

HYDROGEN SULPHIDE OXIDATION UNDER CLAUS FURNACE CONDITIONS

by

HOWARD AUSTIN BENNETT

B.A.Sc. University of Toronto, 1968

M.A.Sc. University of Toronto, 1969

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in

THE FACULTY OF GRADUATE STUDIES

Department of Chemical Engineering

We accept this thesis as conforming

to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

January, 1979

© Howard Austin Bennett, 1979

In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study.

I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Chemical Engineering

The University of British Columbia
2075 Wesbrook Place
Vancouver, Canada
V6T 1W5

Date March 20, 1979

ABSTRACT

The oxidation of hydrogen sulphide under Claus furnace conditions (800 to 1500°K and one atmosphere pressure) was studied theoretically and experimentally.

Equilibrium compositions of mixtures resulting from reactions between H_2S and air were calculated for temperatures and O_2/H_2S ratios ranging from 600 to 2000°K and 0.05 to 1, respectively. Forty-four compounds containing nitrogen, hydrogen, oxygen and sulphur were assumed to be present at equilibrium, but only 25 had concentrations exceeding 0.1 ppm. Eleven carbon compounds were later included, but only five of them had concentrations greater than 0.1 ppm. Sulphur yields in the furnace were found to increase about 10% when O_2/H_2S ratios less than 0.5 (stoichiometric) are used. Feed impurities such as NH_3 (below 1600°K), H_2O and CO_2 diminish the sulphur yields.

A computer model was developed to simulate a Claus plant consisting of a furnace and two catalytic converters operating adiabatically. The model showed that the maximum sulphur yields for the plant are obtainable when operating with stoichiometric air. Preheating the furnace feed or recycling part of the furnace products enhances the overall yield only slightly. Enriching the combustion air with pure oxygen causes the sulphur yield to drop since, with N_2 absent, the furnace temperature rises to over 2200°K. Above 1750°K, the sulphur yield falls with temperature.

To determine equilibrium compositions experimentally, various

mixtures of known H_2S /air ratios were introduced into a quartz vessel located in a furnace and operating between 800 and 1500°K. The contents of this vessel were sampled and analysed by gas chromatography.

Experimental measurements for H_2S dissociation were in excellent agreement with Raymont's¹⁹ results and theoretical predictions. Results for H_2S oxidation showed the same trend as the theoretical predictions, but did not agree quantitatively; the experimental sulphur yields exceeded the predicted values by up to 15%. Reasons for these discrepancies are discussed.

TABLE OF CONTENTS

ABSTRACT	ii
LIST OF TABLES	vii
LIST OF FIGURES	ix
ACKNOWLEDGEMENTS	xi
CHAPTER	
1. INTRODUCTION	1
2. LITERATURE REVIEW	7
2.1 Theory	7
2.2 Experimental	22
2.3 Claus Process	28
2.3.1 Controls	28
2.3.2 Furnace	28
2.3.3 Reheaters	29
2.3.4 Catalytic Converters	29
2.3.5 Sulphur Wash Tower	29
3. THEORY	31
3.1 Equilibrium Compositions	31
3.1.1 Acid Gas Containing Pure H ₂ S Only	31
3.1.2 Impurities in Acid Gas	36
3.1.3 Hydrogen Sulphide Dissociation	38
3.2 Adiabatic Flame Temperature	38
3.3 Recycle	41
3.4 Thermochemical Data	44
3.5 Vapour Pressure of Sulphur	53
4. EXPERIMENTAL APPARATUS	55
4.1 Requirements of the Apparatus	55
4.2 Apparatus and Principles of Operation	55
4.2.1 Feed Mixture Preparation	59
4.2.2 Furnace	59
4.2.3 Quartz Equilibrium Vessel	62
4.2.4 Sampling	62
4.3 Gas Chromatography	63
4.3.1 Requirements of the G.C. Column	63
4.3.2 Analysis of Four Compounds	63
4.3.2.1 Single column operating isothermally	64

4.3.2.2	Three columns operating isothermally	64
4.3.2.3	One column with temperature programming	67
4.3.3	Analysis of Three Compounds	67
4.3.4	Column Packings	69
4.3.5	Calibration of the Gas Chromatograph	72
4.4	Calculation of Mixture Compositions	72
4.4.1	Calculation of the Feed Composition	72
4.4.2	Composition of the Sampled Gases	76
4.4.3	Composition of the Equilibrium Vessel Contents	77
4.4.4	Dissociation of Hydrogen Sulphide	78
5.	THEORETICAL RESULTS	80
5.1	Claus Furnace	80
5.1.1	Acid Gas Containing H ₂ S Only	80
5.1.2	Acid Gas Containing Carbon Compounds	91
5.1.3	Acid Gas Containing Ammonia	102
5.1.4	Hydrogen Sulphide Dissociation	102
5.2	Claus Plant	105
5.2.1	Oxygen Concentration in the Furnace Feed	107
5.2.2	Enriching Combustion Air with Oxygen	109
5.2.3	Preheating the Furnace Feed	109
5.3	Effect of Recycle	115
6.	EXPERIMENTAL RESULTS	125
6.1	Averaging Technique	125
6.2	Comparison of Experimental with Theoretical Results	125
6.2.1	Effect of Temperature	140
6.2.2	Effect of PA	140
6.3	Causes of Deviation between Experimental and Theoretical Results	142
6.3.1	High Temperature Reversion	142
6.3.2	H ₂ S - SO ₂ Reaction at Low Temperatures	145
6.3.3	Sample Size	145
6.3.4	Trace Compounds	147
6.3.5	Theoretical Data	147
6.3.6	Temperature Measurement	149
6.3.7	Error Analysis	149
7.	CONCLUSIONS	153
7.1	Theoretical Equilibrium Compositions and Yields	153
7.2	Claus Plant Model	153
7.3	Experimental Equilibrium Compositions	154
	NOMENCLATURE	155
	REFERENCES	159

APPENDIX

A	EXPERIMENTAL PROCEDURE	163
A.1	Preparing the Feed Mixture	163
A.2	Introducing the Mixture into the Equilibrium Vessel	163
A.3	Sampling the Equilibrium Vessel	164
A.4	Calibration of Gas Chromatograph	164
B	CALCULATOR PROGRAMS AND SAMPLE CALCULATIONS	166
B.1	Constants for Gas Chromatograph Calibration	166
B.2	Equilibrium Vessel Compositions	170
B.2.1	Hydrogen Sulphide Oxidation	170
B.2.2	Hydrogen Sulphide Dissociation	171
B.3	Compositions of a Mixture of H_2S , SO_2 and N_2	173
C	CALIBRATION CURVES FOR ROTAMETERS	175
D	EXPERIMENTAL RESULTS	182
E	COMPUTER PROGRAMS	201
F	ERROR ANALYSIS	231

LIST OF TABLES

Table

2.1	Summary of various theoretical papers on the Claus Process	11
2.2	Experimental sulphur yields found by various authors	23
3.1	Equilibrium equations for the system H_2S -air	34
3.2	Equilibrium equations for the system H_2S - air - CO_2 - NH_3	37
3.3	Equilibrium equations for the system H_2S - CH_4 - NH_3	39
3.4	Thermochemical data not available from McBride et al.	46
3.5	Matrix A	47
3.6	Vector d_1	47
3.7	Heat capacities of gaseous sulphur molecules from Rau et al.	49
3.8	Matrix A	50
3.9	McBride coefficients calculated in this thesis	51
3.10	Comparison of standard errors of data of S_2 generated from McBride coefficients	52
3.11	Equations for vapour pressure of sulphur	54
4.1	List of equipment	60
4.2	Possible chromatographic columns for separating H_2 , N_2 , H_2S and SO_2	65
4.3	Gas chromatography references for separations involving H_2S and/or SO_2	66
4.4	Thermal conductivities of various gases at $0^\circ C$	68
4.5	Operating conditions of the gas chromatograph	70
6.1	Moles of product formed at various temperatures from 100 moles of H_2S and 238 moles of air (stoichiometric air)	141
6.2	Effect of sampling time and P_{2O_5} at $1200^\circ K$	144
6.3	Check for H_2S - SO_2 reaction at low temperatures	146
6.4	Effect of changes in F_T° of H_2S , SO_2 , H_2O or S_2 on compositions at $1300^\circ K$	148
6.5	Comparison of $-F_T^\circ$ for SO_2 computed by McBride coefficients with that listed in McBride or JANAF	150
6.6	Comparison of $-F_T^\circ$ for H_2O computed by McBride coefficients with that listed in McBride or JANAF	151
6.7	Furnace temperature profiles	152
B.1	TI-58 program for calculating G.C. calibration curve constants and for finding equilibrium vessel compositions for H_2S oxidation	167
B.2	Typical calibration data for the gas chromatograph (Run 77)	169
B.3	TI-58 program for calculating equilibrium vessel compositions for H_2S dissociation	172
B.4	TI-58 program for calculating the composition of a mixture of H_2S , SO_2 and N_2	174

D.1	Experimental results of hydrogen sulphide oxidation at 800°K for various PA	183
D.2	Experimental results of hydrogen sulphide oxidation at 900°K for various PA	185
D.3	Experimental results of hydrogen sulphide oxidation at 1000°K for various PA	187
D.4	Experimental results of hydrogen sulphide oxidation at 1100°K for various PA	189
D.5	Experimental results of hydrogen sulphide oxidation at 1200°K for various PA	191
D.6	Experimental results of hydrogen sulphide oxidation at 1300°K for various PA	193
D.7	Experimental results of hydrogen sulphide oxidation at 1400°K for various PA	195
D.8	Experimental results of hydrogen sulphide oxidation at 1500°K for various PA	198
E.1	H ₂ S Dissociation.	202
E.2	H ₂ S Oxidation	207
E.3	Claus Plant	213
E.4	McBride Coefficients	228
F.1	Estimate of errors in stoichiometric air, PA, by flow meters (Run 77)	232
F.2	Estimates of errors in chemical compositions and sulphur yield	233

LIST OF FIGURES

Figure		
1.1	Flowsheet of a typical straight-through Claus plant . .	3
2.1	Theoretical equilibrium conversions	9
3.1	Flowsheet of Claus plant with preheat and recycle . . .	32
4.1	Schematic diagram of the experimental apparatus	56
4.2	Experimental apparatus	57
4.3	Typical chromatogram (Run 77)	71
4.4	Typical calibration curve for H_2 (Run 77)	73
4.5	Typical calibration curve for H_2S (Run 77)	74
4.6	Typical calibration curve for SO_2 (Run 77)	75
5.1	Effect of temperature on the partial pressure of harmless compounds (with the exception of NO)	81
5.2	Effect of temperature on the partial pressure of sulphur compounds	82
5.3	Effect of temperature on the partial pressure of sulphur polymers	83
5.4	Comparison of sulphur yields calculated by various workers ($PA = 100$)	86
5.5	Effect of temperature and PA on sulphur yield	88
5.6	Effect of PA on sulphur yield at various temperatures	89
5.7	Effect of PA on the adiabatic flame temperature and on the corresponding sulphur yield	90
5.8	Effect of temperature on the partial pressure of harmless compounds (with the exception of NO)	92
5.9	Effect of temperature on the partial pressure of sulphur polymers	93
5.10	Effect of temperature on the partial pressure of carbon compounds	94
5.11	Effect of temperature on the partial pressure of sulphur compounds	95
5.12	Effect of temperature and CO_2 on the sulphur yield . .	97
5.13	Effect of temperature and PA on the sulphur yield . . .	98
5.14	Effect of PA on the adiabatic flame temperature and on the corresponding sulphur yield	100
5.15	Effect of H_2O and CO_2 on the sulphur yield	101
5.16	Effect of ammonia on the sulphur yield (sufficient air to oxidise the H_2S only)	103
5.17	Effect of ammonia on the sulphur yield (sufficient air to oxidise both the H_2S and the NH_3)	104
5.18	Effect of ammonia on sulphur yields from H_2S dissociation	106
5.19	Effect of PA on Claus plant yields and temperatures	108

5.20	Effect of enriching combustion air with oxygen on Claus plant yields and temperatures	110
5.21	Effect of temperature of furnace feed on Claus plant yields and temperatures	112
5.22	Effect of temperature of first converter feed on Claus plant yields and temperatures	113
5.23	Effect of temperature of second converter feed on Claus plant yields and temperatures	114
5.24	Effect of recycle on yield at 1300°K with PA = 100 .	116
5.25	Effect of temperature on sulphur yield for various recycles	117
5.26	Effect of recycle on Claus plant yields	118
5.27	Effect of recycle on temperature of the Claus furnace	120
5.28	Effect of recycle on temperature of the catalytic converters	121
5.29	Effect of recycle on yield of the first catalytic converter	122
5.30	Effect of recycle on yield of the second catalytic converter	124
6.1	Effect of PA on H ₂	126
6.2	Effect of PA on H ₂ S	127
6.3	Effect of PA on SO ₂	128
6.4	Effect of PA on N ₂	129
6.5	Effect of PA on H ₂ O	130
6.6	Effect of PA on S ₂	131
6.7	Effect of PA on sulphur yield at 800°K	132
6.8	Effect of PA on sulphur yield at 900°K	133
6.9	Effect of PA on sulphur yield at 1000°K	134
6.10	Effect of PA on sulphur yield at 1100°K	135
6.11	Effect of PA on sulphur yield at 1200°K	136
6.12	Effect of PA on sulphur yield at 1300°K	137
6.13	Effect of PA on sulphur yield at 1400°K	138
6.14	Effect of PA on sulphur yield at 1500°K	139
6.15	Effect of temperature on the concentration of H ₂ formed from H ₂ S dissociation	143
C.1	Calibration of rotameter Ch.E 2912B (Gilmont Model F-2000, Size 10) for H ₂	176
C.2	Calibration of rotameter Ch.E 2912B (Gilmont Model F-2000, Size 10) for H ₂ S	177
C.3	Calibration of rotameter Ch.E 2912B (Gilmont Model F-2000, Size 10), for SO ₂	178
C.4	Calibration of rotameter Ch.E 3107A (Gilmont Model F-1200, Size 2), for N ₂	179
C.5	Calibration of rotameter Ch.E 2600 (Gilmont Model F-1100, Size 1) for air	180
C.6	Calibration of rotameter 2912A (Gilmont Model F-2000, Size 10) for H ₂ S	181

ACKNOWLEDGEMENTS

The author wishes to thank the following:

- Dr. Axel Meisen for his patient help during this work;
- Nina Thurston for her excellent typing;
- Monica Gutiérrez who drew the figures;
- Don Sheraton who took the photograph of the apparatus;
- The workshop of the Chemical Engineering Department and the glassblowing shop of the Physics Department for help in constructing the experimental apparatus;
- The faculty, students and others of the Chemical Engineering Department for their help and encouragement;
- My parents for their patience, love and encouragement.

The financial support from the National Research Council of Canada in the form of a scholarship and research grant is gratefully acknowledged.

CHAPTER 1

INTRODUCTION

Canada is the world's second largest supplier of elemental sulphur, producing seven million tons in 1976.¹ Virtually all Canadian sulphur is produced from hydrogen sulphide by the Claus process. The two major sources of H_2S in Canada arise from natural gas processing and petroleum refining.

Hydrogen sulphide, an undesirable constituent of most Canadian natural gas, is usually removed by absorption into amine solutions. Carbon dioxide, which may also be present in natural gas, is removed together with the H_2S , as are small quantities of methane and higher hydrocarbons.

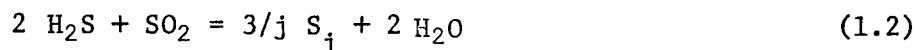
In petroleum refining, H_2S is the by-product of hydrofining (hydrogenation of sulphur-bearing feedstocks), and is also obtained from sour water stripping. Depending on refinery operation, ammonia and CO_2 may also be associated with the H_2S stream.

Thus, H_2S from petroleum refining or natural gas processing can contain ammonia, carbon dioxide, methane and higher hydrocarbons and is usually saturated with water vapour. A mixture of such compounds is often called an "acid gas."

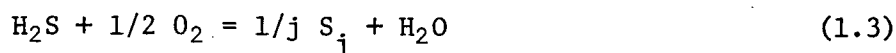
Until fairly recently it was common practice either to vent the acid gas directly to the atmosphere or to incinerate it before discharge. Incineration oxidises the H_2S to SO_2 , which, although less odorous than

H₂S, is still offensive. To minimise pollution, the acid gas nowadays is usually treated by the Claus process, to convert the H₂S to elemental sulphur.

This sulphur recovery process, as developed by C. F. Claus and improved by H. Bähr, is based on the following main reactions:



These equations can be combined to give the so-called "overall Claus reaction,"



Subscript *j* denotes the number of atoms per molecule of sulphur vapour.

At temperatures less than 150°C, *j* ≈ 8, whereas above 800°C, *j* ≈ 2.

For temperatures between 150 and 800°C, *j* lies between 8 and 2.

There are three main variations of the Claus process—"straight through," "split stream," and "direct oxidation."² Since the "straight through" process is the most efficient and hence the preferred version, only it will be discussed in this thesis. However, it cannot be used to treat acid gases containing less than about 50% H₂S, or more than about 2% hydrocarbons.³ For such acid gases, either the split flow or direct oxidation process, described in detail by Estep et al.,³ must be used.

In the straight through process, the entire acid gas is sent to the Claus furnace where it is oxidised with air under free flame conditions at about 1100°C. To achieve maximum conversion, operating experience has shown that the amount of air should be stoichiometric with respect to Eq. 1.3, i.e., the H₂S/O₂ ratio should be 2/1.

The furnace products, which are mainly nitrogen, water vapour, elemental sulphur vapour, SO₂, and unreacted H₂S, are first cooled to

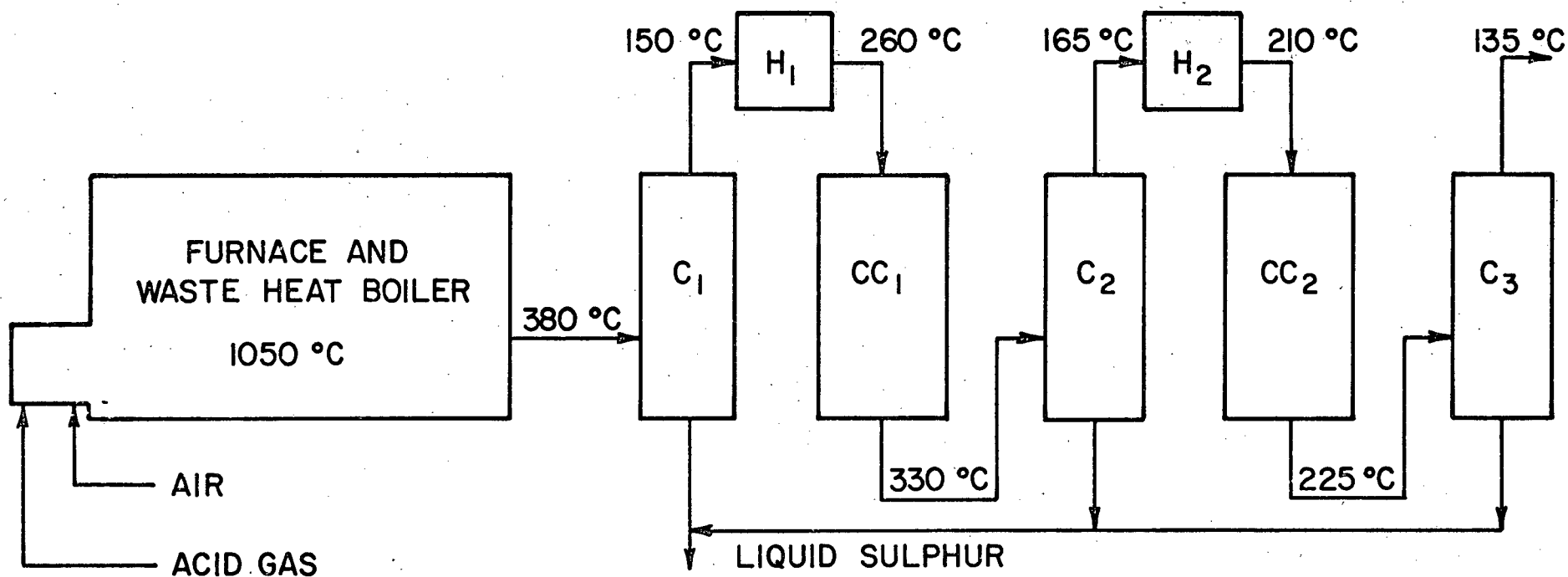


Figure 1.1: Flowsheet of a typical straight-through Claus plant³.

Legend: C--sulphur condenser
 CC--catalytic converter
 H--heater

approximately 380°C in a waste heat boiler. This is followed by further cooling to about 150°C in a condenser, where the elemental sulphur is removed as a liquid. Before entering the catalytic converter, the process gases are reheated to near the optimal temperature for the main converter reaction, Eq. 1.2. Since this reaction is exothermic, low temperatures favour the equilibrium sulphur yield, however, high temperatures are necessary to increase the reaction rate and to prevent sulphur from condensing and fouling the catalyst. The optimal temperature in most plants appears to be about 260°C. To promote this reaction, alumina is the catalyst commonly used. The elemental sulphur produced in the converters is condensed and drained to sulphur storage pits. Most of the elemental sulphur mist from the last condenser is trapped by a coalescer before the gases are incinerated. The primary purpose of the incinerator is to oxidise all sulphur compounds to SO₂ before discharge to the atmosphere.

Well-operated Claus plants with two catalytic converters recover about 95% of the sulphur in the acid gas feed. This recovery is comprised of the following approximate yields: furnace 60%, first catalytic converter 20%, second converter 15%. If a Claus plant, operating at 95% recovery, processes acid gas containing 1000 tons per day of sulphur, it would discharge about 100 tons per day of sulphur dioxide to the atmosphere. Stricter pollution control regulations, such as those in effect in Alberta and other provinces, require that large sulphur plants must reach recoveries of about 99%. Most conventional Claus plants are unable to achieve such performance for the following main reasons:

- (i) Maximum furnace and converter yields are attained only when the combustion air is exactly stoichiometric. For an air surplus

or deficiency of X%, the sulphur loss is also of the order of X%. Sophisticated control systems have been developed to assure that the amount of combustion air is always stoichiometric. Although they can increase sulphur yield as much as 3%, such systems are usually quite costly.⁴

- (ii) The mixing of air and acid gas in the furnace may not be complete because of imperfect burner design.
- (iii) If the acid gas contains carbon compounds, then COS and CS₂ may be formed in the furnace. These compounds pass relatively unaffected through the catalytic converters, and are oxidised to CO₂ and SO₂ only in the incinerator.
- (iv) As catalysts become deactivated, less H₂S and SO₂ are converted to sulphur. After a year or more, the catalysts require regeneration or replacement. In a conventional Claus plant, the gas from the final coalescer, termed the "tail gas," can be treated to improve the overall yield. Usually a unit is added downstream of the coalescer to treat the gas before it is incinerated. However, the cost of such tail-gas conditioning usually exceeds that of the basic Claus plant.

An alternative to tail gas treatment may be to improve the performance of the Claus process itself but this requires a better understanding of the process than is currently available. One important aspect of this is to determine accurately the thermodynamic equilibrium between hydrogen sulphide and air under Claus process conditions. Although equilibria are never exactly achieved in practice because of kinetic limitations, they nevertheless provide useful information on maximum attainable sulphur yields and chemical compounds likely to be formed.

Of special interest is the Claus furnace, since this unit usually converts over 50% of the H_2S in the acid gas to sulphur. Moreover, relatively little research has been done on the furnace.

Although the effect on furnace performances of parameters such as acid gas composition is important, their effect on the entire plant must also be considered. In this thesis, a Claus furnace and two converters are modelled. This model is then used to study the effect of the following on furnace and converter equilibrium compositions:

- acid gas impurities (NH_3 , H_2O , CO_2 and CH_4);
- the amount of air added to the acid gas;
- temperature of the feed stream to the furnace and to each converter.

The results of this thesis should help to provide guidance for the optimal operation of Claus furnaces.

CHAPTER 2

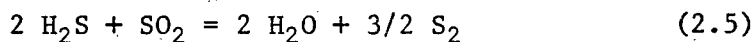
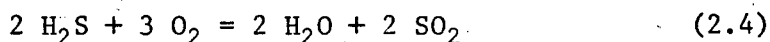
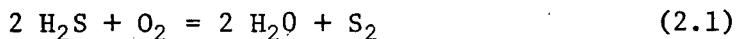
LITERATURE REVIEW

This chapter reviews important papers on the Claus process under the following headings: theory, experiments and industry. For a more general review, the reader is referred to the publication by Estep et al.³

2.1 Theory

Although the Claus process was developed in the 1890's and modern plants date from the 1940's, practically no theoretical investigations were published until 1953, when Gamson and Elkins⁵ presented a major study. They calculated equilibrium compositions of H₂S and air mixtures under Claus process conditions and compared their predictions with their experimental results. The following paragraphs deal with Gamson and Elkins' theoretical work; their experiments are discussed in Sect. 2.2.

Gamson and Elkins considered the following reactions to determine the equilibrium composition:



Furthermore, they made the following assumptions

--Reactions 2.1, 2.4 and 2.6 go to completion. Therefore, no oxygen is present, and only Eqs. 2.2, 2.3 and 2.5 need be considered.

--The only compounds present at equilibrium are H_2S , H_2O , S_2 , S_6 , S_8 , SO_2 and N_2 and they obey the ideal gas law.

--The acid gas is pure H_2S .

--The supply of combustion air is stoichiometric with respect to Eq. 2.1 and contains 21 vol. % O_2 and 79 vol. % N_2 .

--The total pressure is constant at 0.5, 1, or 2 atmospheres.

Gamson and Elkins developed a unique hand computation method to predict equilibrium compositions subject to these assumptions.

The sulphur yields calculated by the authors for a total pressure of one atmosphere are plotted as Curve A of Fig. 2.1. This curve has a minimum which they explained as follows:

The minimum in the equilibrium-conversion curve is caused by the shift in the predominant sulphur specie [sic] with temperature. The formation of diatomic sulphur by reactions (1) and (5) increases with increasing temperature; whereas, the opposite is true with S_6 and S_8 .

This explanation is essentially correct, but more thorough discussion of the shape of this curve is presented in Chapter 5 of this thesis. Gamson and Elkins divided the curve into two regions. To the right of the minimum is the "free flame" region, so called because Claus furnaces operate well above 800°K . At such elevated temperatures, combustion can occur in a free flame and the reaction rates should be sufficiently rapid for thermodynamic equilibrium to be attained. To the left of the minimum is the "catalytic" region, so designated because Claus catalytic converters operate at these lower temperatures.

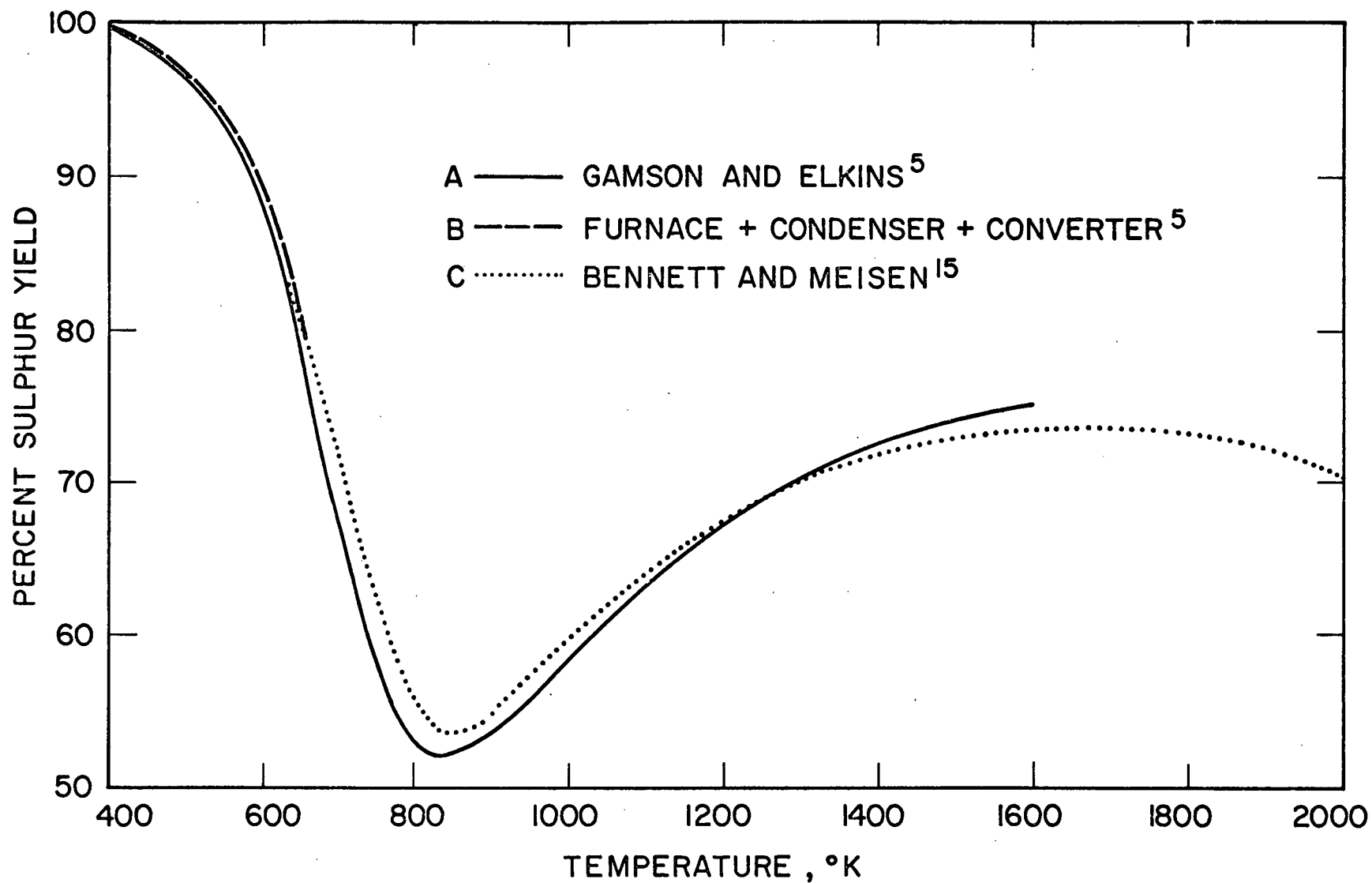


Figure 2.1. Theoretical equilibrium conversions.

Gamson and Elkins predicted overall yields of a Claus plant with a furnace which converted 70% of the acid gas to sulphur, a condenser which removed all the sulphur formed in the furnace, and, finally, a catalytic converter. These total yields are plotted as Curve B of Fig. 2.1 for catalytic converter temperatures from 400 to 650°K. Later in this chapter, Fig. 2.1 will be compared to other equilibrium calculations, experimental results (including those of Gamson and Elkins) and plant data.

The work of Gamson and Elkins, however, had some shortcomings. They assumed only seven species present at equilibrium, since this was the maximum number which could easily be handled by a simple desk calculator. They considered an acid gas of pure H_2S , which was oxidised with *stoichiometric* amounts of air. Finally, Gamson and Elkins used Kelley's thermodynamic data,⁶ published in 1937. More recent and accurate thermodynamic data are available.^{7,8}

Since large digital computers became readily available in the late 1960's, the equilibrium compositions of Claus furnaces with as many as 44 species have since been calculated for various acid gas impurities, and deviations from stoichiometric air. Furthermore, thermodynamic data have recently been published based on the latest theory and experiments.

Numerous workers^{9to21} elaborated on Gamson and Elkins studies in one or more of the following ways: the compounds present in the starting and in the equilibrium mixtures, the temperature range, the thermodynamic data, and the method of calculating the equilibrium compositions. Except where noted in the text, the results agreed substantially with those of Gamson and Elkins. A comparison of the papers is summarised in Table 2.1.

TABLE 2.1

SUMMARY OF VARIOUS THEORETICAL PAPERS ON THE CLAUS PROCESS

Authors*	5	10	11	12	13	14	15	16	17	18	19	20	21	This Thesis
Date	1953	1966	1968	1971	1972	1972	1973	1974	1974	1974	1975	1977	1978	
Feed														
H ₂ S	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
H ₂ O			✓	✓		✓		✓	✓	✓			✓	✓
CO ₂						✓		✓	✓	✓		✓	✓	✓
Hydrocarbons				✓				✓	✓				✓	
Others			✓											✓
O ₂	✓	✓		✓	✓	✓	✓	✓	✓	✓		✓	✓	✓
N ₂	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓
Stoichiometric air (%)	100	100	NS	100		100	10to 200	100	100	10to 200	0	100	100	0-300
Equilibrium Mixture														
N ₂	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓
NH ₃						✓	✓	✓		✓			✓	✓
NO						✓	✓	✓		✓		✓	✓	✓
NO ₂						✓	✓	✓		✓			✓	✓
O ₂		✓	✓	✓	✓	✓	✓	✓	✓	✓				✓
H ₂			✓		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

Table 2.1 continued

Authors* Date	5 1953	10 1966	11 1968	12 1971	13 1972	14 1972	15 1973	16 1974	17 1974	18 1974	19 1975	20 1977	21 1978	This Thesis
H ₂ O	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓
H ₂ S	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
H ₂ S ₂			✓				✓			✓	✓			✓
SO			✓				✓			✓		✓		✓
SO ₂	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓
SO ₃			✓				✓	✓	✓	✓		✓		✓
S		✓			✓		✓			✓	✓	✓		✓
S ₂	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
S ₄			✓				✓			✓	✓	✓	✓	✓
S ₆	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓		✓	✓
S ₈	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓		✓	✓
S ₃ S ₅ S ₇							✓			✓	✓	✓	✓	✓
C(S)								✓						
Hydro- carbons		✓		✓	✓	✓		✓	✓	✓				✓
CO				✓	✓	✓		✓	✓	✓		✓	✓	✓
CO ₂		✓		✓	✓	✓		✓	✓	✓		✓	✓	✓

Table 2.1 continued

Authors*	5	10	11	12	13	14	15	16	17	18	19	20	21	This Thesis
Date	1953	1966	1968	1971	1972	1972	1973	1974	1974	1974	1975	1977	1978	
COS				✓	✓	✓		✓	✓	✓		✓	✓	✓
CS ₂				✓	✓	✓		✓	✓	✓		✓	✓	✓
Others							✓			✓	✓		✓	✓
Thermodynamic data	6	6	7,22, 25	NS	8	7,8	7,23	7,8	NS	7,23	7,22, 23	NS	7,27	7,8,22, 23,24
Temperature (°K)	400 to 1600	NS	823 to 923	500 to 1300	400 to 1750	1073 to 2773	600 to 2000		973 to 1573	600 to 2000	750 to 2000	1450 to 2000	883 to 1712	250 to 2200
Calculations			FEM	FEM	FEM	FEM		FEM	FEM					

*Authors: 5=Gamson and Elkins; 10=Opekar and Goar; 11=Eriksson and Rosén; 12=Boas and Andrade; 13=McGregor; 14=Neumann; 15=Bennett and Meisen; 16=Bragg; 17=Fischer; 18=Meisen and Bennett; 19=Raymont; 20=Kerr and Berlie; 21=Maadah and Maddox

Abbreviations: NS=Not Stated; FEM=Free Energy Minimisation

Opekar and Goar¹⁰ wrote a computer program to calculate equilibrium compositions and mass and heat balances for all units of a Claus plant, i.e., furnace, waste heat boiler, catalytic converters, sulphur condensers, and tail gas incinerator. Details of these computations, however, were not given. A typical optimisation study indicated that overall Claus plant conversions could be increased 2% by changing parameters such as the temperatures of the acid gas and of the first and second condenser outlets.

Eriksson and Rosén¹¹ estimated that free energy data from JANAF was accurate to $\pm 1\%$ (except for SO) and that data for SO from JANAF, S₄, S₆ and S₈ from Braune et al²⁵ and H₂S₂ from Mackle and O'Hare²² were accurate to $\pm 10\%$. Eriksson and Rosen also examined the effect of the ratio of the partial pressures of H₂S to SO₂ on the sulphur yield. They found the yield to be a maximum when this ratio was 2.0, a fact well-known to Claus plant operators.

Boas and Andrade¹² modelled a Claus plant to determine the effect of the following on sulphur yield: feed composition, temperatures of the waste heat boiler, condenser and catalytic converter, furnace conversion, entrainment and the ratio of the partial pressures of H₂S to SO₂. They examined in turn effects of CH₄, H₂O, and N₂ in the acid gas. With 5% CH₄ present, yields decrease 3%, with 5% H₂O, conversion fell only 1%, while with 5% N₂, yields dropped negligibly.

Valdes⁹ plotted equilibrium conversions based on acid gas from refinery operations or from well-head facilities. Valdes noted that

the equilibrium plots were arrived at in much the same manner that Gamson calculated the conversions; namely, satisfying the equilibrium constants for the known predominant reactions occurring in the system. The main difference, however,

consisted in the inclusion here of all the components in the feed gas and all the possible chemical species that might be present in the system at any given temperature.

Although Valdes neither named the species, nor described further his program he did emphasise the importance of CO_2 and hydrocarbons in the starting mixture. His results were similar to those of Gamson and Elkins.

To supplement an experimental investigation into the catalytic reaction of H_2S and SO_2 , McGregor¹³ calculated the thermodynamic equilibria of several sulphur plant reactions. His predicted sulphur yields for the Claus furnace were slightly higher than those of Gamson and Elkins because different thermodynamic data were used. At temperatures above 1200°K , hydrogen concentrations exceeded 10%. For the converters he predicted thermodynamic yields of reactions involving COS , CS_2 , CO_2 , CH_4 , and CO , which he considered important since COS and CS_2 emission can account for about 1/3 of the total sulphur losses from a Claus plant.

Neumann¹⁴ estimated Claus furnace equilibria for various feed gases containing CO_2 and H_2O . For combustion with stoichiometric air, he found practically no CH_4 or NH_3 , concentrations of NO_x , SO_3 and CS_2 at or below the ppm level, and COS about 1%, and concluded that the higher levels of CS_2 obtained by other workers^{26,27} could not be explained by equilibrium considerations alone. Neumann found significant concentrations of H_2 and CO which increased with temperature. He also noted that, under furnace conditions, the reactions forming H_2 and CO increase the consumption of H_2S and S_2 , and lower the flame temperature.

Neumann examined the effect of pressure on sulphur recovery at

1400°C, and like Gamson and Elkins, found that increasing the pressure decreased the yields except at very low temperatures.

Bragg¹⁶ modelled an entire Claus plant, including a furnace, waste heat boiler, catalytic converters, condensers, and tail gas incinerator. For each unit, Bragg computed mass and energy balances, and for the furnace and converters, he calculated the adiabatic flame temperature, allowing for heat losses.

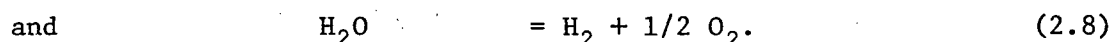
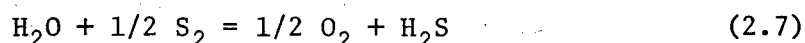
Bragg noted that equilibrium was achieved in the furnace only if the reacting gases were completely mixed and the residence time was sufficiently large. To account for the lack of equilibrium in the furnace, Bragg by-passed some H_2S directly to the first catalytic converter. Side reactions in the catalytic converters involving CO , H_2 , COS and CS_2 were modelled by withholding portions of these compounds from reaction, although, for fresh catalyst and high reactor temperatures, COS and CS_2 did not have to be withheld.

The model could be used for routine plant surveillance and optimisation, for checking the consistency of experimental data, or for predicting sulphur recoveries. Actual and predicted sulphur recoveries agreed within 0.2%. Quantities such as process temperatures and approaches to equilibrium also agreed within experimental error.

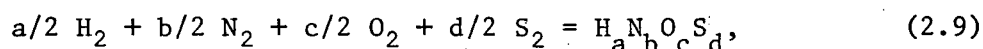
Fischer¹⁷ discussed proper operation of Claus furnaces and he predicted temperatures, compositions and sulphur yields in the furnace. Except for CS_2 , whose concentration was only 1/200 of the measured value, the predicted compositions agreed well with plant data from properly designed furnaces. Sulphur yields of several furnaces exceeded 80% for temperatures above 1000°C and residence times over three seconds, compared to yields of about 70% as reported by earlier workers.^{3,28}

The discrepancy of 10% could be a result either of improved Claus furnace technology or reversion in the sampling lines. Fischer was unable to measure the exact composition of the gas at the furnace exit, and instead took samples at 260°C just upstream of the first catalytic converter. The reactions yielding elemental sulphur probably continued as the gases were cooled, giving apparently high sulphur yields. This "reversion" will be discussed further in the experimental section of this chapter.

Bennett and Meisen¹⁵ computed equilibrium compositions by a method used by Kellogg²³ which seemed simpler than free energy minimisation. First, the partial pressures of "key components" were guessed. For Claus furnace equilibria, S_2 , H_2S , H_2O and N_2 were chosen, as their partial pressures were expected to be among the highest. It was convenient to consider that O_2 and H_2 were formed according to



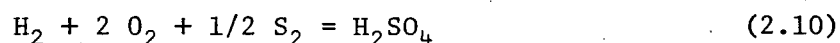
The other products present in the equilibrium mixture resulted from reaction between the elements S_2 , N_2 , O_2 and H_2 , i.e.,



for example, in the case of H_2SO_4 ,

$$a = 2, b = 0, c = 4, d = 1$$

and Eq. 2.9 becomes



The partial pressures of all the components of the equilibrium mixture were then used to evaluate:

- the sum of partial pressures, P_T ;
- the atomic ratios of bound as well as unbound oxygen to sulphur, R_{OS} ;
- ratio of hydrogen to sulphur, R_{HS} ;
- ratio of nitrogen to oxygen, R_{NO} .

Since the total pressure was atmospheric, $P_T = 1$, and since the initial mixture was assumed to be pure H_2S and air (79% N_2 and 21% O_2), the desired magnitudes of R_{HS} and R_{NO} were 2.0 and 3.76 respectively. Although R_{OS} could be freely specified, a value of unity corresponded to stoichiometric air according to Eq. 2.1.

If the total pressure and the three ratios did not agree within 0.1% of the desired values (denoted by *), new partial pressures of the key components were determined from

$$[S_2] = [S_2]_0 \{(P_T^*/P_T) (R_{OS}^*/R_{OS})\}^{\frac{1}{2}} \quad (2.11)$$

$$[H_2S] = [H_2S]_0 \{(P_T^*/P_T) (R_{HS}^*/R_{HS})\}^{\frac{1}{2}} \quad (2.12)$$

$$[H_2O] = [H_2O]_0 (P_T^*/P_T)^{\frac{1}{2}} \quad (2.13)$$

$$[N_2] = [N_2]_0 \{(P_T^*/P_T) (R_{NO}^*/R_{NO})\}^{\frac{1}{2}} \quad (2.14)$$

where [] denoted partial pressure and the subscript "0" referred to the previous iteration. The calculations were repeated until the desired convergence was obtained.

The adiabatic flame temperature was also computed. Details of this calculation, as well as Kellogg's method are given in Chapter 3.

The authors found that, for at least some temperatures between 600 and 2000°K, the following 25 compounds exceeded 0.1 ppm at 1 atmosphere: NH_3 , NO , N_2 , H , H_2 , H_2O , HS , H_2S , H_2S_2 , O , OH , O_2 , SO , SO_2 , SO_3 , S_2O , SN , S , S_2 , S_3 , S_4 , S_5 , S_6 , S_7 and S_8 . Above 1200°K, the concentration of H_2 exceeded 1%, and above 1000°K the concentration of S_2 exceeded 10%, which was more than ten times that of any other sulphur polymer.

Using Kellogg's free energy equations for the sulphur polymers introduced negligible error into the sulphur yields, which are plotted as Curve C of Fig. 2.1.

The authors varied the combustion air from 10% to 200% of

stoichiometric. At fixed temperatures, maximum sulphur yields occurred with less than stoichiometric amounts of air. Under adiabatic conditions, however, stoichiometric air resulted in maximum yields, which confirms plant operating experience.

An important drawback of this paper was that the acid gas was assumed to be pure H_2S . A subsequent paper by Meisen and Bennett¹⁸ examined the effects on yield of having CO_2 and H_2O in the acid gas. In addition to the 25 compounds whose concentrations exceeded 0.1 ppm, the authors assumed the following to be present at equilibrium: CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , HCN , C_2N_2 , CO , CO_2 , COS , CS and CS_2 .

When the acid gas contained CO_2 or H_2O the sulphur yield decreased. For an acid gas containing 10% H_2O only, the yield dropped by only 3%. The yield also fell 3% for 15% CO_2 in the acid gas, provided the equilibrium temperature exceeded 1500°K. At temperatures below 1200°K, as much as 30% CO_2 had no noticeable effect on the sulphur yield.

For an acid gas containing 15% CO_2 , the most abundant carbon compound at equilibrium was CO_2 , with a concentration from 2 to 6%. The non-carbon compounds had a composition similar to those in the authors' previous paper.

No data were available for the polymers S_3 , S_4 , S_5 , S_6 , and S_7 , and their free energies were therefore estimated from equations given by Kellogg,²³ even though they were only strictly valid up to 700°K. At higher temperatures, however, the partial pressures of the heavy sulphur species were extremely small, and consequently, little error was introduced into the sulphur yield, the result of greatest interest. Most other authors, however, considered only S_2 , S_6 and S_8 , because they lacked data for the other polymers.

In 1973, Rau et al.²⁴ published equations, valid between 773 and 1273°K, for calculating the composition of all sulphur polymers from S_2 to S_8 . They based their equations on literature data and their own measurements of sulphur vapour densities between 827°K and 1273°K.

With an upper limit of 1273°K, the equations of Rau et al. should therefore predict more accurately than those of Kellogg the sulphur polymer distribution above 700°K.

The paper of Rau et al. is especially valuable as their equations enable calculating equilibrium constants of sulphur polymers without interpolation. For the other compounds, JANAF data, presented at increments of 100°C, require interpolation, when used to obtain the results described in Sect. 5.1 of this thesis.

Raymont investigated the thermal decomposition of H_2S , which he postulated to be responsible for H_2 concentrations of up to 3% in Claus plants.⁴⁷ He used Kellogg's method²³ to predict the levels of H_2 , H_2S , sulphur vapour and sulphanes (H_2S_j , where $j = 2$ to 9), present at equilibrium.¹⁹

Kerr and Berlie²⁰ predicted equilibrium compositions of the furnace as a function of the H_2S content of the acid gas and found close agreement with actual conversion efficiencies for acid gas streams containing over 90% H_2S . They also concluded that the use of 100% stoichiometric air was not optimal because the furnace produces H_2 and CO which do not undergo subsequent reactions. These compounds reduce the air demand from that calculated by assuming that they are absent.

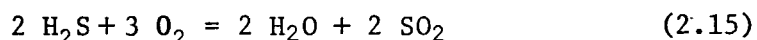
Maadah and Maddox²¹ considered a large number of reactions and impurities. Like Kerr and Berlie, their predicted concentrations of COS and CS_2 were much below those of plant test data. Small amounts

of impurities were found to have only a minor effect on predicted sulphur yields which were about 98% for a furnace and two converters.

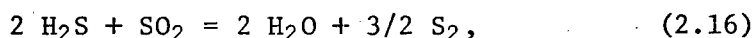
2.2 Experimental

Compared to theoretical work few experimental results have been published on the Claus process, and most of these are concerned not with the furnace, but with the catalytic converters^{30 to 43}. Various papers reporting plant trials or experiments pertinent to Claus furnace operation are summarised in Table 2.2.

Taylor and Livingston³⁶ were among the first to investigate the non-catalytic oxidation of H_2S . However, they added excess oxygen to a batch reactor heated to between 475 and 675°K, a temperature range well below that of the Claus furnace. They detected sulphur and H_2SO_4 in the reaction products, and concluded that the equation,



did not adequately describe the reaction mechanism. Furthermore, this equation predicted a pressure decrease less than that observed during the reaction. The authors postulated that this pressure decrease may be accounted for by a subsequent reaction such as



or by the solubility of the SO_2 in the liquid sulphur formed, or by the production of H_2SO_4 .

Gamson and Elkins⁵ reported that Bähr and Braus had oxidised H_2S in a free flame at temperatures of up to 1000°C, cooled the combustion products and condensed the sulphur. Apparent yields ranging from 80 to 90% were found. As mentioned earlier, Gamson and Elkins calculated the maximum yield to be less than 75%. The high yields of Bähr and Braus may have been caused by "reversion" which could be explained as follows: during cooling, the combustion products continue to react until a sufficiently low temperature is reached to stop the reaction. According

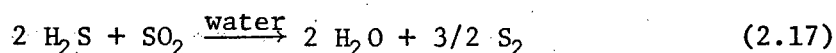
TABLE 2.2

EXPERIMENTAL SULPHUR YIELDS FOUND BY VARIOUS AUTHORS

Author(2)	Bähr and Braus (cited by 5)	Sawyer et al ²⁸				Gamson & Elkins ⁵	Grekel ⁴¹				Fischer ⁴²	Fischer ¹⁷		Bragg ¹⁶	Kerr & Berlie ²⁰	Kopp & Morin ⁴³
Date	1940	1950				1953	1959				1971	1974		1975	1977	1977
Temperature °C	1000	600-750	500	575	650	>1300	205-815	288	371	491	>1035	1240	1120	1110	NS	NS.
Sulphur Yield (%)	80to90	76to82	73	71.7	70.6	90	7to85	8	12	58	66	86	68	NS	50to80	71
Theoretical Yield*	68	55to60	60	55	57	74	63to97	93	77	57	70	73	73	72	NA	NA
Acid gas composition																
% H ₂ S	100	100		96		100	15		100		38	95	62	69	50to98	83
% CO ₂	0	0		0		0	83		0		62	0	38	31	NS	17
others	0	0		4		0	2		0		0	5	0	0	NS	0
Scale of apparatus	NS	Bench		Bench		Bench	Bench		Bench		Plant	Plant		Plant	Plant	Plant

NS=Not stated; NA=Not applicable; *=Theoretical sulphur yield is based on oxidation of pure H₂S with stoichiometric air

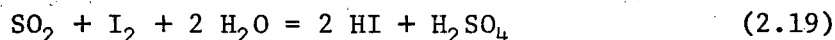
to Fig. 2.1, for an apparent yield of 80 to 90%, this temperature would lie between 565 and 635°K. Another cause of the discrepancy between the experimental and theoretical yields could be the Wackenroder reaction,⁴⁴



which, in the presence of liquid water, is rapid, even at room temperature.

Probably the first important experimental study of the Claus process was published in 1950 by Sawyer et al.²⁸ They operated a tubular laboratory furnace with a 460 mm long quartz tube, 25 mm in diameter. With a flow rate of 60 ml./min. of H₂S and 290 ml./min. air (200% of stoichiometric) and for temperatures between 873 and 1023°K, they obtained sulphur yields of about 80%, compared with theoretical yields of less than 50% for the same amount of air. This discrepancy was probably caused by reversion.

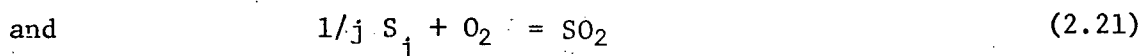
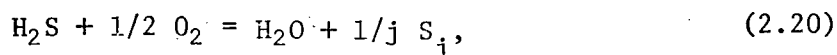
H₂S and SO₂ were analysed by Tutweiler titration, as follows. A sample was taken into the Tutweiler burette by displacing an aqueous starch solution, and was then titrated with iodine to the blue end point:



This titration gave the total concentration of H₂S and SO₂. Then, Na₂S₂O₃ was added to remove the blue colour and the HI and H₂SO₄ were titrated with NaOH to the methyl orange end point. From the normalities and volumes of iodine and bases used in the two titrations, the amounts of H₂S and SO₂ could be calculated.

Sawyer et al. also studied H₂S oxidation at temperatures below 650°K. Reacting 96% H₂S in a porcelain tube, they noted a drop in

yield from 73% at 500°C to 71% at 650°C. They explained the lower conversions at higher temperatures with the following argument, based on kinetic considerations. The oxidation of H_2S was stepwise, the two important steps being



Sulphur and H_2S competed for the oxygen. At lower temperatures, reaction 2.21 was suppressed; hence the high conversions to free sulphur. However, with increasing temperatures, reaction 2.21 became more significant and more sulphur was converted to SO_2 ; hence the lower yields.

In another experiment, Sawyer et al. examined the effect of space velocity on yield. They found that for an increase of residence time from 1.76 sec to 3.55 sec, the apparent yield decreased from 62% to a minimum of 45% and then increased back to 62%. Sawyer et al. postulated that this minimum was due to the presence of free oxygen along the entire length of the furnace. At the lower space velocities, oxygen reacted with both H_2S and sulphur until all the oxygen was used up. Then H_2S reacted with SO_2 , thus increasing the actual conversion. At higher space velocities, oxygen was present at the reactor exit, and this oxygen reacted with H_2S in the sampling lines. A more plausible explanation may be, that under the laminar flow conditions of the experiment, heat transfer was poor and the bulk gas temperature was substantially less than the wall temperature. Higher flow rates resulted in increased gas temperatures, but they also gave lower contact times, which, at low flow rates, outweighed heat transfer considerations. Hence, yield fell with increasing flow rates, until a minimum yield was reached where heat transfer began to play the larger rôle.

Gamson and Elkins⁵ investigated experimentally the free flame combustion of pure H_2S . They used two concentric pyrex tubes 6 and 10 mm. in diameter. Air at 6.0 ml/min ($0.76 \text{ ft}^3/\text{hr}$) flowed through the inner tube, H_2S at 2.4 ml/min ($0.31 \text{ ft}^3/\text{hr}$) flowed through the annulus, and the two streams were mixed in the flame. The reaction products were absorbed by an aqueous NaOH scrubber and subsequently analysed by wet methods.

Gamson and Elkins obtained yields of 90%, compared with their calculated conversions of 75%, and industrial ones of 55%.⁹ There are two possible explanations for the discrepancies. First, as suggested by Sawyer et al., kinetics may play a rôle, if, at high temperatures, H_2S is oxidised more quickly to sulphur, than sulphur is to SO_2 . Second, reversion may be a cause, if the gases are not quenched rapidly enough before sampling, or if H_2S and SO_2 combine at room temperature after sampling to form sulphur. At temperatures below 550°K , reaction after sampling, rather than kinetics should be the major effect. Since Gamson and Elkins operated a catalytic converter at 550°K and found yields similar to the theoretical ones, reaction after sampling is unlikely to have caused the discrepancy in the furnace results.

Levy and Merryman⁴⁵ reacted H_2S with excess O_2 in N_2 or Ar at about 1260°K , and determined levels of N_2 , O_2 , H_2S , H_2 and H_2O by mass spectrometry. They analysed SO_3 as H_2SO_4 and the remaining sulphur oxides by barium chloranilate. Levy and Merryman suggested that the concentrations of the free radicals H, O, OH and SH could then be estimated from the composition profiles obtained from their apparatus. Their results differed substantially from Gamson and Elkins' equilibrium experiments, but this was undoubtedly due to Levy and Merryman using

more than five times stoichiometric oxygen. For example, Levy and Merryman found 11% free O_2 , only 5% H_2O , 6% SO_2 and no free sulphur. They postulated a reaction scheme for the stepwise oxidation of H_2S to SO and further to SO_2 and SO_3 , which may have some application to the study of the Claus process. Levy and Merryman also suggested a reaction mechanism consisting of 23 steps, found a number of significant rate constants, and calculated concentrations of atoms and free radicals.

Hyne⁴⁶ was interested in the behaviour of Claus furnaces and built a "mini-furnace" with variable baffles, ceramic lining and air as well as fuel nozzles. He was especially concerned about "minor" components of the acid gas, such as CH_4 and other hydrocarbons. Hyne presented a sequence of some chain reactions in the furnace, which he felt were necessary (in addition to the reactions considered by Gamson and Elkins) to account for H_2 and SO_3 found in typical Claus plants. These reactions were very sensitive to relatively small amounts (less than 0.1%) of initiators, inhibitors, poisons, etc. Hyne proposed to analyse stable species by a gas chromatograph, and free radicals, which are short-lived, by a mass spectrometer. To date, however, no results have been published in the open literature.

Raymont^{19,47,48} experimented with H_2S dissociation and found, for temperatures above $1250^\circ K$, hydrogen concentrations agreeing with those predicted on the basis of the following reaction,



The agreement suggests his quenching was superior to that of Sawyer et al. as well as Gamson and Elkins. Below $1250^\circ K$, however, the rate of reaction without a catalyst was so low that yields were less than those predicted from thermodynamic calculations.

2.3 Claus Process

In a comprehensive review, Estep et al.³ considered most practical aspects of Claus plant operation, which they illustrated by describing two plants. A typical straight-through plant whose flow sheet is shown in Fig. 1.1, will be discussed in this section in the light of the work of Estep, Valdes⁹ and Fischer.¹⁷

2.3.1 Controls

Ratio flow controls proportion the acid gas and air stoichiometrically. Such a ratio is said to maximise sulphur yield in the furnace.^{3, 43,49,50} The controller must compensate for temperature fluctuations in the air, and both temperature and composition changes in the acid gas. Accurate analysis of the acid gas composition is therefore essential. Once correct ratios have been established and checked by stack gas analysis ($\text{H}_2\text{S}/\text{SO}_2$ ratio should be 2/1) the furnace temperature may be used as a control point, since it will rise with excess combustion air and fall with deficient air. Furthermore, the temperature of the catalytic converter beds drops with any deviation from the correct amount of combustion air. Correct combustion ratios can therefore be maintained by proper metering, stack gas analysis and monitoring of furnace and catalyst bed temperatures.

2.3.2 Furnace

A cylindrical furnace, 3.7 m in diameter contains two burner ports at each end and a chequered baffle wall in the centre. Fischer¹⁷ suggested that improperly designed furnaces achieve often less than 20% conversion, compared to 75% theoretically. Poor furnace design can lead to formation of carbon and ammonical sulphur compounds which impair safety and optimal sulphur recovery in the catalytic converters. Most

combustion chambers should be larger. Burners should mix air with acid gas before these gases reach the combustion chamber. This can be achieved by a multi-burner system distributed over the entire front wall. Proper furnace design, Fischer noted, can increase sulphur recovery of a plant with two catalytic converters to a level not normally achieved in even three converter units.

2.3.3 Reheaters

In the Okotoks plant,³ an acid gas fired reheater brings the gases up to the operating temperature of the catalytic converter. Other methods of reheat are available.⁹ These include direct mixing of combustion products from the waste heat boiler (simpler and cheaper than acid gas fired reheater, but sulphur yields are poorer) and indirect heat exchange (expensive but comparatively high yields). Temperatures downstream of the furnace (except in the condensers) must always exceed the sulphur dew point; otherwise sulphur will condense and plug gas ducts or foul the catalyst.

2.3.4 Catalytic Converters

Valdes noted that two catalytic converters with sulphur condensation in between would recover more sulphur than a single converter with a thicker bed. The extracatalyst in the single converter would achieve little additional conversion, since it would operate at an excessively high temperature which would not favour conversion.

2.3.5 Sulphur Wash Tower

A tower, 3.4 × 3.4 × 10.7 m high circulates cooled molten sulphur counter-current to the gas to condense the sulphur formed in the final catalytic converter. Valdes pointed out that a shell and tube heat exchanger is cheaper than refluxing liquid sulphur.

The Okotoks plant processes 190,000 standard m³/day of acid gas containing 75.1 % H₂S, 24.7% CO₂ and 0.2% hydrocarbons and inerts.

The furnace recovers about 66% of the sulphur of the feed, the first catalytic converter, 21%, the second converter, 6%, for a total recovery of 93.6%. Sulphur production is 160 tons/day.

This section described only a few of the design and operating considerations in Claus plants. The reader is referred to Estep et al., Fischer, and Valdes for more details.

CHAPTER 3

THEORY

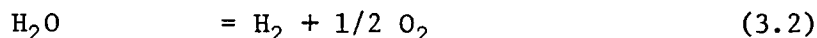
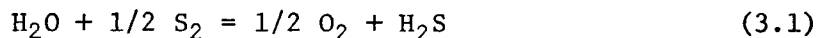
This chapter describes a mathematical model of a Claus plant with recycle whose flow sheet is shown in Fig. 3.1. The model consists of five main parts which calculate the equilibrium compositions, adiabatic flame temperatures, recycle stream compositions, thermochemical properties and check for sulphur condensation in the converters. Each part is subsequently discussed in this chapter.

3.1 Equilibrium Compositions

Equilibrium calculations are based on the following assumptions: all compounds behave as ideal gases, air consists entirely of nitrogen (79%) and oxygen (21%) and the total system pressure is 1 atmosphere.

3.1.1 Acid Gas Containing Pure H₂S Only

For the equilibrium calculations, it is convenient to consider that oxygen and hydrogen are formed according to



and that all other products likely to be present in the equilibrium mixture, i.e., N, NH, NH₂, NH₃, NO, NO₂, NO₃, N₂H₂, N₂H₄, N₂O, N₂O₃, N₂O₄, N₂O₅, H, HNO, cis-HNO₂, trans-HNO₂, HNO₃, HO₂, H₂O₂, H₂SO₄, O, OH, O₃, SO, SO₂, SO₃, S₂O, SH, H₂S₂, SN, S, S₃, S₄, S₅, S₆, S₇, S₈, result from reactions between the elements S₂, N₂, O₂ and H₂. To calculate

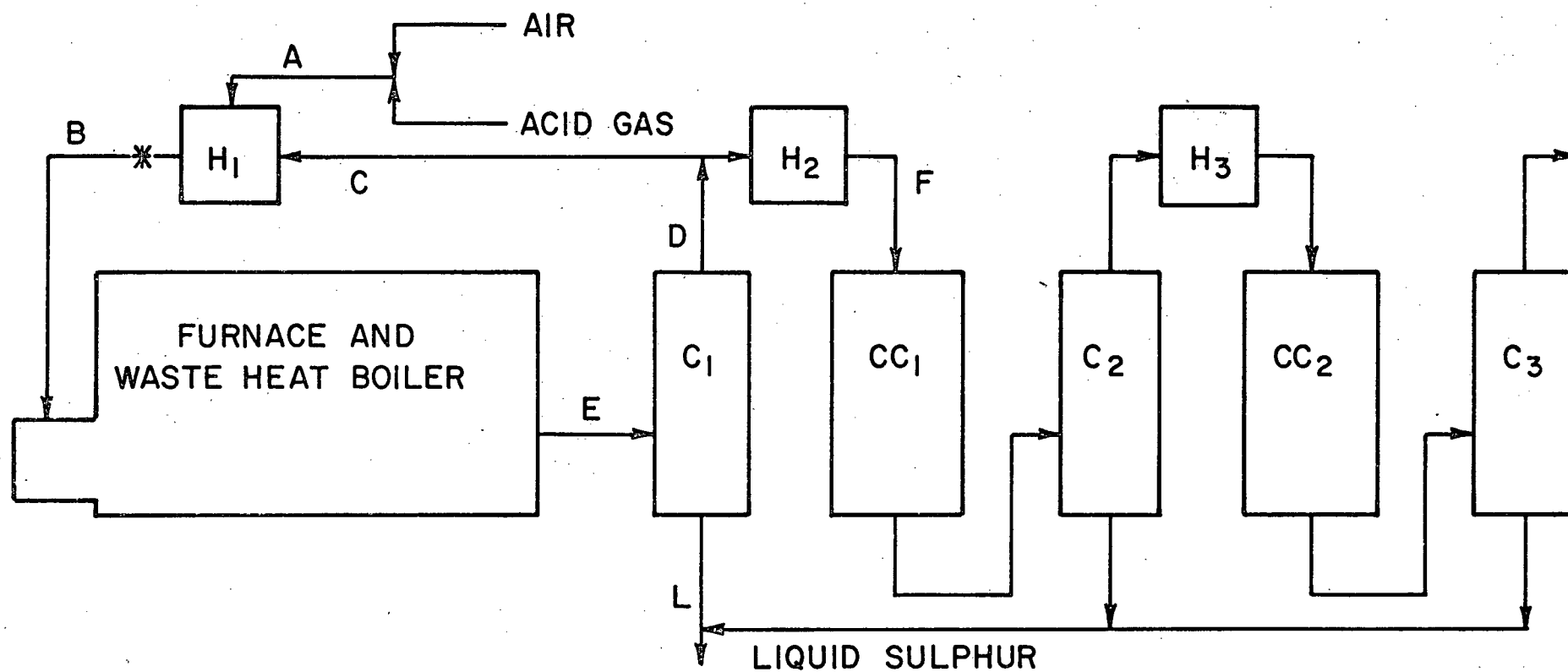


Figure 3.1. Flowsheet of Claus plant with preheat and recycle.

Legend: C--sulphur condenser
 CC--catalytic converter
 H--heater

the equilibrium composition, the following procedure, described in Chapter 2 is used:

(i) The partial pressures of the key components S_2 , H_2S , H_2O and N_2 are guessed.

(ii) The partial pressures of O_2 and H_2 are obtained from the law of mass action applied to Eqs. 3.1 and 3.2, i.e.,

$$[O_2] = K_{O_2}^2 [H_2O]^2 [S_2] / [H_2S]^2 \quad (3.3)$$

and

$$[H_2] = K_H [H_2O] / [O_2]^{\frac{1}{2}}. \quad (3.4)$$

(iii) The partial pressures of the elements S_2 , N_2 , O_2 and H_2 enable the compositions of the remaining species to be calculated from the reactions listed in Table 3.1.

(iv) With all partial pressures known, the total pressure P_T , and the ratios of both bound and free hydrogen to sulphur (R_{HS}), nitrogen to oxygen (R_{NO}) and oxygen to sulphur (R_{OS}) can be found and then compared to the corresponding desired values, P_T^* , R_{HS}^* , R_{NO}^* and R_{OS}^* . Since the total pressure is one atmosphere, $P_T^* = 1.0$; and since the acid gas is pure H_2S , and air is assumed to consist of 79% N_2 and 21% O_2 , $R_{HS}^* = 2$ and $R_{NO}^* = 3.76$. The oxygen to sulphur ratio can be freely specified, but according to Eq. 3.1, $R_{OS}^* = 1$ corresponds to stoichiometric amounts of O_2 and H_2S in the feed mixture.

(v) If P_T , R_{HS} , R_{NO} or R_{OS} deviate by more than 0.1% from the corresponding desired values, partial pressures of the key components are obtained from Eqs. 2.11 to 2.14.

(vi) Steps (ii) to (v) are repeated until convergence is obtained; the sulphur yield is found from

TABLE 3.1

EQUILIBRIUM EQUATIONS FOR THE SYSTEM H₂S-AIR

$1/2 \text{ N}_2$	$= \text{N}$	(1)
$1/2 \text{ N}_2 + 1/2 \text{ H}_2$	$= \text{NH}$	(2)
$1/2 \text{ N}_2 + \text{H}_2$	$= \text{NH}_2$	(3)
$1/2 \text{ N}_2 + 3/2 \text{ H}_2$	$= \text{NH}_3$	(4)
$1/2 \text{ N}_2 + 1/2 \text{ O}_2$	$= \text{NO}$	(5)
$1/2 \text{ N}_2 + \text{O}_2$	$= \text{NO}_2$	(6)
$1/2 \text{ N}_2 + 3/2 \text{ O}_2$	$= \text{NO}_3$	(7)
$\text{N}_2 + \text{H}_2$	$= \text{cis-N}_2\text{H}_2$	(8)
$\text{N}_2 + 2 \text{ H}_2$	$= \text{N}_2\text{H}_4$	(9)
$\text{N}_2 + 1/2 \text{ O}_2$	$= \text{N}_2\text{O}$	(10)
$\text{N}_2 + 3/2 \text{ O}_2$	$= \text{N}_2\text{O}_3$	(11)
$\text{N}_2 + 2 \text{ O}_2$	$= \text{N}_2\text{O}_4$	(12)
$\text{N}_2 + 5/2 \text{ O}_2$	$= \text{N}_2\text{O}_5$	(13)
$1/2 \text{ H}_2$	$= \text{H}$	(14)
$1/2 \text{ H}_2 + 1/2 \text{ N}_2 + 1/2 \text{ O}_2$	$= \text{HNO}$	(15)
$1/2 \text{ H}_2 + 1/2 \text{ N}_2 + \text{O}_2$	$= \text{cis-HNO}_2$	(16)
$1/2 \text{ H}_2 + 1/2 \text{ N}_2 + \text{O}_2$	$= \text{trans-HNO}_2$	(17)
$1/2 \text{ H}_2 + 1/2 \text{ N}_2 + 3/2 \text{ O}_2$	$= \text{HNO}_3$	(18)
$1/2 \text{ H}_2 + \text{O}_2$	$= \text{HO}_2$	(19)
$\text{H}_2 + \text{O}_2$	$= \text{H}_2\text{O}_2$	(20)
$\text{H}_2 + 1/2 \text{ S}_2 + 2 \text{ O}_2$	$= \text{H}_2\text{SO}_4$	(21)
$\text{H}_2 + \text{S}_2$	$= \text{H}_2\text{S}_2$	(22)
$1/2 \text{ O}_2$	$= \text{O}$	(23)
$1/2 \text{ O}_2 + 1/2 \text{ H}_2$	$= \text{OH}$	(24)
$3/2 \text{ O}_2$	$= \text{O}_3$	(25)
$1/2 \text{ S}_2$	$= \text{S}$	(26)
$1/2 \text{ S}_2 + 1/2 \text{ N}_2$	$= \text{SN}$	(27)
$1/2 \text{ S}_2 + 1/2 \text{ H}_2$	$= \text{SH}$	(28)
$1/2 \text{ S}_2 + 1/2 \text{ O}_2$	$= \text{SO}$	(29)
$1/2 \text{ S}_2 + \text{O}_2$	$= \text{SO}_2$	(30)
$1/2 \text{ S}_2 + 3/2 \text{ O}_2$	$= \text{SO}_3$	(31)
$\text{S}_2 + 1/2 \text{ O}_2$	$= \text{S}_2\text{O}$	(32)

Table 3.1 continued

$3/2 S_2$	$= S_3$	(33)
$2 S_2$	$= S_4$	(34)
$5/2 S_2$	$= S_5$	(35)
$3 S_2$	$= S_6$	(36)
$7/2 S_2$	$= S_7$	(37)
$4 S_2$	$= S_8$	(38)

$$Y = 100 [S_T] / \{ [H_2SO_4] + [SN] + [SH] + [H_2S] + 2 [H_2S_2] + [SO] + [SO_2] + [SO_3] + 2 [S_2O] + [S_T] \} \quad (3.5)$$

$$\text{where } [S_T] = \sum_{j=1}^8 j [S_j] \quad (3.6)$$

3.1.2 Impurities in Acid Gas

Under industrial conditions, the acid gas frequently contains CH_4 , CO_2 , H_2O and NH_3 in addition to H_2S . It is therefore desirable to consider carbon and nitrogen compounds as well, and the procedure described in Sect. 3.1.1 is revised slightly as follows:

- (i) Carbon dioxide is chosen as a fifth key component.
- (ii) Compounds whose concentrations were found to be always less than 0.1 ppm in Sect. 3.1.1 are neglected and the following carbon species are included in the calculations: HCN , C_2N_2 , CS_2 , C_2H_2 , CH_4 , C_2H_4 , C_2H_4O , CO , COS , CS as well as the key component, CO_2 . Since elemental carbon does not appear in the equilibrium mixtures to any significant extent, the carbon species are not considered to be formed from their elements, but rather from the equations shown in Table 3.2.
- (iii) In addition to R_{HS} , R_{NO} and R_{OS} , the ratio of carbon to sulphur, R_{CS} , must be considered. Since the feed can contain H_2O and NH_3 , R_{HS} and R_{NO} are no longer constant, but, like R_{OS} and R_{CS} , depend on the composition of the furnace feed.
- (iv) New guesses of the key components are calculated from Eq. 2.11 to 2.14 and from

$$[CO_2] = [CO_2]_0 \{ (P^*/P) (R_{CS}^*/R_{CS}) \}^{\frac{1}{2}} \quad (3.7)$$

The percentage sulphur yield is modified to include carbon compounds:

TABLE 3.2
EQUILIBRIUM EQUATIONS FOR THE SYSTEM
H₂S - AIR - CO₂ - NH₃

$1/2 \text{ N}_2 + 3/2 \text{ H}_2$	$= \text{NH}_3$	(1)
$1/2 \text{ N}_2 + 1/2 \text{ O}_2$	$= \text{NO}$	(2)
$1/2 \text{ H}_2$	$= \text{H}$	(3)
$\text{H}_2 + \text{S}_2$	$= \text{H}_2\text{S}_2$	(4)
$1/2 \text{ O}_2$	$= \text{O}$	(5)
$1/2 \text{ O}_2 + 1/2 \text{ H}_2$	$= \text{OH}$	(6)
$1/2 \text{ S}_2$	$= \text{S}$	(7)
$1/2 \text{ S}_2 + 1/2 \text{ N}_2$	$= \text{SN}$	(8)
$1/2 \text{ S}_2 + 1/2 \text{ H}_2$	$= \text{SH}$	(9)
$1/2 \text{ S}_2 + 1/2 \text{ O}_2$	$= \text{SO}$	(10)
$1/2 \text{ S}_2 + \text{O}_2$	$= \text{SO}_2$	(11)
$1/2 \text{ S}_2 + 3/2 \text{ O}_2$	$= \text{SO}_3$	(12)
$\text{S}_2 + 1/2 \text{ O}_2$	$= \text{S}_2\text{O}$	(13)
$3/2 \text{ S}_2$	$= \text{S}_3$	(14)
2 S_2	$= \text{S}_4$	(15)
$5/2 \text{ S}_2$	$= \text{S}_5$	(16)
3 S_2	$= \text{S}_6$	(17)
$7/2 \text{ S}_2$	$= \text{S}_7$	(18)
4 S_2	$= \text{S}_8$	(19)
$\text{CO}_2 + 1/2 \text{ N}_2 + 1/2 \text{ H}_2$	$= \text{HCN} + \text{O}_2$	(20)
2 HCN	$= \text{C}_2\text{N}_2 + \text{H}_2$	(21)
$\text{CO}_2 + 2 \text{ H}_2\text{S}$	$= \text{CS}_2 + 2 \text{ H}_2\text{O}$	(22)
$2 \text{ CS}_2 + \text{H}_2$	$= \text{C}_2\text{H}_2 + 2 \text{ S}_2$	(23)
$1/2 \text{ C}_2\text{H}_2 + 3/2 \text{ H}_2$	$= \text{CH}_4$	(24)
$\text{C}_2\text{H}_2 + \text{H}_2$	$= \text{C}_2\text{H}_4$	(25)
$\text{C}_2\text{H}_4 + 1/2 \text{ O}_2$	$= \text{C}_2\text{H}_4\text{O}$	(26)
CO_2	$= \text{CO} + 1/2 \text{ O}_2$	(27)
$\text{CO}_2 + \text{H}_2\text{S}$	$= \text{COS} + \text{H}_2\text{O}$	(28)
$\text{COS} + \text{H}_2$	$= \text{CS} + \text{H}_2\text{O}$	(29)

$$Y = 100 [S_T] / \{ [SN] + [SH] + [H_2S] + 2[H_2S_2] + [SO] + [SO_2] + [SO_3] + 2[S_2O] + 2[CS_2] + [COS] + [CS] + [ST] \} \quad (3.8)$$

3.1.3 Hydrogen Sulphide Dissociation

This thesis examines both H_2S oxidation and H_2S dissociation. The latter not only provides insight into Claus plant operation, but also, as will be described in the experimental section, is excellent for checking the operation of the apparatus.

If neither CO_2 nor H_2O is associated with the acid gas, compounds containing oxygen will not be present at equilibrium and the computer program* must therefore be modified to calculate H_2S dissociation. This is done by considering that H_2 is formed by the following reaction:



All other compounds are produced by the reactions shown in Table 3.3.

3.2 Adiabatic Flame Temperature

The method described in the preceding section enables the calculation of equilibrium compositions for given temperatures, pressures and feed compositions. However, since Claus furnaces operate adiabatically (heat losses are usually minor), the compositions and yields should be calculated at the adiabatic flame temperature (AFT). The following procedure was adopted in this study. First, a value of the AFT, say T_G , is guessed and the corresponding equilibrium composition is found by the method described in Sect. 3.1. Then the temperature, T , to which the mixture will rise is obtained from the heats of reaction and thermal data of the compounds. If T_G and T differ by more than $5^\circ K$, the procedure is repeated using T as the new guess, until convergence is reached.

The equation for calculating the AFT is:

*Table E.1 of Appendix E.

TABLE 3.3

EQUILIBRIUM EQUATIONS FOR THE SYSTEM $\text{H}_2\text{S} - \text{CH}_4 - \text{NH}_3$

$1/2 \text{ N}_2 + 3/2 \text{ H}_2 = \text{NH}_3$	(1)
$1/2 \text{ H}_2 = \text{H}$	(2)
$\text{H}_2 + \text{S}_2 = \text{H}_2\text{S}_2$	(3)
$1/2 \text{ H}_2 + 1/2 \text{ S}_2 = \text{SH}$	(4)
$1/2 \text{ N}_2 + 1/2 \text{ S}_2 = \text{SN}$	(5)
$1/2 \text{ S}_2 = \text{S}$	(6)
$3/2 \text{ S}_2 = \text{S}_3$	(7)
$2 \text{ S}_2 = \text{S}_4$	(8)
$5/2 \text{ S}_2 = \text{S}_5$	(9)
$3 \text{ S}_2 = \text{S}_6$	(10)
$7/2 \text{ S}_2 = \text{S}_7$	(11)
$4 \text{ S}_2 = \text{S}_8$	(12)
$1/2 \text{ N}_2 + \text{CH}_4 = \text{HCN} + 3/2 \text{ H}_2$	(13)
$2 \text{ HCN} = \text{C}_2\text{N}_2 + \text{H}_2$	(14)
$2 \text{ CS}_2 + \text{H}_2 = \text{C}_2\text{H}_2 + 2 \text{ S}_2$	(15)
$\text{C}_2\text{H}_2 + \text{H}_2 = \text{C}_2\text{H}_4$	(16)
$\text{CH}_4 + 1/2 \text{ S}_2 = \text{CS} + 2 \text{ H}_2$	(17)
$\text{CS} + 1/2 \text{ S}_2 = \text{CS}_2$	(18)

$$\sum_{i=1}^N n_{0,i} (H_{T_R}^{\circ} - H_{298}^{\circ})_i + \sum_{i=1}^N (n_i - n_{0,i}) (\Delta H_{f,298}^{\circ})_i$$

Heat released on cooling
the reactants to 298°K

Heat produced by the
reactions at 298°K

$$= \sum_{i=1}^N n_i (H_T^{\circ} - H_{298}^{\circ})_i \quad (3.10)$$

Heat required to heat the
products from 298°K to the AFT

where $n_{0,i}$, n_i = number of moles of species i present before reaction

and at the adiabatic flame temperature, respectively.

If species i is absent before reaction, $n_{0,i} = 0$; if

it is absent at the flame temperature, $n_i = 0$.

$H_{T_R}^{\circ}$, H_T° = enthalpy at T_R , and T , respectively, cal/mole

$(\Delta H_{f,298}^{\circ})_i$ = standard heat of formation of species i at 298°K,
cal/mole

N = total number of species

T_R = reactant temperature, °K

T = adiabatic flame temperature °K

Although the first term in Eq. 3.10 is easily calculated, it can usually be neglected, since $T_R \approx 298^{\circ}\text{K}$. Since T is not known, the last term is rewritten as

$$\sum_{i=1}^N n_i (H_T^{\circ} - H_{298}^{\circ})_i = \sum_{i=1}^N n_i \{ (H_{T_G}^{\circ} - H_{298}^{\circ})_i + \int_{T_G}^T C_{p_i}^{\circ} dT \}, \quad (3.11)$$

which may be approximated by

$$\sum_{i=1}^N n_i (H_T^{\circ} - H_{298}^{\circ})_i \approx \sum_{i=1}^N n_i [(H_{T_G}^{\circ} - H_{298}^{\circ})_i + C_{p_i}^{\circ} (T - T_G)] \quad (3.12)$$

The accuracy of this approximation increases as T_G approaches T .

Substituting Eq. 3.12 in 3.10 and solving for T yields:

$$T = T_G + \left\{ \sum_{i=1}^N n_{0,i} (H_{T_R}^\circ - H_{298}^\circ)_i + \sum_{i=1}^N (n_i - n_{0,i}) (\Delta H_{f,298}^\circ)_i \right. \\ \left. - \sum_{i=1}^N n_i (H_{T_G}^\circ - H_{298}^\circ)_i \right\} / \sum_{i=1}^N n_i C_{p,i} \quad (3.13)$$

Since Eq. 3.13 is written in terms of *moles* rather than partial pressures, both the feed and equilibrium compositions must be expressed in terms of moles.

3.3 Recycle

The effect of adding a recycle stream (c.f. Fig. 3.1) on the yield of a Claus furnace is subsequently examined. It is assumed that the condenser removes all elemental sulphur from stream E, i.e., stream D contains *no* elemental sulphur, whereas stream L contains *only* elemental sulphur. The temperature of every stream except E can be freely specified at the start of the recycle calculations, while that of stream E must be found from the adiabatic flame temperature calculations described in the previous section.

The compositions of the streams are computed as follows:

With a basis of 100 moles of acid gas, the moles of H_2S , H_2O , NH_3 , CO_2 and CH_4 in stream A are specified by the acid gas composition; O_2 and N_2 are computed from the amount of combustion air added to the acid gas.

The compositions of the other streams may be obtained from those of stream A by the following mass balances:

$$M_{e,B} = M_{e,A} + M_{e,C} \quad (3.14)$$

$$M_{e,C} = r M_{e,D} \quad (3.15)$$

$$M_{e,D} + M_{e,L} = M_{e,E} \quad (3.16)$$

$$M_{e,E} = M_{e,B} \quad (3.17)$$

$$M_{e,L} = (Y/100) M_{e,E} \quad (3.18)$$

where $M_{e,E}$ represents the total moles of element e (C, H, N, O or S) in stream E, r is the fraction of stream D recycled, subscripts A, B, C, D, E and L refer to the various streams and Y is the percent sulphur yield defined by Eq. 3.8. When the mass balances are made for an element other than sulphur, then $Y = 0$ to make $M_{e,L} = 0$. This follows since only sulphur is present in stream L. Substituting Eqs. 3.15 to 3.18 into Eq. 3.14 gives

$$M_{e,B} = M_{e,A} / (1 - r') \quad (3.19)$$

where r' is defined by

$$r' = r(1 - Y/100) \quad (3.20)$$

Eq. 3.14 to 3.20 enable the number of moles of element e in streams B to F to be calculated from the composition of stream A. The number of moles of compound i in a given stream, say stream E, is related to the total moles of element e by the equation

$$\sum_{i=1}^N j m_{i,E} = M_{e,E} \quad (3.21)$$

where j is the number of atoms of element e in compound i . For example, if e is hydrogen and i corresponds to H_2O , then $j = 2$, but, if i corresponds to C_2N_2 , then $j = 0$. The summation is over the total number of compounds, N .

Since the gases are assumed to be ideal, the number of moles of compound i is proportional to the partial pressure of i , i.e., for stream E,

$$m_{i,E} = \alpha P_i \quad (3.22)$$

Substituting Eq. 3.22 in Eq. 3.21 gives

$$\alpha \sum_{i=1}^N j P_i = M_{e,E} \quad (3.23)$$

Substituting Eq. 3.19 and 3.23 in Eq. 3.17 and solving for α gives

$$\alpha = M_{e,A} / \left[\sum_{i=1}^N P_i (1 - r') \right] \quad (3.24)$$

Since the gases are ideal, α should be the same for each element, but because of computer round-off error, slight variations occur and the mean value is therefore used.

From Eq. 3.22 and 3.24 the number of moles of each species in stream E is computed. Subsequently, the compositions of streams, B, C, D and F are found by mass balances.

The solution of the equations governing the recycle case, like that of the equilibrium compositions, is iterative. First, the ratios R_{CS} , R_{HS} , and R_{OS} at the mixing point * are guessed, then the equilibrium compositions, the yield and finally r' can be computed. For the k^{th} iteration, an improved guess of the ratio R_{eS} is given by

$$(R_{eS})_k = (M_{e,B} / M_{S,B})_k \quad (3.25)$$

where, in the denominator, $e = S$ has been substituted and elsewhere $e = C, H$ or O . Substituting Eq. 3.19 in the R.H.S. of Eq. 3.25, and noting that if $e \neq S$, $r' = r$, gives

$$(R_{eS})_k = [(M_{e,A} / M_{s,A}) (1 - r) / (1 - r')]_k \quad (3.26)$$

Since the fraction recycled (r), and the composition of stream A are both constant,

$$(R_{eS})_k = (M_{e,A} / M_{s,A}) (1 - r) / (1 - r'_k) \quad (3.27)$$

$$\text{Letting} \quad \beta = M_{e,A} / M_{s,A} \quad (3.28)$$

$$\text{and} \quad f_k = (1 - r) / (1 - r'_k) \quad (3.29)$$

and substituting Eqs. 3.28 and 3.29 in Eq. 3.27 yields

$$(R_{eS})_k = \beta f_k \quad (3.30)$$

or for the next iteration,

$$(R_{eS})_{k+1} = \beta f_{k+1} \quad (3.31)$$

From Eqs. 3.30 and 3.31,

$$(R_{es})_{k+1} = (R_{es})_k f_{i+1}/f_k. \quad (3.32)$$

If f_{k+1}/f_k deviates from unity by more than 0.1%, new ratios are obtained from Eq. 3.32; this enables the computation of revised equilibrium compositions, sulphur yield, r' , and finally k_{i+2} for the next iteration. For the first iteration, f_1 is set to unity, although a better procedure may be to guess the yield and substitute the resulting r' into Eq. 3.29 to obtain a guess of f_1 .

3.4 Thermochemical Data

In order to compute the equilibrium compositions and the adiabatic flame temperatures, thermochemical data are needed. For most compounds, data are listed in JANAF tables at intervals of 100°K and interpolation is therefore required. Thermochemical data in the form of power series offer the possibility of faster, more precise computation. For most compounds considered in this thesis, McBride et al.⁸ have published sets of coefficients a_1 to a_7 for the following equations:

$$\frac{C_p^\circ}{R} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 \quad (3.33)$$

$$\frac{H_T^\circ}{RT} = a_1 + \frac{a_2}{2} T + \frac{a_3}{3} T^2 + \frac{a_4}{4} T^3 + \frac{a_5}{5} T^4 + \frac{a_6}{T} \quad (3.34)$$

$$\frac{S_T^\circ}{R} = a_1 \ln T + a_2 T + \frac{a_3}{2} T^2 + \frac{a_4}{3} T^3 + \frac{a_5}{4} T^4 + a_7 \quad (3.35)$$

$$\frac{F_T^\circ}{RT} = a_1 (1 - \ln T) - \frac{a_2}{2} T - \frac{a_3}{6} T^2 - \frac{a_4}{12} T^3 - \frac{a_5}{20} T^4 + \frac{a_6}{T} - a_7 \quad (3.36)$$

The equilibrium constants may be obtained from

$$K_T = \exp(-\Delta F_T^\circ/RT), \quad (3.37)$$

where

$$\Delta F_T^\circ = \sum_{i=1}^N n_i (F_T^\circ)_i - \sum_{i=1}^N n_{0,i} (F_T^\circ)_i \quad (3.38)$$

For the species listed in Table 3.4, coefficients are not available. The coefficients for these compounds are found by simultaneous least squares approximation. This method, described in detail by Zeleznik and Gordon⁵¹ is used by McBride et al. for their calculations, yields the equation,

$$\underline{A} \underline{x}_i = \underline{d}_i, \quad (3.39)$$

where $\underline{x}_i^T = [a_1, a_2, \dots, a_{10}]$, and a_1 to a_7 are the coefficients, in Eq. 3.33 to 3.36 and a_8 to a_{10} are Lagrange multipliers. Matrix \underline{A} is constant but \underline{d}_i is a function of heat capacity, enthalpy and entropy of specie i . Zeleznik and Gordon noted that two sets of coefficients, one from 300°K to T_0 , the other from T_0 to 5000°K, gave a better fit of the data than just one set. McBride found that $T_0 = 1000^\circ\text{K}$ gave good results for most compounds. The elements of \underline{A} and of \underline{d}_i are listed in Tables 3.5 and 3.6 respectively.

Since \underline{A} is very ill-conditioned, it must be scaled by multiplying with \underline{F} which is given by

$$\underline{F} = \text{diag}[10^{-7}, 10^{-9}, 10^{-12}, 10^{-15}, 10^{-18}, 10^{-3}, 10^{-6}, 10^{-6}, 10^{-5}, 10^{-5}] \quad (3.40)$$

Multiplying both sides of Eq. 3.39 by \underline{F} , and solving for \underline{x}_i gives

$$\underline{x}_i = (\underline{F} \underline{A})^{-1} \underline{F} \underline{d}_i \quad (3.41)$$

the matrix $\underline{F} \underline{A}$ must be inverted by a double precision routine; single precision inversion gives erroneous results. For each compound in Table 3.4, two sets of coefficients are generated, one for temperatures below 1000°K, the other for temperatures above 1000°K.

McBride coefficients are calculated for the sulphur polymers S_3 to S_7 even though Rau et al.²⁴ provide an equation and coefficients for

TABLE 3.4

THERMOCHEMICAL DATA NOT AVAILABLE FROM McBRIDE ET AL.

Compound	Source of Data	Form of Data
H ₂ S ₂	Mackle and O'Hare ²²	300 to 1000°K in increments of 100°K
S ₃ to S ₇	Rau et al. ²⁴	Coefficients of equation for C _p
S ₈ , S ₂ O, C ₂ H ₄ O	JANAF ⁷	0 to 6000°K in increments of 100°K

TABLE 3.5

MATRIX \underline{A}

(See reference 51)

TABLE 3.6

VECTOR \underline{d}_i

(See reference 51)

heat capacity. Although this equation may be more accurate, the convenience of having the data in the same form for all the compounds, outweighs this advantage. To generate McBride coefficients for these sulphur polymers (S_3 to S_7), the heat capacity, enthalpy and entropy are needed in intervals of 100°K , from 300 to 5000°K . These data were generated from the equation given for C_p° by Rau et al.

$$C_p^\circ = A + (B \times 10^{-3}) T + (C \times 10^5) T^{-2} \quad (3.42)$$

and its derived functions,

$$\begin{aligned} H_T^\circ - H_{298}^\circ &= \int_{298}^T C_p^\circ dT \\ &= AT + 1/2(B \times 10^{-3}) T^2 - (C \times 10^5) T^{-1} + \Delta H_{f,298}^\circ \end{aligned} \quad (3.43)$$

$$\begin{aligned} \text{and } \Delta S^\circ &= \int_{298}^T (C_p^\circ/T) dT \\ &= A \ln T + (B \times 10^{-3}) T - 1/2(C \times 10^5) T^{-2} + S_{298}^\circ \end{aligned} \quad (3.44)$$

where the coefficients, A, B and C are listed for S_3 to S_7 in Table 3.7.

McBride coefficients for all compounds in Table 3.4 (except H_2S_2) were calculated for two temperature ranges: 300 to 1000°K and 1000. to 5000°K .

For H_2S_2 the second range was 1000 to 2000°K . [Data for H_2S_2 above 1000°K were estimated by plotting the given data (300 to 1000°K) and extrapolating to 2000°K .] Table 3.8 lists the elements of the symmetric matrix A of Eq. 3.39 for each of the three temperature ranges. Table 3.9 lists the McBride coefficients for H_2S_2 , S_3 , S_4 , S_5 , S_6 , S_7 , S_8 , S_2O , and C_2H_4O .

In summary, McBride coefficients for the thirty-six species assumed to be present at equilibrium were obtained from three sources:

- McBride et al.⁸ (most compounds);
- Data from JANAF tables⁷ (S_8 , S_2O , C_2H_4O) or Mackle and O'Hare²² (H_2S_2);
- Data generated by Eqs. 3.42 to 3.44 (S_3 to S_7).

TABLE 3.7
HEAT CAPACITIES OF GASEOUS SULPHUR MOLECULES
FROM RAU ET AL.²⁴

Polymer	$C_p = A + 10^{-3} BT + 10^5 C T^{-2}$			(T in °K) ^a	
	A	B	C	ΔH_f° Kcal/mol	S° cal/mol/°K
S ₂	8.54	0.28	-0.79	31.20	54.40
S ₃	12.854	1.04	-1.554	33.81	64.39
S ₄	19.092	0.783	-2.820	34.84	74.22
S ₅	25.558	0.253	-3.771	26.14	73.74
S ₆	31.580	0.120	-4.400	24.36	84.60
S ₇	37.038	0.613	-4.723	27.17	97.41
S ₈	42.670	0.860	-5.110	24.32	102.76

^aEquation in the authors' computer program was used instead of that given in their Table 1, as the latter appeared to have an incorrect sign for an exponent.

TABLE 3.8

MATRIX A

(A) For $300 < T < 1000^{\circ}\text{K}$

3.45563D 02	4.18165D 04	1.76839D 07	1.05141D 10	7.31261D 12	1.42897D-02	5.12526D 01	1.00000D 00	1.00000D 00	6.90776D 00
4.18165D 04	8.55000D 06	5.02666D 09	3.69192D 12	2.98069D 15	4.00000D 00	5.20000D 03	1.00000D 03	5.00000D 02	1.00000D 03
1.76839D 07	5.02666D 09	3.44579D 12	2.75990D 15	2.35752D 18	1.73333D 03	1.90000D 06	1.00000D 06	3.33333D 05	5.00000D 05
1.05141D 10	3.69192D 12	2.75990D 15	2.32180D 18	2.04910D 21	9.50000D 05	1.00533D 09	1.00000D 09	2.50000D 08	3.33333D 08
7.31261D 12	2.98069D 15	2.35752D 18	2.04910D 21	1.84924D 24	6.03200D 08	6.32900D 11	1.00000D 12	2.00000D 11	2.50000D 11
1.42897D-02	4.00000D 00	1.73333D 03	9.50000D 05	6.03200D 08	2.99768D-05	0.00000D-01	0.00000D-01	1.00000D-03	0.00000D-01
5.12526D 01	5.20000D 03	1.90000D 06	1.00533D 09	6.32900D 11	0.00000D-01	8.00000D 00	0.00000D-01	0.00000D-01	1.00000D 00
1.00000D 00	1.00000D 03	1.00000D 06	1.00000D 09	1.00000D 12	0.00000D-01	0.00000D-01	0.00000D-01	0.00000D-01	0.00000D-01
1.00000D 00	5.00000D 02	3.33333D 05	2.50000D 08	2.00000D 11	1.00000D-03	0.00000D-01	0.00000D-01	0.00000D-01	0.00000D-01
6.90776D 00	1.00000D 03	5.00000D 05	3.33333D 08	2.50000D 11	0.00000D-01	1.00000D 00	0.00000D-01	0.00000D-01	0.00000D-01

(B) For $1000 < T < 5000^{\circ}\text{K}$

2.65844D 03	1.17937D 06	2.31782D 09	6.51016D 12	2.15458D 16	1.67024D-02	3.24488D 02	1.00000D 00	1.00000D 00	6.90776D 00
1.17937D 06	9.59400D 08	2.70600D 12	9.57415D 15	3.72991D 19	2.05000D 01	1.23000D 05	1.00000D 03	5.00000D 02	1.00000D 03
2.31782D 09	2.70600D 12	8.93587D 15	3.45362D 19	1.42493D 23	4.10000D 04	2.13200D 08	1.00000D 06	3.33333D 05	5.00000D 05
6.51016D 12	9.57415D 15	3.45362D 19	1.40334D 23	5.98688D 26	1.06600D 08	5.41200D 11	1.00000D 09	2.50000D 08	3.33333D 08
2.15458D 16	3.72991D 19	1.42493D 23	5.98688D 26	2.61365D 30	3.24720D 11	1.64128D 15	1.00000D 12	2.00000D 11	2.50000D 11
1.67024D-02	2.05000D 01	4.10000D 04	1.06600D 08	3.24720D 11	8.53650D-06	0.00000D-01	0.00000D-01	1.00000D-03	0.00000D-01
3.24488D 02	1.23000D 05	2.13200D 08	5.41200D 11	1.64128D 15	0.00000D-01	4.10000D 01	0.00000D-01	0.00000D-01	1.00000D 00
1.00000D 00	1.00000D 03	1.00000D 06	1.00000D 09	1.00000D 12	0.00000D-01	0.00000D-01	0.00000D-01	0.00000D-01	0.00000D-01
1.00000D 00	5.00000D 02	3.33333D 05	2.50000D 08	2.00000D 11	1.00000D-03	0.00000D-01	0.00000D-01	0.00000D-01	0.00000D-01
6.90776D 00	1.00000D 03	5.00000D 05	3.33333D 08	2.50000D 11	0.00000D-01	1.00000D 00	0.00000D-01	0.00000D-01	0.00000D-01

(C) For $1000 < T < 2000^{\circ}\text{K}$

6.07116D 02	1.45790D 05	1.29811D 08	1.56548D 11	2.16469D 14	7.68771D-03	8.01907D 01	1.00000D 00	1.00000D 00	6.90776D 00
1.45790D 05	5.81625D 07	7.01250D 10	1.03153D 14	1.64868D 17	5.50000D 00	1.65000D 04	1.00000D 03	5.00000D 02	1.00000D 03
1.29811D 08	7.01250D 10	9.62759D 13	1.52656D 17	2.56777D 20	5.50000D 03	1.29250D 07	1.00000D 06	3.33333D 05	5.00000D 05
1.56548D 11	1.03153D 14	1.52656D 17	2.52887D 20	4.38510D 23	6.46250D 06	1.40250D 10	1.00000D 09	2.50000D 08	3.33333D 08
2.16469D 14	1.64868D 17	2.56777D 20	4.38510D 23	7.76965D 26	8.41500D 09	1.76833D 13	1.00000D 12	2.00000D 11	2.50000D 11
7.68771D-03	5.50000D 00	5.50000D 03	6.46250D 06	8.41500D 09	5.63955D-06	0.00000D-01	0.00000D-01	1.00000D-03	0.00000D-01
8.01907D 01	1.65000D 04	1.29250D 07	1.40250D 10	1.76833D 13	0.00000D-01	1.10000D 01	0.00000D-01	0.00000D-01	1.00000D 00
1.00000D 00	1.00000D 03	1.00000D 06	1.00000D 09	1.00000D 12	0.00000D-01	0.00000D-01	0.00000D-01	0.00000D-01	0.00000D-01
1.00000D 00	5.00000D 02	3.33333D 05	2.50000D 08	2.00000D 11	1.00000D-03	0.00000D-01	0.00000D-01	0.00000D-01	0.00000D-01
6.90776D 00	1.00000D 03	5.00000D 05	3.33333D 08	2.50000D 11	0.00000D-01	1.00000D 00	0.00000D-01	0.00000D-01	0.00000D-01

TABLE 3.9

MCBRIDE COEFFICIENTS CALCULATED IN THIS THESIS

H2S2	A	2.983841E 00	1.827030E-02	-3.377943E-05	3.191604E-08	-1.133443E-11	-1.504930E 04	1.012199E 01	
	C	-4.006376E 00	3.825903E-02	-4.484299E-05	2.276628E-08	-4.119618E-12	-1.352112E 04	4.519797E 01	
S3	A	1.994550E 00	2.214285E-02	-4.199058E-05	3.693052E-08	-1.216380E-11	1.573815E 04	1.600090E 01	
	B	6.192672E 00	8.281507E-04	-1.300452E-07	2.445527E-11	-1.693141E-15	1.503796E 04	-3.352772E 00	
S4	A	1.419415E 00	4.014523E-02	-7.755356E-05	6.849166E-08	-2.264341E-11	1.588457E 04	2.017998E 01	
	B	9.087337E 00	9.843155E-04	-2.587690E-07	4.996914E-11	-3.547584E-15	1.461462E 04	-1.512070E 01	
S5	A	1.889776E 00	5.343961E-02	-1.040888E-04	9.198493E-08	-3.042697E-11	1.096717E 04	1.428267E 01	
	B	1.216487E 01	9.189248E-04	-3.478061E-07	6.733600E-11	-4.793224E-15	9.267043E 03	-3.301131E 01	
S6	A	3.111956E 00	6.210307E-02	-1.210310E-04	1.068742E-07	-3.532800E-11	9.444715E 03	1.083229E 01	
	B	1.507760E 01	9.862620E-04	-4.067890E-07	7.873088E-11	-5.602093E-15	7.463789E 03	-4.425087E 01	
S7	A	4.977823E 00	6.648612E-02	-1.289477E-04	1.135838E-07	-3.749137E-11	1.016442E 04	5.633759E 00	
	B	1.777322E 01	1.285839E-03	-4.266613E-07	8.207413E-11	-5.806909E-15	8.040461E 03	-5.330151E 01	
S8	A	8.134380E 00	6.201076E-02	-1.145798E-04	9.744235E-08	-3.135071E-11	7.830715E 03	-8.797317E 00	
	B	2.074677E 01	1.422980E-03	-6.253405E-07	1.211831E-10	-8.636866E-15	5.589266E 03	-6.770522E 01	
S20	A	2.981449E 00	1.117787E-02	-1.345013E-05	7.617597E-09	-1.632645E-12	-8.074227E 03	1.231663E 01	
	B	5.904741E 00	1.235819E-03	-5.453139E-07	1.065669E-10	-7.670578E-15	-8.775336E 03	-2.289682E 00	
C2H4O	A	9.748182E-01	1.200106E-02	2.404282E-05	-3.976852E-08	1.657641E-11	-7.099223E 03	1.933131E 01	
	B	4.341626E 00	1.423433E-02	-5.734252E-06	1.058247E-09	-7.337582E-14	-8.533711E 03	-7.169849E-01	
S2	R	A	2.062335E 00	1.084251E-02	-2.060508E-05	1.798278E-08	-5.884028E-12	1.475241E 04	1.316049E 01
S2	J	A	2.712902E 00	6.210468E-03	-9.188907E-06	6.495227E-09	-1.783368E-12	1.450320E 04	1.047553E 01
S2	M	A	2.699935E 00	6.274953E-03	-9.287078E-06	6.539327E-09	-1.780228E-12	1.450493E 04	1.053422E 01
S2	R	B	4.155184E 00	2.994199E-04	-6.805589E-08	1.286454E-11	-8.945445E-16	1.440128E 04	3.497378E 00
S2	J	B	4.192687E 00	3.777821E-04	-1.513399E-07	2.928021E-11	-2.086213E-15	1.418747E 04	3.277442E 00
S2	M	B	4.189693E 00	3.846970E-04	-1.556663E-07	3.036801E-11	-2.179585E-15	1.418813E 04	3.293030E 00

LEGEND: A--FOR 300 < T < 1000 K
 B--FOR 1000 < T < 5000 K
 C--FOR 1000 < T < 2000 K
 R--CALCULATED FROM RAU'S EQUATIONS
 J--CALCULATED FROM JANAF DATA
 M--COEFFICIENTS AS LISTED IN MCBRIDE ET AL

TABLE 3.10

COMPARISON OF STANDARD ERRORS OF DATA OF S_2
GENERATED FROM McBRIDE COEFFICIENTS

Source	C_p		$H_T - H_{298}$		S_T	
	σ_1	σ_2	σ_1	σ_2	σ_1	σ_2
McBride et al. ⁸	0.001	0.002	0.000	0.144	0.000	0.064
This thesis + JANAF ⁷	0.001	0.002	0.001	0.144	0.000	0.063
This thesis + Eqs. 3.42 to 3.44	0.028	0.058	0.008	0.189	0.052	0.047

$$\sigma_1 = \left[\frac{1000 \sum_{T=300} (X_T - \hat{X}_T)^2}{n_1 - 1} \right]^{\frac{1}{2}}$$

$$\sigma_2 = \left[\frac{5000 \sum_{T=1000} (X_T - \hat{X}_t)^2}{n_2 - 1} \right]^{\frac{1}{2}}$$

where $X = C_{p_T}$, $H_T - H_{298}$ or S_T listed in JANAF tables for temperature T

$\hat{X} = C_{p_T}$, $H_T - H_{298}$ or S_T calculated from McBride coefficients

for temperature T

T = temperature in °K

n_1, n_2 = the number of temperature intervals in the summation

($n_1 = 8$; $n_2 = 41$)

Since McBride coefficients for S_2 can be obtained from each of these three sources, a comparison of their accuracy could be made. Table 3.10 shows that the standard error of thermochemical data generated by McBride coefficients from each of the three sources is less than 10%.

Thus, McBride coefficients are an accurate, convenient way of representing thermochemical data.

3.5 Vapour Pressure of Sulphur

Sulphur condenses when the sum of the partial pressures of the various sulphur species, i.e.,

$$P_s = \sum_{j=1}^8 [S_j], \quad (3.45)$$

exceeds the saturated vapour pressure of sulphur. An equation for the latter can be obtained by fitting a curve to the data of West.⁵²

The author reported vapour pressure-temperature data for sulphur between 393 and 919°K and two equations, listed in Table 3.11, one valid below 573°K, the other for temperatures between 573 and 823 °K. At 573°K, however, the vapour pressures given by the two equations differed by almost 20%. Likewise two equations provided by *The Sulphur Data Book*⁵³ disagreed by over 4% at the common point. The single equation given by Rau et al.⁵⁴ did not cover the entire range desired. It was therefore decided to fit the data of West et al. to a single equation valid from 393 to 919°K. The equation used is

$$\ln P_v = 3.77978 + 1.91809 \times 10^{-6} T^2 - 796.138 T^{-1} - 1,883,640 T^{-2} \quad (3.46)$$

where P_v is in atmospheres and T is in °K. The coefficient of determination (r^2) was 0.99999. This equation gives a better fit to the experimental data of West et al. than any of the equations listed in Table 3.11.

TABLE 3.11

EQUATIONS FOR VAPOUR PRESSURE OF SULPHUR

Source	Range (°K)	Equation
West ⁵²	373 to 573	$\log_{10} P = 6.04892 - 4087.8/T$
	573 to 823	$\log_{10} P = 4.57579 - 3288.5/T$
Sulphur Data Book ⁵³	393 to 598	$\log_{10} P = 11.8 - 0.006228T - 5405.1/T$
	598 to 823	$\log_{10} P = 4.57579 - 3288.5/T$
Rau et al. ⁵⁴	590 to 1313	$\log_{10} P = 60.9106 - 24,971/T + 1.0817 \times 10^7/T^2$ $- 2.2060 \times 10^9/T^3 - 14.4102 \log_{10} T$

P is in atmospheres; T in °K

CHAPTER 4

EXPERIMENTAL APPARATUS

4.1 Requirements of the Apparatus

The experimental equipment must be capable of providing feed mixtures having known ratios of air to hydrogen sulphide, heating these mixtures to a given temperature (between 800 and 1500°K) and letting the mixtures come to equilibrium at one atmosphere pressure.

In situ analysis of the gas mixture in the equilibrium vessel was rejected because of complexity and expense. The reaction products therefore had to be sampled before analysis. The sampling procedure had to have the following characteristics:

- speed to quench the gases rapidly and prevent reversion;
- removal of condensed sulphur before it could clog the valves and lines;
- removal of condensed water which catalyses the reaction between H_2S and SO_2 .

Since theory predicts that H_2 , H_2S , SO_2 , N_2 , H_2O and sulphur vapour are present in quantities exceeding 1%, and since the water and sulphur are removed during sampling, an analysis technique was sought which determined the concentrations of just H_2 , H_2S , SO_2 and N_2 .

4.2 Apparatus and Principles of Operation

The following sections describe the apparatus and how it was designed to meet the requirements given in the previous section. The equipment is shown in Figs. 4.1 and 4.2 and important components of the

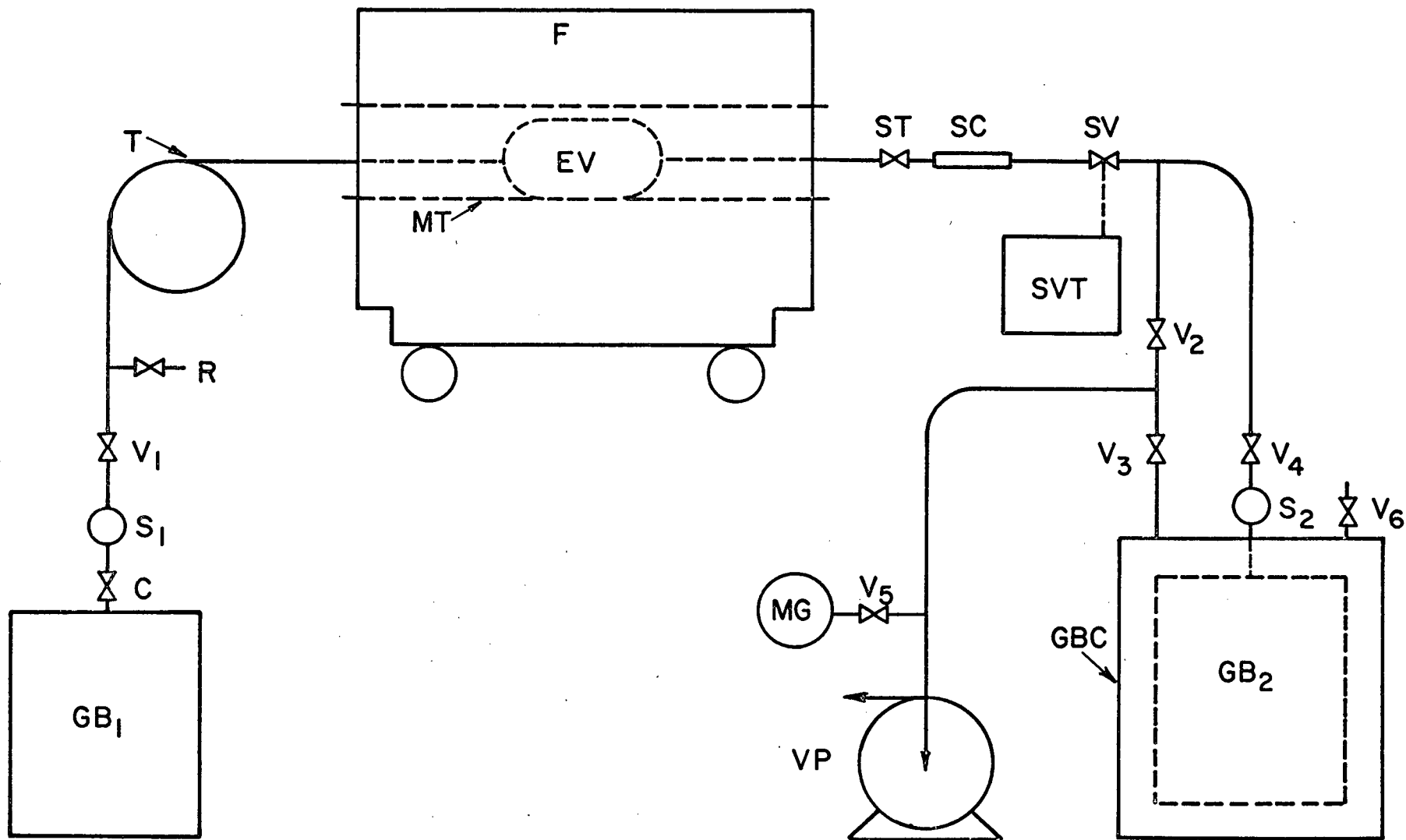


Figure 4.1. Schematic diagram of the experimental apparatus.
The legend is on page 58.

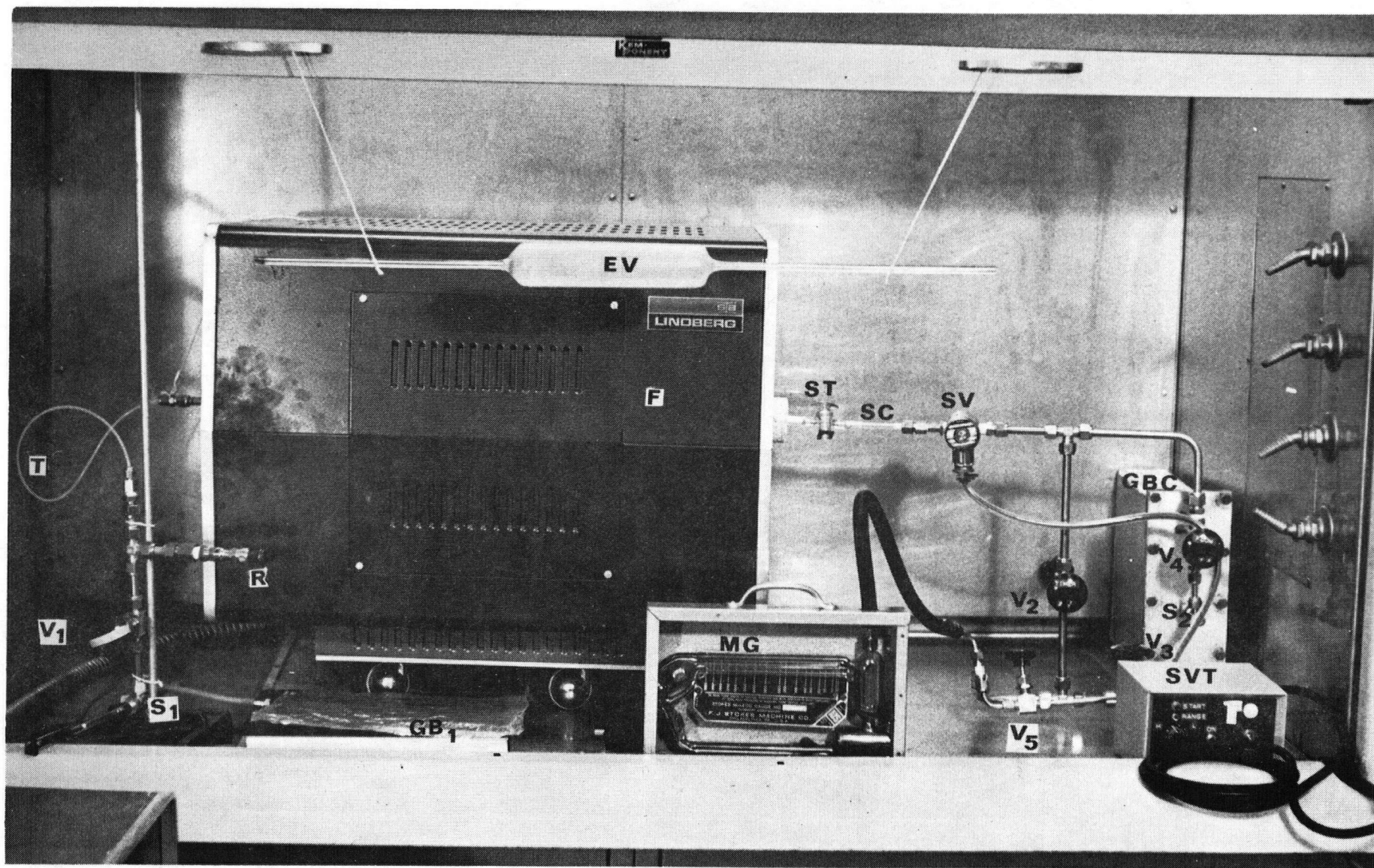


Figure 4.2. Experimental apparatus. (The equilibrium vessel has been removed from the furnace to show its shape and size.)

The legend is on page 58.

Legend for Figures 4.1 and 4.2

C	Clamp
EV	Equilibrium vessel
F	Furnace
GB ₁ ,GB ₂	Gas bag for feed and product mixtures, respectively
GBC	Gas bag container
MG	McLeod gauge
MT	Mullite tube
R	Pressure relief valve
S ₁ and S ₂	Septums
SC	P ₂ O ₅ scrubber
ST	Stopcock
SV	Solenoid valve
SVT	Solenoid valve timer
T	Tygon tubing
V ₁ to V ₆	Stainless steel valves
VP	Vacuum pump

apparatus are listed in Table 4.1. Details of the operating procedure are given in Appendix A.

4.2.1 Feed Mixture Preparation

The feed mixtures were prepared by blending streams of air and hydrogen sulphide in the desired ratios. The flow of C.P. grade H_2S (from a lecture bottle) was metered by a Gilmont rotameter (model F2000, size 10) whereas the air flow was determined with another Gilmont rotameter (model F1100, size 1). The feed mixture was stored in 2-litre Tedlar gas bags (supplied by Environmental Measurements Inc.) until needed.

Instead of first collecting the air- H_2S mixture in a gas bag, one might also consider passing it directly through the equilibrium vessel. In a series of experiments, metered flows of air and H_2S were passed through a 10 mm ID Vycor tube located in a small furnace. Reaction products were sampled from the exit of the tube. The apparatus, however, was unsatisfactory for two main reasons:

- At low flow rates, the residence time was sufficient for the gases to attain chemical equilibrium, but the heat transfer was poor and the gases did not reach the desired temperature.
- At high flow rates, the heat transfer was good, but residence times were too low for the gases to reach chemical equilibrium.

4.2.2 Furnace

A Lindberg furnace (model 54233), capable of attaining a temperature of $1500^{\circ}C$, and controllable to within $\pm 1^{\circ}C$, was chosen for this work. The furnace, which is 635 mm long, contains eight SiC heating elements which are spaced in such a way that a 200 mm long zone is created where the temperature is uniform within $\pm 5^{\circ}C$. To enable easy positioning,

TABLE 4.1
LIST OF EQUIPMENT

Code used in Figs.4.1 and 4.2	Item	Supplier	Model	Comments
	<i>Gases</i>			
-	Nitrogen	Air Liquide	Cylinder	-
-	Hydrogen	Air Liquide	Cylinder	-
-	Hydrogen sulphide	Matheson	Lecture bottle	-
-	Sulphur dioxide	Matheson	Lecture bottle	-
	<i>Chromatograph</i>			
-	Gas Chromatograph	Beckman	GC-2	-
-	Recorder	Sargent	SRG	with Disc integrator
-	Chart paper	Graphic Controls	S-72168	-
-	Gas drier	Chemical Research Supplies	-	-
S	Septa	Chromatograph Specialities	Grey	silicone rubber 12.5 mm and 9.5 mm dia.
-	Syringe	Hamilton	1005 LLCH	5 ml capacity
-	Syringe needles	Hamilton	N722, Pt 3. 50 mm long	22 gauge
	<i>Gas bags</i>			
GB	Gas bag	Environmental Measurements, Inc.	10-011	du Pont Tedlar, 240mm×300mm (2 litres)
GBC	Gas bag container	-	-	60mm×230mm× 310mm
	<i>Valves, etc.</i>			
-	N ₂ regulator	Air Liquide	1040	-
-	H ₂ regulator	Air Liquide	1040	-
-	Lecture bottle valves (2)	Air Liquide	2080	For hose connection
ST	Stopcock	Corning	-	
V ₁ -V ₄	Valves (4)	Whitey	SS-IRS4	1/4"
V ₅	Valve	Whitey	SS-IRS6	1/8"

Table 4.1 continued

Code used in Figs. 4.1 and 4.2	Item	Supplier	Model	Comments
SV	Solenoid	Skinner Electric	V52 DB2100	1/8" orifice diam.
SVT	Solenoid timer	-	-	0.05 to 2.3 seconds range
R	Pressure Relief Valve	Swagelok	SS-6R-10	Releases at 5 psig
T	Teflon Tubing	Cadillac Plas- tics	2mm ID×3mm OD	-
SC	P ₂ O ₅ Scrubber	-	5mm ID×7mm OD ×100mm long	Tube filled with P ₂ O ₅ ; ends plugged with glass wool
<i>Rotameters</i>				
-	Rotameters (2)	Gilmont	F2000 Size 10	0.2-90ml/min air
-	Rotameter	Gilmont	F1100 Size 1	1-280ml/min air
-	Rotameter	Gilmont	F1200 Size 2	20-2100ml/min air
<i>High Temp. Equipment</i>				
F	Furnace	Lindberg	54233	50mm 300mm heated zone
-	Controller	Lindberg	59545	-
MT	Mullite Tube	McDanel Refractory	PT134	46mm ID×51mm OD×635mm
QT	Quartz Tubing	Quartz Scientific	QT2E QT40D	2mm ID×8mm OD 40mm ID×44mm OD
<i>Vacuum Equipment</i>				
VP	Vacuum Pump	W. M. Welch	"Duo Seal"	-
MG	McLeod Gauge	F. J. Stokes	-	-

the furnace was placed on a pallet equipped with wheels.

4.2.3 Quartz Equilibrium Vessel

Quartz was selected as the material of construction of the vessel because it can withstand temperatures of up to 1250°C, yet is comparatively easy to work into the desired "pipette" shape. Such a shape takes advantage of the "flat zone" of the furnace. The "bulb" of the pipette, 40mm ID × 200mm long and containing about 250 ml, lies entirely within the flat temperature zone of the furnace. Gases are supplied to, and withdrawn from the vessel through two quartz capillary tubes (2mm ID × 8mm OD × 280mm long) which have a combined capacity of 2ml, and which extend beyond the flat zone. The pipette shape of the vessel therefore enables over 99% of its contents to attain a uniform temperature and composition, provided the residence time is sufficiently long. The quartz equilibrium vessel rests on a mullite tube (46mm ID × 51mm OD × 635mm long) which was inserted into the furnace chamber.

4.2.4 Sampling

The sampling system consists of a gas bag (placed inside a metal container), valves, fittings and a vacuum pump. Before a sample can be taken, both the gas bag and its container are evacuated to about 300 μ Hg vacuum (valves $V_2 - V_5$ of Fig. 4.1 open, V_6 and the solenoid closed). To sample, valve V_2 is first closed (to prevent the sample from being drawn into the vacuum pump), the stopcock ST is opened and the solenoid valve is activated. A timing circuit opens the solenoid valve for a predetermined period, e.g., two seconds. Sampled gases flow rapidly into the gas bag because of the pressure difference. Initially the pressure in the vessel is one atmosphere, whereas the pressure inside the gas bag is about 300 μ Hg. After sampling, the corresponding

pressures are about 0.8 and 0.02 atm., assuming that a 50ml sample (at S.T.P.) is taken. Opening valve V_6 restores the pressure in the container and gas bag to one atmosphere. Opening clamp C and valve V_1 restores the reactor pressure to atmospheric conditions by drawing an additional amount of the air- H_2S feed mixture into the equilibrium vessel. To ensure that equilibrium had been attained, samples were withdrawn after the gas mixtures had resided in the equilibrium vessel for various periods of time.

A glass tube containing phosphorus pentoxide (P_2O_5) is located in the sampling line just upstream of the solenoid valve. The purpose of the P_2O_5 is to remove liquid water which is capable of catalysing the reaction between H_2S and SO_2 . The desiccant is periodically replaced to ensure adequate absorbancy. The stopcock ST isolates the contents of the equilibrium vessel from the P_2O_5 and is opened only just before sampling.

4.3 Gas Chromatography

Gas chromatography was chosen as the method of analysis because it is fairly simple, rapid and inexpensive. Furthermore, a Beckman GC-2 chromatograph was available.

4.3.1 Requirements of the G.C. Column

The column used in the gas chromatograph should have the following properties:

- separate H_2 , N_2 , H_2S and SO_2 , which are the gases expected to be present in significant concentrations;
- operate at close to ambient temperature to minimise reaction of H_2S with SO_2 in the column.

4.3.2 Analysis of Four Compounds

An attempt was made to devise a chromatographic system to separate and detect the following four compounds: H_2 , N_2 , H_2S and SO_2 . Three

pressures are about 0.8 and 0.02 atm., assuming that a 50ml sample (at S.T.P.) is taken. Opening valve V_6 restores the pressure in the container and gas bag to one atmosphere. Opening clamp C and valve V_1 restores the reactor pressure to atmospheric conditions by drawing an additional amount of the air- H_2S feed mixture into the equilibrium vessel. To ensure that equilibrium had been attained, samples were withdrawn after the gas mixtures had resided in the equilibrium vessel for various periods of time.

A glass tube containing phosphorous pentoxide (P_2O_5) is located in the sampling line just upstream of the solenoid valve. The purpose of the P_2O_5 is to remove liquid water which is capable of catalysing the reaction between H_2S and SO_2 . The desiccant is periodically replaced to ensure adequate absorbancy. The stopcock ST isolates the contents of the equilibrium vessel from the P_2O_5 and is opened only just before sampling.

4.3 Gas Chromatography

Gas chromatography was chosen as the method of analysis because it is fairly simple, rapid and inexpensive. Furthermore, a Beckman GC-2 chromatograph was available.

4.3.1 Requirements of the G.C. Column

The column used in the gas chromatograph should have the following properties:

- separate H_2 , N_2 , H_2S and SO_2 , which are the gases expected to be present in significant concentrations;
- operate at close to ambient temperature to minimise reaction of H_2S with SO_2 in the column.

4.3.2 Analysis of Four Compounds

An attempt was made to devise a chromatographic system to separate and detect the following four compounds: H_2 , N_2 , H_2S and SO_2 . Three

different arrangements were examined. Although none proved to be successful, each method is described briefly in the following section and summarised in Table 4.2.

4.3.2.1. Single column operating isothermally. The simplest way is to separate H_2 , N_2 , H_2S and SO_2 with a single column maintained at a constant temperature. Table 4.3 summarises references dealing with the chromatographic separation of gas mixtures containing H_2S and/or SO_2 . None of these references describes single columns which operate isothermally and are capable of separating H_2 , N_2 , H_2S and SO_2 in percent quantities. Supelco⁵⁵ suggested a 1.8m column of Porapak Q for the separation of N_2 , H_2S and SO_2 . To separate H_2 and N_2 as well would require a column about 6m long and this was excessive for the Beckman GC-2, due to pressure drop considerations.

4.3.2.2. Three columns operating isothermally. A 1.8m \times 3mm column of molecular sieve 5A (80/100 mesh) separated H_2 and N_2 but permanently adsorbed H_2S and SO_2 . On the other hand, a 1.8m column of Porapak Q separated N_2 , H_2S and SO_2 (H_2 and N_2 eluted together, forming a composite peak). An analysis of all four compounds could therefore be achieved, at least in principle, by using three columns in series. The first column would be Porapak Q, which separates H_2S and SO_2 . This is followed by a column of KOH to remove H_2S and SO_2 before the remaining gases pass into the third column containing the molecular sieve. The last column then separates H_2 and N_2 . However, due to pressure drop restrictions, the available chromatograph could not handle columns longer than about 3m. The total length of the three column system was, however, greater than this and the arrangement had to be abandoned.

TABLE 4.2

POSSIBLE CHROMATOGRAPHIC COLUMNS FOR SEPARATING
H₂, N₂, H₂S AND SO₂

	Supplier		
	Supelco ⁵⁵	Chromatographic Specialities ⁵⁶	Analabs ⁵⁷
Column	6m Porapak QS	0.5m×3mm Porapak QS and 1.8m×3mm molecular sieve 5A	1m×3mm Spherocarb
Operating Conditions	Isothermal	Porapak QS separates H ₂ S and SO ₂ which are analysed and then absorbed by KOH. The molecular sieve then separates H ₂ and N ₂	H ₂ and N ₂ are separated at 40°C; H ₂ S and SO ₂ are separated at 180°C
Reason for Rejection	Column is too long for available G.C. due to pressure drop restriction	Columns are too long for available G.C.	The "Thermotrac" temperature programming attachment for the Beckman GC-2 did not work properly

TABLE 4.3

GAS CHROMATOGRAPHY REFERENCES FOR SEPARATIONS INVOLVING

 H_2S AND/OR SO_2

Unless otherwise noted, a thermal conductivity detector and H₂ carrier gas were used

Abbreviation: NS = not stated

Authors										
Robbins et al ⁵⁸ 1964		Hodges and Matson ⁵⁹ 1964			Koppe and Adams ⁶⁰ 1967		Jones ⁶¹ 1967	Obermiller and Charlier ^{62 63} 1967 1968		Applebury & Schaer ⁶⁴ 1970
Column: Length(m) OD(mm)	6×6	1.8×6	1.8×6	0.3×6	2.4×5	1.8×5	3×6	3×3	1.5×1.5	1.8×6
Packing material	Dibutyl Sebacate on Fluoropak	Triton X-305 on Dia- toport S	Benzo cello- solve	Silica gel	Triton X-305 on Chromo- sorb G	PorapakQ	PorapakQ	PorapakQ	PorapakQ	PorapakQ
Temperature(°C)	60	25to75	30	100	30to70	60to140	ambto125	90	75	90
Gases of inter- est separated	H ₂ ,N ₂ ,H ₂ S,SO ₂	Air, H ₂ S, SO ₂			H ₂ S,SO ₂		H ₂ ,N ₂ ,H ₂ S	N ₂ ,H ₂ S,SO ₂		H ₂ S,SO ₂
SO ₂ elution(min)	15	6	12	10	7	NS	-	6	4	NS
Comments	-Three columns were needed, each operated at a different temperature -Total length of 6m was excessive	-Authors found silica gel best -Best temperature was 120°C			-Triton X gave better separ- ation than did PorapakQ (ppb quantities) -Microcoulo- metric detector (M.C.D.) was used		-Two columns, one "hot" and one "cold" were required -He/H ₂ carrier was used	-Two columns were required one at -70°C and the other at 90°C		-PorapakQ absorbed small quantities of SO ₂ (ppm quantities) -M.C.D. used

Thornsberry ⁶⁵ 1971			Anon ⁶⁶ 1972	Bollman and Mortimore ⁶⁷ 1972	Bremner and Banwart ⁶⁸ 1974	Murdock and Atwood ⁶⁹ 1974	de Souza et al ⁷⁰ 1975	Supelco Inc ⁷¹ 1976	Supelco Inc ⁷² 1977	Analabs Inc ⁵⁷ 1977
1.8×6	0.6×6	1×3	0.6×6	1.8×2 ID	3.7×5	0.5×3	0.5×3	1.8×4	0.9×3	
PorapakQS	Acid-washed Deactigel	Acid-washed Deactigel	Carbon molecular sieve	Chromosil 310	PorapakQS and Porapak R in series	Acetone- washed PorapakQS	Carbo- sieve S	Chromosil 310	Sphero- carb	
98	122	50-150	175	40	95	30to210	100to250	40	150to200	
H ₂ S	SO ₂	H ₂ S	H ₂ S,SO ₂	H ₂ S,SO ₂	N ₂ ,H ₂ ,H ₂ S, SO ₂	H ₂ S,SO ₂	H ₂ S,SO ₂	H ₂ S,SO ₂	H ₂ S,SO ₂	
6	9	NA	6	2.5	NS	NS	7	6	5	
-Authors preferred Deactigel		-Tailing and adsorptive losses were noted -Flame photometric detector (F.P.D.) used with air as carrier gas	-Conditioning with H ₂ S was required -Best separation for H ₂ S was at 175°C	-Chromosil was best -Trace quantities of gases were studied -F.P.D. used with N ₂ as carrier gas	-	-Excessive SO ₂ tail- ing with acid- washed Deactigel -F.P.D. used	-No tailing	-Excellent separation of percent quantities	-A 2.9m column separated H ₂ and N ₂ at 40°C -May catalyse H ₂ S dissociation	

4.3.2.3. One column with temperature programming. A 0.9m x 3 mm column of Sphero carb separated H_2 and N_2 at 40°C, and H_2S and SO_2 between 150 and 200°C.* However, the available Beckman "Thermotrac" temperature programming system proved to be unsatisfactory, since it required two columns with identical pressure drops. If a more modern gas chromatograph had been available, then temperature programming would have been very promising.

4.3.3 Analysis of Three Compounds

Since no satisfactory method could be found to separate H_2 , N_2 , H_2S and SO_2 using the available gas chromatograph, it was decided to separate only H_2 , H_2S and SO_2 . If N_2 is chosen as the carrier gas, then the nitrogen of the sample passes through the gas chromatograph undetected and does not interfere with the hydrogen analysis. Hydrogen, H_2S and SO_2 are measured directly, whereas N_2 must be determined by difference.

The accuracy of this method is determined to a large degree by the response of H_2 , H_2S , and SO_2 obtained with N_2 as the carrier gas. Since the GC-2 was fitted with a thermal conductivity detector, the response to any compound is proportional to the difference between the thermal conductivity of the carrier gas and that of the compound. Table 4.4 shows that, although N_2 produces only a relatively fair response with H_2S and SO_2 , it results in a quite good response for H_2 . Since samples usually contain only about 2% H_2 , but as much as 10% H_2S and SO_2 , nitrogen nevertheless is an excellent carrier gas because it gives the highest sensitivity for the least plentiful compound. Furthermore, since N_2 constitutes up to 75% of the sample, little accuracy is lost by measuring the N_2 by difference. Consequently, this method of analysis can be

*The carrier gas was a H_2/He mixture.

TABLE 4.4

THERMAL CONDUCTIVITIES OF VARIOUS GASES
 AT 0°C⁷³. (The units for thermal
 conductivity are kerg/sec/°C/cm.)

Compound	Thermal Conductivity	Differences in Thermal Conductivity		
		He	N ₂	Ar
He	13.9	0.	-11.62	-12.32
N ₂	2.28	11.62	0.	-0.70
Ar	1.58	12.32	0.70	0.
H ₂	15.9	-2.0	-13.62	-14.32
H ₂ S	1.20	12.70	1.08	0.38
SO ₂	0.77	13.13	1.51	0.81

expected to have an accuracy similar to an arrangement capable of separating H_2 , N_2 , H_2S , and SO_2 .

4.3.4 Column Packings

Three column packings suggested in the literature were chosen for experimental evaluation: acid-washed Deactigel, Spherocarb and Porapak QS.

Acid-washed Deactigel was unsatisfactory because of excessive SO_2 tailing. For example, SO_2 injected into a $0.5m \times 3mm$ column at $70^\circ C$ with 40ml/min. N_2 carrier gas started to elute after 5 min., but had not completely eluted after over 15 min.

Spherocarb was rejected because it absorbed H_2S and SO_2 at temperatures below $100^\circ C$. Above $100^\circ C$, it appeared to catalyse H_2S dissociation, to some extent. Injecting H_2S into a $1.8m \times 3mm$ stainless steel column of 100/120 mesh Spherocarb and using 40ml/min of N_2 as carrier gas, produced a single *negative* peak although H_2S should have given a *positive* peak. It is possible that this negative peak can be produced even when H_2 and H_2S occur simultaneously. With N_2 as the carrier gas, a thermal conductivity detector is over twelve times as sensitive to H_2 as it is to H_2S , and hence would produce a negative peak even if both gases were present in similar concentrations.

The third material tested, Porapak QS, proved to be excellent for separating H_2 , H_2S and SO_2 . Operating under the conditions listed in Table 4.5, chromatograms of the type shown in Fig. 4.3 could be obtained. Sulphur dioxide tailing was small, and the analysis could be completed in just over three minutes. Reproducibility was excellent, with typical errors for H_2 , H_2S and SO_2 being 2, 3 and 5%, respectively. Due to its excellent performance, Porapak QS was chosen as the column packing.

Teflon was selected as the tubing material because Koppe and Adams⁶⁰

TABLE 4.5

OPERATING CONDITIONS OF THE GAS CHROMATOGRAPH

Tubing:	1.1m × 3mm F.E.P. (Teflon)
Packing:	Porapak QS, 80/100 mesh
Column Temperature:	40°C
Carrier gas:	Nitrogen
Inlet pressure:	20 psig
Flow rate:	60ml/min at 25°C and 1 atmosphere
Detector:	Thermal conductivity
Current:	150 mA
Attenuation:	-5.0 for H ₂ ; 1.0 for H ₂ S and for SO ₂
Sample size:	5 ml
Composition:	H ₂ 0.5%
	H ₂ S 4.7%
	SO ₂ 7.1%
	N ₂ 87.7% (by difference)
Chart speed:	0.5 in/min

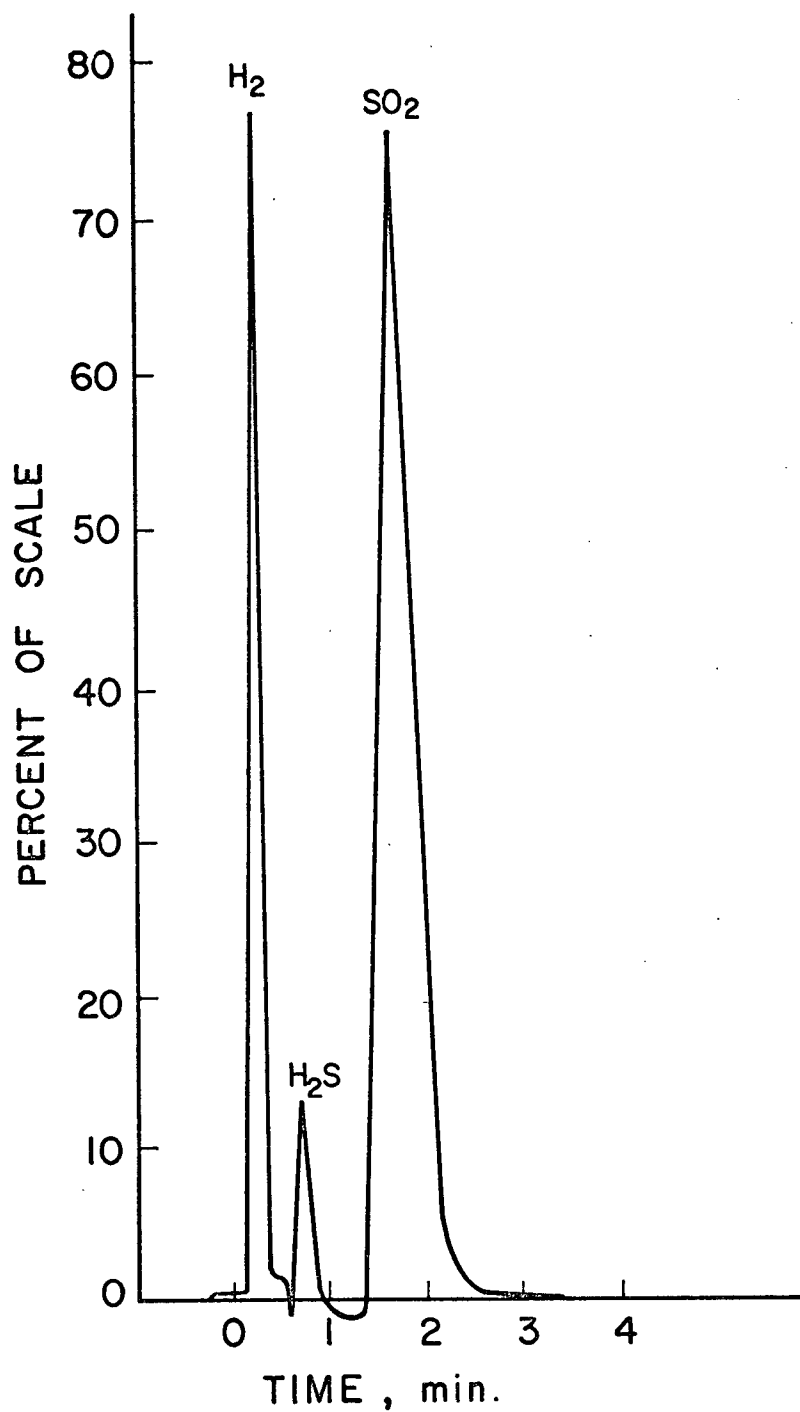


Figure 4.3. Typical chromatogram (Run 77).

found that it adsorbed less H_2S and SO_2 at 70°C than glass or stainless steel. Moreover, a Teflon tube is easy to pack and coil.

4.3.5 Calibration of the Gas Chromatograph

Calibration mixtures were prepared by combining, in the desired ratios, streams of H_2S (measured by Gilmont rotameter F2000, size 1) and N_2 (measured by Gilmont rotameter F1200, size 2). The mixture was sampled with a 5ml syringe inserted into a septum port in the lines. The sample was injected into the gas chromatograph and the area of the resulting peak measured. This procedure was repeated at other flow-rates of H_2S and N_2 to produce the compositions needed for the calibration curve. Curves for H_2 and SO_2 were obtained with the same apparatus in a similar manner. Using N_2 rather than air eliminated air peaks which interfere with the detection of H_2 . Sample calculations are presented in Appendix B.

Typical calibration curves are shown in Figs. 4.4 to 4.6. The data are fitted almost perfectly by straight lines with correlation coefficients (r^2) exceeding 0.9900. The data were processed by a Texas Instruments TI58 pocket programmable calculator using the program listed in Table B.1 of Appendix B.

4.4 Calculation of Mixture Compositions

This section develops the equations necessary for computing the composition of the air- H_2S feed mixture and the equilibrium vessel.

4.4.1 Calculation of the Feed Composition

In preparing a feed mixture it was necessary to know what rotameter positions corresponded to a given percent of stoichiometric air, P_A . If the amount of air is stoichiometric according to the reaction,

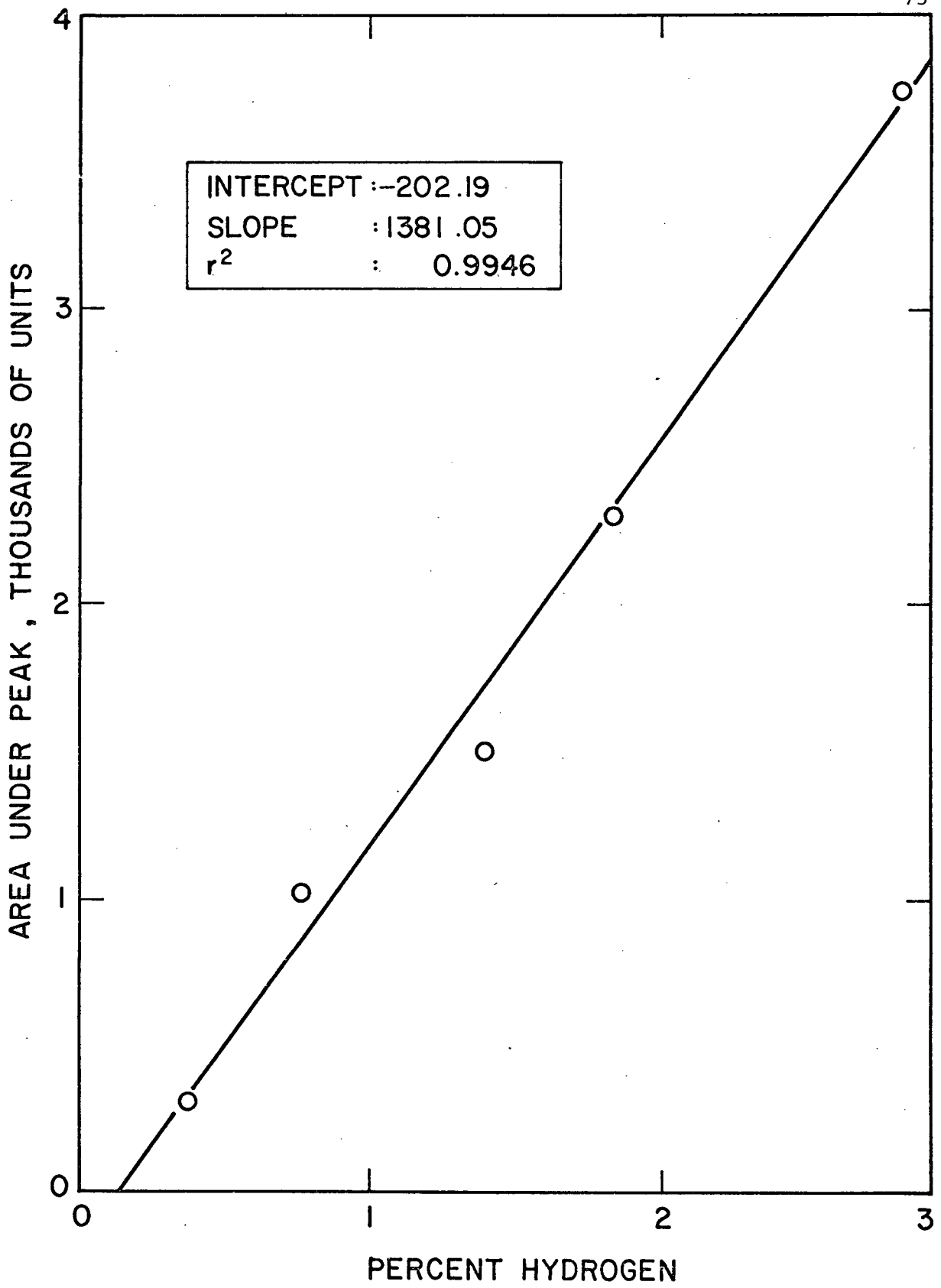


Figure 4.4. Typical calibration curve for H_2 (Run 77).

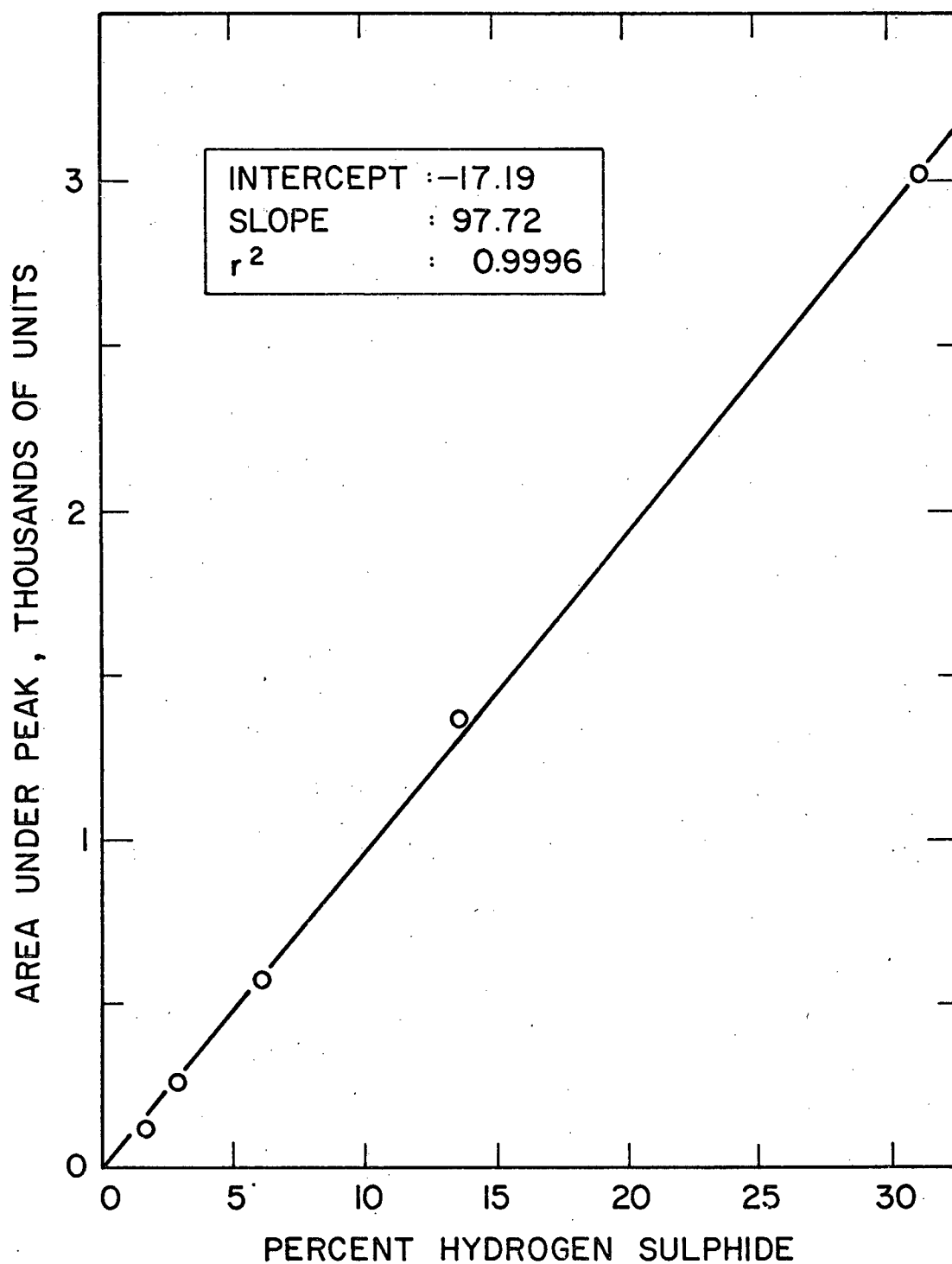


Figure 4.5. Typical calibration curve for H_2S (Run 77).

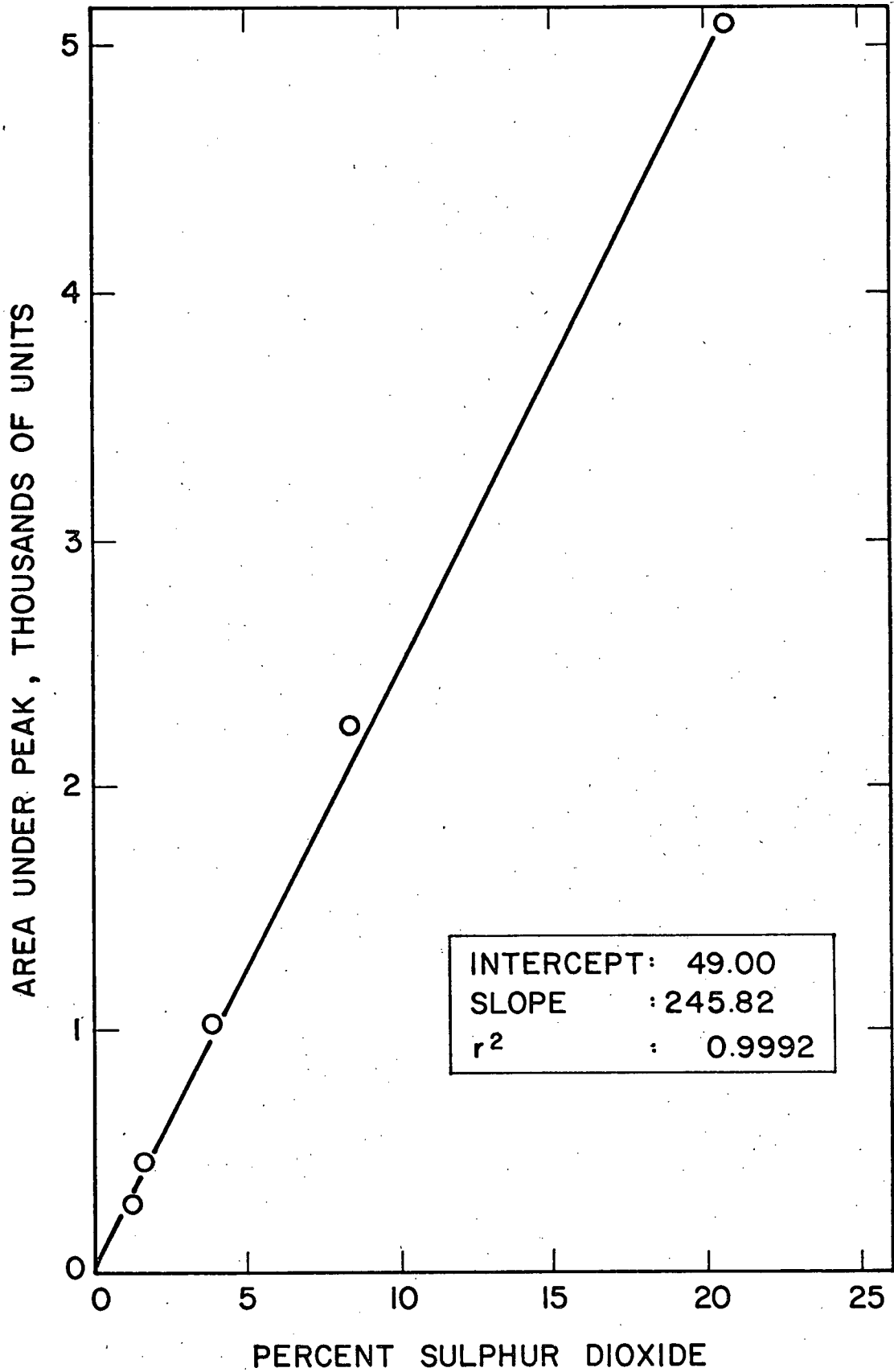
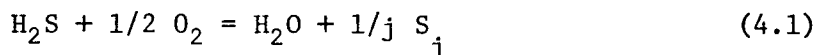


Figure 4.6. Typical calibration curve for SO_2 (Run 77).



then, the ratio of oxygen to H_2S is 0.5. The ratio of air to H_2S is therefore $(100/21) \times 0.5$, or 50/21. For any amount of air, then,

$$P_A = (Q_A/Q_{\text{H}_2\text{S}}) (21/50) \times 100 \quad (4.2)$$

where Q_A and $Q_{\text{H}_2\text{S}}$ are the flow rates of air and H_2S , respectively. The calibration curves for air and H_2S (Figs. C.5 and C.2 in Appendix C) may be represented by the following equations:

$$Q_A = m_A x_A + b_A \quad (4.3)$$

$$Q_{\text{H}_2\text{S}} = m_{\text{H}_2\text{S}} x_{\text{H}_2\text{S}} + b_{\text{H}_2\text{S}} \quad (4.4)$$

where m , b and x denote the slope, intercept and rotameter float position, respectively. Substituting Eqs. 4.3 and 4.4 into Eq. 4.2 gives

$$P_A = 42(m_A x_A + b_A)/(m_{\text{H}_2\text{S}} x_{\text{H}_2\text{S}} + b_{\text{H}_2\text{S}}) \quad (4.5)$$

or

$$x_A = P_A m_{\text{H}_2\text{S}} / (42 m_A) x_{\text{H}_2\text{S}} + [P_A b_{\text{H}_2\text{S}} / (42 m_A) - b_A / m_A] \quad (4.6)$$

Since it was difficult to set the flowrates precisely, the actual P_A was calculated from Eq. 4.5. The TI58 program for this calculation is listed in Table B.1.

4.4.2 Composition of the Sampled Gases

The composition of a sample taken from the product gas bag was determined from the peak areas of H_2 , H_2S and SO_2 and their corresponding calibration curves. Since the curves are linear, it follows that

$$y_i = (A_i - b_i)/m_i \quad (4.7)$$

where i refers to H_2 , H_2S or SO_2 ,

y_i is the percent of compound i in the gas bag

A_i is the area under the chromatographic peak

m and b are the slope and intercept, respectively, of the calibration curve.

The nitrogen content is obtained by difference, i.e.,

$$y_{N_2} = 100 - (y_{H_2} + y_{H_2S} + y_{SO_2}) \quad (4.8)$$

4.4.3 Composition of the Equilibrium Vessel Contents

When the equilibrium vessel is sampled, sulphur and water are condensed. Since the sample volumes are small (typically less than 50 ml) it was impractical to measure sulphur and water gravimetrically. These compounds were therefore calculated from mass balances and using the following assumptions:

- the gases are ideal;
- the equilibrium vessel pressure is atmospheric;
- air consists of 21% O_2 and 79% N_2 ;
- only H_2 , H_2S , SO_2 , N_2 , H_2O and S_2 are present in the equilibrium vessel;
- water and sulphur are removed completely. Consequently, the sample contains only H_2 , H_2S , SO_2 and N_2 .

These assumptions enable mass balances to be set up as follows. The atomic ratios of the elements in the feed and in the products must be identical. For example, the ratio of bound as well as unbound nitrogen to oxygen atoms, R_{NO} , is given by

$$R_{NO} = (2 \times 79) / (2 \times 21) = 2n_{N_2} / (2n_{SO_2} + n_{H_2O}) \quad (4.9)$$

where n_i refers to the number of moles of compound i in the sample taken from the equilibrium vessel before the sulphur and water are condensed.

Likewise,

$$R_{HS} = 2 = (2n_{H_2} + 2n_{H_2S} + 2n_{H_2O}) / (n_{H_2S} + n_{SO_2} + 2n_{S_2}) \quad (4.10)$$

$$R_{OH} = PA/200 = (2n_{SO_2} + n_{H_2O}) / (2n_{H_2} + 2n_{H_2S} + 2n_{H_2O}) \quad (4.11)$$

If 100 moles of sample are chosen as a basis, then

$$n_{H_2} = y_{H_2}, \quad (4.12)$$

$$n_{H_2S} = y_{H_2S}, \quad (4.13)$$

$$n_{SO_2} = y_{SO_2}, \quad (4.14)$$

$$n_{N_2} = y_{N_2}, \quad (4.15)$$

since these compounds are not removed during sampling. The number of moles of water and sulphur follow from Eqs. 4.9 and 4.10, i.e.,

$$n_{H_2O} = 0.532 n_{N_2} - 2n_{SO_2} \quad (4.16)$$

and

$$n_{S_2} = 0.5(n_{H_2} - n_{SO_2} + n_{H_2O}) \quad (4.17)$$

Hence

$$P_i = 100 n_i / n_T \quad (4.18)$$

where P_i represents the percent of compound i (H_2 , H_2S , SO_2 , N_2 , H_2O or S_2) in the equilibrium vessel, and

$$n_T = n_{H_2} + n_{H_2S} + n_{SO_2} + n_{N_2} + n_{H_2O} + n_{S_2}. \quad (4.19)$$

The sulphur yield is given by

$$Y = 2n_{S_2} / (2n_{S_2} + n_{H_2S} + n_{SO_2}) \quad (4.20)$$

The experimental error may be estimated by comparing the P_A value of the feed mixture with that given by

$$P_A = 100 / [1.88 / n_{N_2} (n_{H_2} + n_{H_2S} - 2n_{SO_2}) + 1] \quad (4.21)$$

This equation follows from substituting Eq. 4.16 into Eq. 4.11.

Equations 4.9 to 4.20 may be used to calculate the compositions and sulphur yields provided $P_A > 0$. For H_2S dissociation, where $P_A = 0$, the equation developed in the next section must be used.

4.4.4 Dissociation of Hydrogen Sulphide

The calculation for determining gas compositions is similar to that of the previous section, except that the equilibrium vessel is assumed to

contain H_2 , H_2S and S_2 only. Equation 4.10 reduces to

$$R_{HS} = 2 = (2n_{H_2} + 2n_{H_2S}) / (n_{H_2S} + 2n_{S_2}) \quad (4.22)$$

or

$$n_{S_2} = 0.5 n_{H_2}. \quad (4.23)$$

The quantities n_{H_2S} and n_{H_2} are found from Eqs. 4.12 and 4.13, respectively.

The equation for the sulphur yield becomes

$$Y = 2n_{S_2} / (2n_{S_2} + n_{H_2S}) \quad (4.24)$$

and the composition of the gases in the equilibrium vessel is given by

$$P_i = 100 n_i / n_T \quad (4.25)$$

where

$$n_T = n_{H_2} + n_{H_2S} + n_{S_2} \quad (4.26)$$

TI58 programs for calculating the reactor compositions and yields based on the mass balances are listed in Appendix B for both H_2S dissociation and oxidation.

CHAPTER 5

THEORETICAL RESULTS

5.1 Claus Furnace

5.1.1 Acid Gas Containing H_2S Only

The compositions of equilibrium mixtures were calculated* at oxygen to sulphur ratios, R_{OS} , ranging from 0.1 to 2.0 and a total pressure of 1.0 atm. The latter is close to industrial conditions. The concentrations of the following compounds were usually in excess of 0.1 ppm for at least some temperatures lying between 600 and 2000°K: O_2 , O , H_2 , H , OH , H_2O , N_2 , NO , NH_3 , SO , SO_2 , SO_3 , S_2O , SH , H_2S , H_2S_2 , SN and S_j where $j = 1, 2, \dots 8$. The other species, which were mentioned earlier, could therefore be neglected in the equilibrium calculations. Although the list of compounds considered in this study does not contain all possible combinations of oxygen, hydrogen, sulphur and nitrogen, it is unlikely that any additional species could be formed in appreciable proportions.

Figures 5.1 to 5.3 depict the variation in partial pressure of the most significant compounds as a function of temperature for $PA = 100$. The first figure shows, with the exception of nitric oxide, those species which may be regarded as harmless to the environment and the Claus process itself. The appreciable concentrations of hydrogen in the reaction mixture are well known to Claus plant operators but have generally been omitted from theoretical calculations. McGregor¹³ found partial pressures of H_2 similar to those shown in Figure 5.1 but he did not consider

*Computer programs for calculating the results in this chapter are listed in Appendix E.

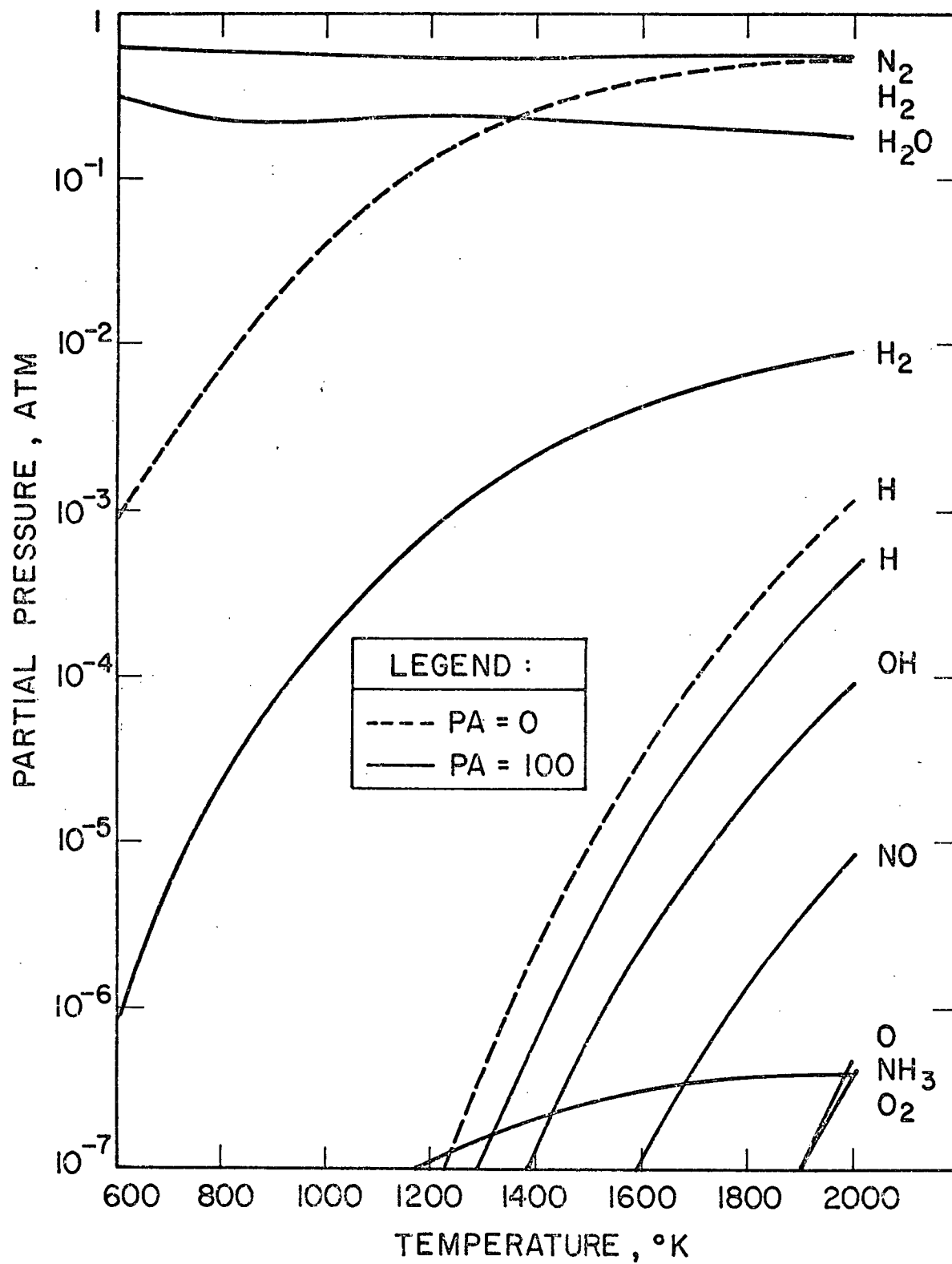


Figure 5.1. Effect of temperature on the partial pressure of harmless compounds (with the exception of NO).

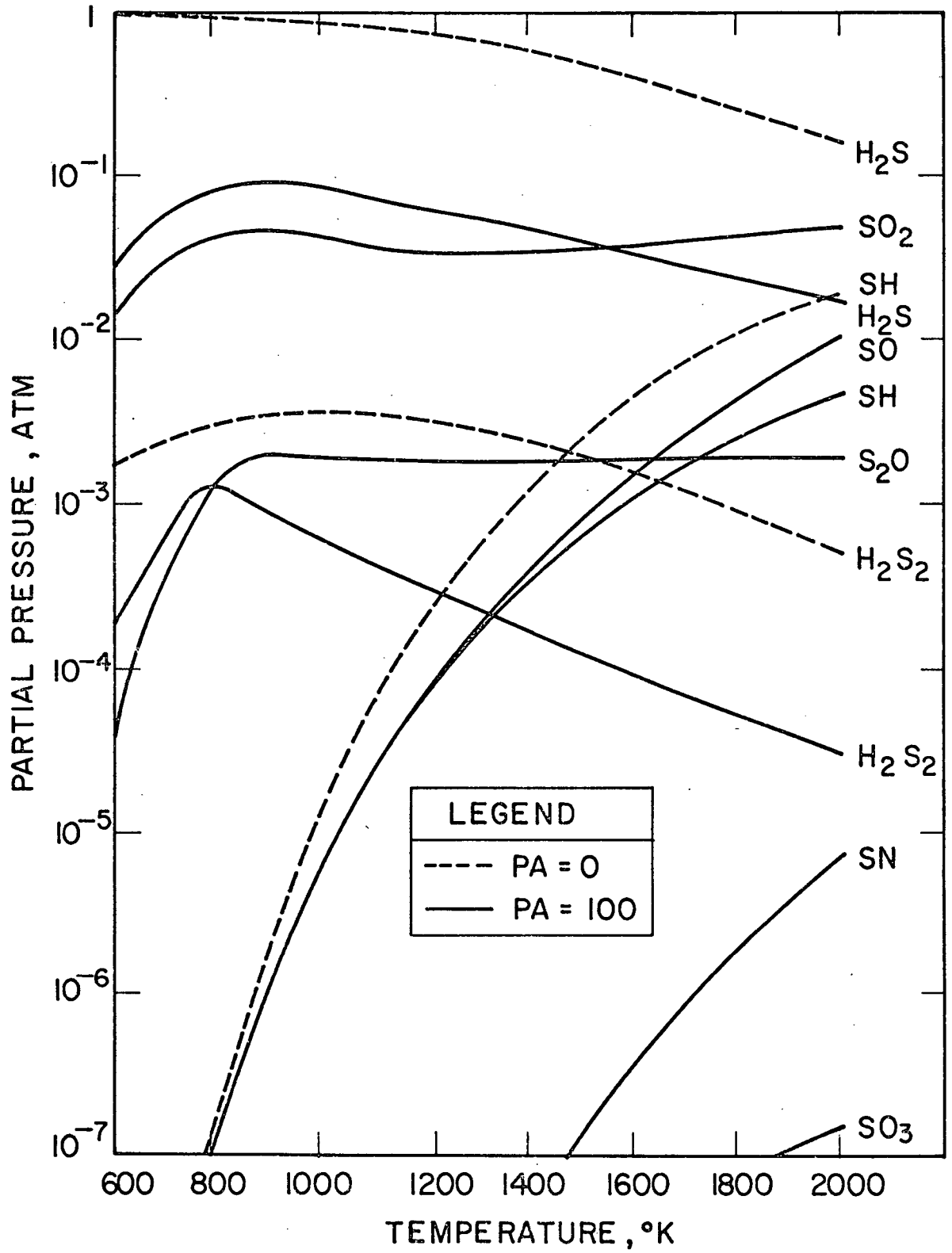


Figure 5.2. Effect of temperature on the partial pressure of sulphur compounds.

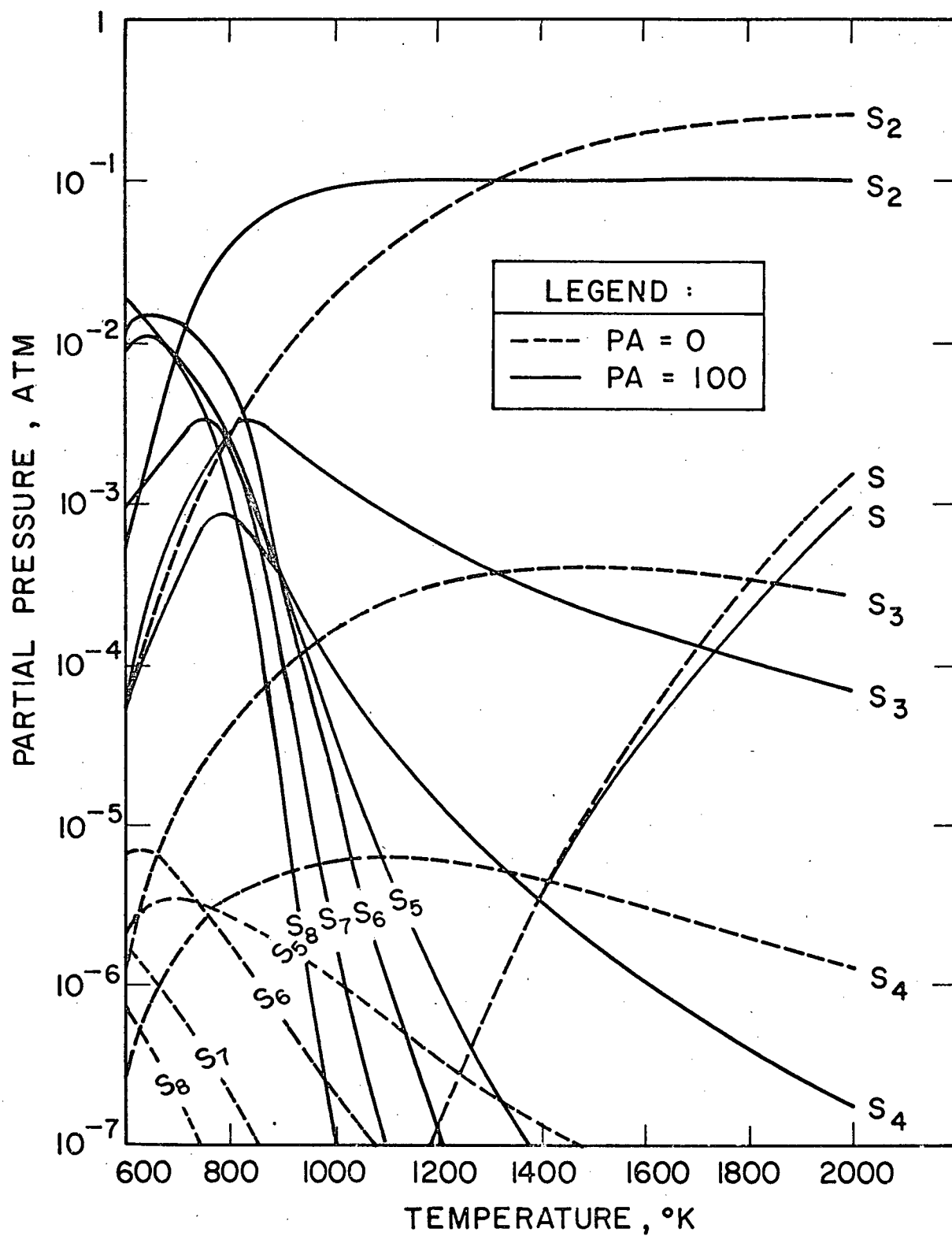


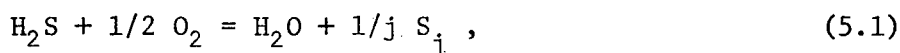
Figure 5.3. Effect of temperature on the partial pressure of sulphur polymers.

the formation of atomic hydrogen. The latter becomes significant only at elevated temperatures. Ammonia is also known to occur in Claus furnaces but in view of the low concentrations predicted by the equilibrium calculations, it is unlikely to be formed by the reduction of atmospheric nitrogen. More probable explanations are that it is introduced with the feed gas or results from amines carried over from the absorption units. The presence of nitrogen oxides except perhaps NO can be discounted. Hydrogen and sulphur are therefore more successful scavengers of oxygen than nitrogen. At temperatures exceeding 2000°K, the concentration of nitrogen compounds however would be expected to become significant.

Figure 5.2 shows the variation in partial pressure with temperature of those sulphur compounds which are undesirable and lower the conversion efficiency of the Claus furnace. H_2S and SO_2 are the most abundant sulphur compounds and their concentrations are fairly independent of temperature. The presence of other sulphur oxides, however, is also significant. Although the concentration of SO_3 is less than 1 ppm, it may contribute to sulphation, i.e., deactivation of the converters downstream from the Claus furnace due to the formation of sulphate layers on the catalyst surface. Other factors such as those cited by Pearson⁷⁴ may however also be responsible for sulphation. The remaining sulphur compounds, although present in smaller concentrations than either SO_2 or H_2S , should not be omitted from equilibrium calculations. In particular H_2S_2 and SH are present in significant proportions, with the latter approaching that of hydrogen sulphide at elevated temperatures. The role which these compounds play in the Claus process and whether they in fact pass through the boiler and sulphur condenser downstream of the furnace is presently unknown.

As seen from Fig. 5.3, a complex equilibrium exists between the various sulphur polymers with the lighter molecules being favoured by elevated temperatures. As mentioned previously no reliable free energy data are available for the heavy sulphur polymers at elevated temperature and caution should therefore be exercised in using Fig. 5.3. The curves agree moderately well with those of Gamson and Elkins⁵ and McGregor¹³. Any discrepancies are likely caused by the different free energy data used in the present study. The aforementioned authors also omitted certain sulphur polymers (viz., S_3 , S_4 , S_5 , S_7 and also S in the case of Gamson and Elkins) which is justifiable only for some restricted temperature ranges.

The relationship between sulphur yield and temperature is presented in Fig. 5.4. The data were calculated for stoichiometric amounts of oxygen in the feed mixture. The agreement with results obtained by earlier workers is generally good and any discrepancies are traceable to using either different free energies or compounds. The validity of the present calculations is therefore established. Gamson and Elkins⁵ were the first to suggest that the minimum in the yield curve arises from the complex equilibrium between the sulphur polymers. Since the strongly exothermic reaction,



can be regarded as dominating the H_2S -air equilibrium and S_6 , S_7 , S_8 are the main polymers formed at low temperatures, the sulphur yield must decrease with temperature according to Le Chatelier's principle. These polymers dissociate endothermically at more elevated temperatures and Eq. 5.1 therefore becomes less exothermic. The sulphur yield consequently rises. Fig. 5.4 also indicates that the yield passes through a

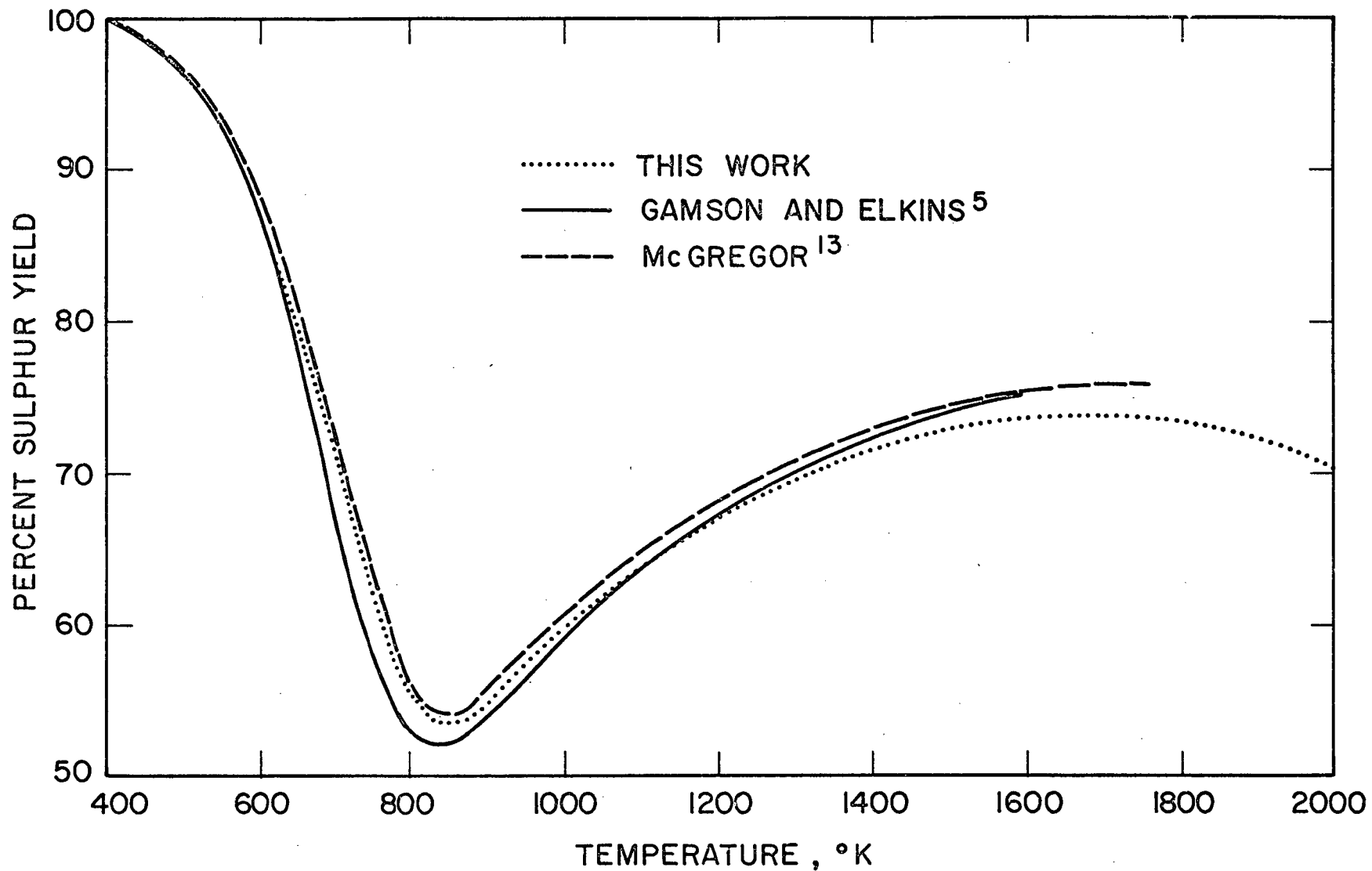


Figure 5.4. Comparison of sulphur yields calculated by various workers (PA = 100).

maximum at approximately 1700°K. This behaviour has not been reported previously and is observed only when H_2 and either SH or SO are included in the equilibrium calculations. The physical reason for the maximum is probably the fact that elemental sulphur undergoes oxidation at elevated temperatures. This is partly confirmed by Fig. 5.2 which shows that the partial pressures of most sulphur oxides increase with temperature.

Further support is given to the conjecture by Fig. 5.5 which shows the relationship between sulphur yield and percentage stoichiometric air in the feed mixture so that a value of 100 corresponds to an O_2/H_2S ratio of 0.5 in the initial mixture. The special case of $P_A = 0$, i.e., H_2S dissociation, will be discussed in section 5.1.4 of this chapter. As seen from Fig. 5.5, the yield is lowered when air in excess of stoichiometric proportions is used. To suppress formation of sulphur oxides at elevated temperatures, the air content in the starting mixture should therefore be reduced. For example, at 2000°K, P_A values of 20% and 60% raise the sulphur yield by approximately 10% over that attainable with stoichiometric amounts of air. Similar conclusions can be drawn from Fig. 5.6 which indicates that high temperatures and low oxygen to hydrogen sulphide ratios lead to the best yields.

The operating conditions maximizing the conversion to elemental sulphur are however only achievable industrially if the feed gases to the Claus furnace are preheated. The effect of preheating the feed gases is investigated more thoroughly later in this chapter. Without such provisions a decrease in P_A reduces the furnace temperature and conversion efficiency. The latter is apparent from Fig. 5.7 which shows the sulphur yield at the adiabatic flame temperature. This temperature

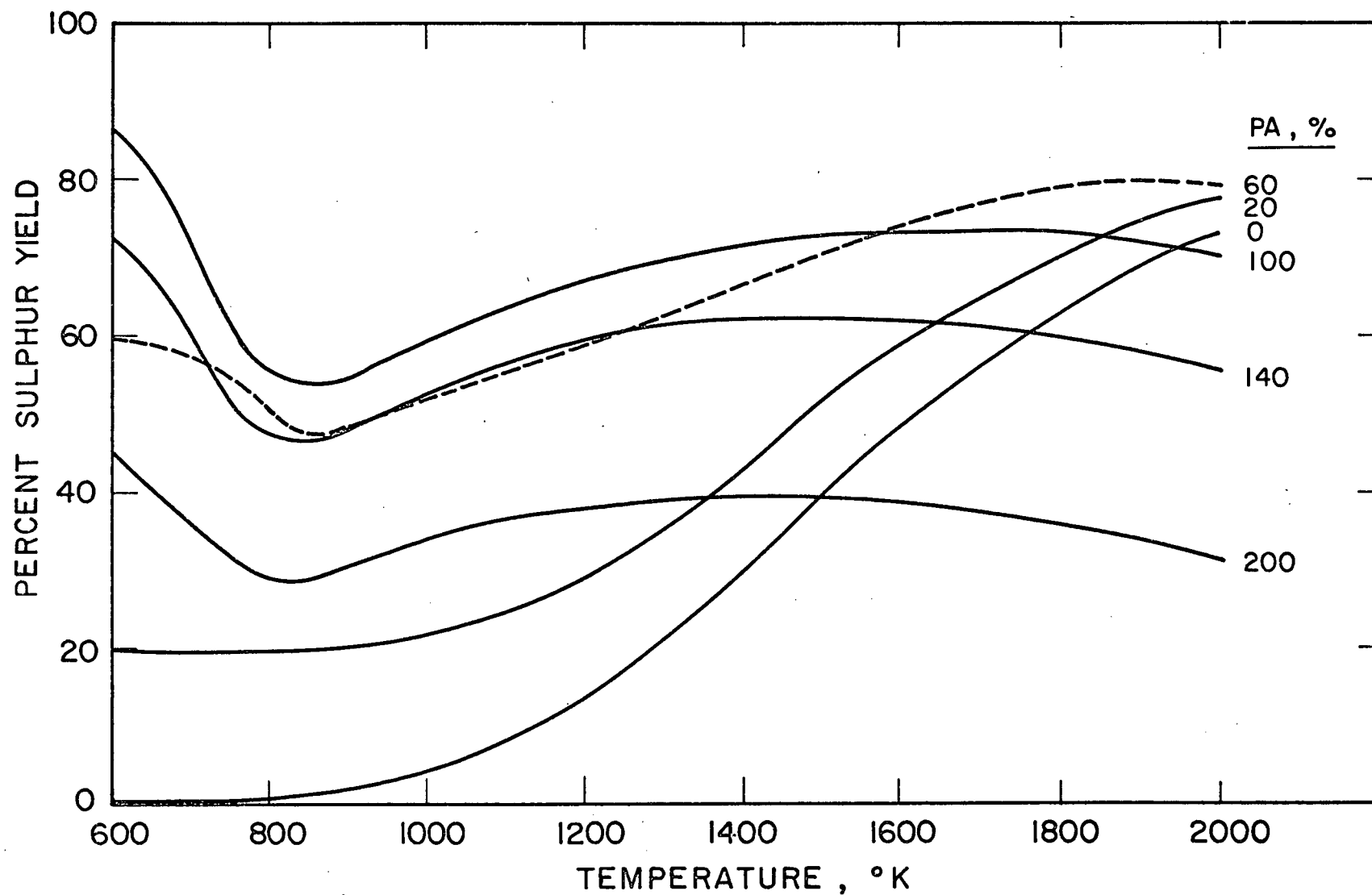


Figure 5.5. Effect of temperature and PA on sulphur yield.

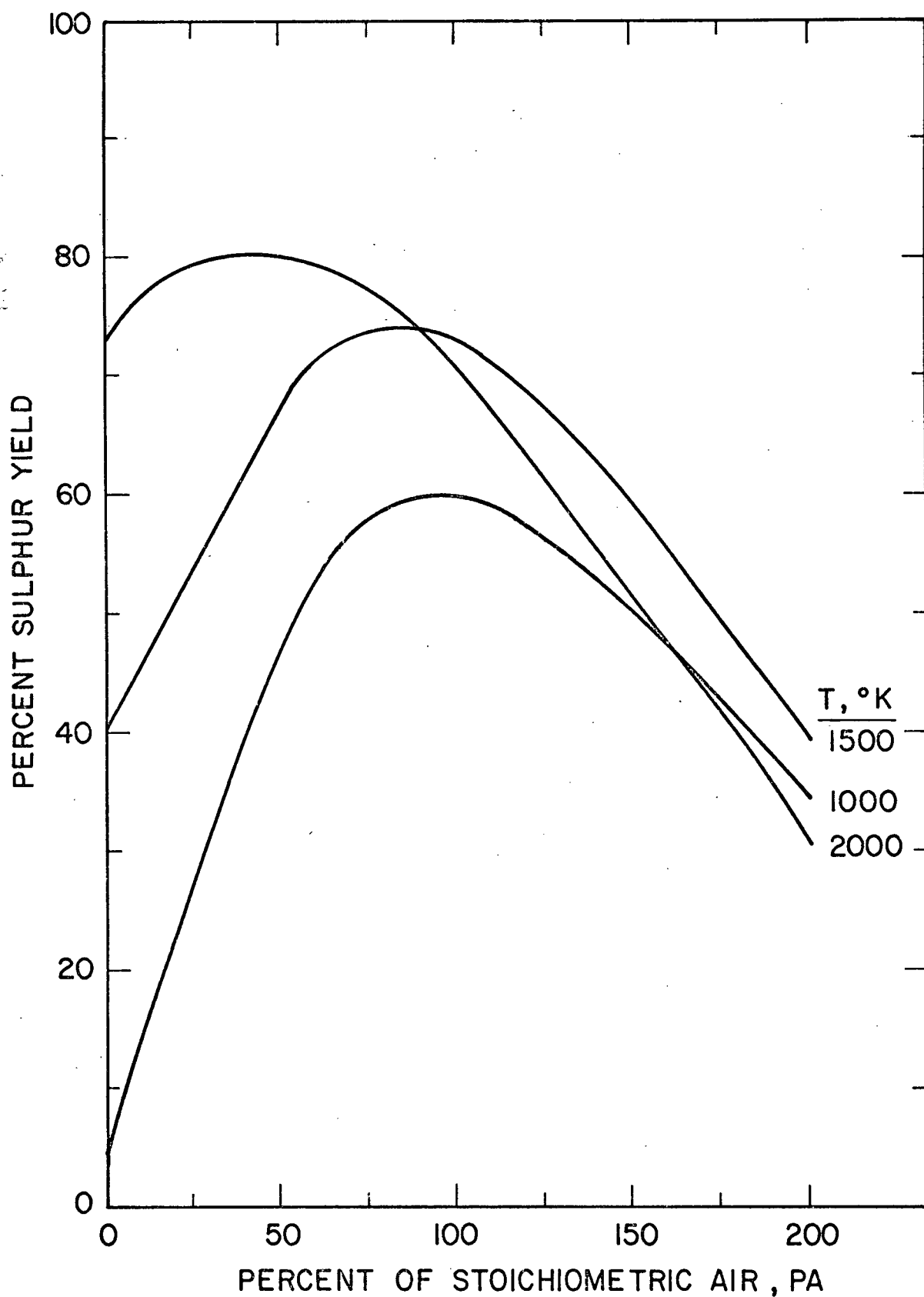


Figure 5.6. Effect of PA on sulphur yield at various temperatures.

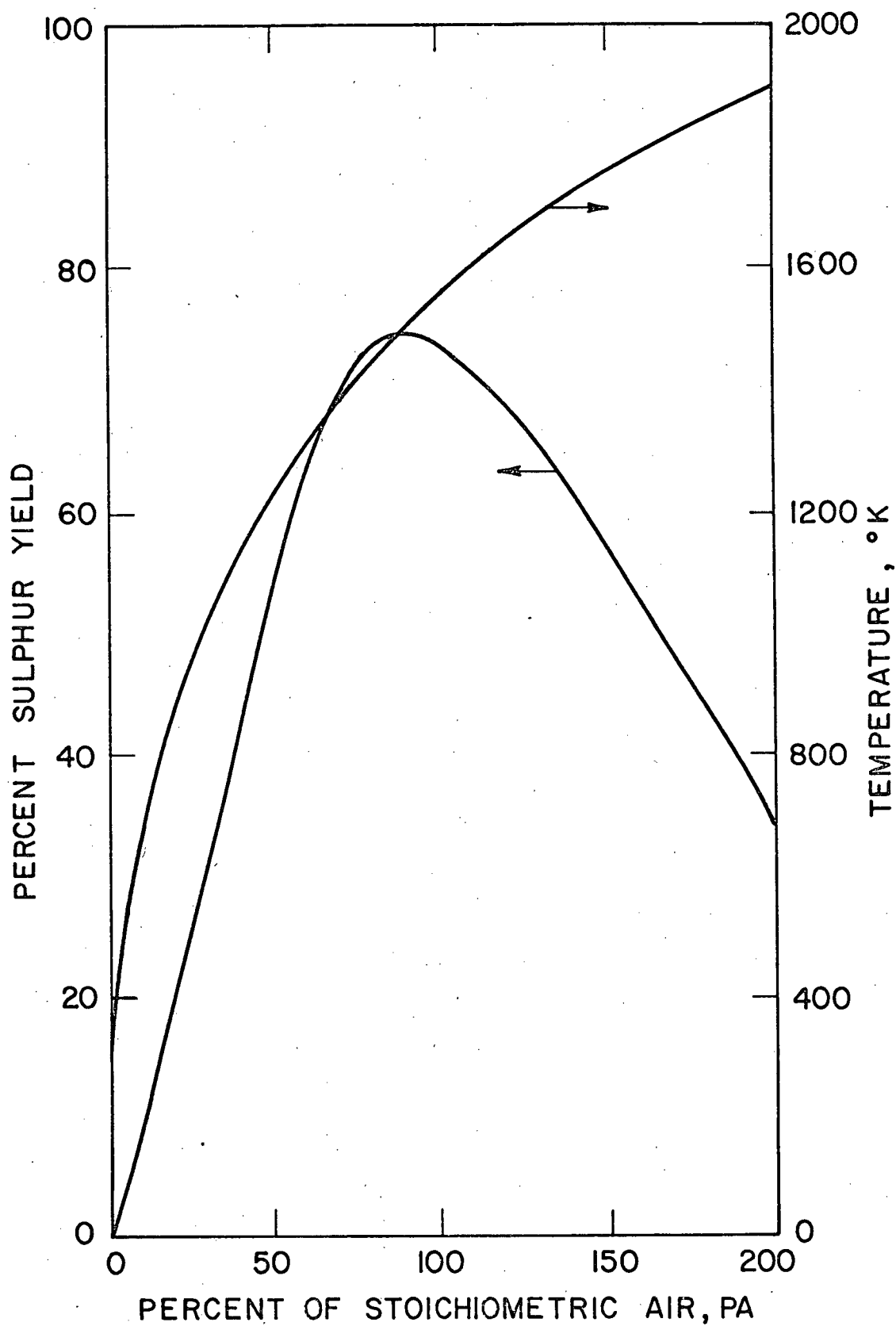


Figure 5.7. Effect of PA on the adiabatic flame temperature and on the corresponding sulphur yield.

closely approximates that of industrial furnaces since they suffer only minor heat losses. Figure 5.7 also indicates that the current industrial practice of operating with stoichiometric amounts of air in the absence of preheat is sound. The yield is reduced when $P_A < 100$ due to lowered furnace temperatures and when $P_A > 100$ due to enhanced formation of sulphur oxides.

5.1.2 Acid Gas Containing Carbon Compounds

The following parameters were varied: temperature (600 to 2000°K), air (20 to 300 percent of stoichiometric), acid gas composition (H_2O and CO_2 concentrations up to 10 and 30 percent, respectively). Of the 36 compounds considered all except HCN, C_2N_2 , CH_4 , C_2H_2 , C_2H_4 and C_2H_4O had partial pressures exceeding 0.1 ppm for at least some temperatures between 600 and 2000°K. The 30 remaining species should, therefore, not be omitted from the equilibrium calculations.

Figures 5.8 to 5.11 show the partial pressures of the most important compounds present when H_2S containing 15 percent CO_2 is oxidized with a stoichiometric amount of air. As seen from Fig. 5.8, nitrogen, the most abundant substance, undergoes little change except for the production of small quantities of NH_3 , NO and SN. The high ammonia concentrations sometimes found in industry are probably produced not from atmospheric nitrogen but rather amines carried over from absorption towers. The partial pressures of both molecular and atomic hydrogen are appreciable.

The distribution of sulphur polymers (shown in Fig. 5.9) is similar to that for pure hydrogen sulphide. Although the dimer S_2 predominates, other sulphur species are also significant at some temperatures and therefore, none of them should be omitted as did most earlier workers.^{5,10,11,12,13,14,16,17,26}

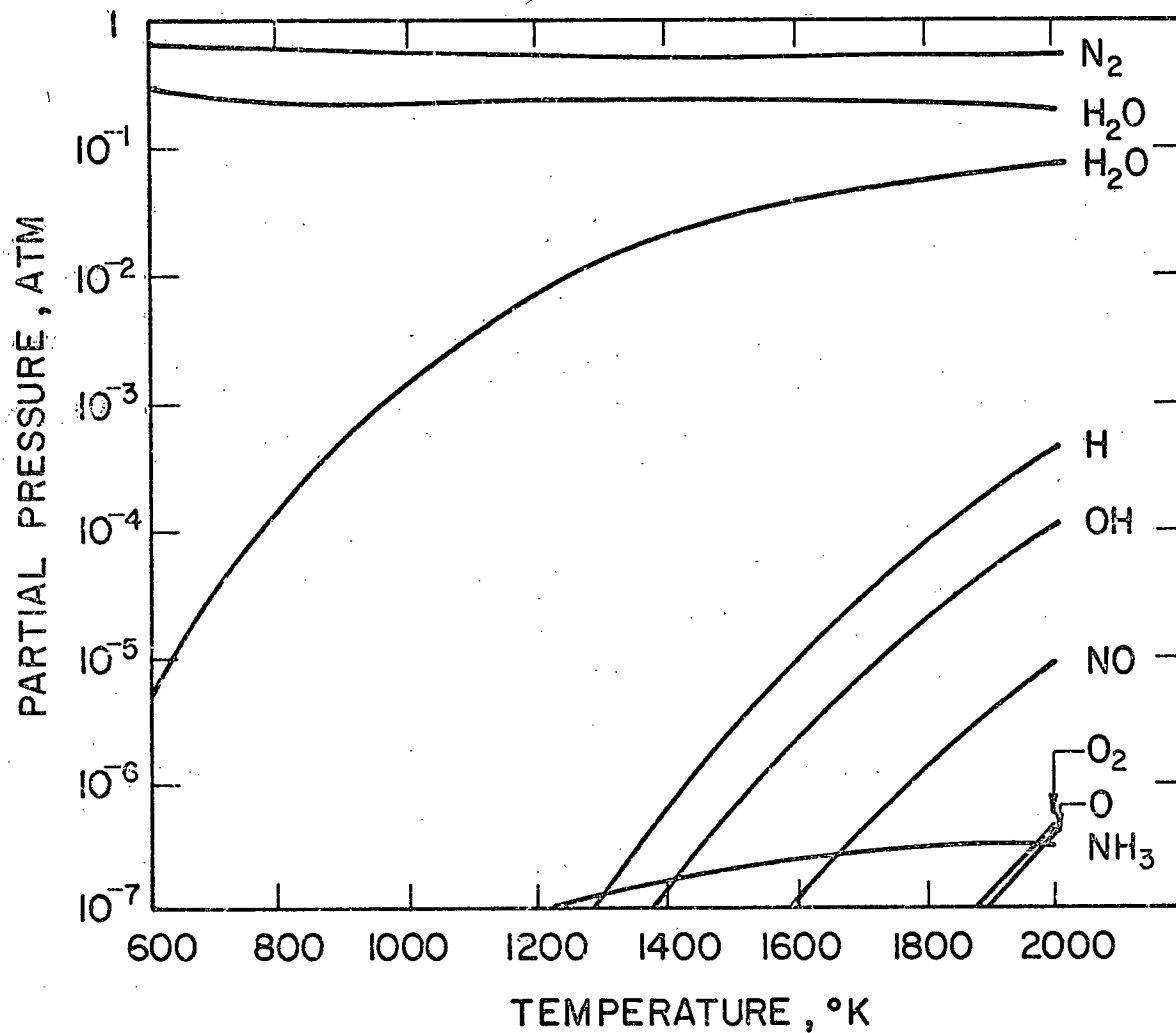


Figure 5.8. Effect of temperature on the partial pressure of harmless compounds (with the exception of NO).

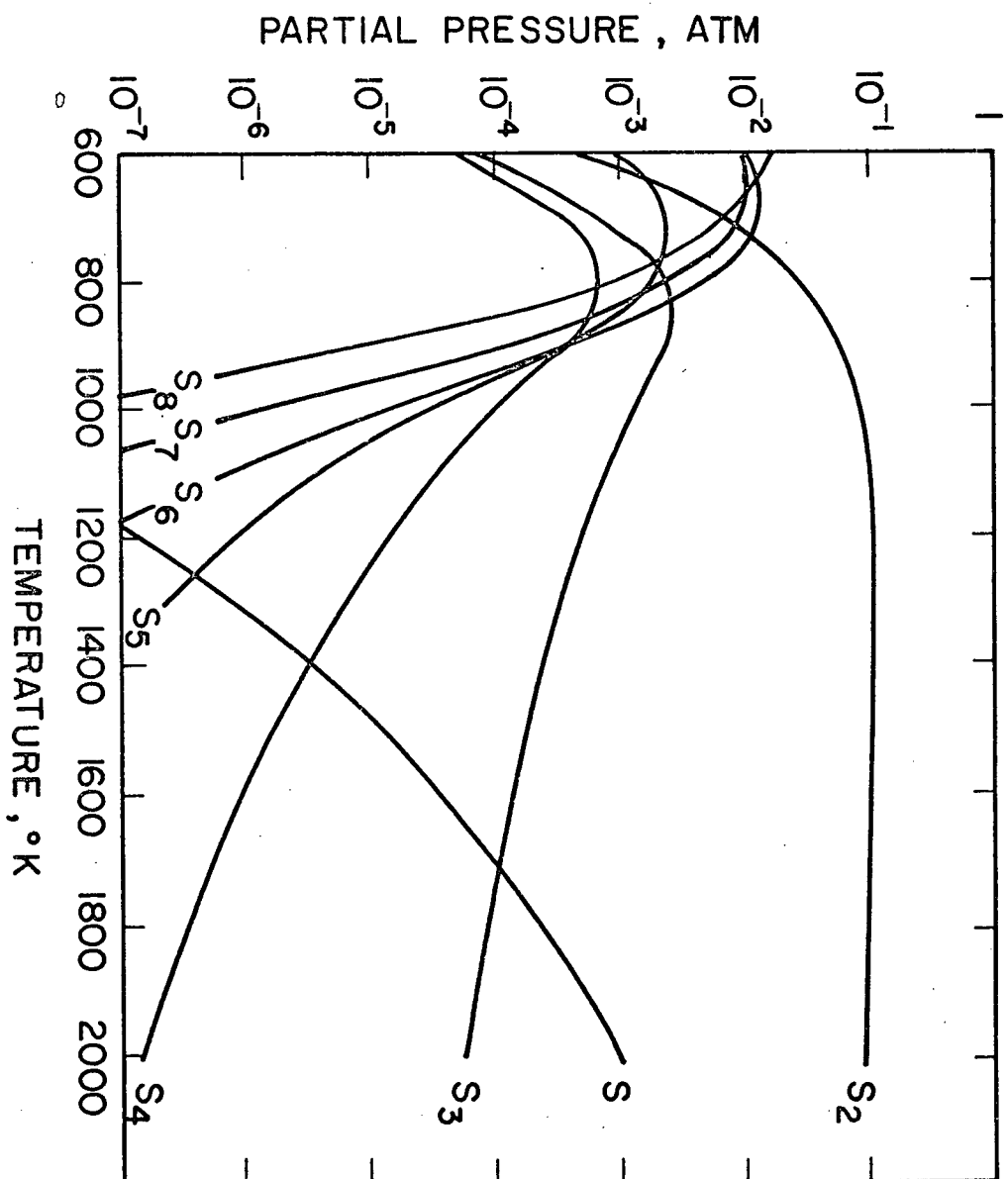


Figure 5.9. Effect of temperature on the partial pressure of sulphur polymers.

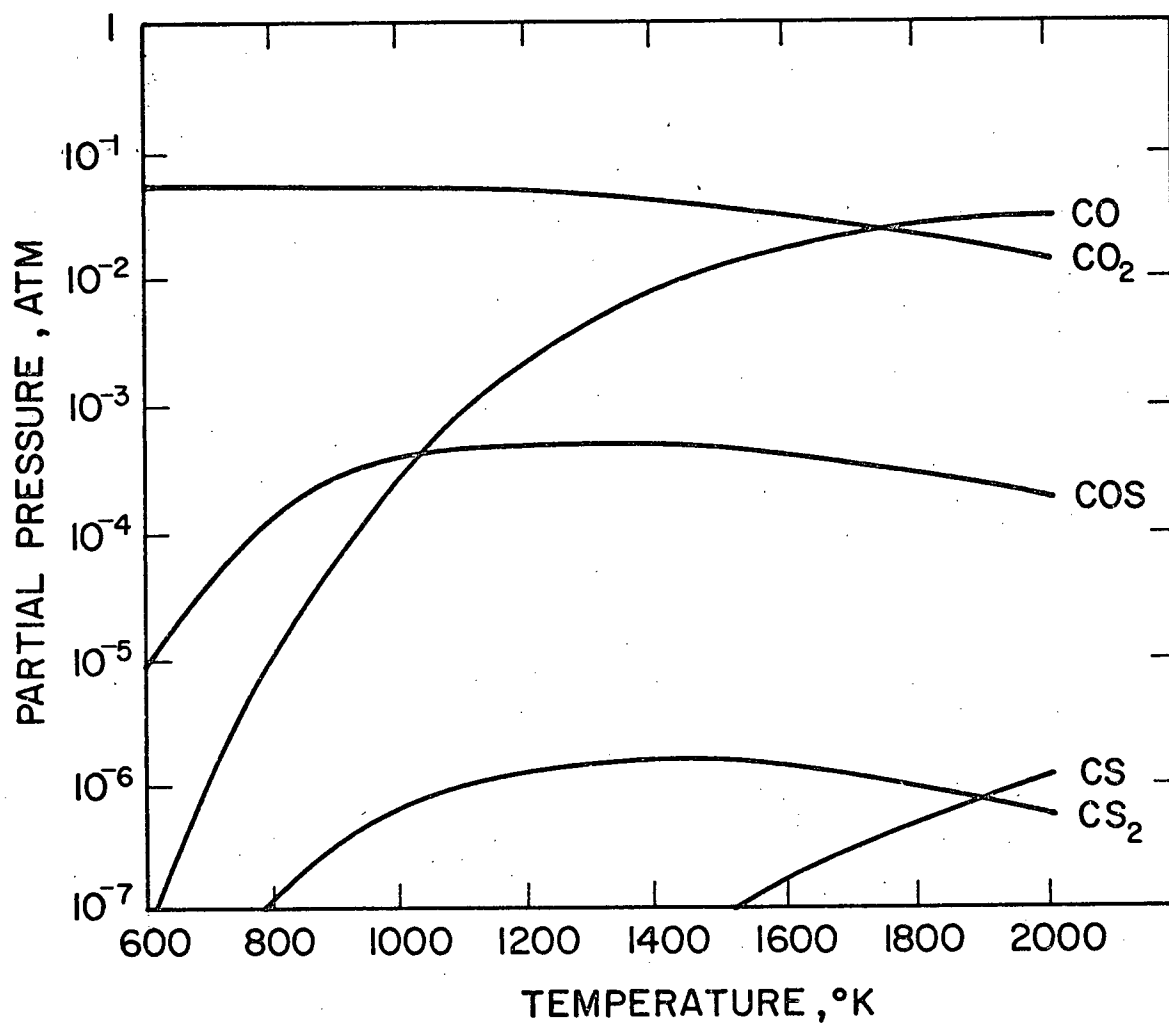


Figure 5.10. Effect of temperature on the partial pressure of carbon compounds.

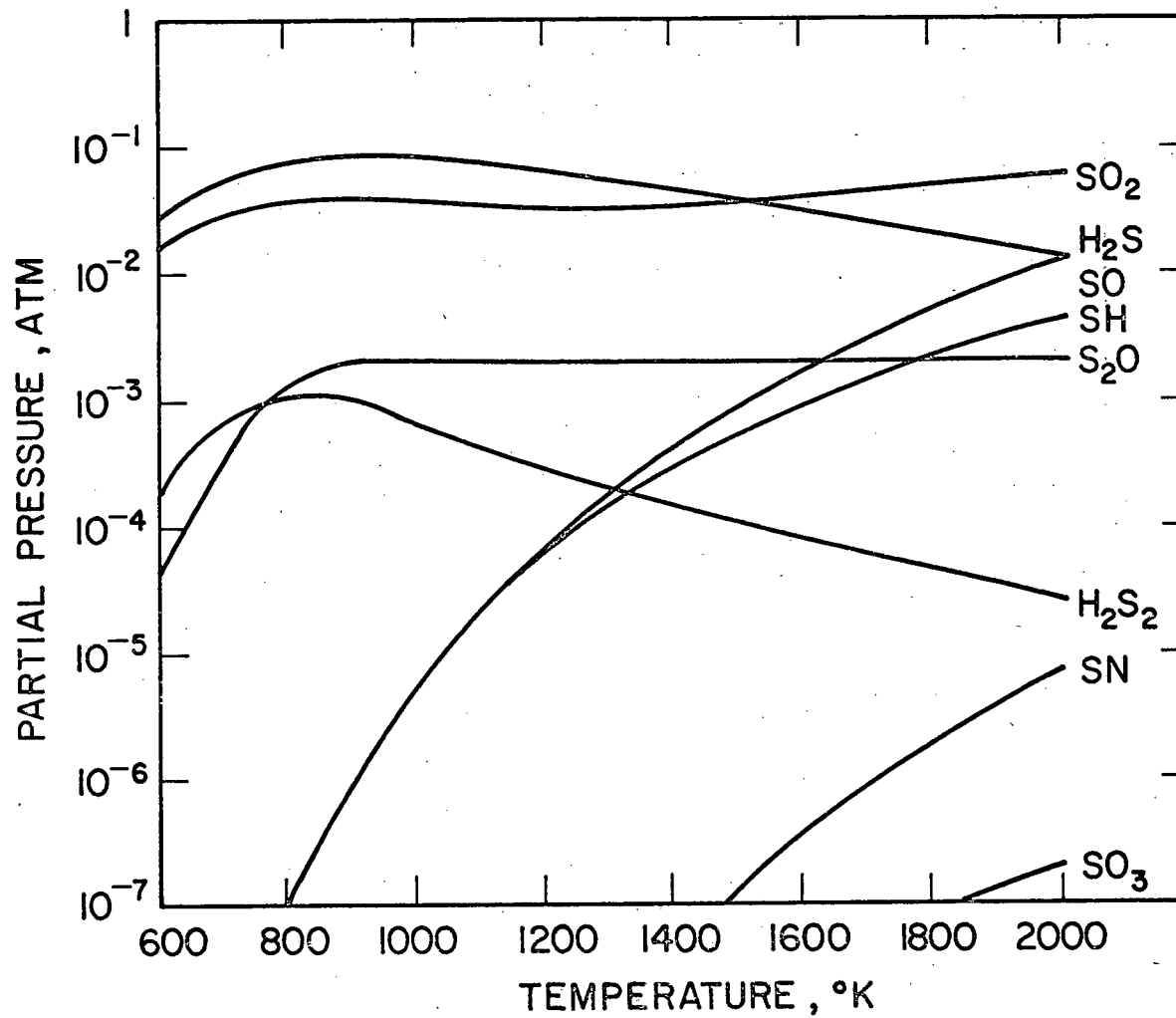


Figure 5.11. Effect of temperature on the partial pressure of sulphur compounds.

Figure 5.10 shows the partial pressures of carbon compounds of which CO_2 and CO are the most abundant. Since at high temperatures CO_2 dissociates into oxygen and CO , and since the latter can further react with elemental sulphur, the formation of COS , CS and CS_2 is not surprising. These compounds not only lower the sulphur yield in the furnace but are also unaffected by the usual Claus catalysts and therefore present a pollution problem.

The other main compounds which impair the furnace performance are H_2S and sulphur oxides. At elevated temperatures SO_2 is more abundant than H_2S and this suggests that elemental sulphur competes successfully for oxygen, as seen from Fig. 5.11. Since the dissociation of CO_2 releases oxygen, smaller sulphur yields are expected with increasing CO_2 concentrations.

This conjecture is confirmed by Fig. 5.12 which gives the sulphur yield as a function of temperature and for various CO_2 concentrations in the acid gas. At low temperatures the curves coincide thus indicating that CO_2 undergoes no appreciable reaction. However, at temperatures exceeding about 1200°K , the curves part because carbon sulphides and additional sulphur oxides are formed. These compounds cause the maxima in the yield curves; the maxima become more pronounced for higher initial CO_2 concentrations.

To reduce the oxidation of elemental sulphur, the amount of initial air can be decreased. Figure 5.13 shows that the sulphur yield is considerably increased at elevated temperatures by lowering P_A . Conversely, increasing P_A reduces the yields. Although the percentage air does not significantly affect the extent to which carbon sulphides are formed, it changes their partial pressures due to the

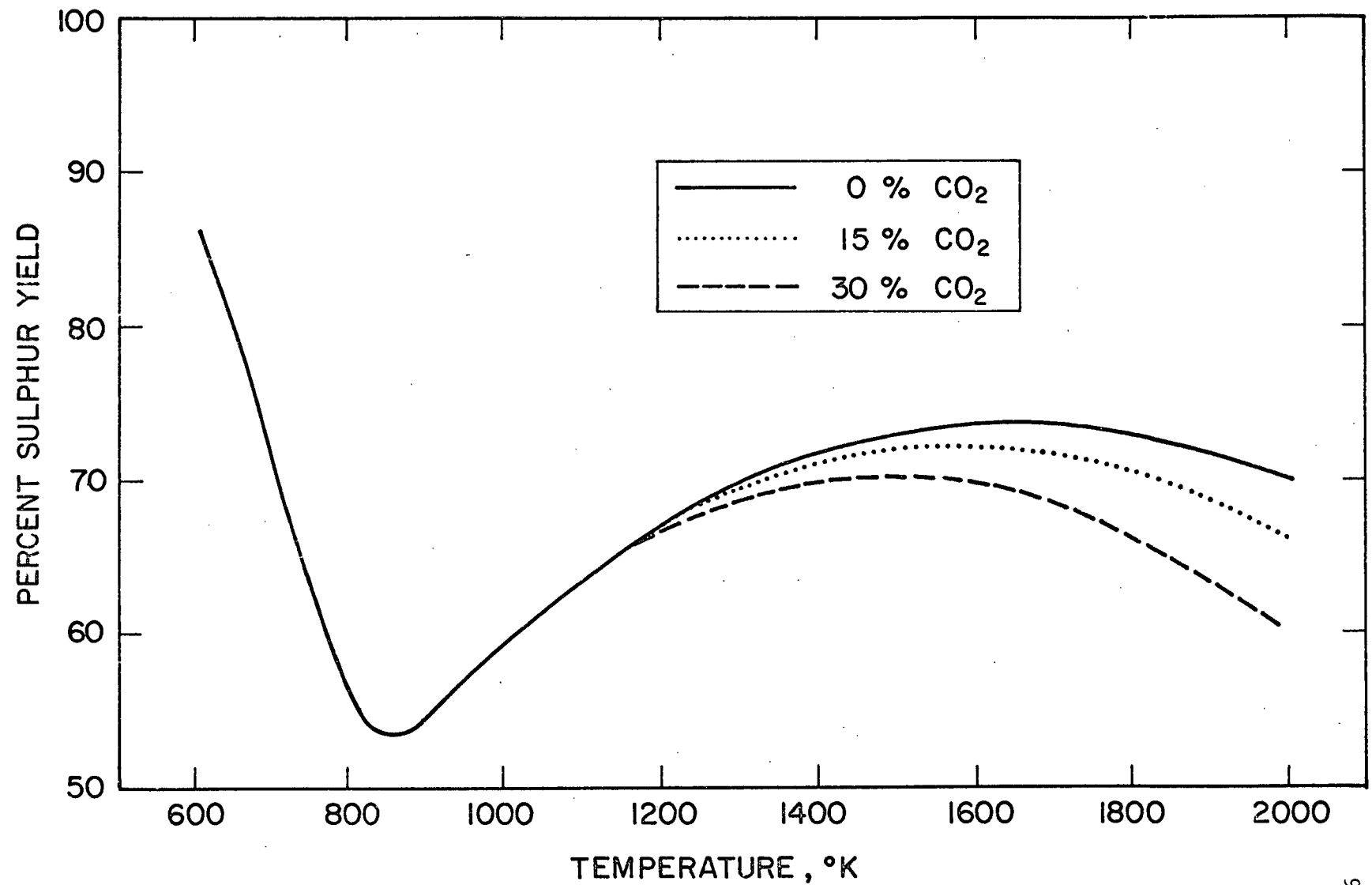


Figure 5.12. Effect of temperature and CO₂ on the sulphur yield.

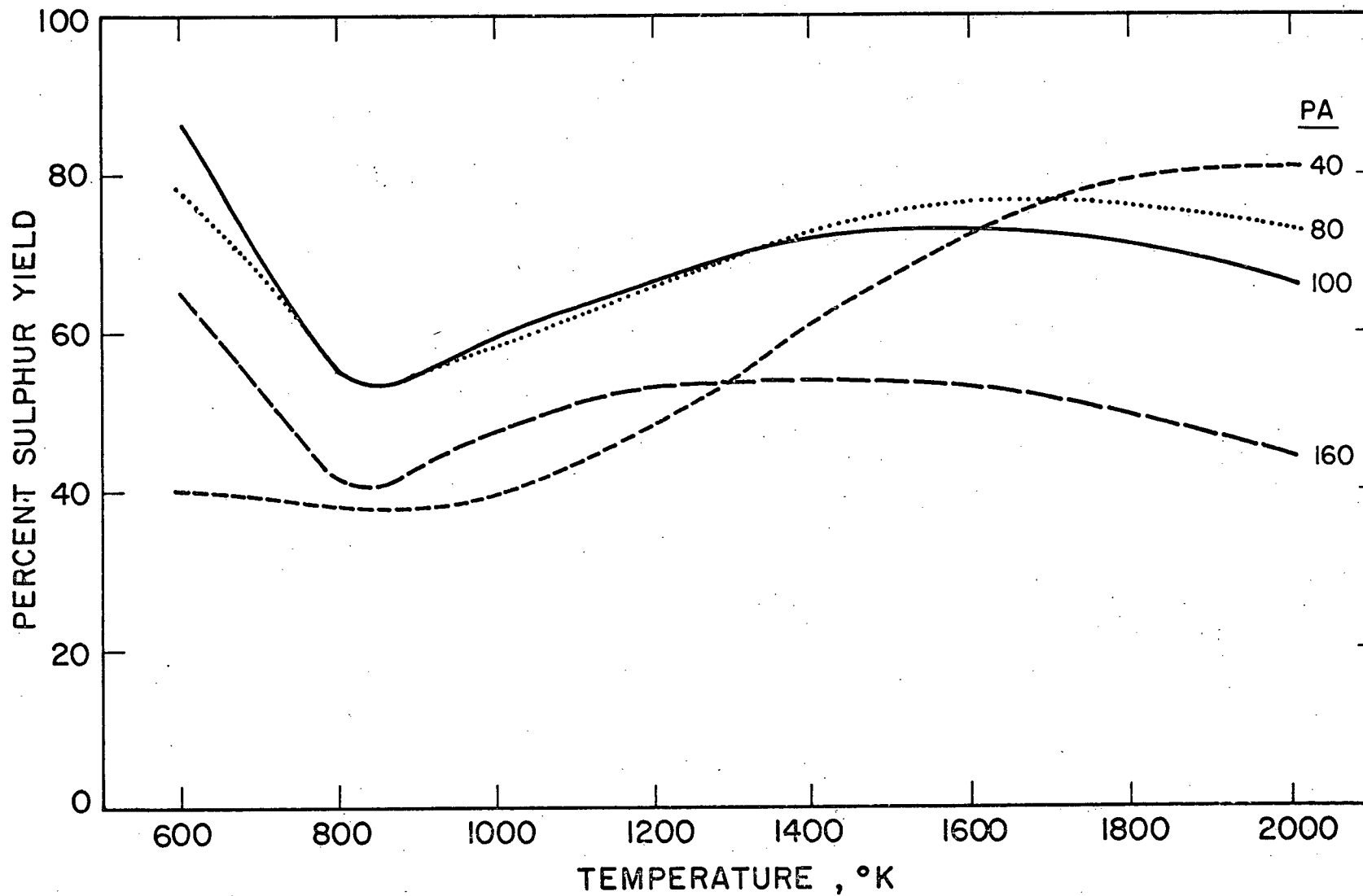


Figure 5.13. Effect of temperature and PA on the sulphur yield.

dilution provided by the nitrogen.

Whereas the sulphur yield can be enhanced by lowering the amount of air in the feed, this improvement may not be realizable in practice because Claus furnaces operate under virtually adiabatic conditions. The yields at the adiabatic flame temperatures were, therefore, calculated by the method described previously. The results for a feed gas at 298°K are shown in Fig. 5.14. The best yields obtainable under adiabatic conditions occur with stoichiometric amounts of oxygen, a fact well-known to Claus plant operators. When $P_A < 100$ the yield falls due to the reduced flame temperature and when $P_A > 100$ it declines on account of the oxidation of elemental sulphur. Hence, in practice the feed gases to the Claus furnace must be preheated to achieve the enhanced yields possible with less than stoichiometric amounts of air.

If the acid gas contains water vapour, the sulphur yield is diminished as seen from Fig. 5.15. This behaviour follows from Eq. 5.1. Since the yield is reduced by only 2 percent for 10 percent H₂O it would be uneconomical to dry the acid gas before it enters the furnace.

If the acid gas contains more than 30 percent CO₂, the "split-stream" process must be adopted as mentioned in the introduction. Equilibrium compositions were, therefore, calculated for an acid gas containing 30 percent CO₂ and for $P_A = 300$, i.e., using a stoichiometric amount of air according to Eq. 1.1. The primary reaction products were SO₂ and H₂O with virtually no elemental sulphur being formed. The partial pressures of the carbon sulphides were always less than 1 ppm for temperatures between 600 and 2000°K thus supporting the earlier contention that they are produced by the reaction between CO and elemental sulphur.

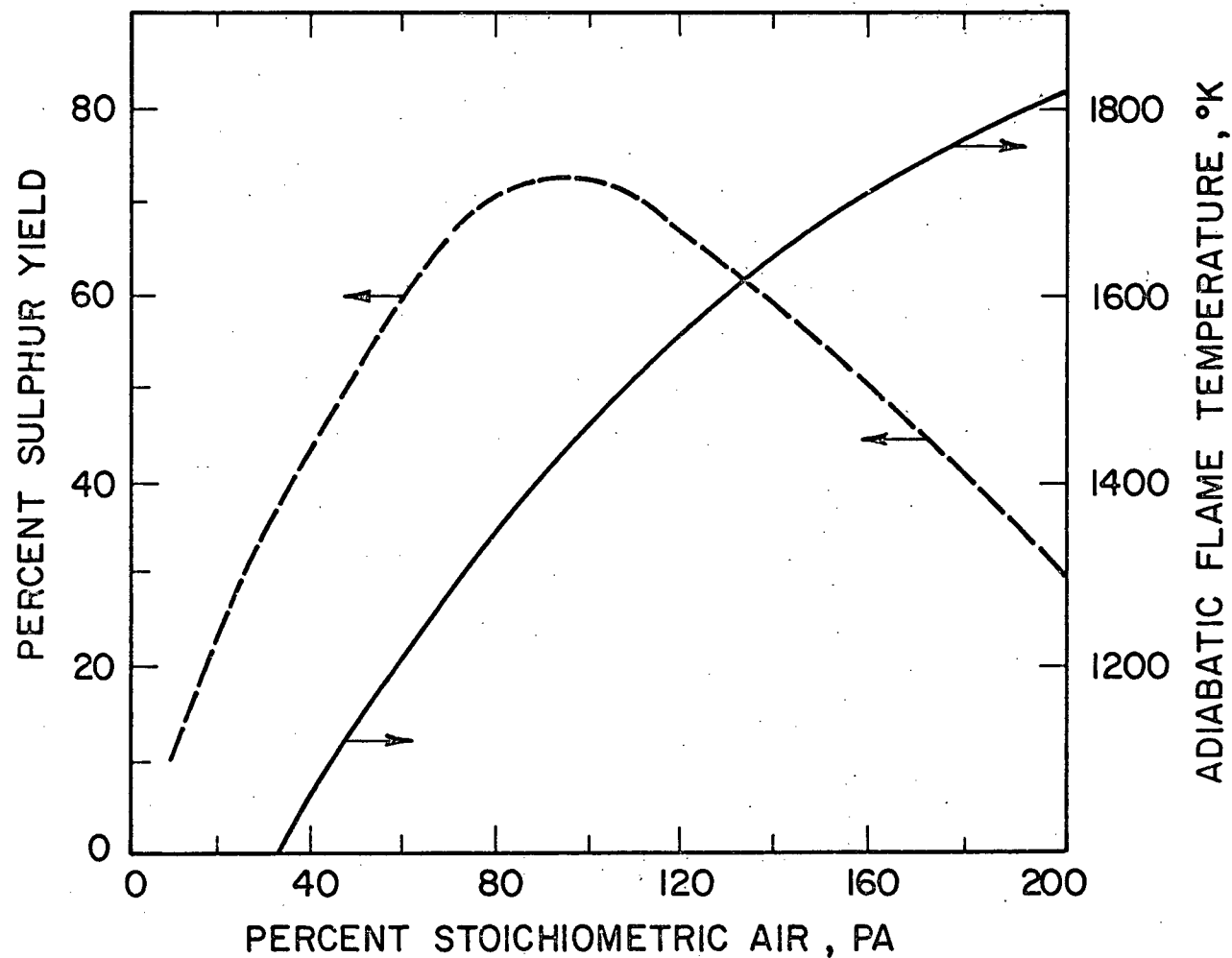


Figure 5.14. Effect of PA on the adiabatic flame temperature and on the corresponding sulphur yield.

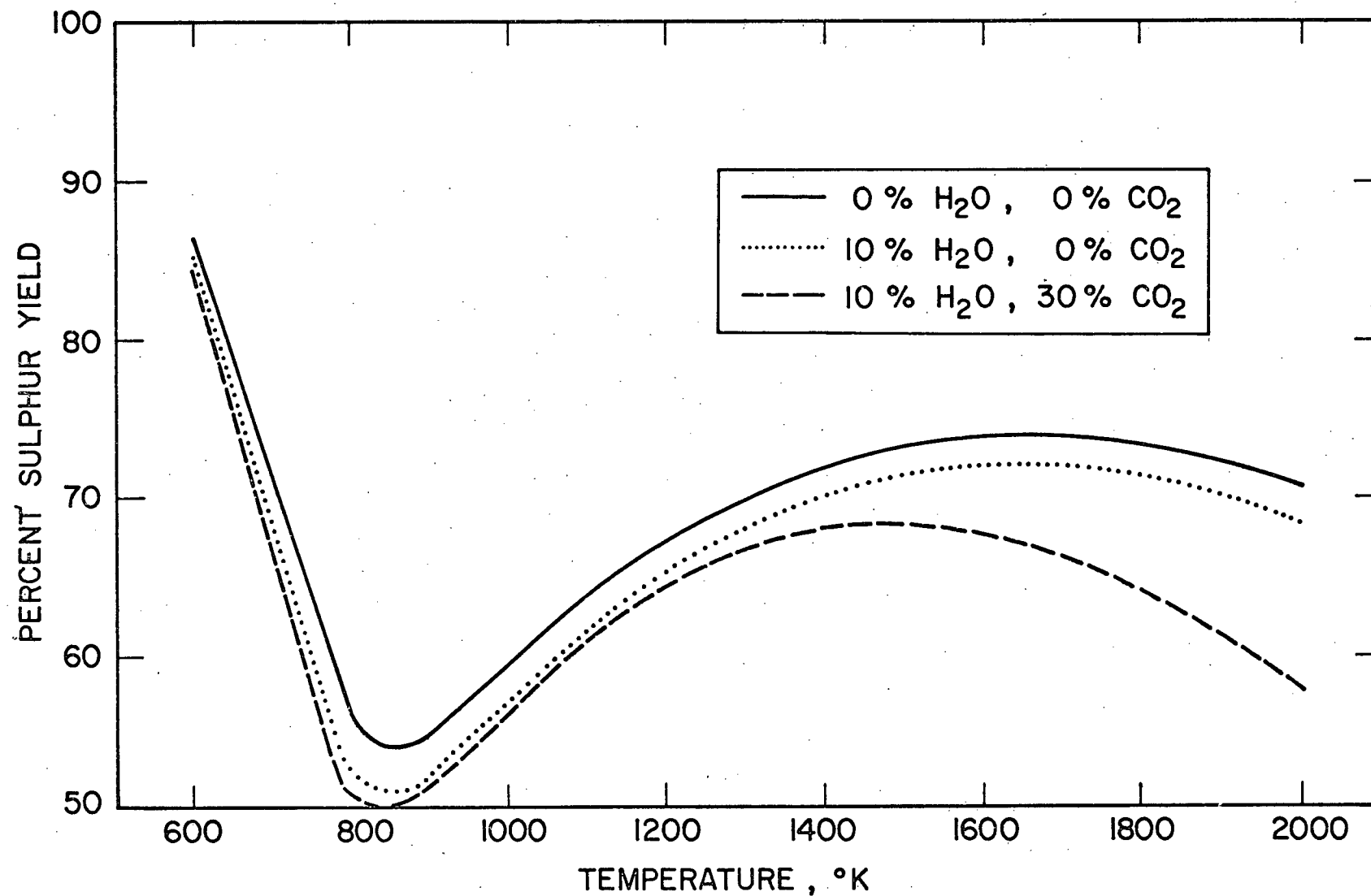
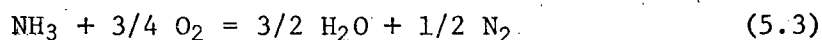
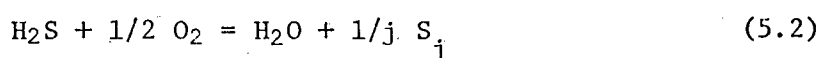


Figure 5.15. Effect of H₂O and CO₂ on the sulphur yield.

5.1.3 Acid Gas Containing Ammonia

Ammonia, as well as CO_2 and water, can be associated with the acid gas. Figure 5.16 shows that below 1600°K , NH_3 lowers the sulphur yield of a furnace but, above 1600°K , it enhances the yield. Since both NH_3 and H_2S are oxidised in the furnace, they compete for combustion air; less oxygen is therefore available for reaction with H_2S . Consequently, an acid gas containing NH_3 results in yields similar to those obtained when operating with $P_A < 100$. This is shown by the similarities of Figs. 5.13 and 5.16 which both exhibit cross-overs in the curves near 1600°K . Temperatures less than 1600°K favour the oxidation of H_2S to elemental sulphur rather than to SO_2 . Hence with less oxygen available (either because $P_A < 100$ or because some O_2 has combined with NH_3), the sulphur yield falls. Temperatures above 1600°K , however, enhance the oxidation of sulphur to SO_2 rather than to elemental sulphur, and an oxygen deficiency therefore *enhances* sulphur yield.

Sufficient air can be provided for complete oxidation of both H_2S and NH_3 according to the reactions:



The similarity of Fig. 5.17 to Fig. 5.15 suggests that, even with enough O_2 for complete oxidation of both NH_3 and H_2S , the presence of ammonia in the acid gas lowers the yield. This is probably so because NH_3 oxidation produces water which tends to shift the equilibrium of Eq. 5.2 to the left.

5.1.4 Hydrogen Sulphide Dissociation

As shown by Fig. 5.5, H_2S dissociation produces much lower sulphur yields than H_2S oxidation at temperatures below about 1500°K . In spite

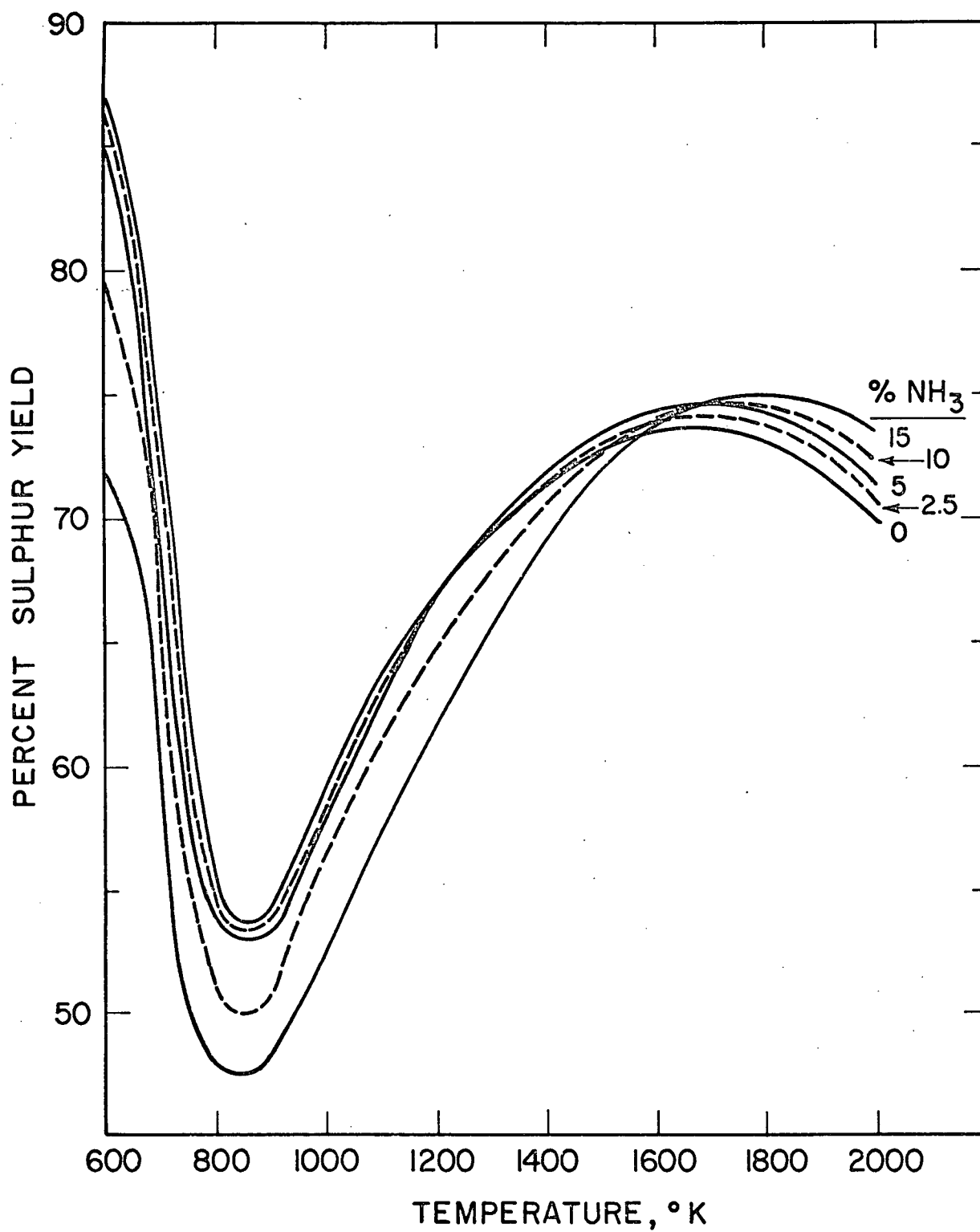


Figure 5.16. Effect of ammonia on the sulphur yield (sufficient air to oxidise the H_2S only).

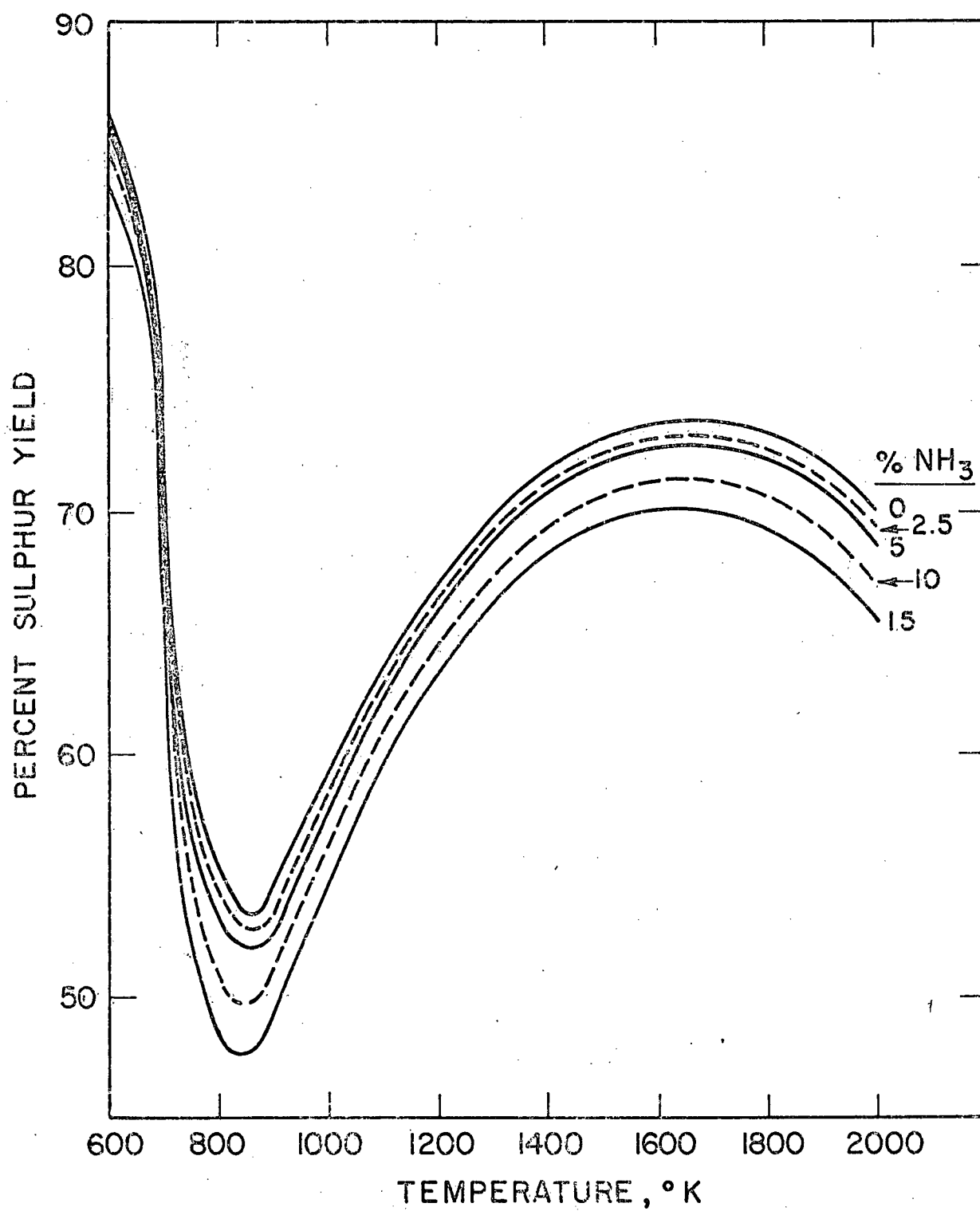


Figure 5.17. Effect of ammonia on the sulphur yield (sufficient air to oxidise both the H_2S and the NH_3).

of this, concentrations of the heavier sulphur polymers resulting from H_2S dissociation are higher above 1400°K , because of the absence of N_2 and H_2O (see Fig. 5.3). Figure 5.1 shows that, for all temperatures, the concentration of hydrogen is at least ten times greater for H_2S dissociation than it is for H_2S oxidation. Raymont⁴⁸ examined this reaction and concluded that it may produce an attractive alternative to the Claus process, since it yields two useful products, viz., hydrogen and sulphur. The dashed lines of Figs. 5.1 and 5.3 agree well with Raymont's theoretical results.¹⁹

As in the case of H_2S oxidation, ammonia adversely affects H_2S dissociation, as shown in Fig. 5.18. With no oxygen present, the decomposition equations corresponding to Eqs. 5.2 and 5.3 become



The hydrogen from NH_3 decomposition inhibits the H_2S dissociation, thus lowering the sulphur yield.

5.2 Claus Plant

In order to further the understanding of the Claus process, an entire plant, consisting of a furnace plus two catalytic converters was modelled.

The yield and temperature of each unit of the plant are examined as a function of the following variables:

- the amount of combustion air in the furnace;
- the oxygen concentration of acid gas;
- temperature of the feed to the furnace and/or converters;
- recycle ratio of the first converter's feed back to the furnace.

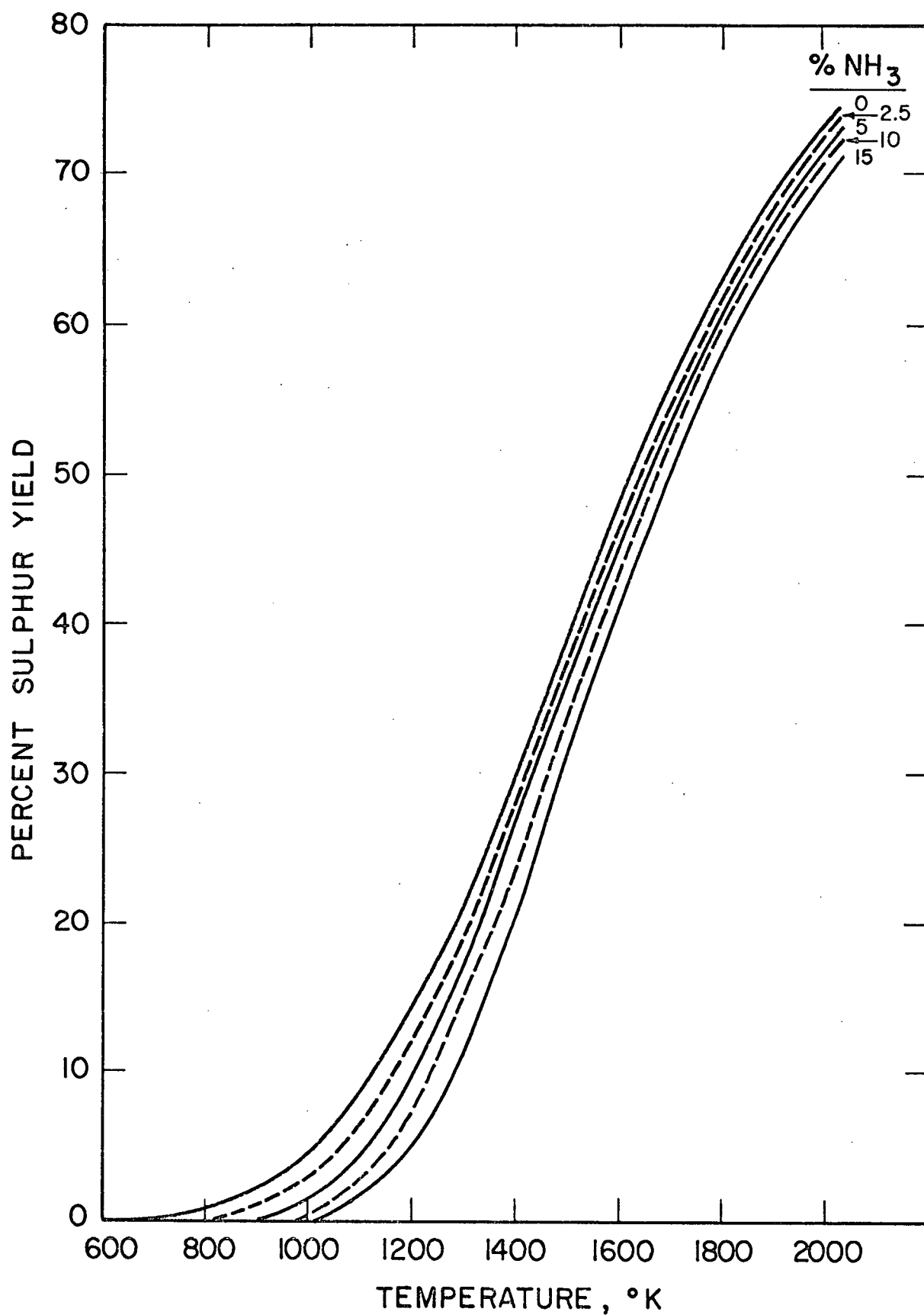


Figure 5.18. Effect of ammonia on sulphur yields from H_2S dissociation.

The Claus plant was assumed to operate adiabatically. Unless otherwise noted, the temperatures of both the combustion air and the acid gas are 298°K; the temperatures of the feeds to the first and second converters are 530 and 480°K, respectively.

5.2.1 Oxygen Concentration in the Furnace Feed

Figure 5.19 shows that operating with 100% of stoichiometric air ($P_A = 100$) maximises the yield of the entire plant, a fact well-known to Claus plant operators. Sulphur yields in the combustion chamber, first converter and second converter are highest with P_A about 90, 120 and 105 respectively.

The furnace temperature rises with P_A (see Fig. 5.19) because adding air favours H_2S oxidation. As discussed in Sect. 1 of this chapter, the furnace yield rises until P_A reaches about 90 because of rising furnace temperature, and then declines on account of the oxidation of elemental sulphur to SO_2 .

In the catalytic converters, sulphur yields rise when $P_A > 50$ as more SO_2 becomes available to react with the H_2S . (Oxygen must be excluded from the converters to prevent catalyst sulphation.) Between 90 and 110% air, the converter yields are high because of favourable H_2S/SO_2 ratios. When P_A exceeds 200, the yield drops sharply because most of the sulphur is present in the converters as SO_2 . When $P_A \approx 100$, the yield in the second converter, which operates at a more favourable temperature, exceeds the yield in the first converter. However, when $P_A < 80$ or $P_A > 120$, the sulphur yield in the second converter is worse than that in the first, because a poor H_2S/SO_2 ratio in the first converter becomes worse downstream.⁹

The temperature of each converter, like that of the furnace, rises

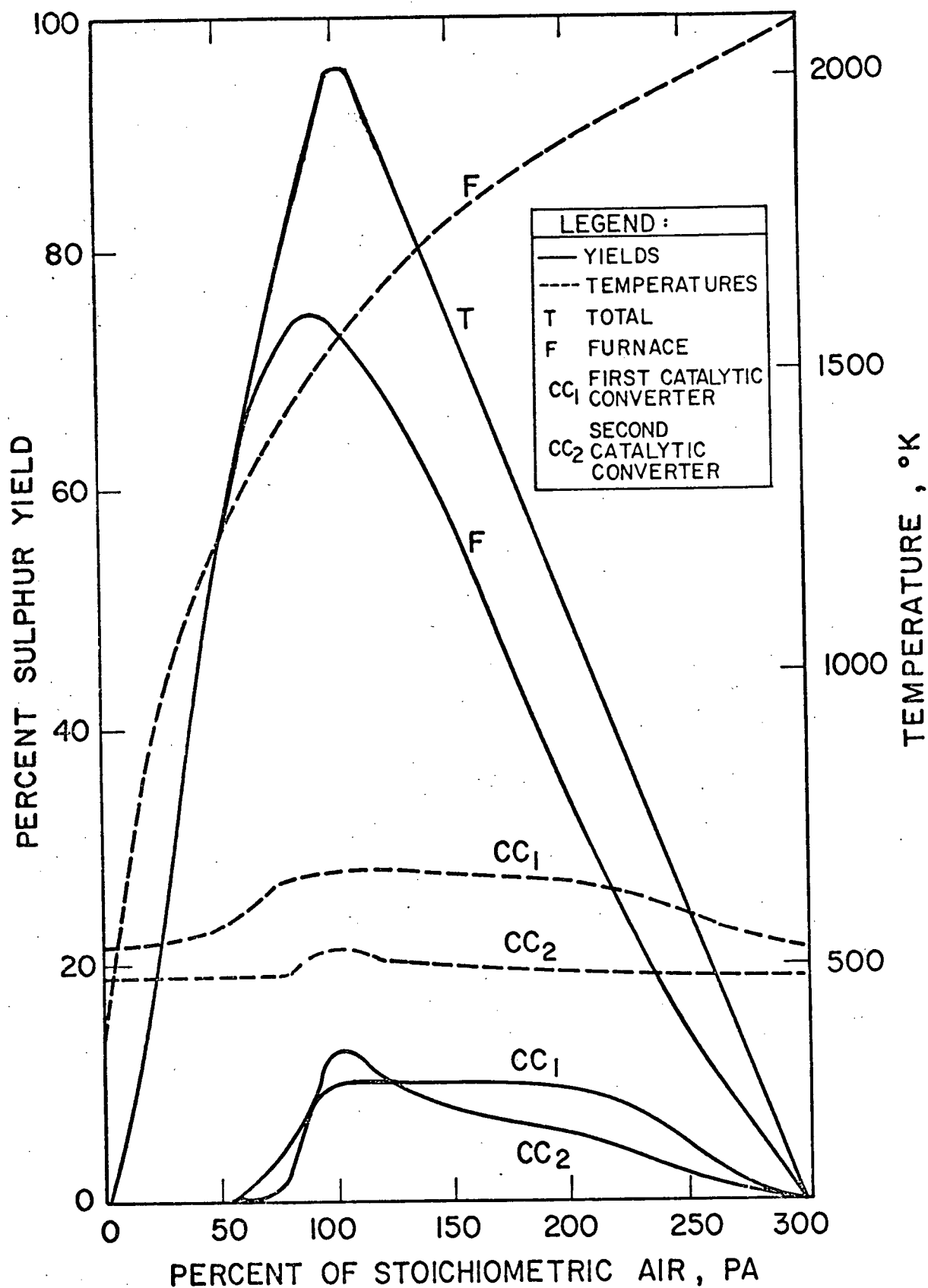


Figure 5.19. Effect of PA on Claus plant yields and temperatures.

and falls with the yield, as shown in Fig. 5.19. This is of course caused by the exothermic nature of the reaction between H_2S and SO_2 .

5.2.2 Enriching Combustion Air with Oxygen

In this section, the effect of varying not the *amount* but the "quality" of the air to the furnace is examined. By decreasing the air while simultaneously adding more pure oxygen to the acid gas, the total oxygen in the furnace remains stoichiometric, and only the concentration of the nitrogen, a diluent, is reduced. This increases the concentration of the reactants, and might be expected to enhance the sulphur yield. However, as shown by Fig. 5.20, the presence of nitrogen is actually beneficial. Without nitrogen present (100% oxygen in Fig. 5.20), the Claus furnace temperature rises to 2220°K . This is detrimental since above 1700°K the sulphur yield in the furnace falls with increasing temperature, as shown in Fig. 5.4.

The minimum yield of the first converter occurs at 750°K and 40% oxygen. Since the minimum in the yield vs temperature plot (Fig. 5.4) corresponds to 850°K , temperature may not be the most important factor affecting yield. The increasing yields in the first converter may rather be a result of falling furnace conversions. This leaves the feed to the first converter rich in H_2S , which reacts with the SO_2 . The converter, therefore, compensates for lower sulphur production in the furnace. The complementary shapes of the yield curves for the two converters indicate that the second converter behaves similarly, offsetting any decrease in the yield in the first.

5.2.3 Preheating the Furnace Feed

It was shown earlier in this chapter that furnace yields are enhanced when operating with less than stoichiometric air, provided the

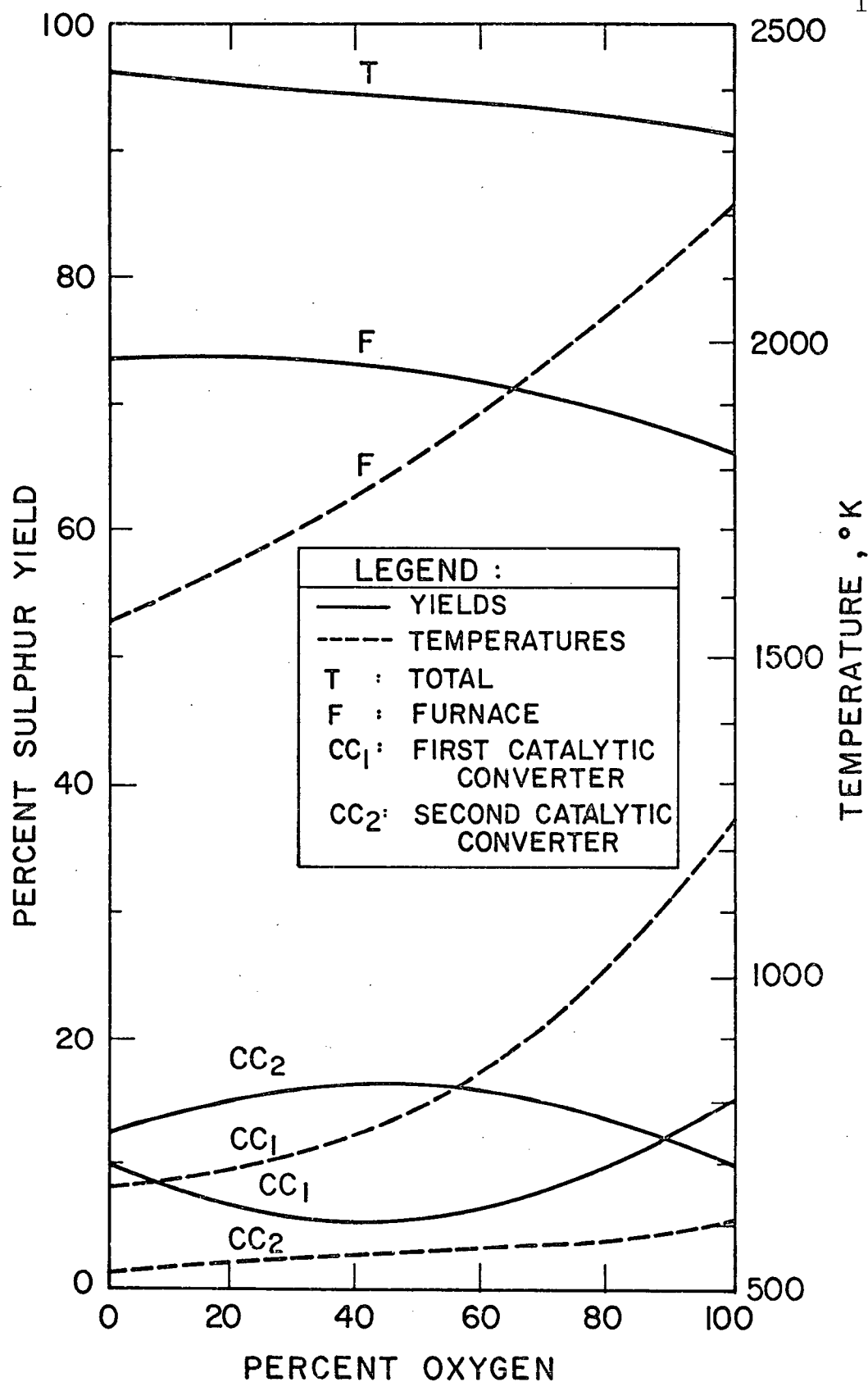


Figure 5.20. Effect of enriching combustion air with oxygen on Claus plant yields and temperatures.

furnace feed is preheated. This section investigates how preheating affects not only the Claus furnace, but also the two converters.

Figure 5.21 shows that preheating the feed to a Claus plant operating with stoichiometric air enhances the overall yield only slightly. When the temperatures of the air and acid gas are raised by 250°K, the furnace temperature rises by 150°K. The furnace yield increases slightly, but the yield of the first converter falls substantially. A higher furnace temperature promotes the oxidation of H_2S to SO_2 ; this adversely affects the $\text{H}_2\text{S}/\text{SO}_2$ ratio and causes the yield in the first catalytic converter to drop. The yield in the second converter, however, rises as that in the first falls. Thus the second converter again compensates for the poor performance of the first. The temperature of the second converter rises with yield because of the exothermic heat of reaction.

Heating the feed to the first converter causes its temperature to increase and its yield to decrease; the yield of the second converter rises to compensate, with a subsequent rise in temperature, as shown in Fig. 5.22. The overall Claus plant yield falls from 97 to 95%.

Figure 5.23 shows that the second catalytic converter should be operated at as low a temperature as possible; heating the feed only causes the yield to fall drastically.

These results show that, for $\text{PA} = 100$, preheating the feed to any unit has a detrimental effect on Claus plant yield. In practice, preheating the feed to the converters would still be necessary, to avoid sulphur condensation on the catalyst.

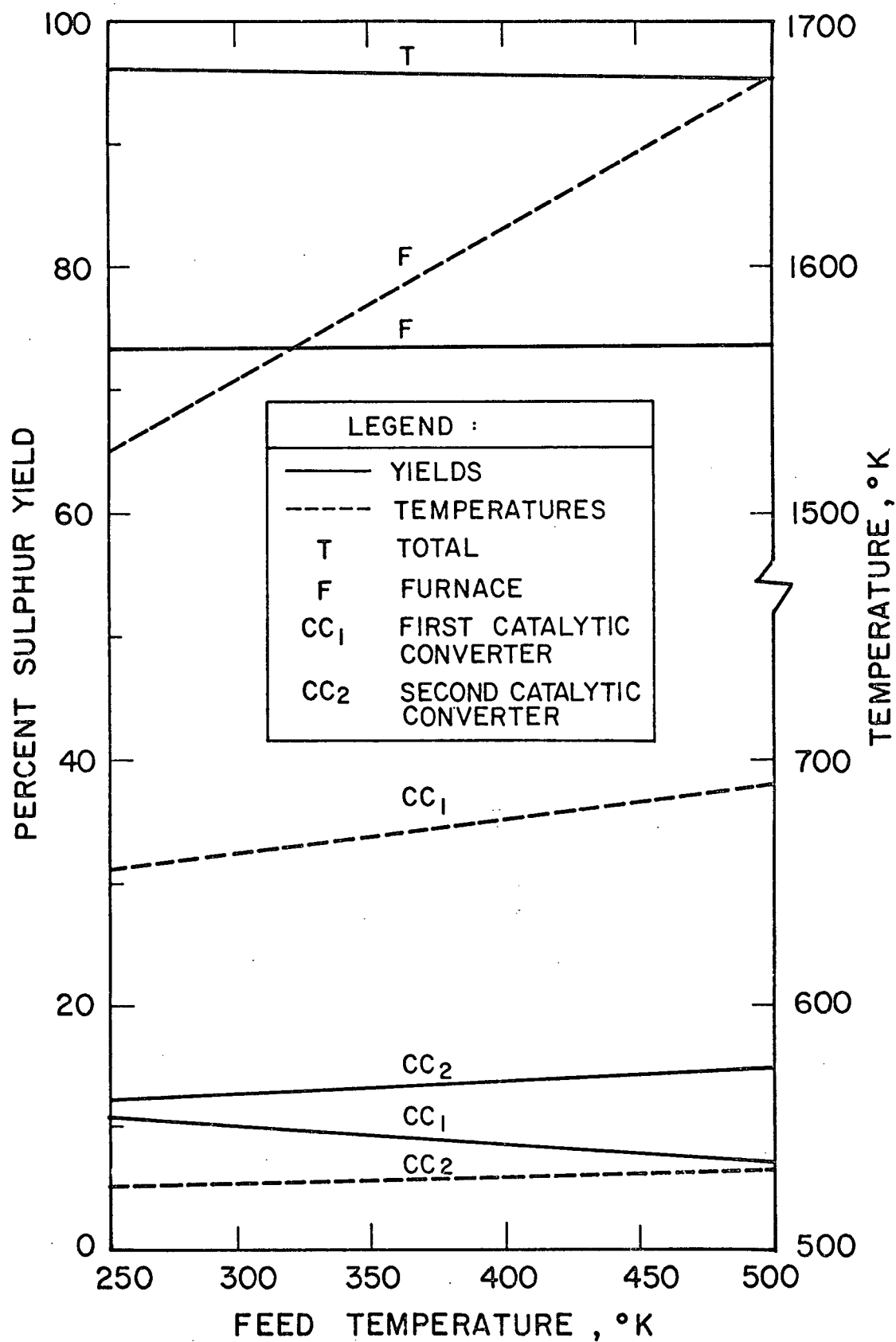


Figure 5.21. Effect of temperature of furnace feed on Claus plant yields and temperatures.

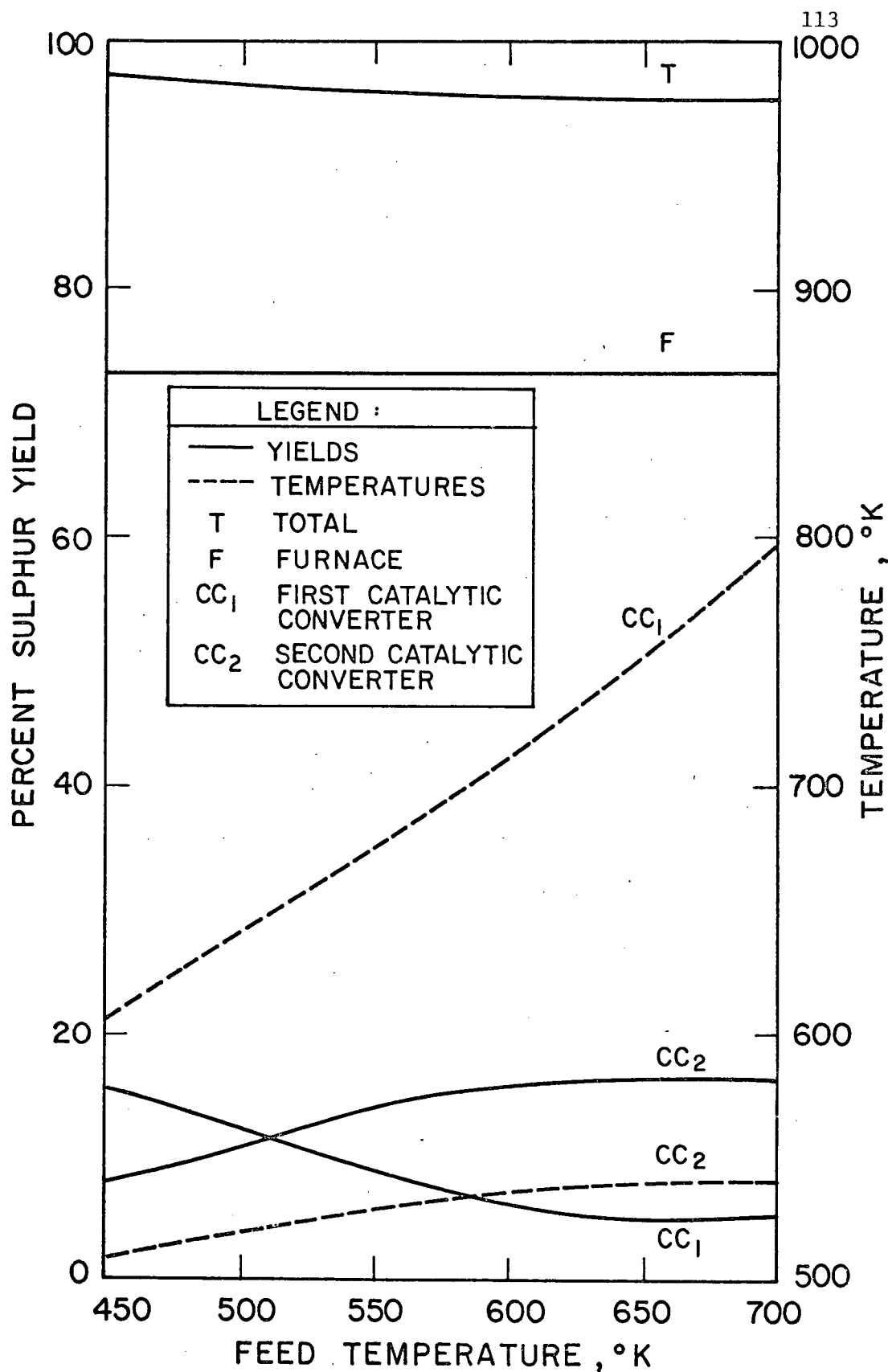


Figure 5.22. Effect of temperature of first converter feed on Claus plant yields and temperatures.

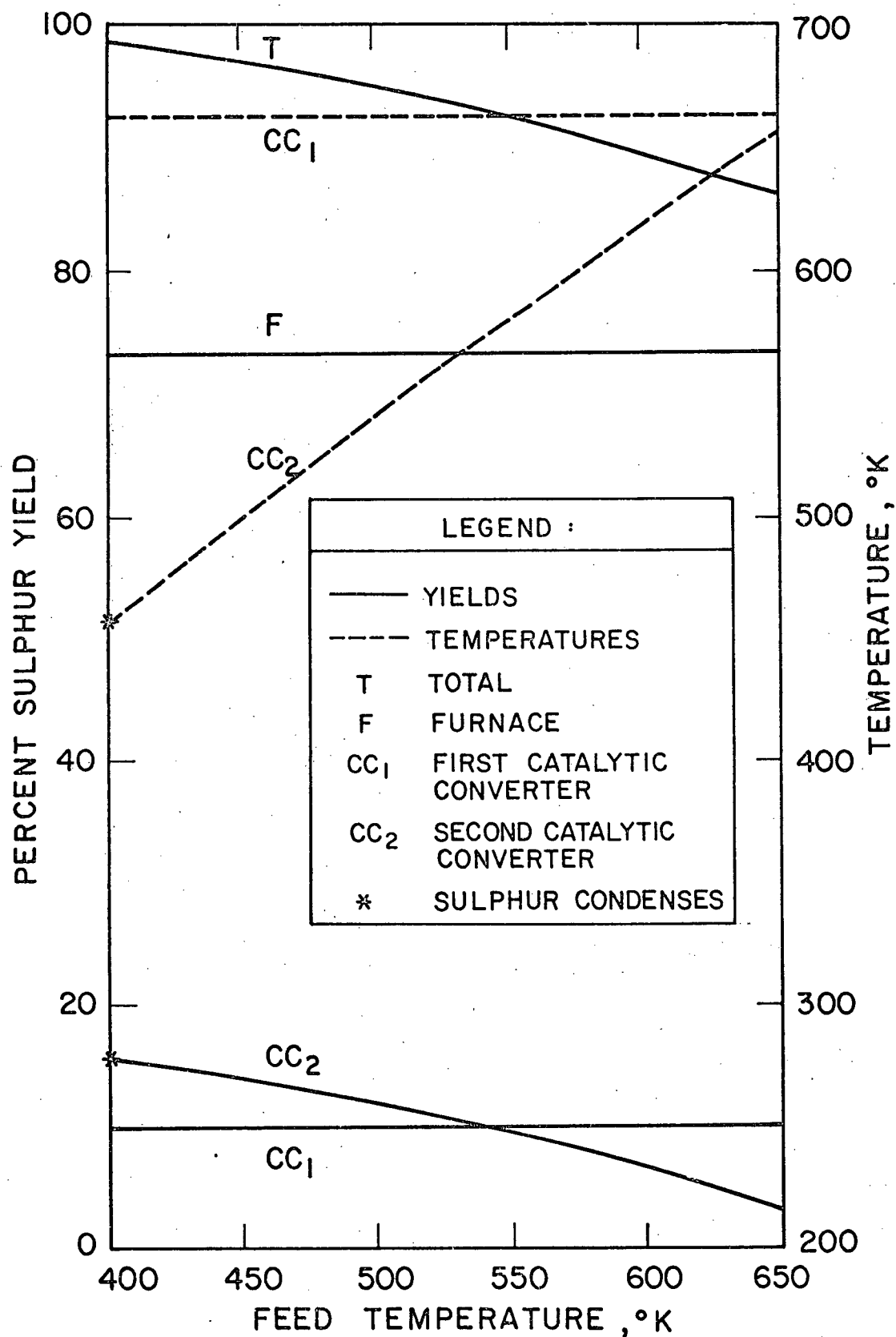


Figure 5.23. Effect of temperature of second converter feed on Claus plant yields and temperatures.

5.3 Effect of Recycle

In many chemical processes, part of the product stream is recycled to undergo additional reaction. This section investigates the effect of recycle, first for the Claus furnace alone, and then for the entire plant.

Figures 5.24 and 5.25 show that increasing the recycle enhances the yield of a Claus furnace operating isothermally and with $PA = 100$. In this thesis, yield is defined as the percentage of sulphur recovered based on the *feed* to the furnace. The reason for the rise in yield with recycle is that elemental sulphur is removed from the system, thus shifting the equilibrium of the Claus reactions to the right.

Although recycle promises greatly improved conversion under isothermal conditions, Claus plants behave more nearly adiabatically. The following sections investigate how recycle affects the yield of each unit of an adiabatic Claus plant operating at 100, 90 or 110% of stoichiometric air.

When $PA = 100$, then $R_{OS} = 1$ in the furnace. This corresponds to $R_{OH} = 0.5$, which, unlike R_{OS} , remains constant throughout the entire plant, because only *sulphur* is condensed downstream from the furnace. However, when $PA \neq 100$, $R_{OH} \neq 0.5$; this adversely affects the overall plant performance. Sufficient air to restore R_{OH} to 0.5 could be supplied to the first converter. Similarly, if $PA = 110$, additional H_2S may be supplied to the converter to restore R_{OH} to 0.5. These two examples are denoted by $PA = 90^*$ and $PA = 110^*$ respectively.

As shown in Fig. 5.26 recycle tends to lower the sulphur yield in the adiabatic furnace. Since recycling the product stream, which contains over 60% nitrogen, increases the volume of inerts in the furnace,

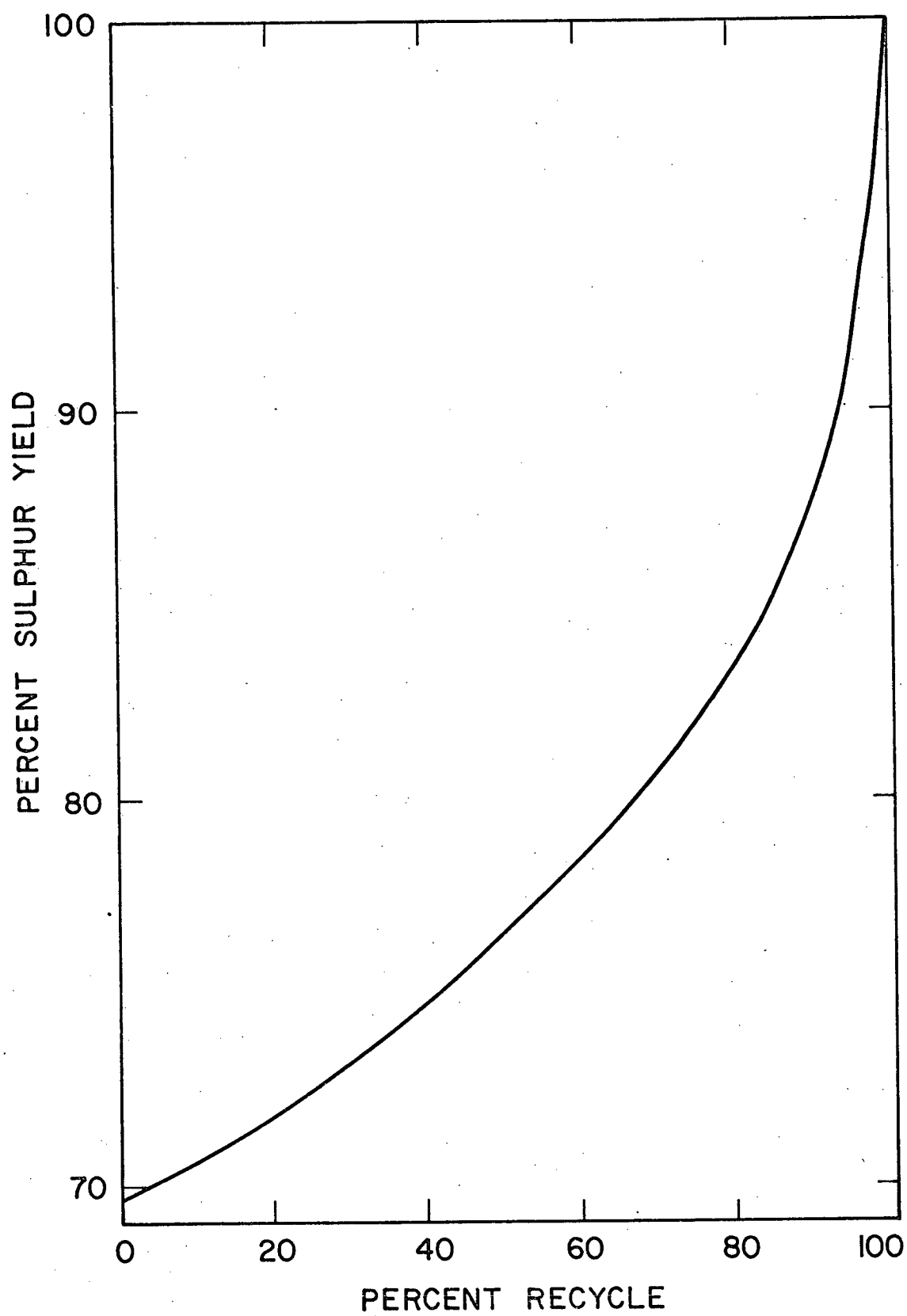


Figure 5.24. Effect of recycle on yield at 1300°K with PA = 100.

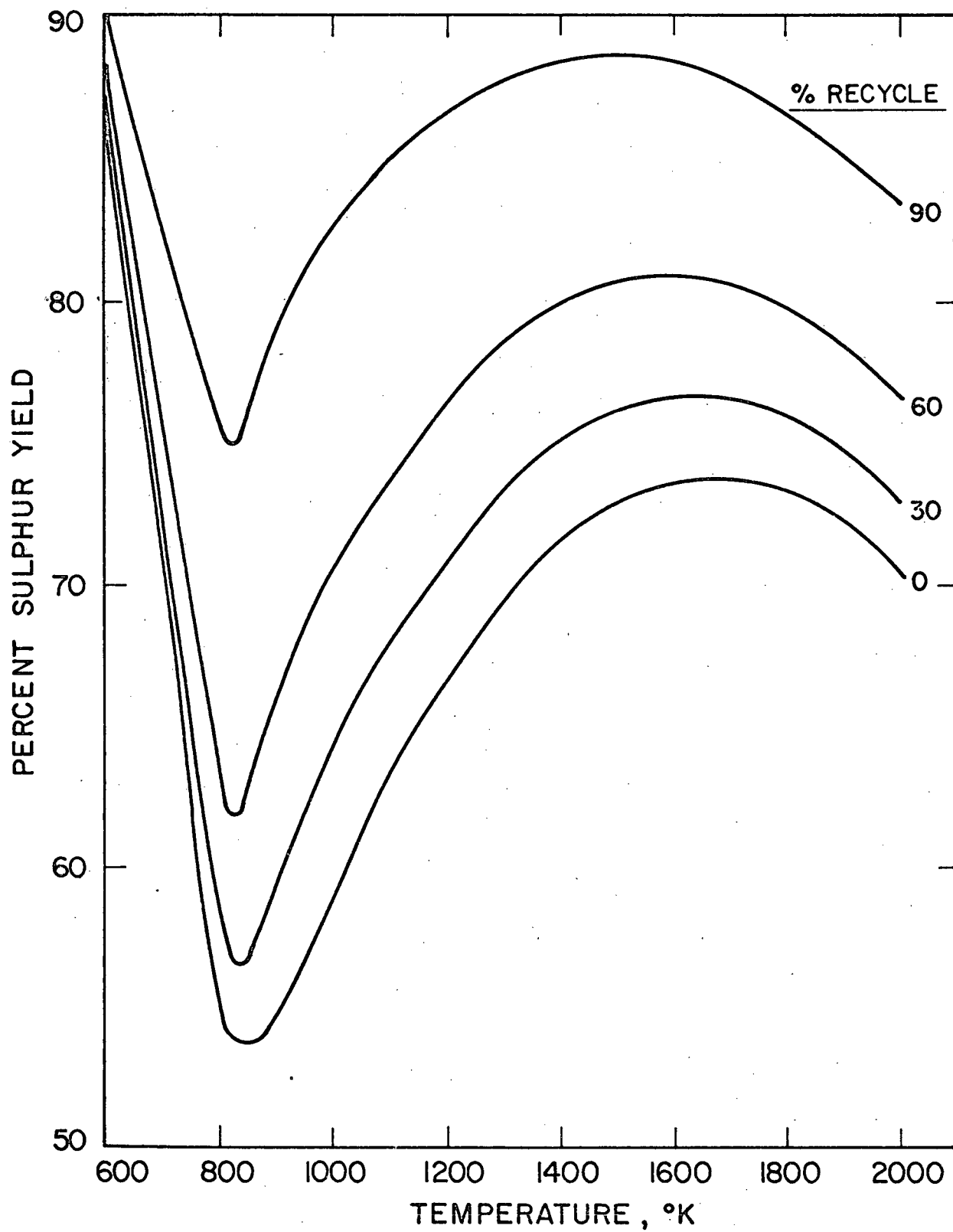


Figure 5.25. Effect of temperature on sulphur yield for various recycles.

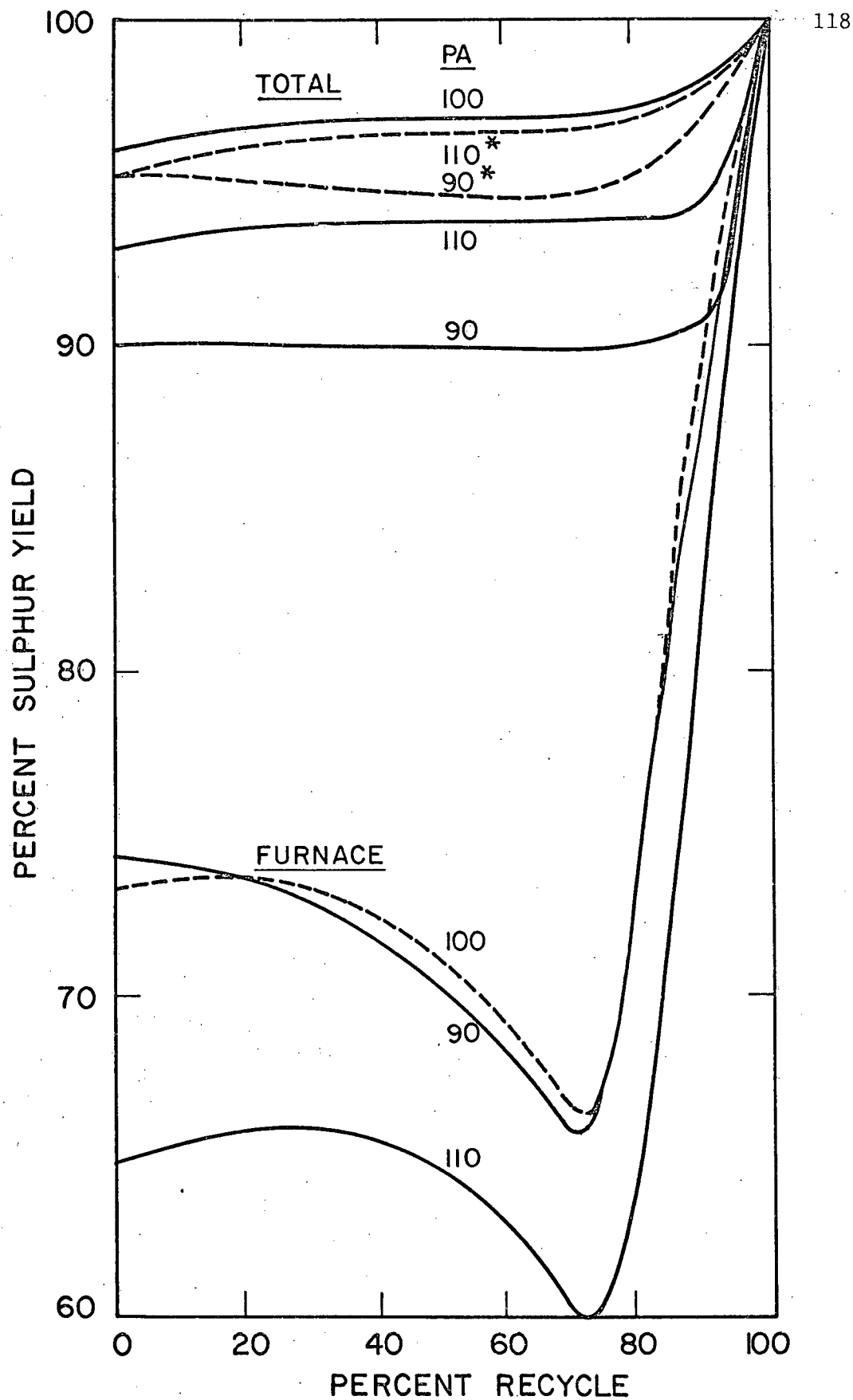


Figure 5.26. Effect of recycle on Claus plant yields.

PA = 90*: air added to feed of first converter.
 PA = 110*: H_2S added to feed of first converter.

and decreases the H_2S available for oxidation, less heat is produced. Therefore, the furnace temperature falls as shown in Fig. 5.27. The minimum sulphur yields in Fig. 5.26 occur at a recycle of slightly over 70% corresponding to a temperature of about 850°K on Fig. 5.27. This temperature results in the minimum yield for all recycles shown in Fig. 5.25. When the recycle exceeds 70%, the temperature lies in the "catalytic region" (i.e., below 850°K) where the yield increases with decreasing temperature.

Although consideration was given to recycling only the furnace gases, such recycle also influences the performance of the catalytic converters. Figure 5.28 shows that the temperature in the first converter, like that of the furnace, falls with increasing recycle. Since the converter operates below 850°K , the yield rises, as shown in Fig. 5.29. Between 50 and 75% recycle, temperature *increases* slightly but nevertheless, yield continues to rise. This is probably due to the drop in furnace yield resulting in an increase in unreacted H_2S in the converter feed which combines with SO_2 to form sulphur and gives off heat. Thus, despite the increased volume of inerts in the converter, its temperature rises slightly with recycle in this range. Above 75% recycle, however, most of the H_2S is oxidised to sulphur in the furnace, thus increasing its yield, but leaving little H_2S for the converter. The converter yield therefore drops sharply, with a corresponding fall in temperature.

The value of PA significantly affects the yield of the first converter only if air or H_2S is added to its feed. For $\text{PA} = 90\%$ the yield is halved, and the temperature rises over 100°K for all recycles. The extra air appears merely to oxidise the sulphur formed in the converter

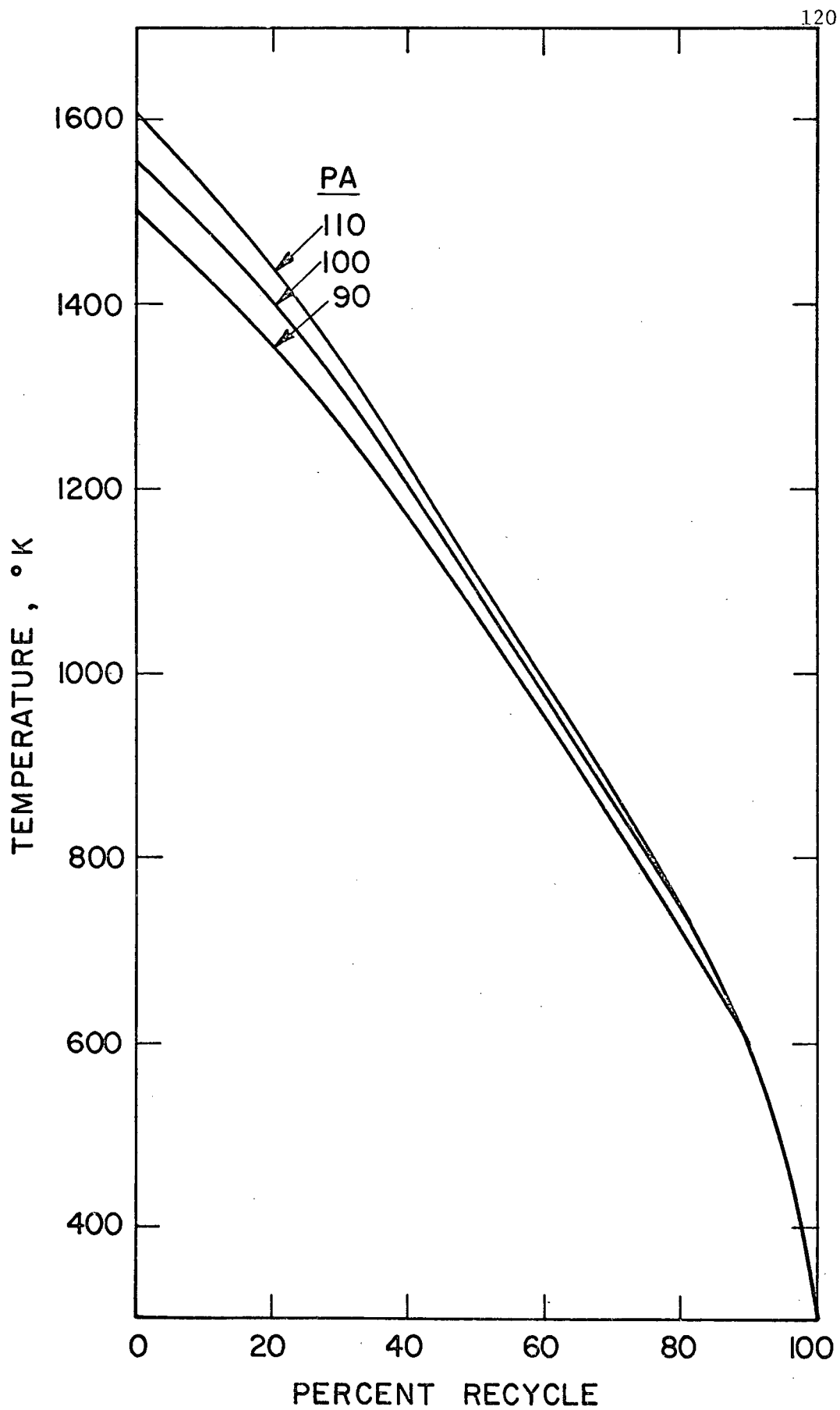


Figure 5.27. Effect of recycle on temperature of the Claus furnace.

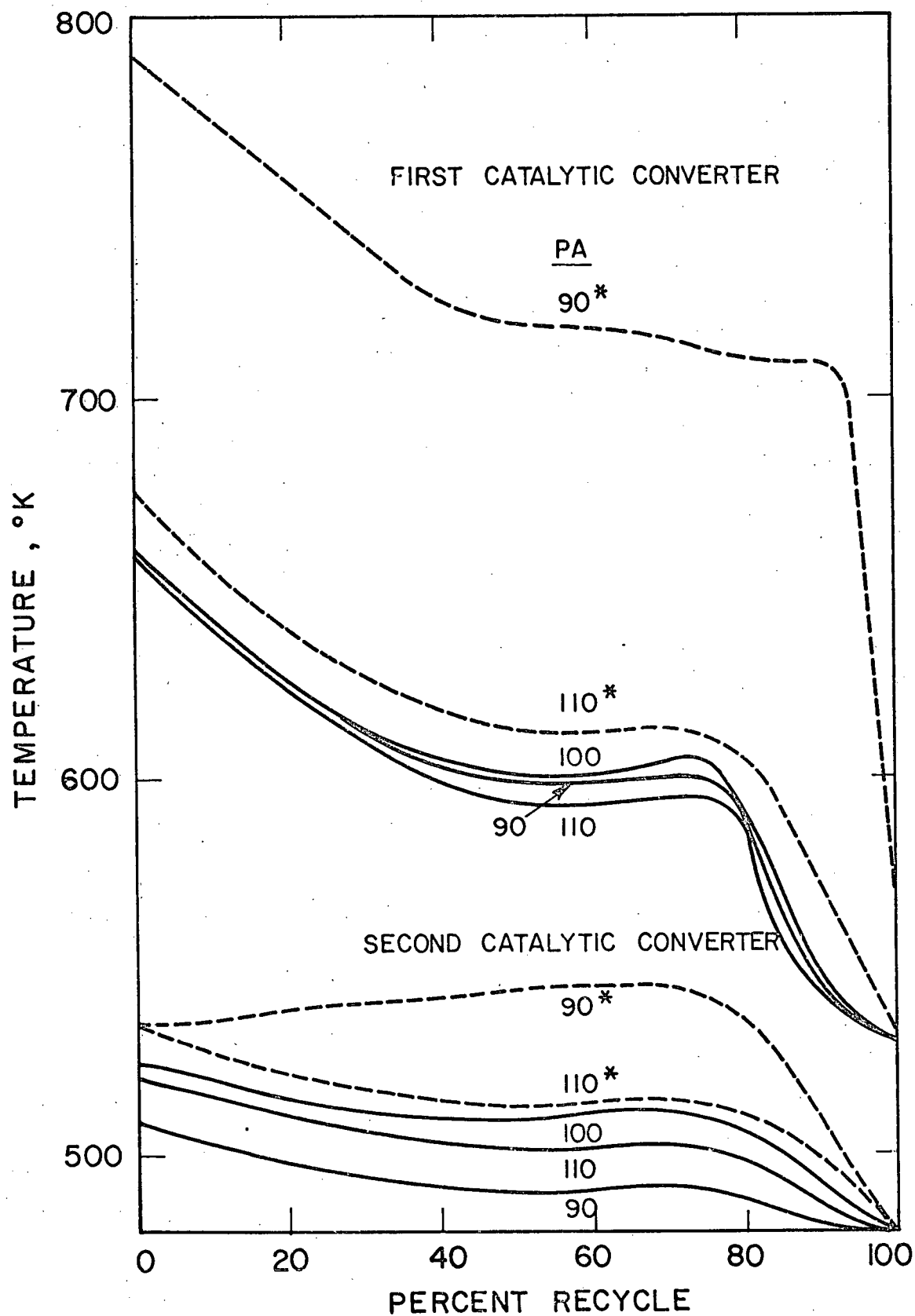


Figure 5.28.. Effect of recycle on temperature of the catalytic converters.
 PA = 90*: air is added to first converter feed.
 PA = 110*: H_2S is added to first converter feed.

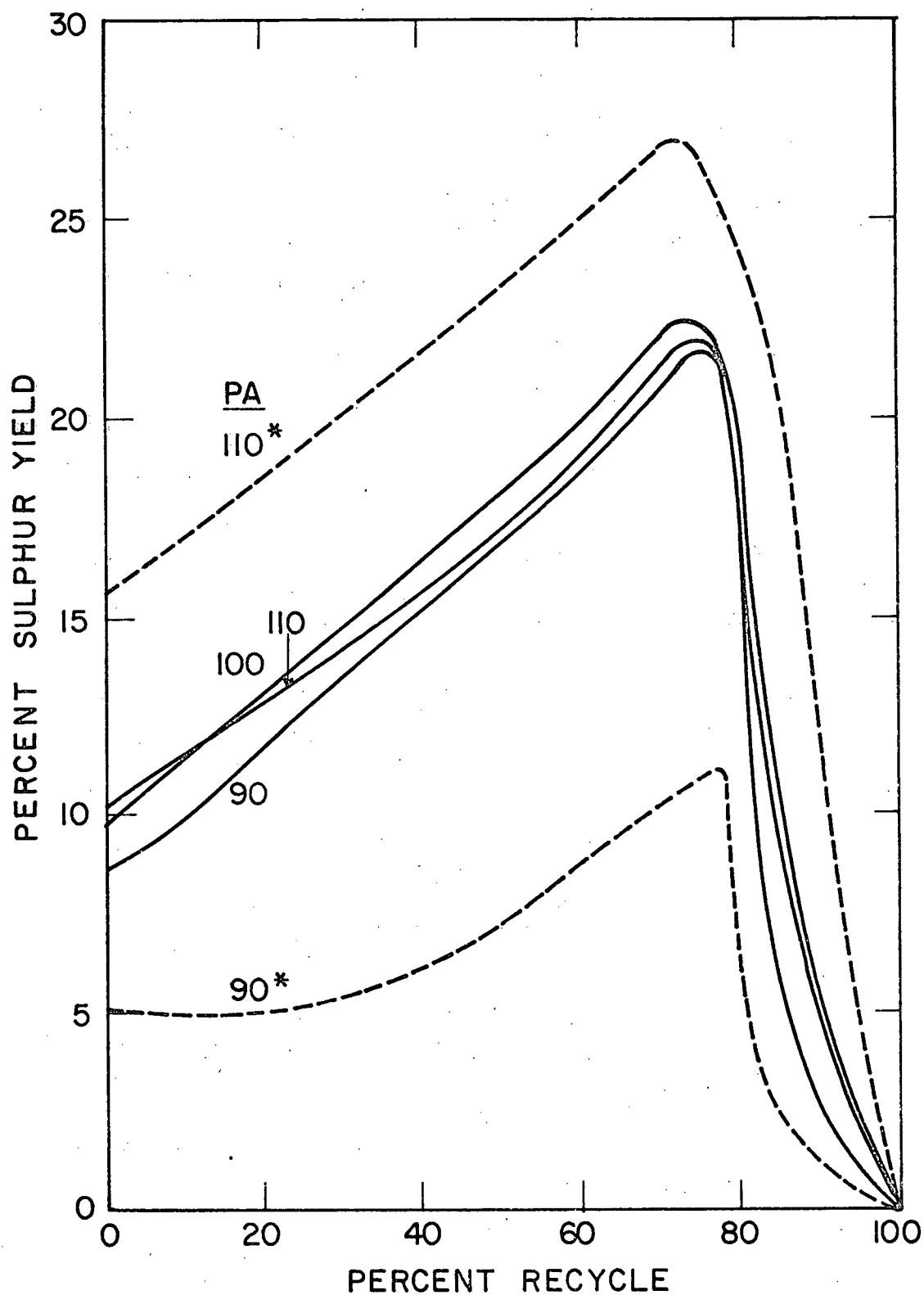


Figure 5.29. Effect of recycle on yield of the first catalytic converter.
 PA = 90*: air is added to first converter feed.
 PA = 110*: H_2S is added to first converter feed.

thus causing the yield to fall and the temperature to rise. The yield is highest for $PA = 110^*$, since the added H_2S reacts in the converter with the large amounts of SO_2 produced.

The second converter produces the highest yield when $PA = 90^*$, as shown in Fig. 5.30. This is probably a result of this unit's compensating for $PA = 90^*$ giving the lowest yield in the first converter. The next highest yields in the second converter correspond to $PA = 110^*$, 100, 110 and 90, the same order as for the first.

The effect of air and recycle on the overall yield of the Claus plant is shown on Fig. 5.26. It is clear that the best performance is obtained operating with 100% stoichiometric air and without any recycle. The increase in yield in the converters resulting from operation at $PA = 110^*$ does not compensate sufficiently for the poor yield in the furnace. For $PA = 90^*$, 110, or 90, yields are even poorer. The negligible gains obtained with recycle are probably not worth the cost of the larger furnace and additional piping and controls required. Thus, it appears that conventional operation at 100% stoichiometric air with no recycle is best.

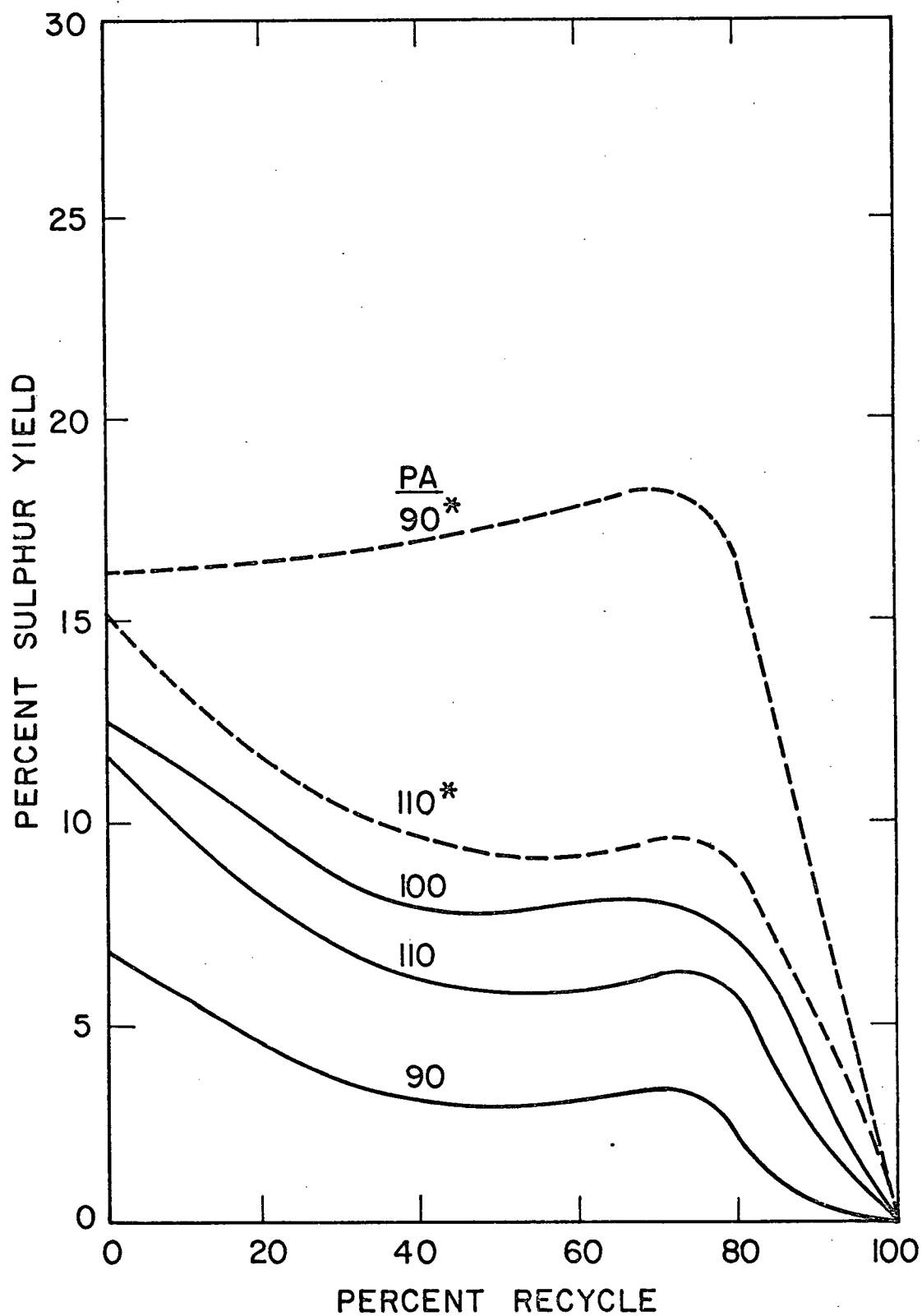


Figure 5.30. Effect of recycle on yield of the second catalytic converter.
PA = 90*: air is added to first converter feed.
PA = 110*: H_2S is added to first converter feed.

CHAPTER 6

EXPERIMENTAL RESULTS

Experimental results for temperatures between 800 and 1500°K are presented in Appendix D. Figures 6.1 to 6.6 illustrate the effect of stoichiometric air (P_A) on the concentrations of H_2 , H_2S , SO_2 , N_2 , H_2O and S_2 in the product mixture. Figures 6.7 to 6.14 show the effect of P_A on sulphur yield.

6.1 Averaging Technique

Since the P_A values were determined several times for each run, both by the flow method (cf Sect. 4.4.1) and mass balance calculations (cf Sect. 4.4.3), an average value was obtained before plotting. For example, point A in Fig. 6.10 was calculated as follows. The mean P_A value found by the flow method is 119.5, whereas the corresponding quantity from the mass balances is 127.4 (see Table D.4, run 77). The average is therefore 123.4. Similarly, the equilibrium vessel compositions and the corresponding sulphur yield were also averaged for each set of experimental conditions. The data points in Figs. 6.7 to 6.14 were plotted with bars, showing the range of P_A values and sulphur yields.

6.2 Comparison of Experimental with Theoretical Results

Figures 6.1 to 6.6 clearly show that the experimental and theoretical results follow the same general trends. However, substantial differences in the compositions and sulphur yields may also be noted.

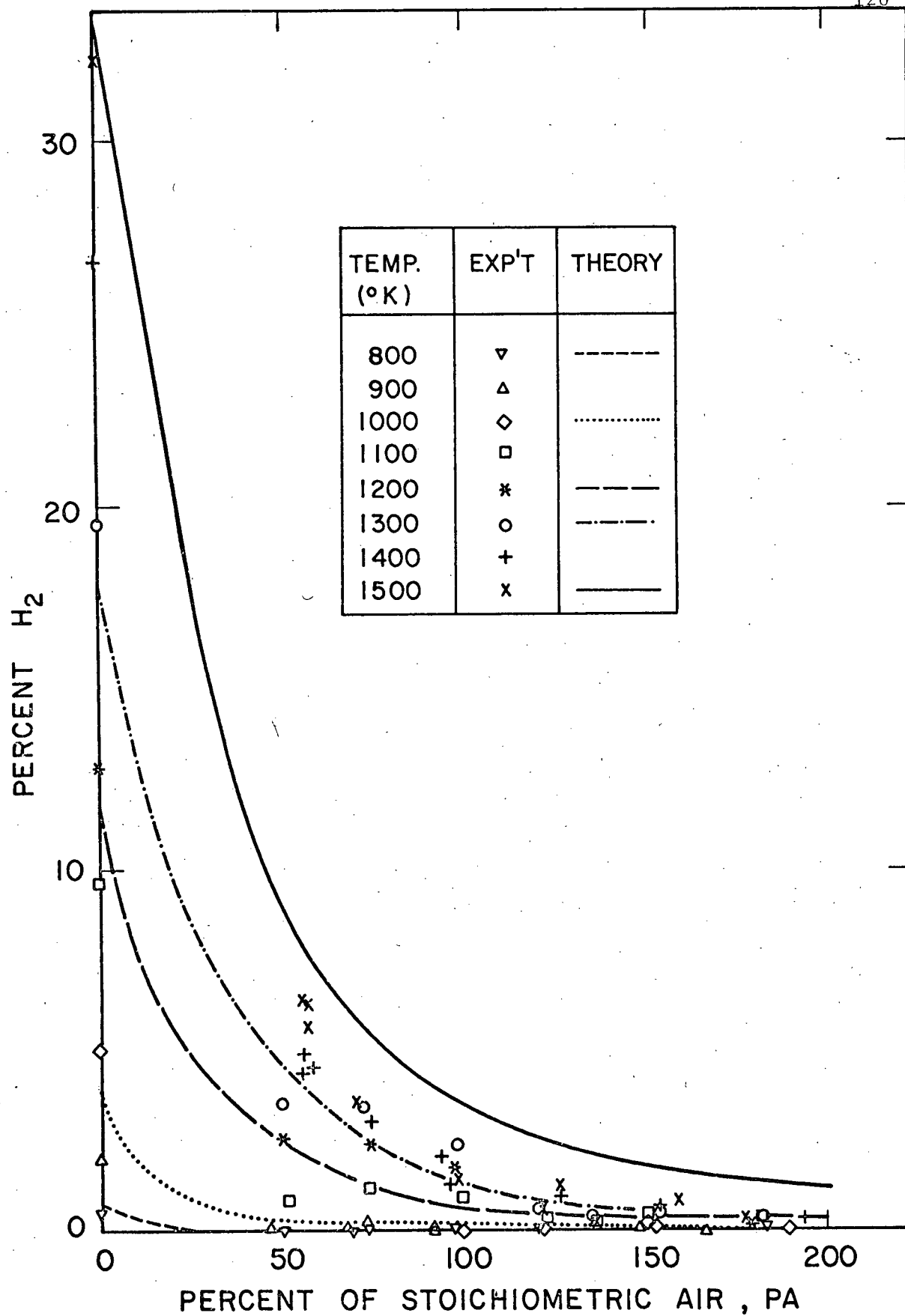


Figure 6.1. Effect of PA on H_2 .

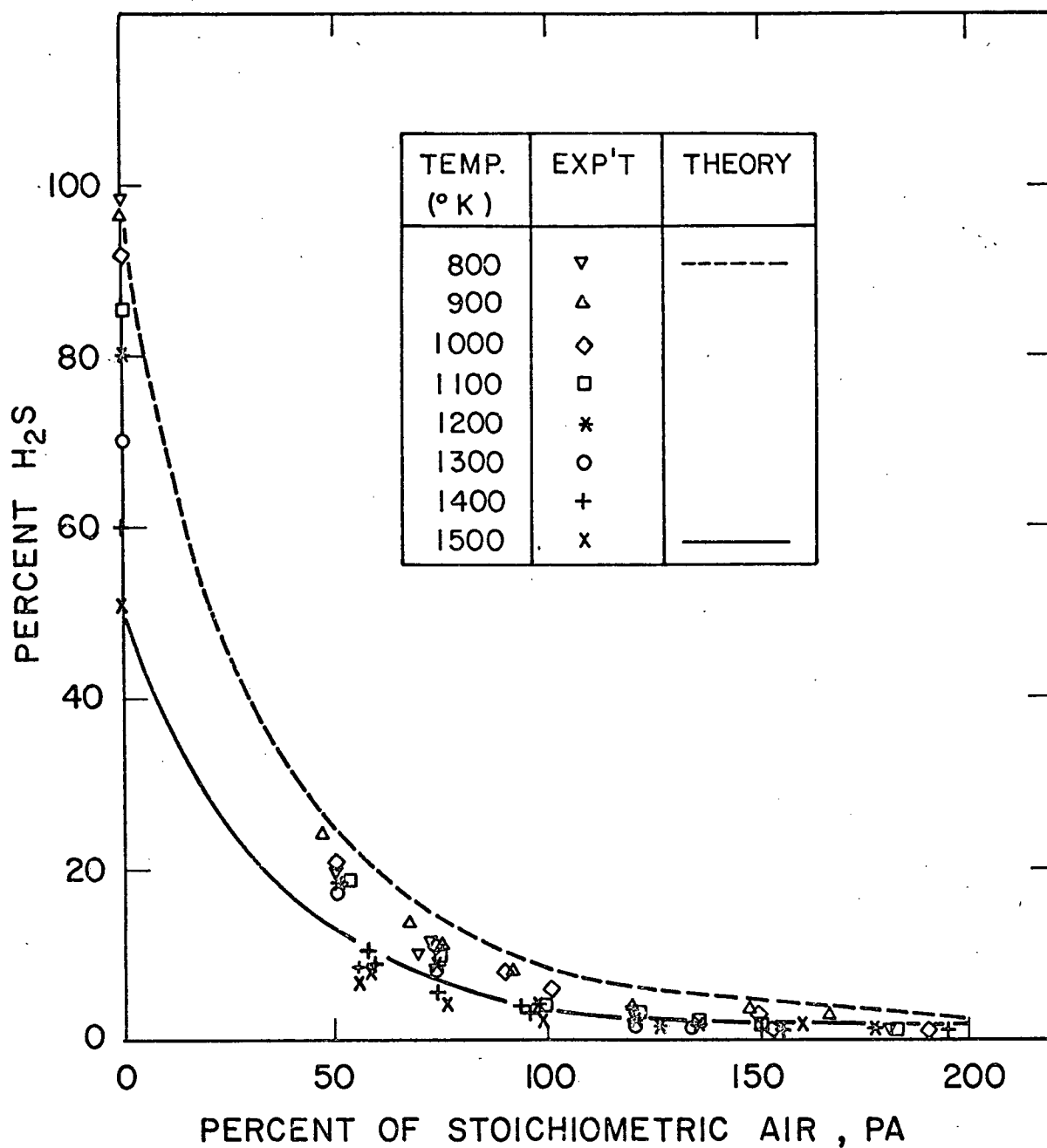


Figure 6.2. Effect of PA on H_2S .

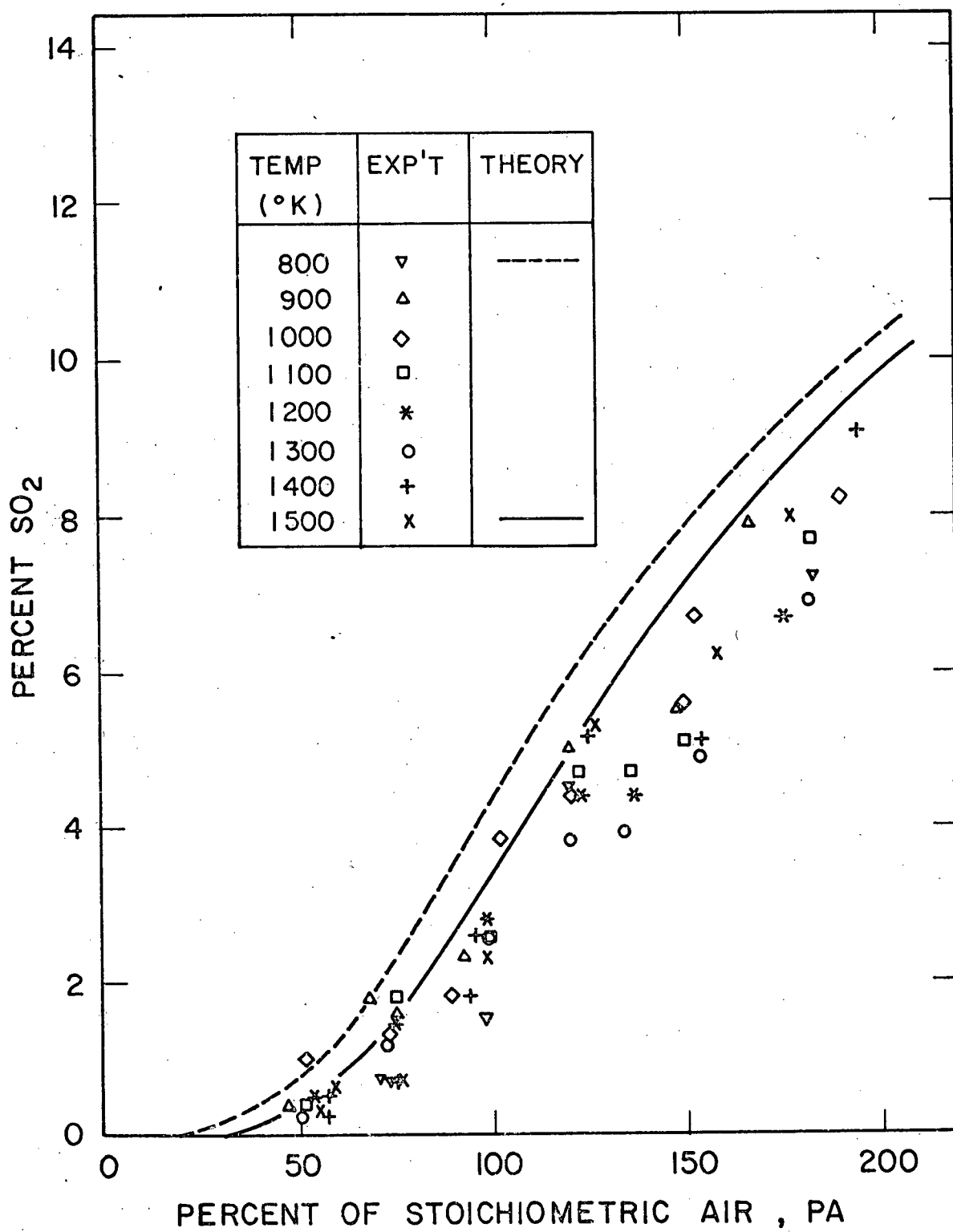


Figure 6.3. Effect of PA on SO_2 .

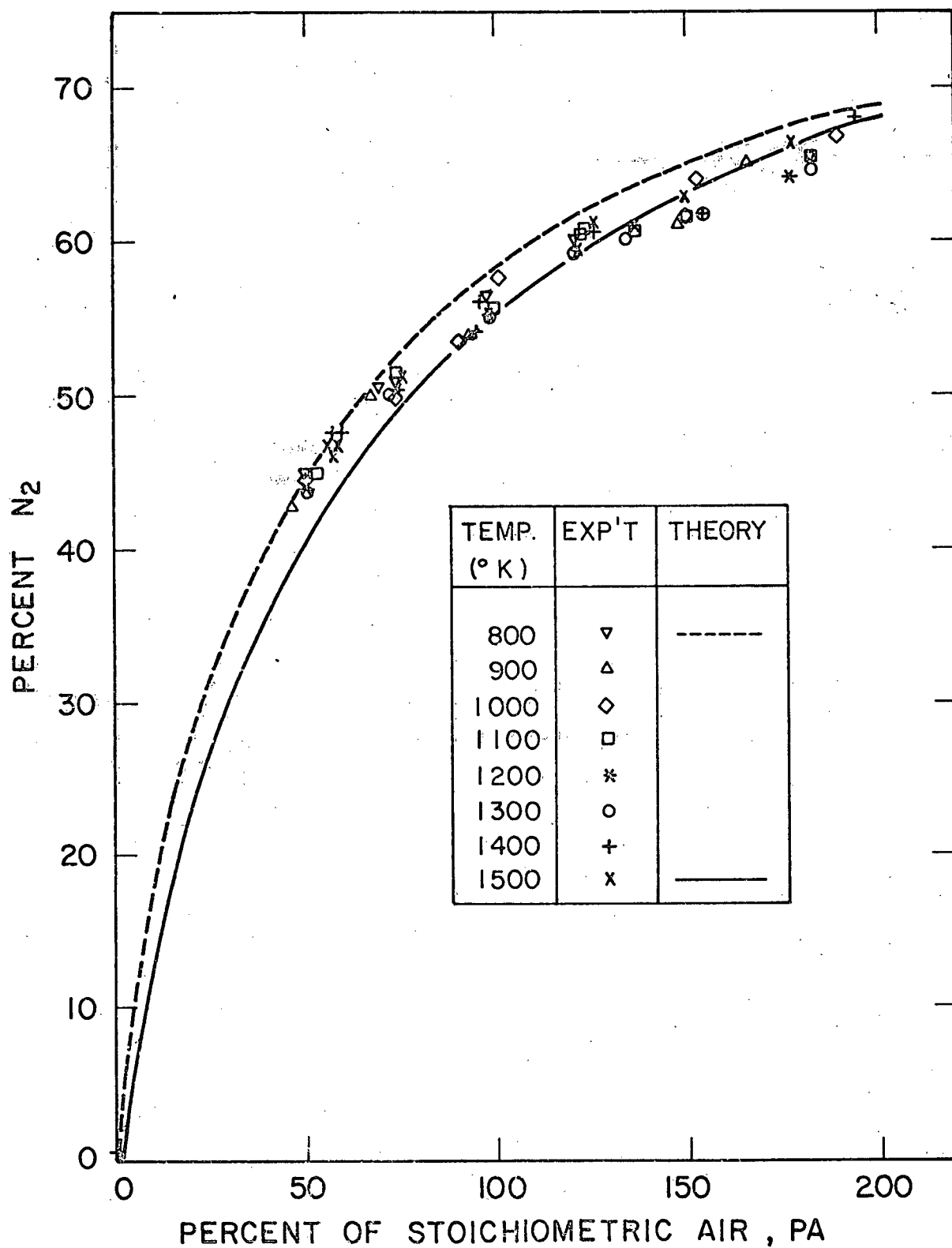


Figure 6.4. Effect of PA on N_2 .

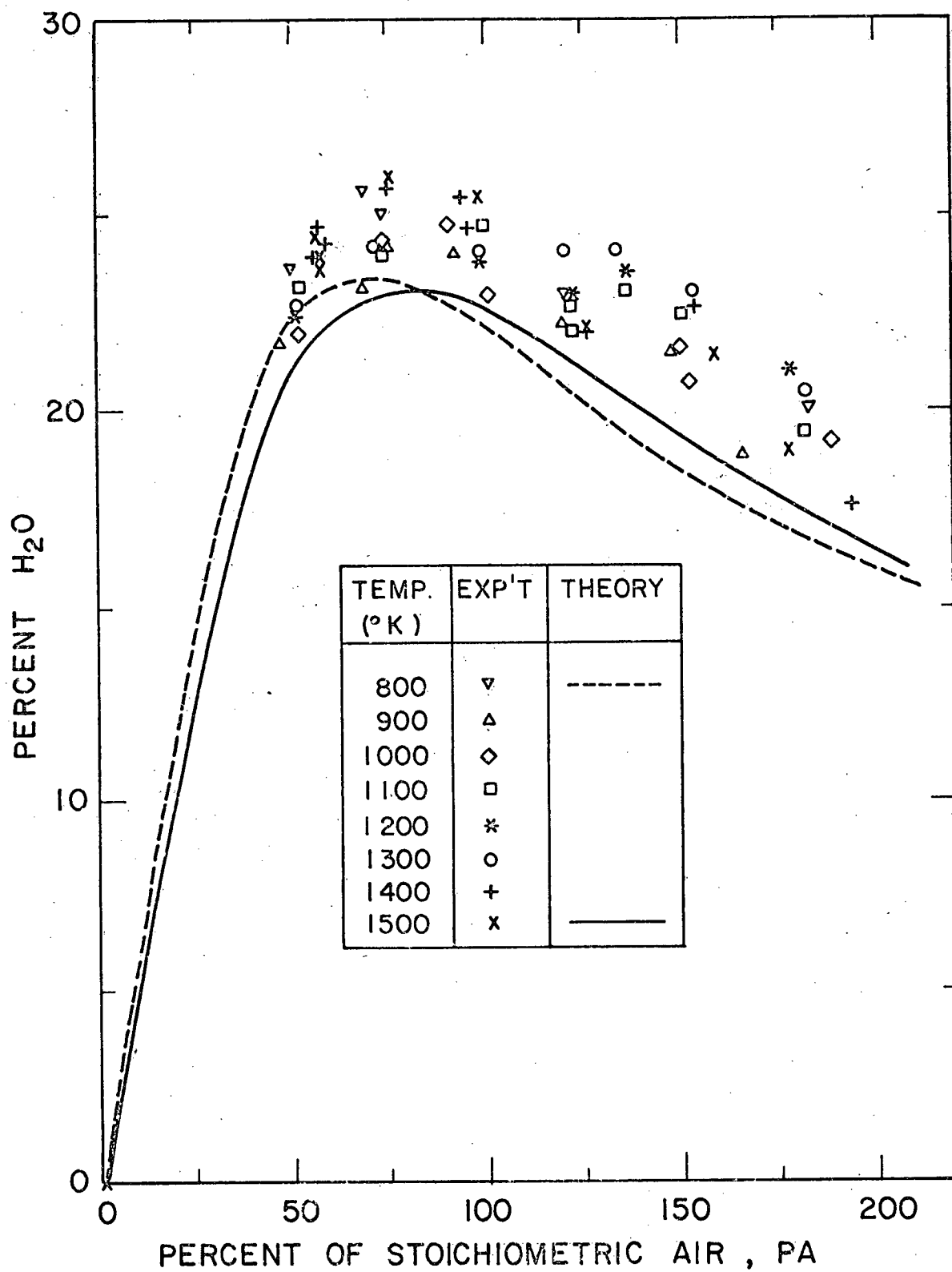
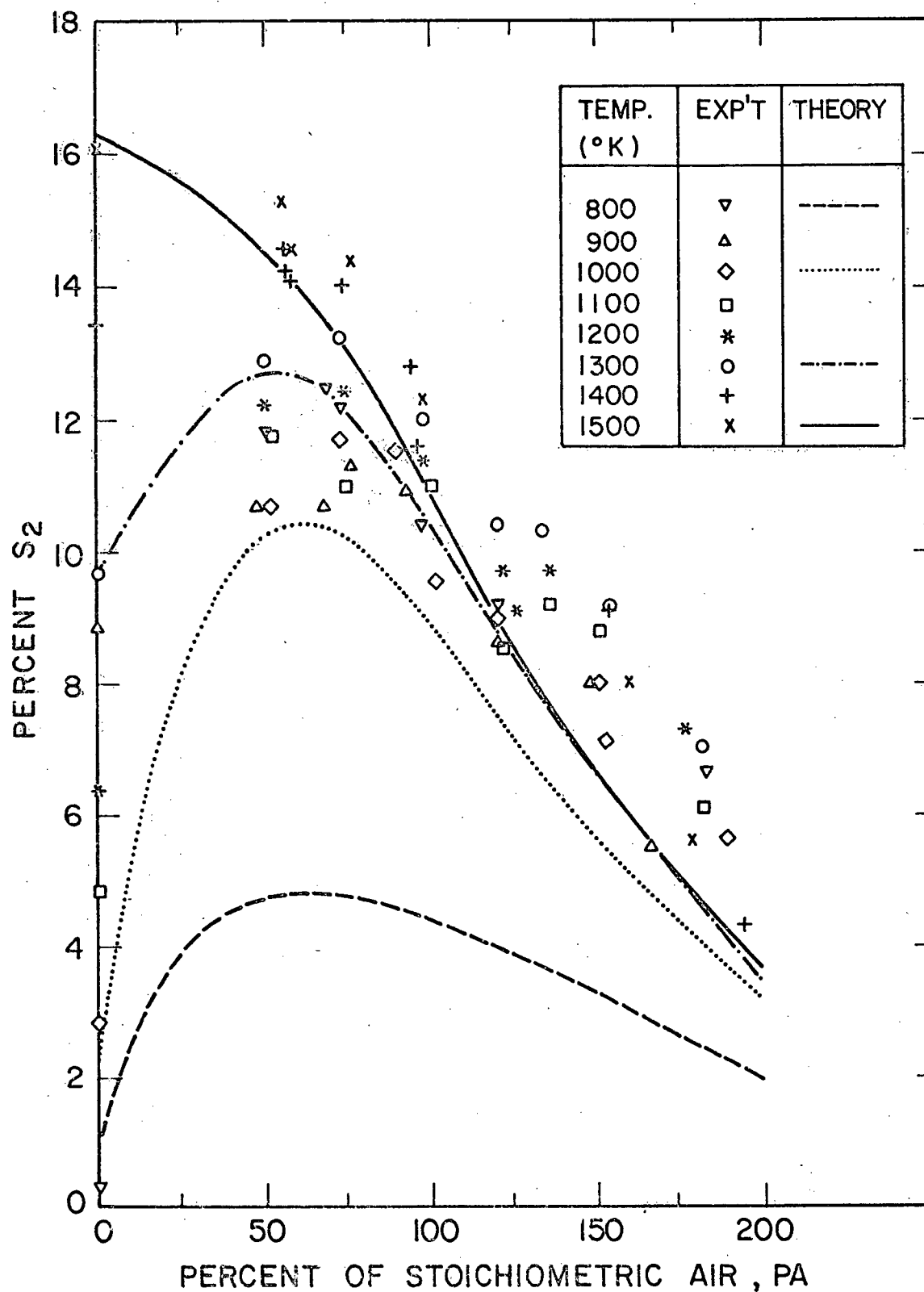


Figure 6.5. Effect of PA on H_2O .

Figure 6.6. Effect of PA on S_2 .

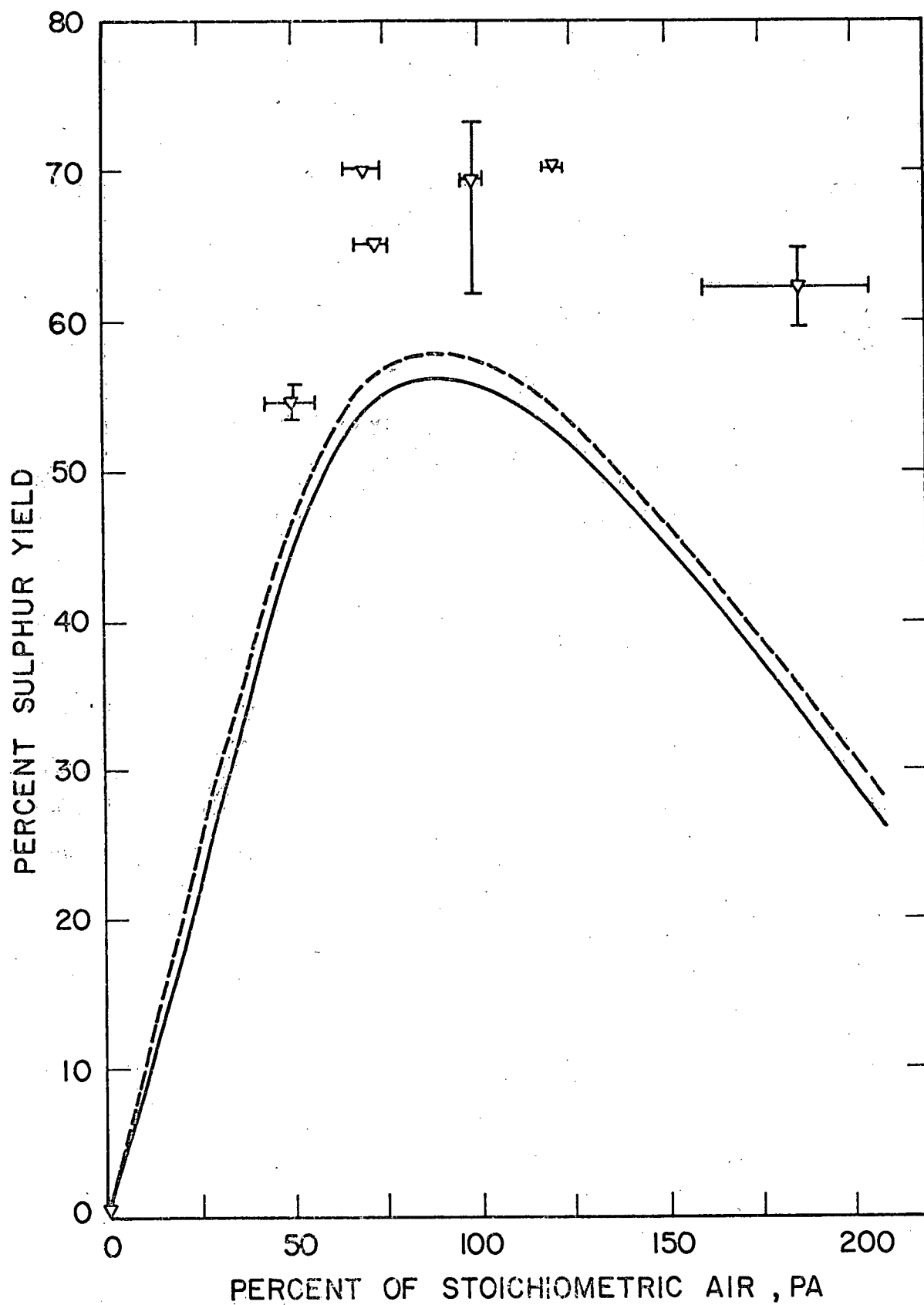


Figure 6.7. Effect of PA on sulphur yield at 800°K.

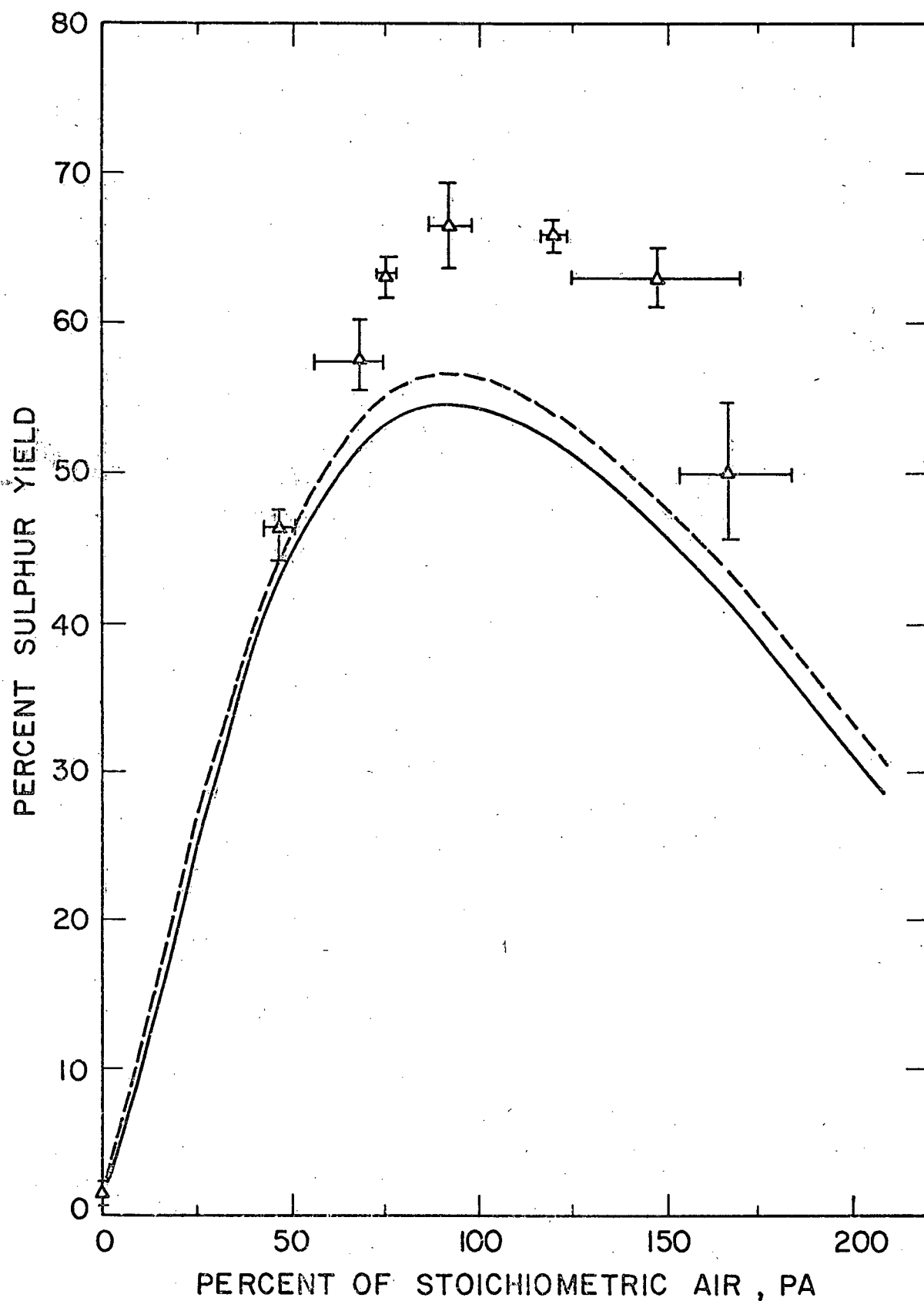


Figure 6.8. Effect of PA on sulphur yield at 900°K.

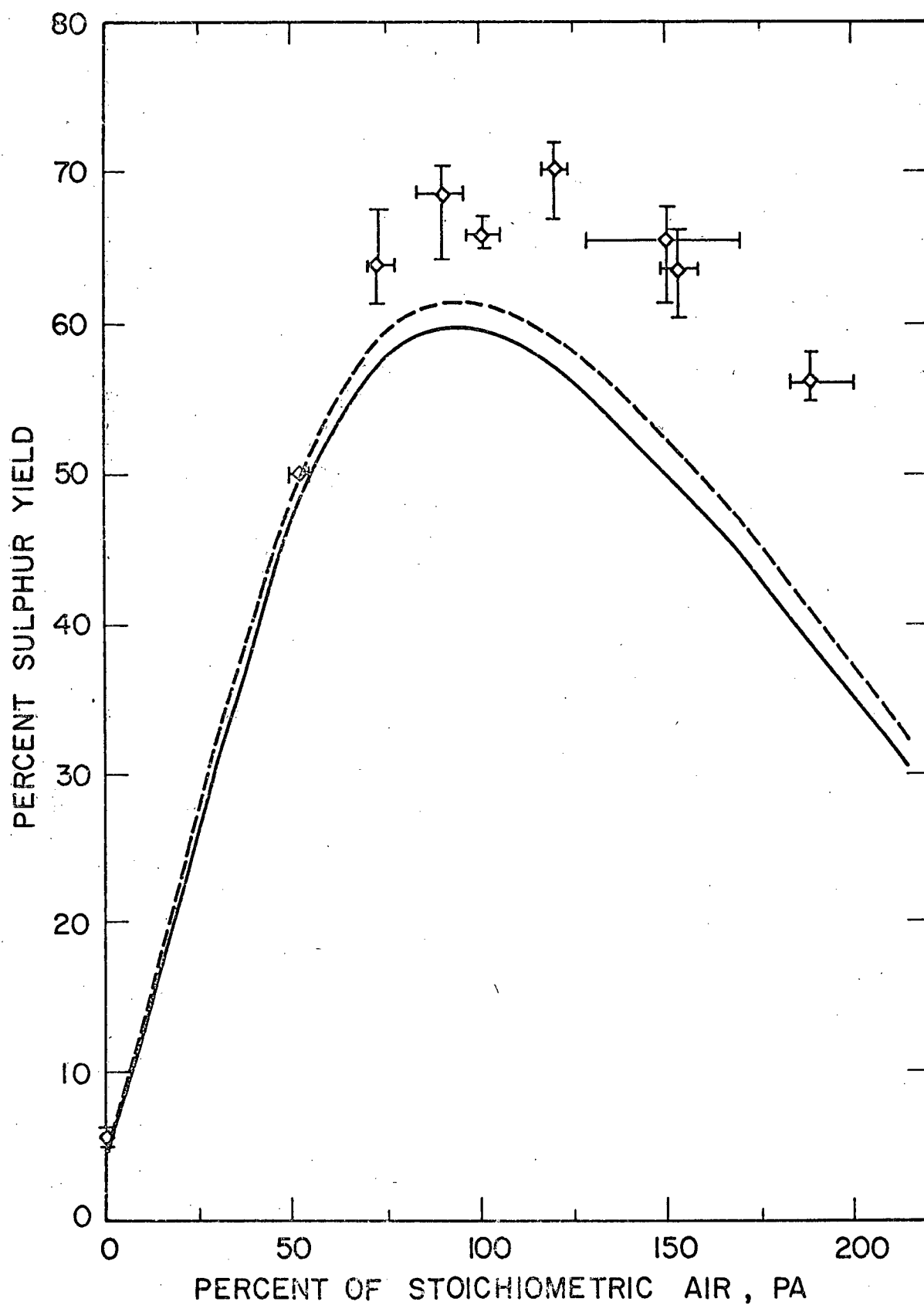


Figure 6.9. Effect of PA on sulphur yield at 1000°K.

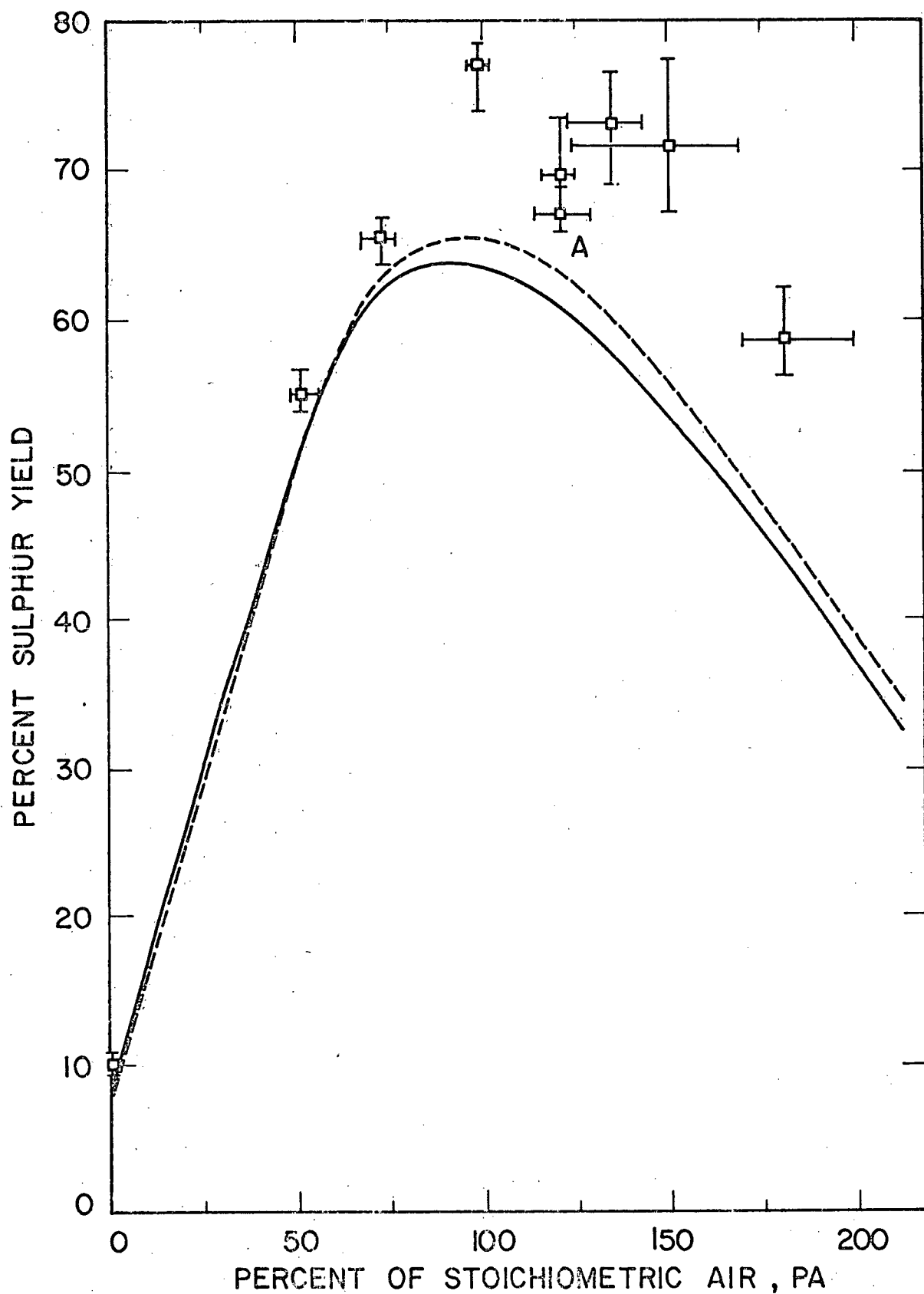


Figure 6.10. Effect of PA on sulphur yield at 1100°K.

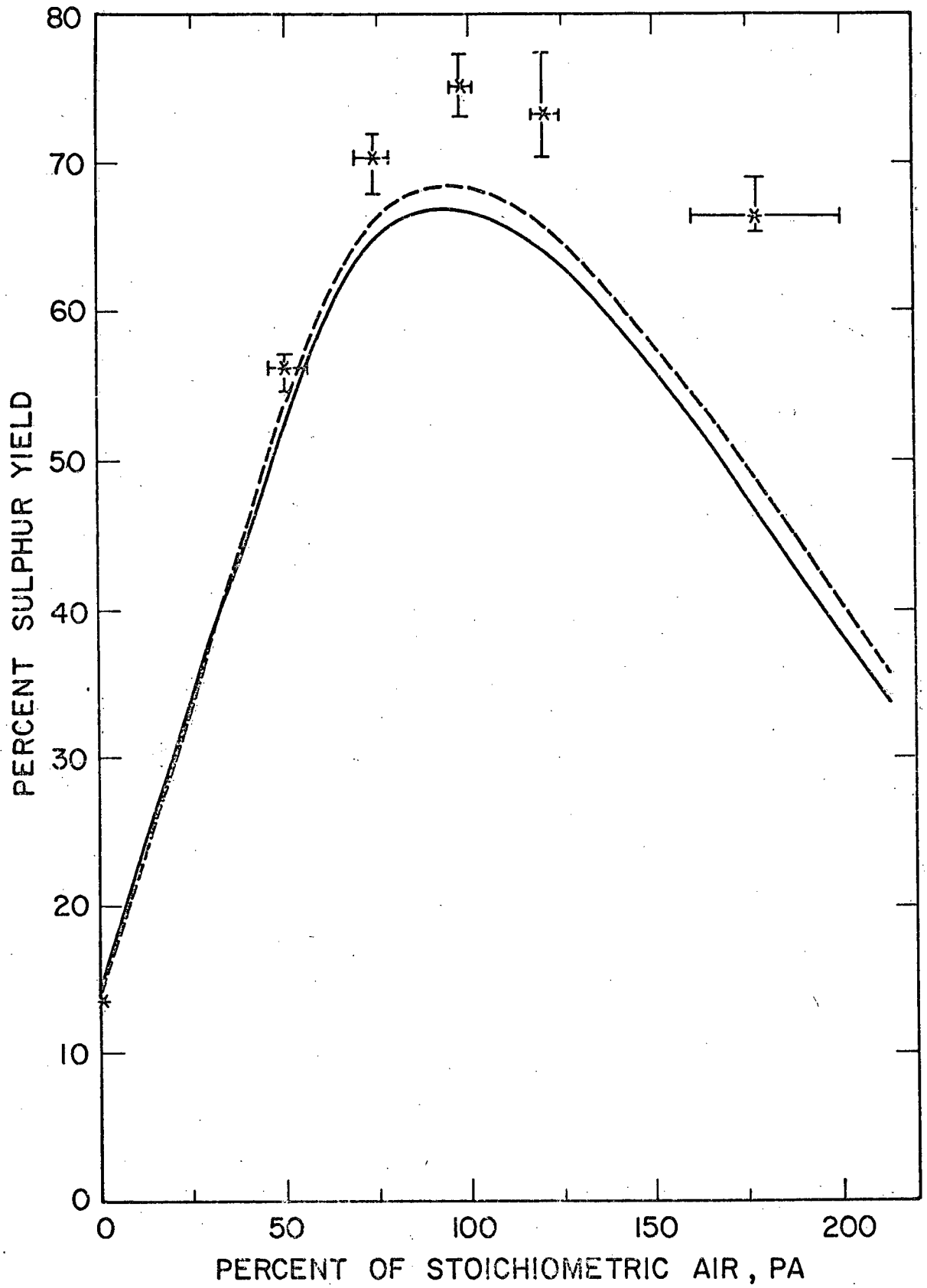


Figure 6.11. Effect of PA on sulphur yield at 1200°K.

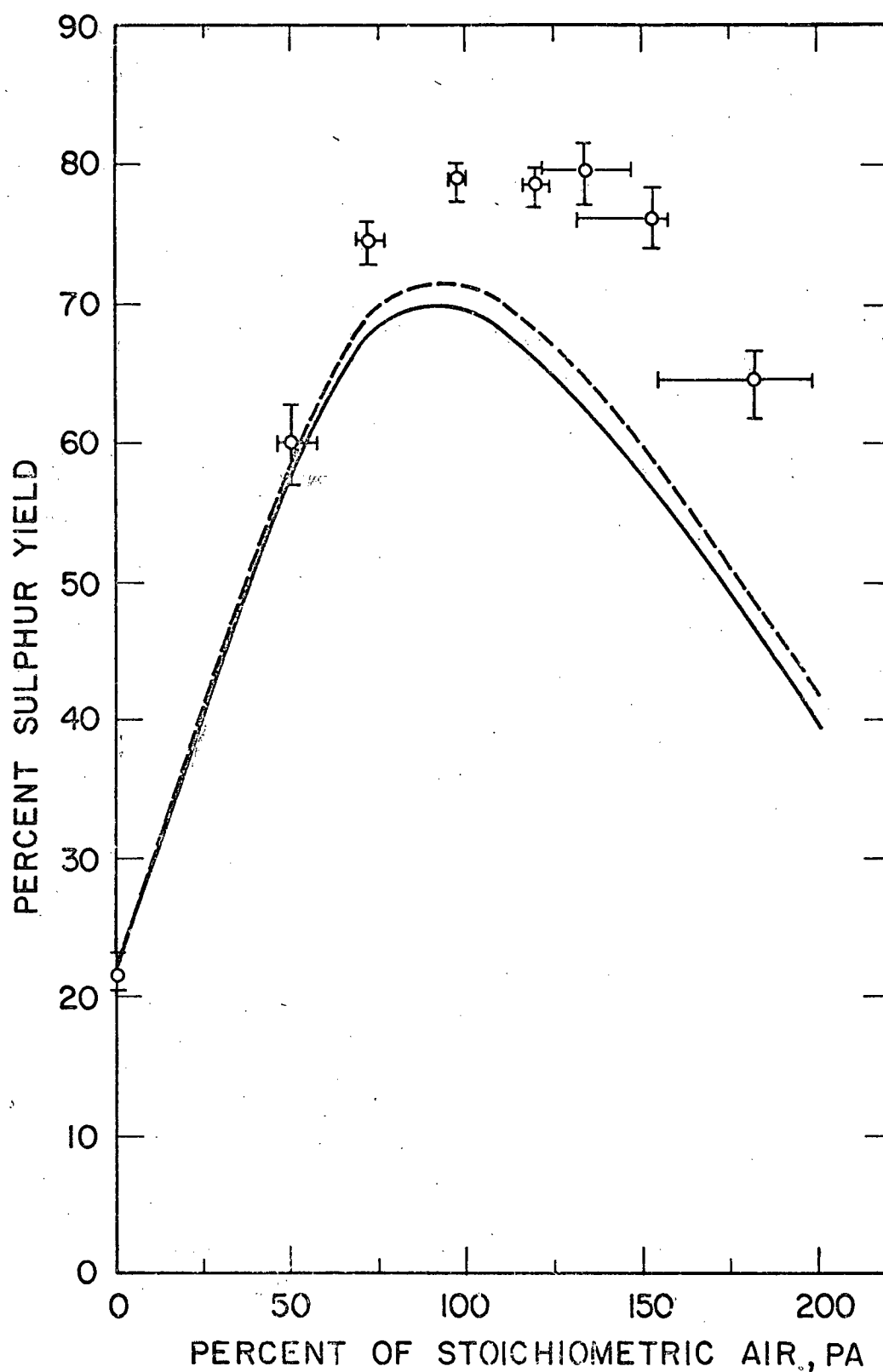


Figure 6.12. Effect of PA on sulphur yield at 1300°K.

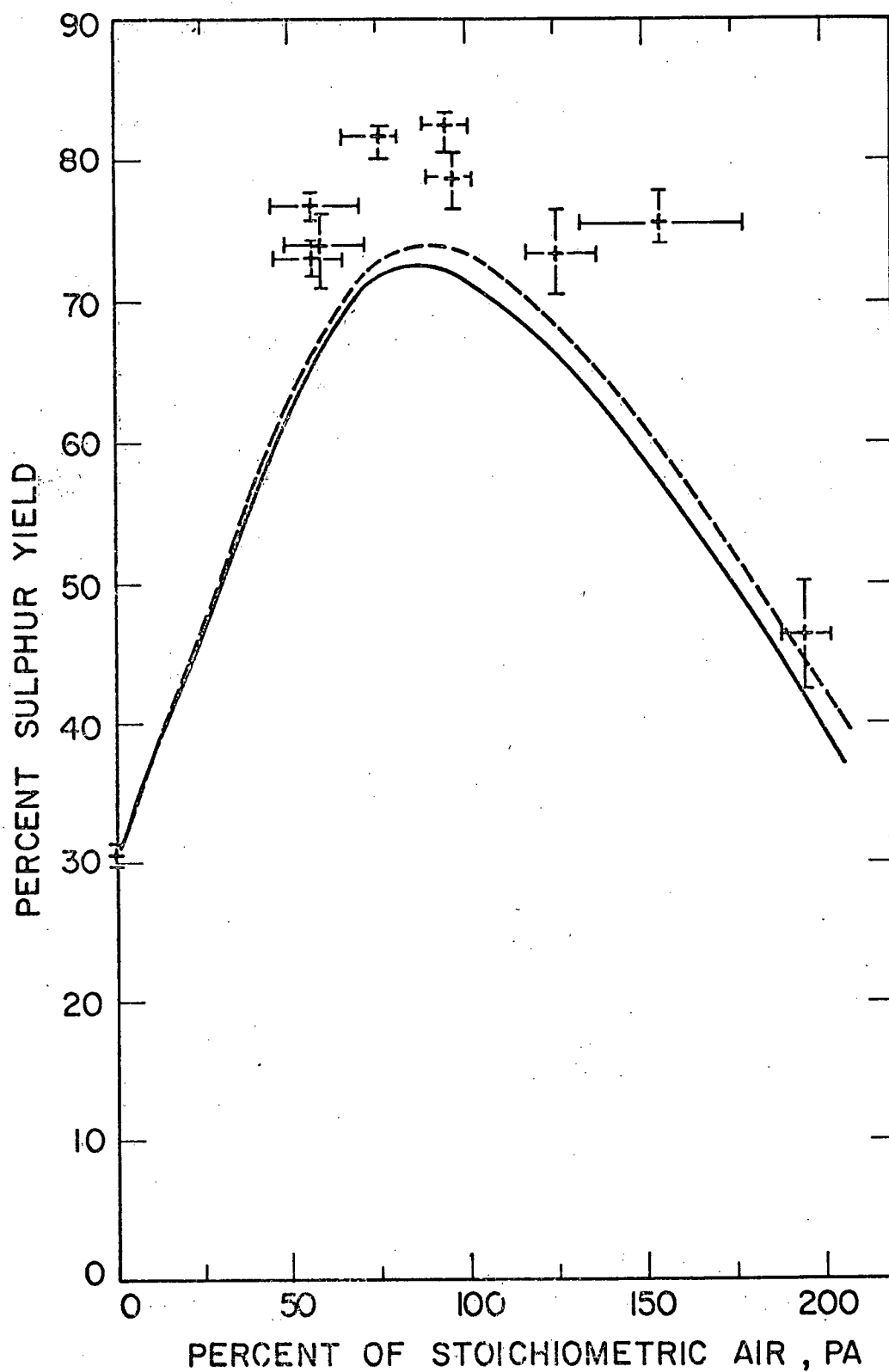


Figure 6.13. Effect of PA on sulphur yield at 1400°K.

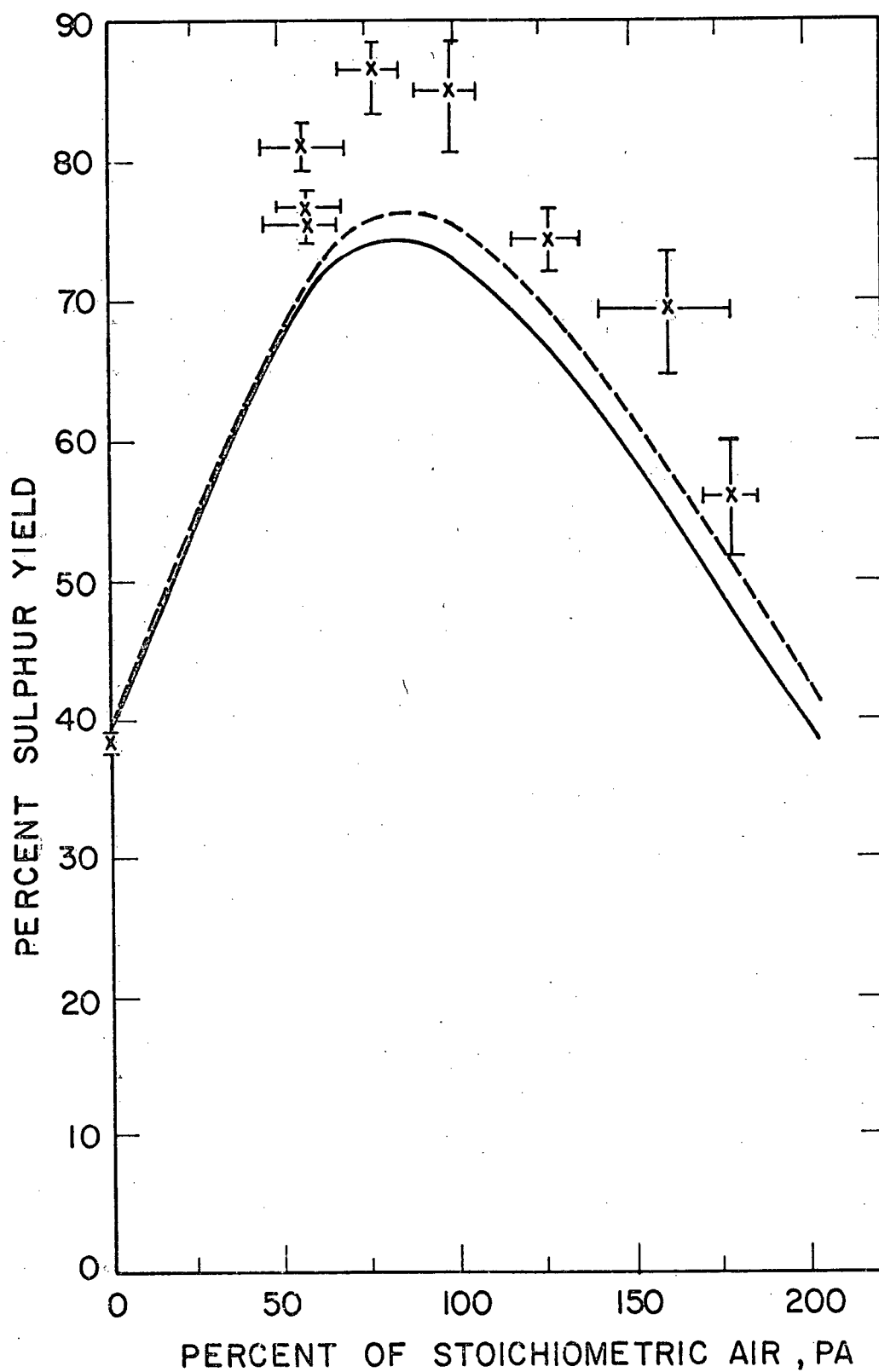


Figure 6.14. Effect of PA on sulphur yield at 1500°K.

Possible causes of these discrepancies are discussed in Sect. 6.3.

6.2.1 Effect of Temperature

The effect of temperature on the concentration of H_2 , H_2S , SO_2 , N_2 , H_2O , S_2 and sulphur yield is best seen in Figs. 5.1 to 5.4. It is believed that an increase in temperature (at constant P_A) promotes the dissociation of H_2S into H_2 and sulphur; thus, the concentration of H_2S falls while the amount of H_2 and S_2 rises.

The concentrations of SO_2 and H_2O are virtually independent of temperature. This may be due to the fact that an increase in temperature not only favours the formation of SO_2 and H_2O via H_2S oxidation, but also promotes their dissociation.

The concentration of N_2 drops slightly with rising temperature. Although the number of moles of N_2 is almost constant for a specified P_A , since N_2 is virtually inert, the total number of moles in the gas mixture increases with rising temperature, as shown in Table 6.1. A slight drop in the N_2 concentration is therefore observed.

6.2.2 Effect of P_A

The percent of stoichiometric air (P_A) has a strong effect on product composition and sulphur yield. It may be reasoned that, for a given temperature, increasing P_A promotes the conversion of H_2 to H_2O , H_2S to S_2 and S_2 to SO_2 . Consequently, the concentrations of H_2 and H_2S fall while those of SO_2 rise with temperature. Likewise, the amounts of S_2 (at temperatures below $1500^\circ K$) and H_2O exhibit a maximum corresponding to a P_A of about 70 (see Figs. 6.5 and 6.6). Since comparatively little H_2 and H_2S are available when P_A values exceed 70, most of the oxygen reacts with the S_2 to form SO_2 , rather than with H_2 or H_2S . Consequently, the concentration of H_2O and S_2 drops while that of SO_2 continues to rise.

TABLE 6.1

MOLES OF PRODUCT FORMED AT VARIOUS TEMPERATURES
FROM 100 MOLES OF H_2S AND 238 MOLES OF AIR
(STOICHIOMETRIC AIR)

Compound	Moles in Product		
	800°K	1300°K	1500°K
H_2	0.06	4.81	10.84
H_2S	29.16	17.94	13.54
SO_2	14.54	11.08	11.81
N_2	187.91	187.93	187.91
H_2O	70.46	77.19	75.52
ΣS_j	19.52	34.61	36.34
Others	<u>0.85</u>	<u>0.80</u>	<u>1.14</u>
Total:	322.50	334.36	337.10

6.3 Causes of Deviation between Experimental and Theoretical Results

Excellent agreement between the experimental and theoretical compositions and yields was found for H_2S dissociation ($P_A = 0$). Furthermore, the H_2 concentrations agree well with those of Raymont,⁴⁷ as shown by Fig. 6.15.

When P_A is greater than zero, the experimentally determined compositions of H_2 , H_2S , SO_2 and N_2 tend to fall below their theoretical values. For H_2O , S_2 and the sulphur yield, the experimentally derived results lie above the theoretical quantities; the difference is especially noticeable for the sulphur yields. Although the experimental data exhibit some scatter, their deviation from the theoretical predictions cannot be explained in this manner.

Six possible causes for the discrepancies between the theoretical and experimental sulphur yields are discussed below.

6.3.1 High Temperature Reversion

One possible explanation for the high experimental sulphur yields could be "reversion" at high temperatures. Although Gamson and Elkins⁵ suggested that

yields greater than the theoretical equilibrium at the flame temperature would be obtained if reaction continued during cooling until the equilibrium was frozen at a temperature where the reaction rates became slow,

they considered this unlikely because

the actual conversion corresponds to the equilibrium at a temperature of 300°C so that the reaction rates would have to be extremely rapid down to that temperature.

To test for possible reversion, the sampling time (the duration the solenoid valve is open) was varied from 0.5 to 10 seconds. Table 6.2 shows that the effect of sampling time on product compositions and

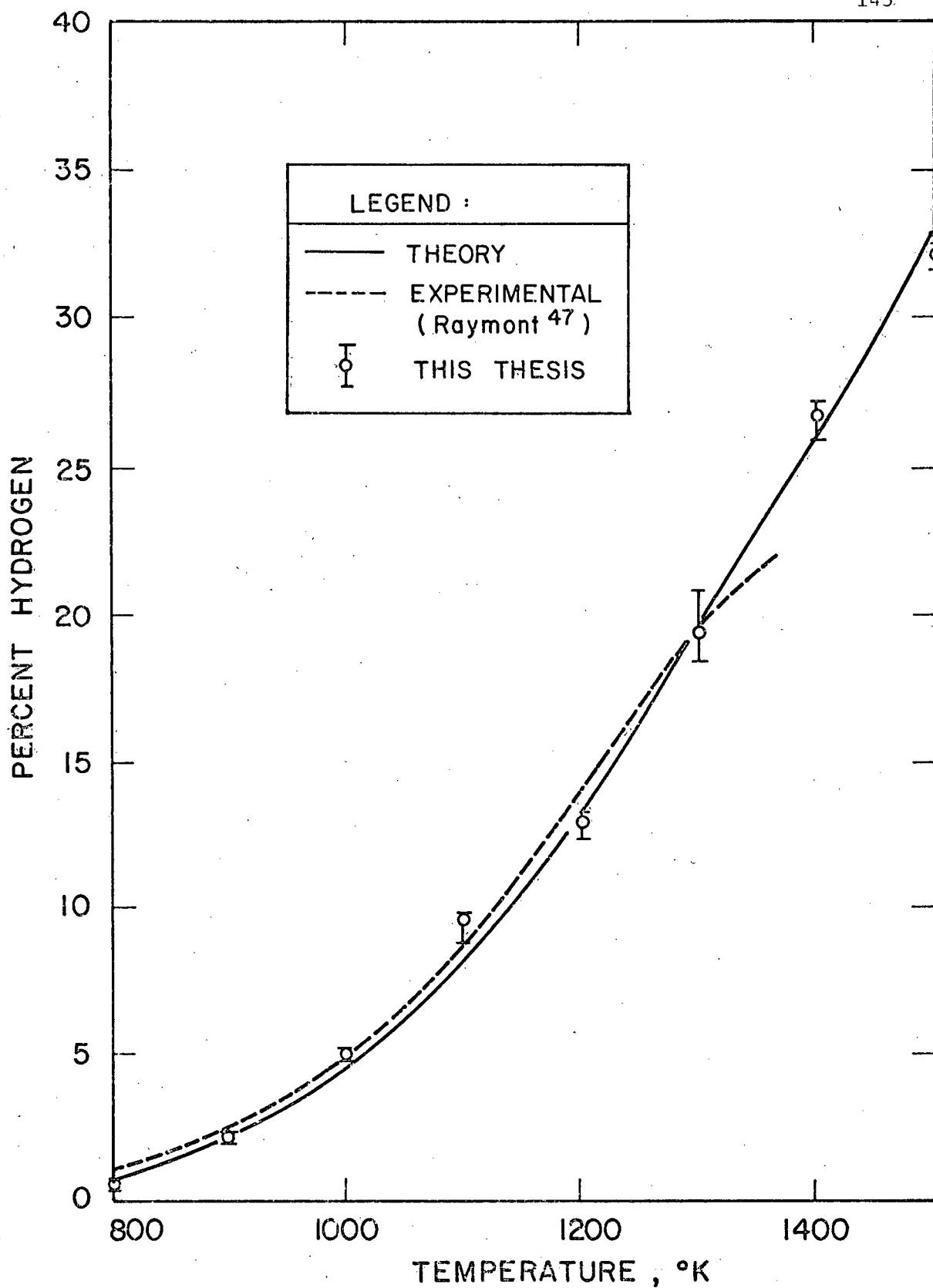


Figure 6.15. Effect of temperature on the concentration of H_2 formed from H_2S dissociation.

TABLE 6.2

EFFECT OF SAMPLING TIME AND P_2O_5 AT $1200^\circ K$

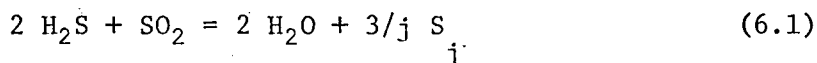
Time (sec)	P_A by Mass Balance	Product Compositions (%)						Sulphur Yield(%)
		H ₂	H ₂ S	SO ₂	N ₂	H ₂ O	S ₂	
0.5	98.8	0.7	4.0	2.1	55.8	25.4	12.0	79.7
1	99.5	0.7	3.8	2.2	56.0	25.4	12.0	79.8
2	99.1	0.8	3.9	2.2	55.9	25.3	11.9	79.5
2	100.2	0.7	4.8	2.8	56.2	24.3	11.1	74.1
2	99.7	0.8	4.6	2.6	56.1	24.5	11.4	75.9
2*	99.5	0.9	3.5	2.1	55.9	25.5	12.1	81.1
4	99.5	0.5	4.4	2.4	56.1	25.1	11.6	77.3
6	100.6	0.6	4.5	2.6	56.3	24.6	11.3	76.1
10	99.9	1.0	4.6	2.8	56.1	24.3	11.3	75.4

*No P_2O_5 present

sulphur yield was fairly small. Furthermore, since the experimental results for H_2S dissociation agree well with the theoretical values, the sampling time was probably sufficiently short to render reversion negligible.

6.3.2 $\text{H}_2\text{S} - \text{SO}_2$ Reaction at Low Temperatures

As mentioned before, the reaction



is catalysed by water and proceeds rapidly, even at room temperature.

If this reaction should occur during sampling, excessive sulphur yields would be noted. The gas samples were therefore passed through a tube filled with phosphorus pentoxide. Table 6.2 shows that the P_2O_5 reduced the apparent sulphur yield by about 5%. The effectiveness of the P_2O_5 was further confirmed by the sampling time experiments, since the sulphur yields would otherwise have increased substantially with sampling time.

To test for reaction of H_2S and SO_2 in the *gas chromatograph*, known mixtures containing about 10% H_2S , 10% SO_2 and 80% N_2 were made up and analysed chromatographically. As seen from Table 6.3, the agreement is good and reaction in the G.C. column did therefore not occur to any significant extent.

Likewise, mixtures of H_2S , SO_2 and N_2 were analysed after passing them through a tube containing P_2O_5 , to test for possible catalytic effects of the P_2O_5 . As seen from Table 6.3, no significant effect of P_2O_5 was observed.

6.3.3 Sample Size

Insufficient sample size may cause errors in the sulphur yield. If not enough sample is taken into the gas bag GB_2 , then air will be sucked

TABLE 6.3

CHECK FOR H₂S OR SO₂ REACTION
AT LOW TEMPERATURES

a) In gas chromatograph

Gas composition (%)			
from rotameter settings		from G.C. analysis	
H ₂ S	SO ₂	H ₂ S	SO ₂
3.6	4.5	3.8	4.6
3.7	2.9	3.7	3.1
6.1	11.4	6.6	11.2
10.2	4.7	10.0	4.8
10.2	6.3	10.5	6.2

b) In phosphorous pentoxide drier

Gas composition by G.C. analysis (%)			
upstream of P ₂ O ₅		downstream of P ₂ O ₅	
H ₂ S	SO ₂	H ₂ S	SO ₂
1.8	-	1.4	-
3.0	-	2.9	-
6.0	-	6.2	-
11.8	-	11.6	-
-	3.8	-	3.0
-	6.7	-	6.4
-	11.4	-	11.4
5.0	5.0	4.2	4.4
5.6	5.8	5.0	5.3
9.4	3.5	9.4	3.9

into the syringe when it is removed from the septum S_2 . Consequently, the compositions of H_2 , H_2S and SO_2 will appear to be low, causing an apparently high sulphur yield. Tests showed that reliable results would be obtained with the syringe set at 5 ml, provided the gas bag GB_2 contained at least 25 ml of the product mixture.

6.3.4 Trace Compounds

The assumption that the equilibrium vessel contains only H_2 , H_2S , SO_2 , N_2 , H_2O and S_2 may introduce errors. Theory predicts that H_2S_2 , HS , SO , S_2O , and S_3 to S_8 all exceed 0.1% in the range of 800 to 1500°K and 0 to 200 percent air.

To examine the effect of omitting these compounds, the theoretical values of the compositions of H_2 , H_2S , SO_2 and N_2 were substituted into the mass balance equations. The concentrations of H_2O and S_2 , as well as the sulphur yield were then calculated. As seen from the dashed lines in Figs. 6.7 to 6.14 the sulphur yields are up to 3% higher than the theoretical values.

6.3.5 Theoretical Data

Since the equilibrium constants are exponential functions of the free energies of formation, a small error in free energy can greatly affect the theoretical equilibrium compositions and sulphur yields. To examine the sensitivity of the results to the free energies, F_T° of each compound was raised by 10% in turn. Increasing F_T° of H_2S , SO_2 , H_2O and S_2 (the most abundant species) caused the greatest changes in the sulphur yields; the results are shown in Table 6.4. Reducing the F_T° of SO_2 by 2.88% at 1300°K brought the theoretical and experimental sulphur yields into good agreement. Similar results were obtained by altering F_T° of H_2S , H_2O or S_2 by appropriate amounts, as shown in Table 6.4.

TABLE 6.4

EFFECT OF CHANGES IN F_T° OF H_2S , SO_2 , H_2O OR S_2
ON COMPOSITIONS AT $1300^\circ K^*$

Compound	Percent Change in ΔF°	Product Compositions						Sulphur Yield
		H_2	H_2S	SO_2	N_2	H_2O	S_2	
-	0	1.4	5.4	3.3	56.2	23.1	10.3	69.5
H_2S	+10	0.4	16.2	8.3	57.9	14.1	3.0	19.5
SO_2	+10	6.2	13.3	9.8	56.7	10.5	3.4	22.9
H_2O	+10	0.1	0.3	0.2	55.7	29.2	14.3	98.0
S_2	+10	1.4	2.3	1.9	55.8	25.9	12.7	85.4
Experimental		2.3	3.8	2.6	55.3	24.1	12.0	78.9
H_2S	-2.57	1.8	3.3	2.5	55.9	24.5	11.6	78.9
SO_2	-2.88	0.9	3.5	2.0	56.1	25.5	11.6	78.9
H_2O	+1.55	0.9	3.7	2.2	56.0	25.1	11.6	78.8
S_2	+5.13	1.5	3.6	2.5	55.9	24.7	11.7	78.9

*PA = 100

Errors in the free energies of formation of SO_2 and H_2O alone, compounds which are not formed from H_2S dissociation, would result in the experimental and theoretical compositions being similar for $P_A = 0$, but different for $P_A > 0$. Therefore the accuracy of the McBride data for these two compounds was examined. Tables 6.5 and 6.6 compare F_T° for SO_2 and H_2O generated by McBride coefficients with the original data listed by McBride et al. The average deviations for both SO_2 and H_2O are less than 0.01% and thus indicate negligible error in the fit for the range 800 - 1500°K. The errors in the original JANAF data were estimated by Eriksson and Rosén to be about $\pm 1\%$ for both SO_2 and H_2O . Thus, the error in the data used in this thesis is expected to be under 1%.

6.3.6 Temperature Measurement

Table 6.7 shows the axial temperature profile of the furnace as measured by a chromel-alumel thermocouple inserted in the mullite tube. The maximum temperature of 837°C is 10°C higher than that indicated by the platinum - platinum/13% rhodium thermocouple attached to the controller. This is close to the limits of experimental errors of $\pm 3/4$ and $\pm 1/4\%$ for chromel-alumel and Pt - Pt/13% Rh thermocouples, respectively. The temperature is uniform to within $\pm 5^\circ\text{C}$ for a distance of 150 mm instead of for 200 mm as stated by the furnace manufacturer. For the entire 200 mm, the temperature is uniform to within $\pm 10^\circ\text{C}$.

6.3.7 Error Analysis

Errors in stoichiometric air, equilibrium vessel compositions and sulphur yields are estimated in Appendix F. For example, the estimated error in the sulphur yield of about 12% compares with typical errors based on repeated measurements (see $100 \sigma/\bar{x}$ in Tables D.1 to D.8) of about 5%.

TABLE 6.5

COMPARISON OF $-F_T^\circ$ FOR SO_2 COMPUTED BY McBRIDE COEFFICIENTS
WITH THAT LISTED IN McBRIDE⁸ OR IN JANAF⁷

Temp °K	$-F_T^\circ$		Error, Δ%	$-F_T^\circ$ from JANAF	Error, Δ%
	by coefficients	from McBride Table			
800	121436.48	121435.8	-0.00056	121438.0	0.00125
900	128531.93	128531.1	-0.00065	128533.7	0.00137
1000	135769.78	135768.9	-0.00065	135772.0	0.00164
Mean error	-	-	-0.00062	-	0.00142
1000	135769.77	135768.9	-0.00064	135772.0	0.00164
1100	143137.87	143136.9	-0.00067	143140.3	0.00170
1200	150625.76	150625.0	-0.00051	150630.6	0.00321
1300	158224.56	158224.2	-0.00023	158230.0	0.00344
1400	165926.62	165926.9	0.00017	165933.0	0.00385
1500	173725.30	173726.4	0.00063	173734.0	0.00501
Mean Error	-	-	-0.00021	-	0.00314

TABLE 6.6

COMPARISON OF $-F_T^\circ$ FOR H_2O COMPUTED BY McBRIDE COEFFICIENTS
WITH THAT LISTED IN McBRIDE⁸ OR IN JANAF⁷

Temp °K	$-F_T^\circ$		Error, Δ%	$-F_T^\circ$ from JANAF	Error, Δ%
	by coefficients	from McBride Table			
800	96269.42	96269.2	-0.00023	96269.1	-0.00033
900	101672.12	101671.8	-0.00032	101670.9	-0.00120
1000	107181.10	107180.8	-0.00028	107180.9	-0.00018
Mean error	-	-	-0.00027	-	-0.00057
1000	107181.10	107180.8	-0.00028	107180.9	-0.00018
1100	112788.79	112788.4	-0.00034	112787.4	-0.00123
1200	118489.06	118488.5	-0.00047	118487.1	-0.00165
1300	124276.66	124276.8	-0.00070	124274.3	-0.00190
1400	130147.03	130145.7	-0.00010	130142.7	-0.00333
1500	136096.10	136094.2	-0.00014	136091.4	-0.00345
Mean Error	-	-	-0.00070	-	-0.00196

TABLE 6.7

FURNACE TEMPERATURE PROFILES

(Temperature controller set to 827°C)

Axial distance from centre of furnace mm	Temperature °C
-280	379
-230	518
-180	670
-125	795
-100	816
-75	828
-50	837
-25	837
0	835
+25	835
+50	830
+75	826
+100	814
+125	789
+180	652
+230	481
+280	356

The difference is to be expected, since 12% represents the *maximum possible*, rather than the *most likely* error in the sulphur yield. Similar statements may be made with respect to the chemical compositions and stoichiometric air (PA). The error analysis should, therefore, be regarded only as a means of comparing the relative importance of error sources.

In view of the reproducibility of the results and systematic trends of the dependent variables (such as sulphur yield and composition), the experimental measurements may be regarded as reliable. A certain degree of scatter in the data was unavoidable due to the limitations in the experimental technique and difficulties of investigating highly reactive chemical compounds at elevated temperatures.

CHAPTER 7

CONCLUSIONS

7.1 Theoretical Equilibrium Compositions and Yields

Equilibrium mixtures resulting from the reaction among H_2S , CO_2 , H_2O , NH_3 and air at atmospheric pressure were found to contain the following compounds whose partial pressures exceeded 10^{-7} atm. for at least some temperatures between 600 and 2000 °K: N_2 , NH_3 , NO , O , O_2 , OH , H , H_2 , H_2O , H_2S , H_2S_2 , SH , SN , SO , SO_2 , SO_3 , S_2O , S to S_8 , CO_2 , CO , COS , CS and CS_2 . These compounds should therefore not be omitted from equilibrium calculations. It was shown that sulphur yields in Claus furnaces could be increased significantly by operating with PA less than 100, since this suppressed the further oxidation of elemental sulphur. In practice, such ratios require preheating of the feed gases for the Claus furnace.

The presence of impurities, such as NH_3 (below 1600°K), H_2O and CO_2 was shown to diminish the sulphur yields.

Between 600 and 1850°K, H_2S dissociation was predicted to produce lower sulphur yields than did H_2S oxidation.

7.2 Claus Plant Model

Modelling a Claus plant consisting of a furnace and two catalytic converters, which operate adiabatically gave the following results:

--The maximum overall sulphur yield occurs when operating with

stoichiometric air.

- Enriching this air with oxygen causes the overall sulphur yield to fall.
- Preheating the feed to the furnace or converters enhances the sulphur yield only marginally.
- Recycling part of the first converter's feed back to the furnace improves the yield slightly; these minor gains are probably not worth the additional cost encountered in practice.

Consequently, it seems preferable to operate Claus plants with 100% of stoichiometric air, without oxygen enrichment and without recycle.

7.3 Experimental Equilibrium Compositions

Compositions of H_2 , H_2S , SO_2 , N_2 , H_2O and S_2 and the sulphur yield were obtained experimentally at one atmosphere pressure and between 800 and 1500°K. The experimental results followed the same trend as the theoretical ones, but did not coincide exactly with them. The sulphur yields were up to 15% higher than the theoretical ones; random error alone did not account for the difference. Six possible causes were investigated:

- high temperature reversion (unlikely);
- reaction of H_2S with SO_2 at room temperatures, either in the sampling lines or in the gas chromatograph (possible, not not likely);
- taking insufficient sample (possible);
- neglecting important species (results in an apparent increase in yield of up to 3%);
- errors in the theoretical data (possible, but not likely);
- errors in temperature measurement (unlikely).

NOMENCLATURE

a	coefficient in Eq. 2.9
a_1, a_2, \dots, a_7	McBride coefficients
a_8, a_9, a_{10}	Lagrange multipliers
A	coefficient in Eq. 3.42
\tilde{A}	symmetric matrix of temperature summations
A_i	area under chromatographic peak
b	coefficient in Eq. 2.9
b_A, b_{H_2S}	intercept of air and H_2S flowmeter calibration curve, respectively
B	coefficient in Eq. 3.42
b_i	intercept of GC calibration curve for compound i (H_2 , H_2S or SO_2)
c	coefficient in Eq. 2.9
$C_{P_i}^\circ$	standard heat capacity of a species i
C	coefficient in Eq. 3.42
d	coefficient in Eq. 2.9
\tilde{d}_i	vector of thermochemical properties of species i
f_k	factor defined by Eq. 3.29 = $(1-r)/(1-r'_k)$
F_T°	standard free energy of a species at temperature T
ΔF_T°	free energy of reaction at temperature T
\tilde{F}	diagonal matrix for scaling \tilde{A}
$H_T^\circ, H_{T_R}^\circ, H_{T_G}^\circ$	enthalpy of a compound at temperatures T , T_R and T_G respectively
H_{298}°	enthalpy of a compound at 298.16°K

$\Delta H_{f,298}^{\circ}$	standard enthalpy of formation of a compound at 298.16°K from its elements
i	compound number
j	number of atoms per molecule of sulphur vapour or number of atoms of element e in compound i
K_T	equilibrium constant at temperature T
K_{O_2}	equilibrium constant for the formation of O_2 (Eq. 3.3)
K_{H_2}	equilibrium constant for the formation of H_2 (Eq. 3.4)
m_A, m_{H_2S}	slope of air and H_2S rotameter calibration curve
m_i	slope of G.C. calibration curve for compound i (H_2 , H_2S or SO_2)
$M_{e,A}, M_{e,B}, M_{e,C}, M_{e,D}, M_{e,E}, M_{e,L}$	number of moles of element e (C, H, N, O or S) in streams A, B, C, D, E, and L, respectively of Fig. 3.1
$m_{i,E}$	number of moles of compound i in stream E
n_i	number of moles of compound i present at the adiabatic flame temperature after reaction
$n_{0,i}$	number of moles of compound i before reaction
N	total number of species
p	number of temperature intervals summed in obtaining McBride coefficients
P_A or PA	percent of stoichiometric air in the feed mixture ($= 100 R_{OS}$)
P_i	partial pressure of compound i (atm)
P_S	sum of the partial pressures of the various sulphur species
P_T	total pressure ($=$ sum of the partial pressures of all the compounds)
P_V	vapour pressure of sulphur
Q_A, Q_{H_2S}	flowrates of air and H_2S respectively
r	fraction of stream D recycled
r'	modified fraction recycled defined by Eq. 3.20
r^2	correlation coefficient

R	gas constant ($= 1.98726 \text{ cal/mole/}^\circ\text{K}$)
R_{CS}	ratio of carbon to sulphur
R_{eS}	ratio of element e (carbon, hydrogen or nitrogen) to sulphur
R_{HS}	ratio of hydrogen to sulphur
R_{NO}	ratio of nitrogen to oxygen
R_{OS}	ratio of oxygen to sulphur
S_T°	standard entropy of a species at temperature T
S_T	$= \sum_j [S_j]$ (Eq. 3.6)
T	adiabatic flame temperature, $^\circ\text{K}$
T_G	guess of adiabatic flame temperature, $^\circ\text{K}$
T_R	temperature of the reactants, $^\circ\text{K}$
T_0	common temperature for the two sets of McBride coefficients
\bar{x}_i	vector of McBride coefficients for compound i
$x_A, x_{\text{H}_2\text{S}}$	rotameter float position for air and H_2S , respectively
y_i	percent of compound i (H_2 , H_2S or SO_2) in gas bag
Y	sulphur yield defined by Eqs. 3.5 and 3.8

Greek

α	proportionality constant in Eq. 3.22
β	constant in Eq. 3.28 ($= M_{\text{e,A}}/M_{\text{s,A}}$)

Subscripts

A,B,C,D,E,L	streams in Fig. 3.1
e	element (either C, H, N, O or S)
G	guessed
HS	hydrogen to sulphur
i	compound number
k	iteration number
NO	nitrogen to oxygen
OS	oxygen to sulphur
R	reactant
S	sulphur
T	total
V	vapour
O	previous iteration

Superscripts

T	transpose of a vector
*	desired value in Eqs. 2.11 to 2.14 and 3.7

Miscellaneous

[]	partial pressure
-----	------------------

REFERENCES

1. Anon, Hydrocarbon Process. 57 (1) 181 (1978).
2. Grekel, H., Kunkel, L. V., and McGalliard, R., Chem. Eng. Progr. 61 (9) 70 (1965).
3. Estep, J. W., McBride, G. T., and West, J. R., in McKetta, J. J. (ed.), *Advances in Petroleum Chemistry and Refining*, Vol. 6, Chapt. 7 Interscience, New York, NY (1962).
4. Goar, B. G., Hydrocarbon Process, 47 (9), 248 (1968).
5. Gamson, B. W., and Elkins, R. H., Chem. Eng. Progr. 49, 203 (1953).
6. Kelley, K. K., U. S. Bur. Mines, Bull. 406 (1937).
7. Stull, D. R., and Prophet, H., (ed.) *JANAF Thermochemical Tables*, 2nd Ed., National Bureau of Standards, Washington, DC (1971).
8. McBride, B. J., Heimel, S., Ehlers, J. G., and Gordon, S., *Thermodynamic Properties to 6000°K for 210 Substances Involving the First 18 Elements*, NASA SP-3001, Washington, DC (1963).
9. Valdes, A. R., Hydrocarbon Process. Petrol. Refiner, 43 (3) 104 (1964).
10. Opekar, P. C., and Goar, B. G., Hydrocarbon Process., 45 (6) 181 (1966).
11. Eriksson, G., and Rosén, E., Proceedings of the Symposium on Recovery of Pulping Chemicals, Helsinki (1968).
12. Boas, A. H., and Andrade, R. C., Hydrocarbon Process 50, (3) 81 (1971).
13. McGregor, D. E., Ph.D. Thesis, University of Alberta, Edmonton, Alta. (1971).
14. Neumann, K. K., Erdöl, Kohle, Erdgas; Petrochem. vereinigt mit Brennst. Chem., 25, 656 (1972).
15. Bennett, H. A., and Meisen, A., Can. J. Chem. Eng., 51, 720 (1973).
16. Bragg, J. R., 76th National AIChE Meeting, Tulsa, Okla, Mar 10-13, (1974).
17. Fischer, H., Hydrocarbon Process., 53 (10), 125 (1974).

18. Meisen, A., and Bennett, H. A., Hydrocarbon Process., 53 (11), 171 (1974).
19. Raymont, M. E. D., Ph.D. Thesis, University of Calgary, Calgary, Alta. (1974).
20. Kerr, R. K., and Berlie, E. M., Energy Process./Can., May-June, 42 (1977).
21. Maadah, A. G., and Maddox, R. N., Hydrocarbon Process. 57, (8) 143 (1978).
22. Mackle, H., and O'Hare, P.A.G. Trans. Faraday Soc., 59, 309 (1963).
23. Kellogg, H. H., Met. Trans., 2, 2161 (1971).
24. Rau, H., Kutty, T. R. N., and Guedes de Carvalho, J. R. F., J. Chem. Thermodynamics 5, 833 (1973).
25. Braune, H., Peter, S., und Neveling, V., Z. Naturforsch. 6a, 32 (1951).
26. Peter, S., und Woy, H., Chem. Ing. Techk., 41, 1 (1969).
27. Pasternak, R., Brennst. Chem. 50, 200 (1969).
28. Sawyer, F. G., Hader, R. N., Herndon, L. K., and Morningstar, E., Ind. Eng. Chem., 42, 1938 (1950).
29. Kerr, R. K., Energy Process/Can., July-Aug., 28 (1976).
30. Kerr, R. K., Paskall, H. G., and Ballash, N., Energy Process./Can., Sept-Oct., 66 (1976).
31. Kerr, R. K., and Paskall, H. G., Energy Process./Can., Nov-Dec., 38 (1976).
32. Kerr, R. K., Paskall, H. G., and Ballash, N., Energy Process./Can., Jan-Feb., 40 (1977).
33. Kerr, R. K., and Berlie, E. M., Energy Process./Can., July-Aug., 48 (1977).
34. Randall, M., and von Bichowsky, F. R., J. Amer. Chem. Soc. 40, 368 (1918).
35. Taylor, H. A., and Wesley, W. A., J. Phys. Chem., 31, 216 (1927).
36. Taylor, H. A., and Livingston, E. M., J. Phys. Chem. 35, 2676 (1931).
37. Murthy, A. R. V., and Rao, B. S., Proc. Indian Acad. Sci., 34A, 283 (1951).

38. Deo, A. V., Dalla Lana, I. G., and Habgood, H. W., J. Catal. 21, 270 (1971).
39. Dalla Lana, I. G., McGregor, D. E., Liu, C. L., and Cormode, A. E., University of Alberta Report, Proceedings of the 5th European/2nd International Symposium on Chemical Reaction Engineering, Paper B (1972).
40. Diah, I. G., Ponter, A. B., and Shemilt, L. W., Ind. Eng. Chem. Process. Des. Develop., 11, 458 (1972).
41. Grekel, H., Oil Gas J., 57 (30) 76 (1959).
42. Fischer, H., Chem. Ing. Techk., 43, 1168 (1971).
43. Kopp, S. P., and Morin, M. M., Gas Conditioning Conference, Paper G (1977).
44. Meyer, B., *Sulphur, Energy and Environment*, Elsevier, Amsterdam (1977).
45. Levy, A., and Merryman, E. L., Combust. Flame, 9, 229 (1965).
46. Hyne, J. B., Alberta Sulphur Research Ltd. Report.
47. Raymont, M. E. D., Hydrocarbon Process., 54 (5) 177 (1975).
48. Raymont, M. E. D., Hydrocarbon Process., 54 (7) 139 (1975).
49. Carmassi, M. J., and Zwilling, J. P., Hydrocarbon Process., 46 (4) 117 (1967).
50. Smith, D. E., and Funk, G. L., Gas Conditioning Conference, Paper Q (1977).
51. Zeleznik, F. J., and Gordon, S., NASA Tech. Note D-767 Washington, D.C. (1961).
52. West, J. R., Ind. Eng. Chem., 42, 713 (1950).
53. Tuller, W. N. (ed.), *The Sulphur Data Book*, McGraw Hill, New York, NY (1954).
54. Rau, H., Kutty, T. R. N., and Guedes de Carvalho, J. R. F., J. Chem. Thermodynamics 5, 291 (1973).
55. Supelco, Inc., Bellefonte, Pa., Priv. Comm. (1976).
56. Chromatographic Specialities, Ltd., Brockville, Ont., Priv. Comm. (1976).

57. *Spherocarb*, Analabs, Inc., North Haven, Conn (1977).
58. Robbins, L. A., Bethea, R. M., and Wheelock, T. D., *J. Chromatogr.* 13, 361 (1964).
59. Hodges, C. T., and Matson, R. F., *Anal. Chem.* 37, 1065 (1965).
60. Koppe, R. K., and Adams, D. F., *Environ. Sci. Technol.*, 1, 479 (1967).
61. Jones, C. N., *Anal. Chem.*, 39, 1858 (1967).
62. Obermiller, E. L., and Charlier, G. O., *J. Gas Chromatogr.*, 6 446 (1968).
63. Obermiller, E. L., and Charlier, G. O., *J. Gas Chromatogr.*, 7 580 (1969).
64. Applebury, T. E., and Schaer, M. J., *J. Air Pollut Contr. Ass.*, 20, 83 (1970).
65. Thornsberry, W. L., *Anal. Chem.* 43, 452 (1971).
66. *Deactigel*, Applied Science Laboratories, Inc., State College PA (1971).
67. Bollman, D. H., and Mortimore, D. M., *J. Chromatogr. Sci.*, 10, 523 (1972).
68. Bremner, J. M., and Banwort, W. L., *Sulphur Inst. J.*, 10, (1), (1974).
69. Murdock, D. L., and Atwood, G. A., *Ind. Eng. Chem. Process. Des. Develop.*, 13, 254 (1974).
70. de Souza, T. L. C., Lane, D. C., and Bhatia, S. P., *Anal. Chem.*, 47, 543 (1975).
71. Bulletin 712A, Supelco. Inc., Bellafonte Pa. (1976).
72. Catalog 11, p 19, Supelco Inc, Bellafonte Pa. (1977).
73. *International Critical Tables*, Vol V, p. 213 McGraw Hill, New York, NY (1926).
74. Pearson, M. J., *Hydrocarbon Process.*, 52 (2), 81 (1973).

APPENDIX A

EXPERIMENTAL PROCEDURE

The following section lists each step in operating the apparatus shown in Figs. 4.1 and 4.2.

- (i) Fill the gas sampling bag GB_1 with the desired mixture of air and H_2S .
- (ii) Introduce this mixture into the equilibrium vessel.
- (iii) After one hour (or more) sample the equilibrium vessel.
- (iv) Calibrate the gas chromatograph. (This may be done between steps (ii) and (iii).)
- (v) Analyse the sample.
- (vi) Calculate the composition of the equilibrium vessel.

A.1 Preparing the Feed Mixture

A gas bag is filled with a feed mixture of air and H_2S as follows:

- (i) Set the H_2S flow rate to at least 20 as indicated by the rotameter.
- (ii) Set the air flowrate according to Eq. 4.6 to produce the desired P_A .
- (iii) Evacuate gas bag GB_1 .
- (iv) Fill the bag with air and H_2S .
- (v) When the bag is full, connect it to the apparatus as shown in Fig. 4.1.

A.2 Introducing the Mixture into the Equilibrium Vessel

The feed mixture is admitted into the equilibrium vessel as follows:

- (i) Close all valves except C, ST, SV, V_2 and V_5 of Fig. 4.1, turn pump VP on, and evacuate the reaction vessel until its pressure falls below about 300μ Hg.

- (ii) Close stopcock ST then open valve V_1 to admit the feed mixture into the vessel. After about 10 seconds, close V_1 again.

A.3 Sampling the Equilibrium Vessel

After equilibrium has been attained, which may require an hour or more, the gases in the equilibrium vessel are sampled as follows:

- (i) After closing valve V_6 and opening valves V_2 , V_3 , V_4 and V_5 , evacuate the product gas bag and its container.
- (ii) When the pressure falls below about 300 μ Hg, open stopcock ST and close valve V_2 . Take a sample by actuating the solenoid SV with the timer set for 2 seconds.
- (iii) As soon as the solenoid closes again, close V_4 and ST; turn off the vacuum pump and open release valve V_6 .
- (iv) Open valve V_1 to admit sufficient feed mixture into the equilibrium vessel to replace the volume withdrawn by sampling.
- (v) Take a 5 ml sample from gas bag GB₂ with a syringe; leave the needle in the septum for about thirty seconds to allow the syringe contents to reach atmospheric pressure.
- (vi) Inject the sample into the gas chromatograph.

A.4 Calibration of Gas Chromatograph

Separate calibration curves for H_2 , H_2S and SO_2 were prepared for most experimental runs. Typical composition ranges used are: 0-10% for H_2 , 0-25% for H_2S , and 0-10% for SO_2 ; the ranges vary, depending on the expected composition in the equilibrium vessel.

The chromatograph is calibrated for H_2S as follows:

- (i) Set the H_2S and N_2 (diluent) flow rates, and then allow about one minute for the lines to be purged by the H_2S/N_2 mixture.
- (ii) From the rotameter float positions compute the percent H_2S .

- (iii) Insert syringe needle through septum S_1 , withdraw a 5 ml sample, but leave the needle in the septum for about one minute to allow the pressure inside the syringe to reach one atmosphere.
- (iv) Inject sample into gas chromatograph. Wait five seconds before withdrawing the needle, to avoid loss of sample through the G.C. septum.
- (v) Measure the area of the gas chromatograph peak from the trace of the Disc integrator (built into the recorder) and plot this area against the corresponding percent H_2S .
- (vi) Repeat steps (i) to (v) at least three times for a range of flow rates and thus obtain a calibration curve. Then fit the points to a straight line using the program listed in Appendix B.
- (vii) Repeat steps (i) to (vi) for H_2 and then for SO_2 .

APPENDIX B

CALCULATOR PROGRAMS AND SAMPLE CALCULATIONS

Programs were written for the Texas Instruments TI-58 programmable pocket calculator to compute:

- gas chromatograph calibration constants;
- equilibrium vessel compositions for both H_2S oxidation and dissociation;
- composition of a gas stream containing H_2S , SO_2 and N_2 .

The use of these programs is described in the following sections with results of sample calculations in brackets.

B.1 Constants for Gas Chromatograph Calibration

Table B.1 lists a TI-58 program which calculates the intercept and slope of the calibration curves for hydrogen, hydrogen sulphide and sulphur dioxide. The calibration constants are found as follows:

- (i) Key in the program listed in Table B.1.
 - (ii) Key in the constants for the flowmeters:
 - For N_2 : -213.403 STO 18; 24.991 STO 19
 - For H_2 : -3.698 STO 16; 2.119 STO 17
 - (iii) Clear the statistical registers: press 2nd E'
 - (iv) Key in flowmeter float positions, x:
 - Key x_{H_2} (5.5) press A, see x_{H_2} (5.50)
 - Key x_{N_2} (93.5), press B, see x_{N_2} (93.50)
 - (v) Press 2nd C', see % H_2 (0.37)
 - (vi) Key in area under H_2 peak (298), press 2nd D' see n (1.00),
the number of points on the calibration curve entered so far.
 - (vii) Repeat steps (iv) to (vi) for each point on the calibration curve.
- (See Table B.2 for the values.)

TABLE B.1

TI-58 PROGRAM FOR CALCULATING G.C. CALIBRATION CURVE CONSTANTS
AND FOR FINDING EQUILIBRIUM VESSEL COMPOSITIONS
FOR H₂S OXIDATION

LOC	CODE	KEY	041	92	RTN	083	95	=
000	76	LBL	042	76	LBL	084	94	+/-
001	11	A	043	15	E	085	42	STD
002	42	STD	044	58	FIX	086	03	03
003	00	00	045	01	01	087	55	÷
004	58	FIX	046	43	RCL	088	01	1
005	02	02	047	00	00	089	93	.
006	91	R/S	048	75	-	090	08	8
007	76	LBL	049	43	RCL	091	08	8
008	12	B	050	10	10	092	75	-
009	42	STD	051	95	=	093	02	2
010	07	07	052	55	÷	094	65	×
011	91	R/S	053	43	RCL	095	43	RCL
012	76	LBL	054	11	11	096	04	04
013	13	C	055	95	=	097	95	=
014	42	STD	056	42	STD	098	42	STD
015	09	09	057	06	06	099	02	02
016	91	R/S	058	43	RCL	100	85	+
017	76	LBL	059	07	07	101	43	RCL
018	14	D	060	14	D	102	06	06
019	75	-	061	43	RCL	103	75	-
020	43	RCL	062	09	09	104	43	RCL
021	12	12	063	75	-	105	04	04
022	95	=	064	43	RCL	106	95	=
023	55	÷	065	14	14	107	55	÷
024	43	RCL	066	95	=	108	02	2
025	13	13	067	55	÷	109	95	=
026	95	=	068	43	RCL	110	42	STD
027	42	STD	069	15	15	111	01	01
028	05	05	070	95	=	112	85	+
029	76	LBL	071	42	STD	113	43	RCL
030	16	A*	072	04	04	114	02	02
031	35	1/X	073	85	+	115	85	+
032	65	×	074	43	RCL	116	01	1
033	04	4	075	05	05	117	00	0
034	02	2	076	85	+	118	00	0
035	00	0	077	43	RCL	119	95	=
036	00	0	078	06	06	120	55	÷
037	75	-	079	75	-	121	01	1
038	04	4	080	01	1	122	00	0
039	02	2	081	00	0	123	00	0
040	95	=	082	00	0	124	95	=

LEAF 168 OMITTED IN PAGE NUMBERING.

TABLE B.2

TYPICAL CALIBRATION DATA FOR THE GAS
CHROMATOGRAPH (Run 77)

Gas	Float Positions		% Gas	Peak Area
	Gas	N ₂		
H ₂	5.5	93.5	0.37	298
	9.5	94	0.76	1020
	16	95	1.38	1500
	14.5	66.5	1.83	2310
	14.5	46	2.81	3740
H ₂ S	89	19.5	31.11	3000
	63	31	13.57	1365
	40	44.5	5.92	565
	27	61	2.87	255
	22	86	1.62	113
SO ₂	84	21.5	20.68	5086
	65	37.5	8.42	2247
	46	56	3.94	1011
	21	68.5	1.64	450
	21	91	1.20	272

Gas	Intercept	Slope	Correlation Coefficient
H ₂	-202.19	1381.05	0.9946
H ₂ S	-17.19	97.72	0.9996
SO ₂	49.00	245.82	0.9992

- (viii) Compute correlation coefficient (r^2): press 2nd Op 13, see r^2 . (0.99).
- (ix) Calculate intercept and slope and store for use in the mass balance part of the programme:
press 2nd Op 12, see intercept (-202.19), press STO 10;
press $x \rightleftharpoons t$, see slope (1381.05), press STO 11.
- (x) Key in the data for the calibration of the flowmeter for H_2S :
1.789 STO 16; 1.370 STO 17.
- (xi) Repeat steps (iii) to (ix) to calculate the intercept (-17.19) and slope (97.72) for the H_2S calibration curve, but store these in registers 12 and 13 respectively.
- (xii) Key in the data for the calibration of the flowmeter for SO_2 :
5.262 STO 16; 0.9427 STO 17.
- (xiii) Repeat steps (iii) to (ix) but store intercept (49.00) and slope (245.82) in registers 14 and 15 respectively.
- (xiv) To calculate the percent of stoichiometric air (P_A) by flowmeter, key in flowmeter constants for H_2S and air respectively: 1.789 STO 16, 1.370 STO 17; -75.884 STO 18, 3.975 STO 19. Then key in float positions, x:
Enter x_{H_2S} (36), press A, see x_{H_2S} (36.00).
Enter x_A (54.5), press B, see x_A (54.50).
Press 2nd C', see % H_2S (26.64). Then press 2nd A' see P_A (115.67).

B.2 Equilibrium Vessel Compositions

B.2.1 Hydrogen Sulphide Oxidation

The programme listed in Table B.1 also calculates vessel compositions from the G.C. calibration data and mass balance equations as

follows:

- (i) Ensure that the G.C. calibration data are in registers 10 to 15.
- (ii) Key in the areas under the gas chromatograph peaks, A:
 Key in A_{H_2} (546), press A, see A_{H_2} (546.00).
 Key in A_{H_2S} (412), press B, see A_{H_2S} (412.00).
 Key in A_{SO_2} (2005), press C, see A_{SO_2} (2005.00).
- (iii) To calculate the composition of the equilibrium vessel, press E, see percent hydrogen (% H_2) in the vessel (0.4). Press R/S, see % H_2S (3.1). Continue pressing R/S and see, in turn, % SO_2 (5.6), % N_2 (61.4), % H_2O (21.4), % S_2 (8.1), % sulphur yield (65.1) and P_A by mass balance (131.1).
- (iv) Repeat steps (i) to (iii) for new A_{H_2} , A_{H_2S} and A_{SO_2} .

B.2.2 Hydrogen Sulphide Dissociation

The program listed in Table B.3 calculates G.C. calibration curves for H_2 and H_2S and computes the composition of the vessel for H_2S dissociation as follows:

- (i) Key in the program.
- (ii) Calculate and store calibration data for H_2 and H_2S as described in Section B.1, steps (ii) to (xi). For Table D.4, run 83, the intercept and slope for H_2 are 500.28 (STO 10) and 382.86 (STO 11), respectively; for H_2S the numbers are -42.46 (STO 12) and 53.35 (STO 13).
- (iii) Key in the areas under the gas chromatograph peaks, A:
 Key in A_{H_2} (4560), press A, see A_{H_2} (4560.00).
 Key in A_{H_2S} (4890), press B, see A_{H_2S} (4890.00).
- (iv) To calculate equilibrium vessel compositions: press E, see percent hydrogen (9.8). Press R/S, see % H_2S (85.3). Continue pressing

R/S and see, in turn, % S_2 (4.9), % sulphur yield (10.3),
and % H_2 + % H_2S in the syringe (103.1).

B.3 Compositions of a Mixture of H_2S , SO_2 and N_2

The program listed in Table B.4 calculates the % H_2S and SO_2 in a mixture of H_2S , SO_2 and N_2 , as follows:

(i) Key in rotameter calibration constants:

For H_2S : 0.3219 STO 10; 1.3213 STO 11

For SO_2 : 5.2624 STO 12; 0.9427 STO 13

For N_2 : -213.403 STO 14; 24.991 STO 15.

(ii) Key in rotameter float positions, x:

Key X_{H_2S} (25), press A, see x_{H_2S} (25.00)

Key X_{SO_2} (60), press B, see x_{SO_2} (60.00)

Key X_{N_2} (26.5), press C, see x_{N_2} (26.50).

(iii) Calculate composition of mixture:

Press D see % H_2S (6.13)

Press E see % SO_2 (11.36).

LEAF 174 OMITTED IN PAGE NUMBERING.

APPENDIX C

CALIBRATION CURVES FOR ROTAMETERS

Four rotameters were required for the experiments: ChE 2912A and B (both Gilmont Instruments, Size 10), ChE 2600 (Gilmont Size 1), and ChE 3107A (Gilmont Size 2). The rotameters were used as follows:

- ChE 2912B (calibrated for H_2 , H_2S , and SO_2) and ChE 3107A (N_2): for gas chromatograph calibration;
- ChE 2912B (H_2S) and 2600 (air): to set the ratio of air to H_2S for filling gas bags;
- ChE 2912A (H_2S), 2912B (SO_2) and 3107A(N_2): to examine the reaction of H_2S with SO_2 .

Rotameters ChE 2600 and ChE 2912A and B were calibrated with a stopwatch and a 50 ml soap bubble flowmeter; ChE 3107, with a stopwatch and a 200 ml soap bubble flowmeter. The data are plotted in Figs. C.1 to C.6. Linear regression was applied to find the best straight line for each plot; the data are fitted very well as the correlation coefficients (r^2) exceed 0.996.

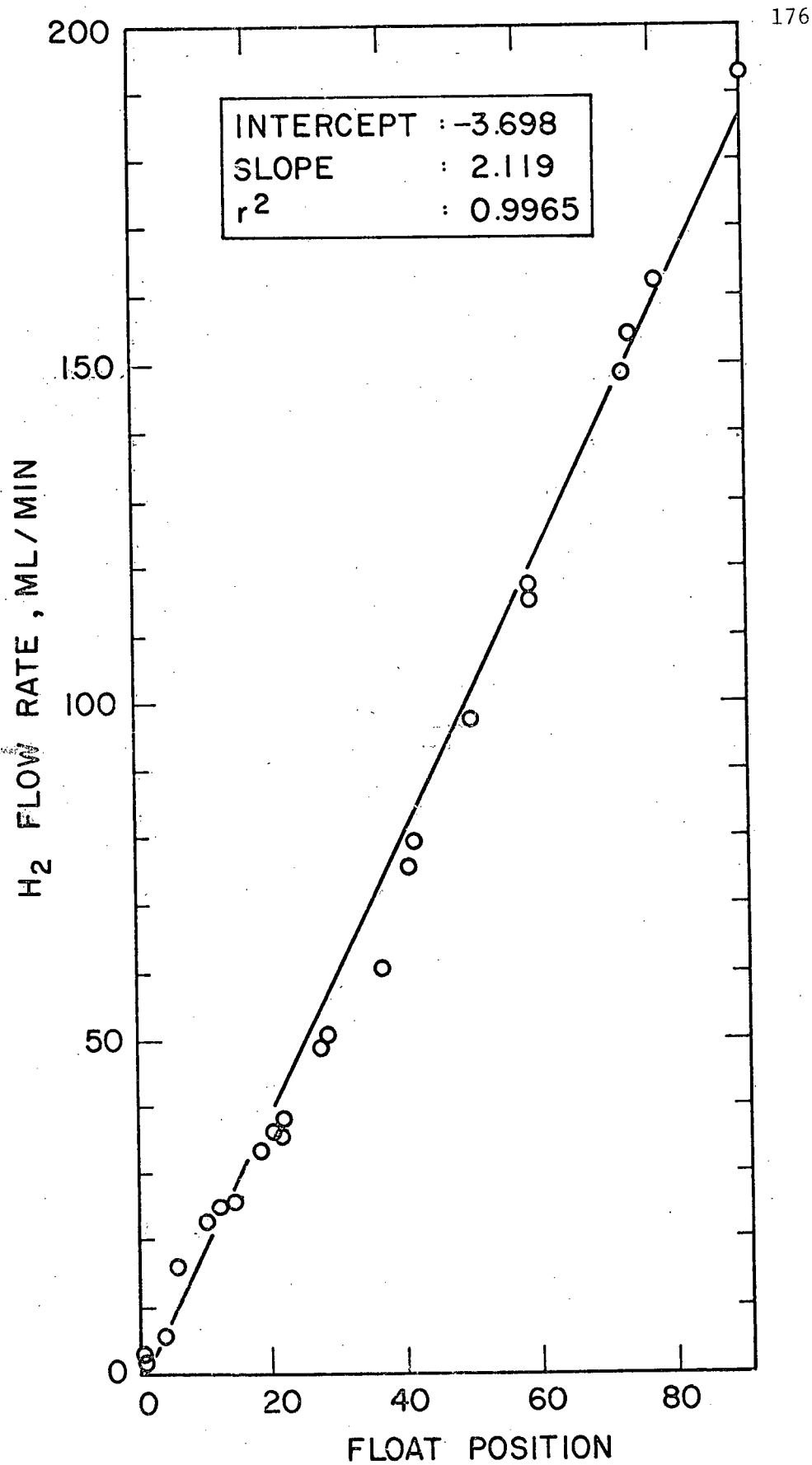


Figure C.1. Calibration of rotameter Ch.E 2912B (Gilmont Model F-2000, Size 10) for H₂.

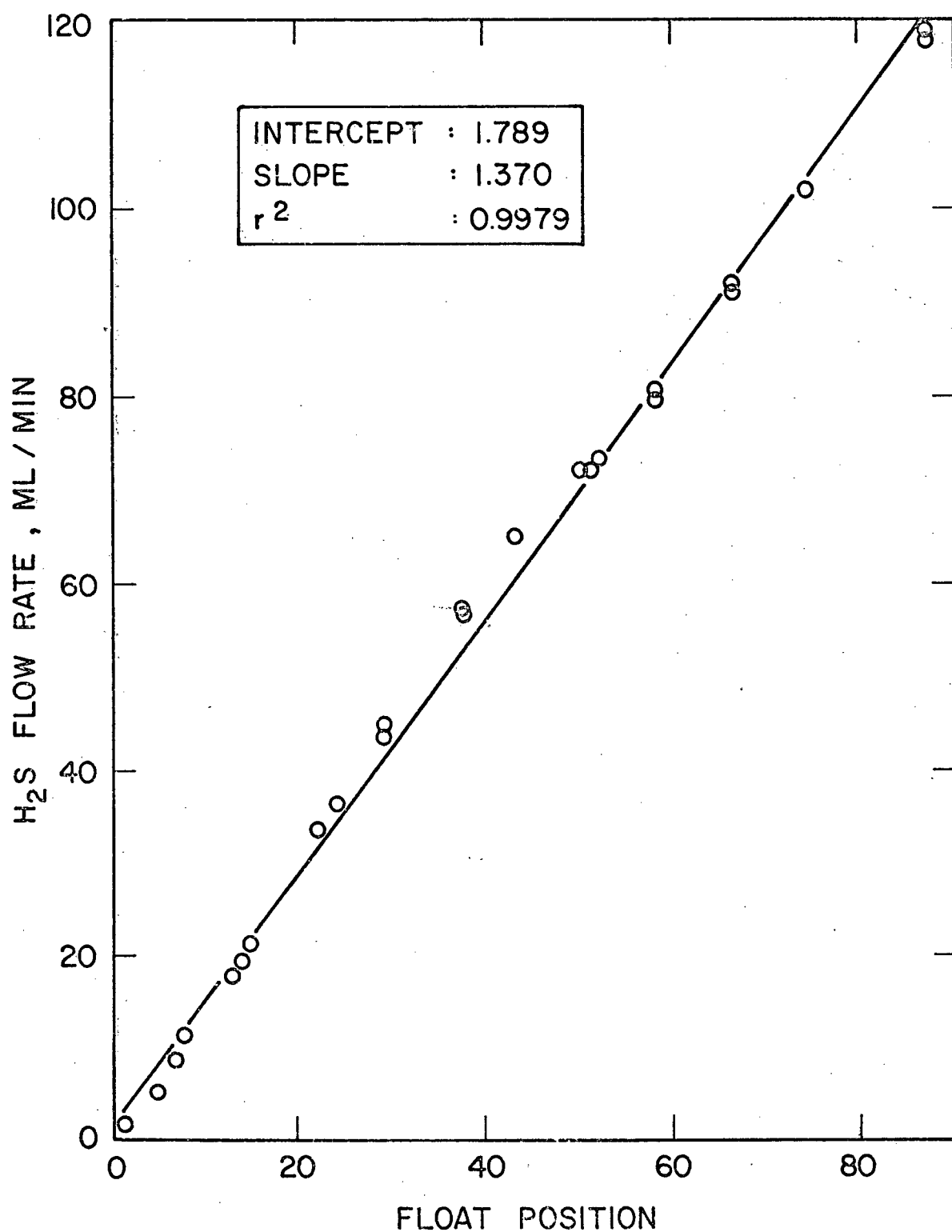


Figure C.2. Calibration of rotameter Ch.E 2912B (Gilmont Model F-2000, Size 10) for H₂S.

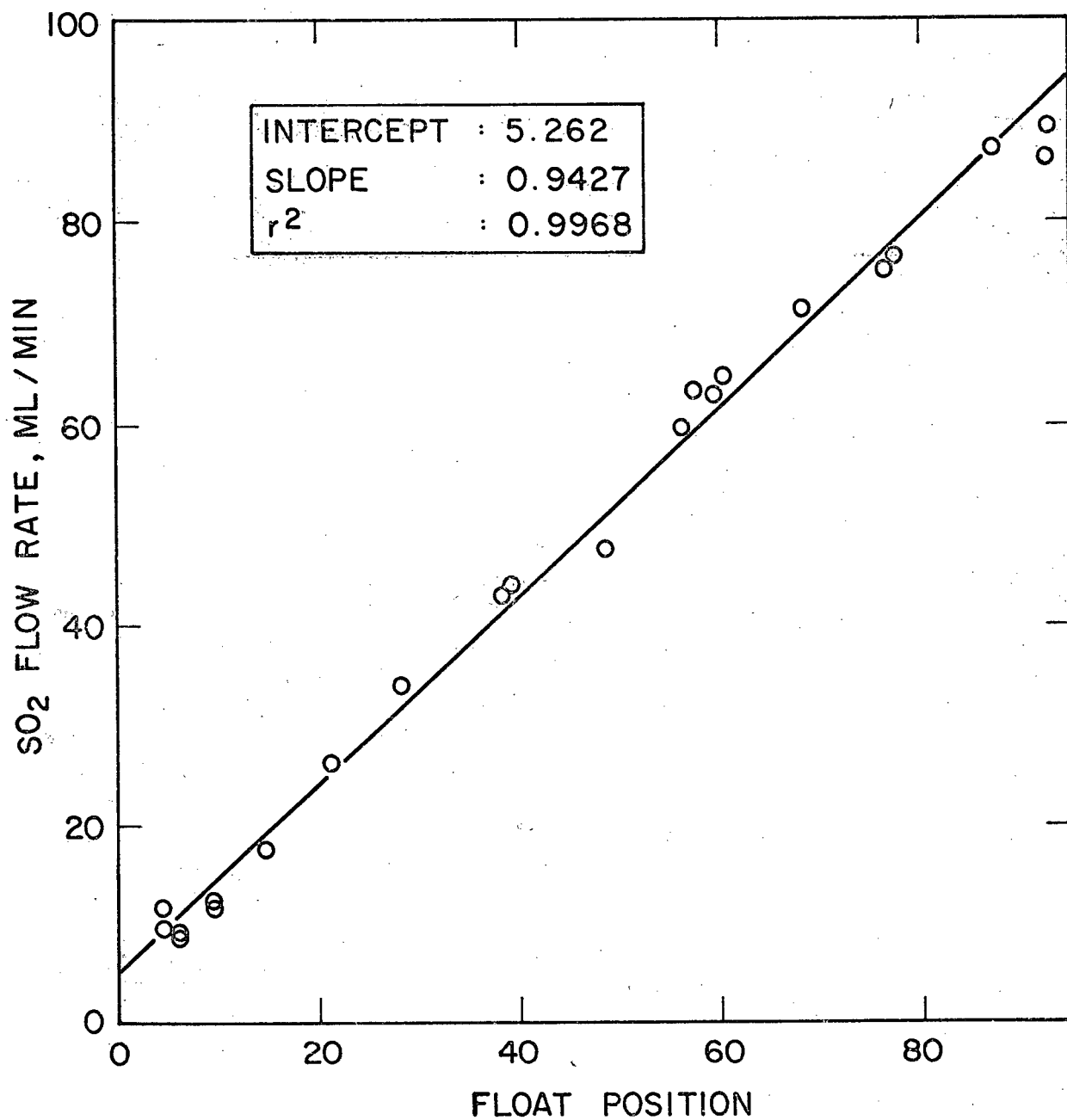


Figure C.3. Calibration of rotameter Ch.E. 2912B (Gilmont Model F-2000, Size 10)for SO₂.

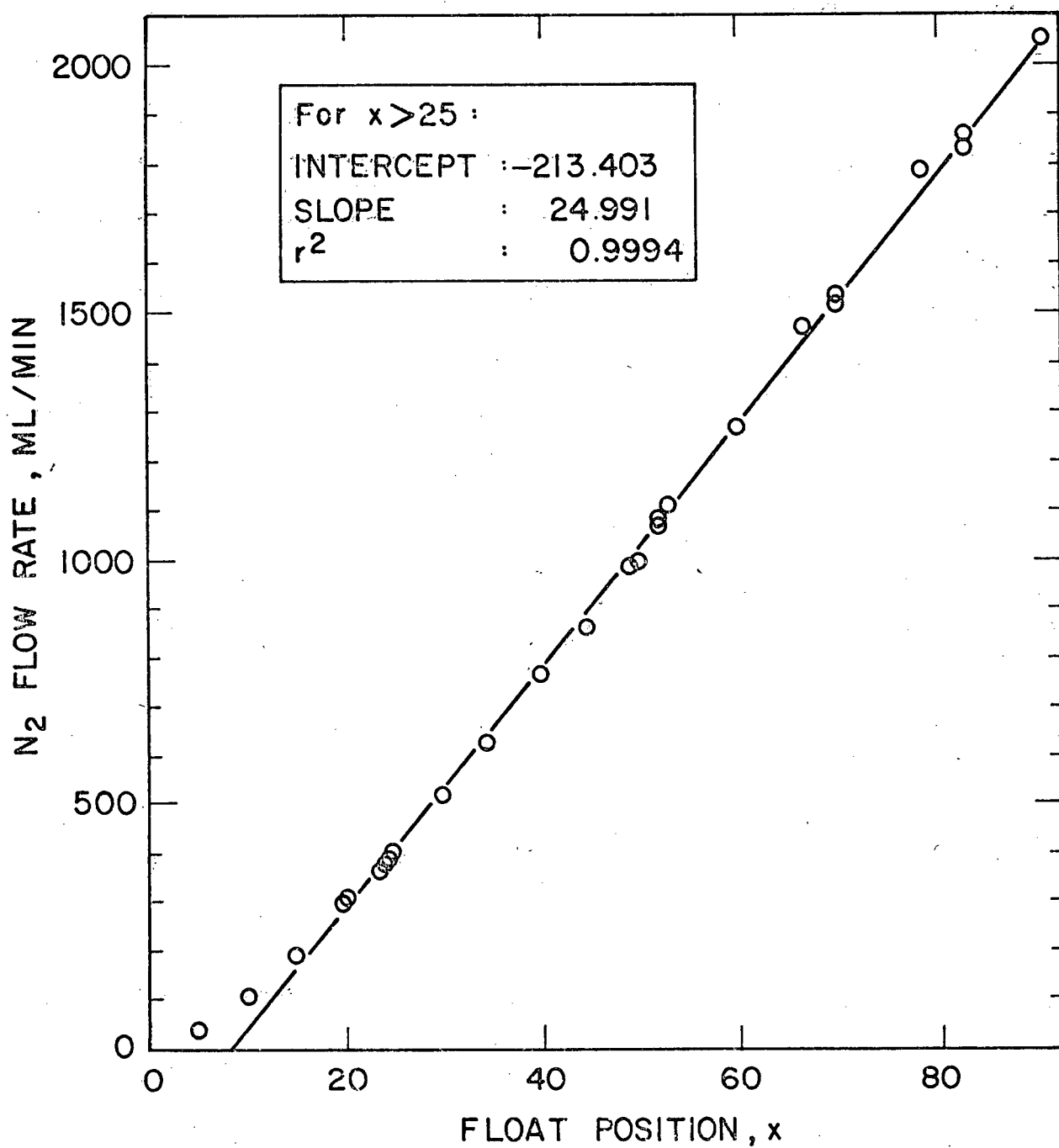


Figure C.4. Calibration of rotameter Ch.E. 3107A (Gilmont Model F-1200, Size 2), for N₂.

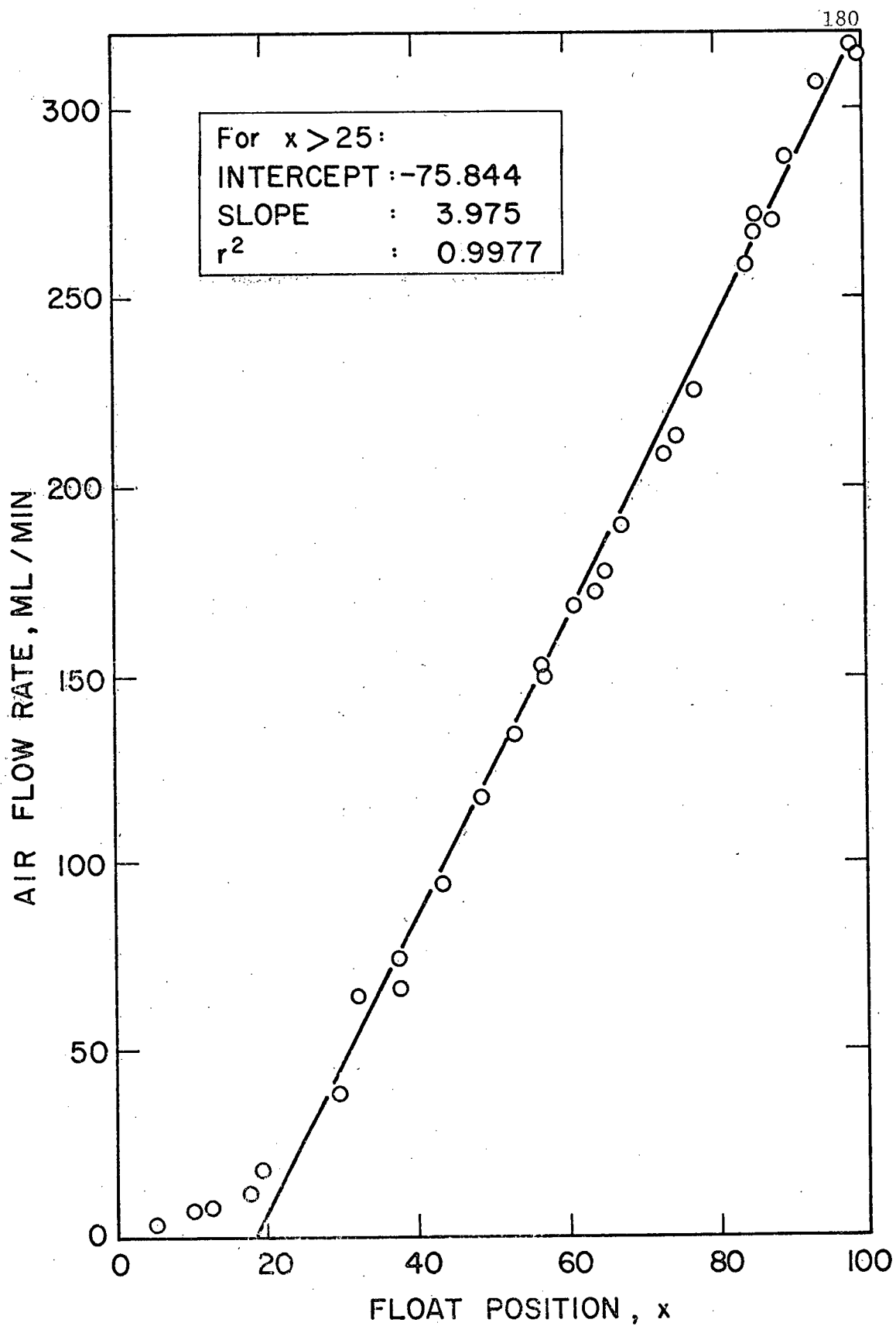


Figure C-5. Calibration of rotameter Ch.E. 2600 (Gilmont Model F-1100, Size 1) for air.

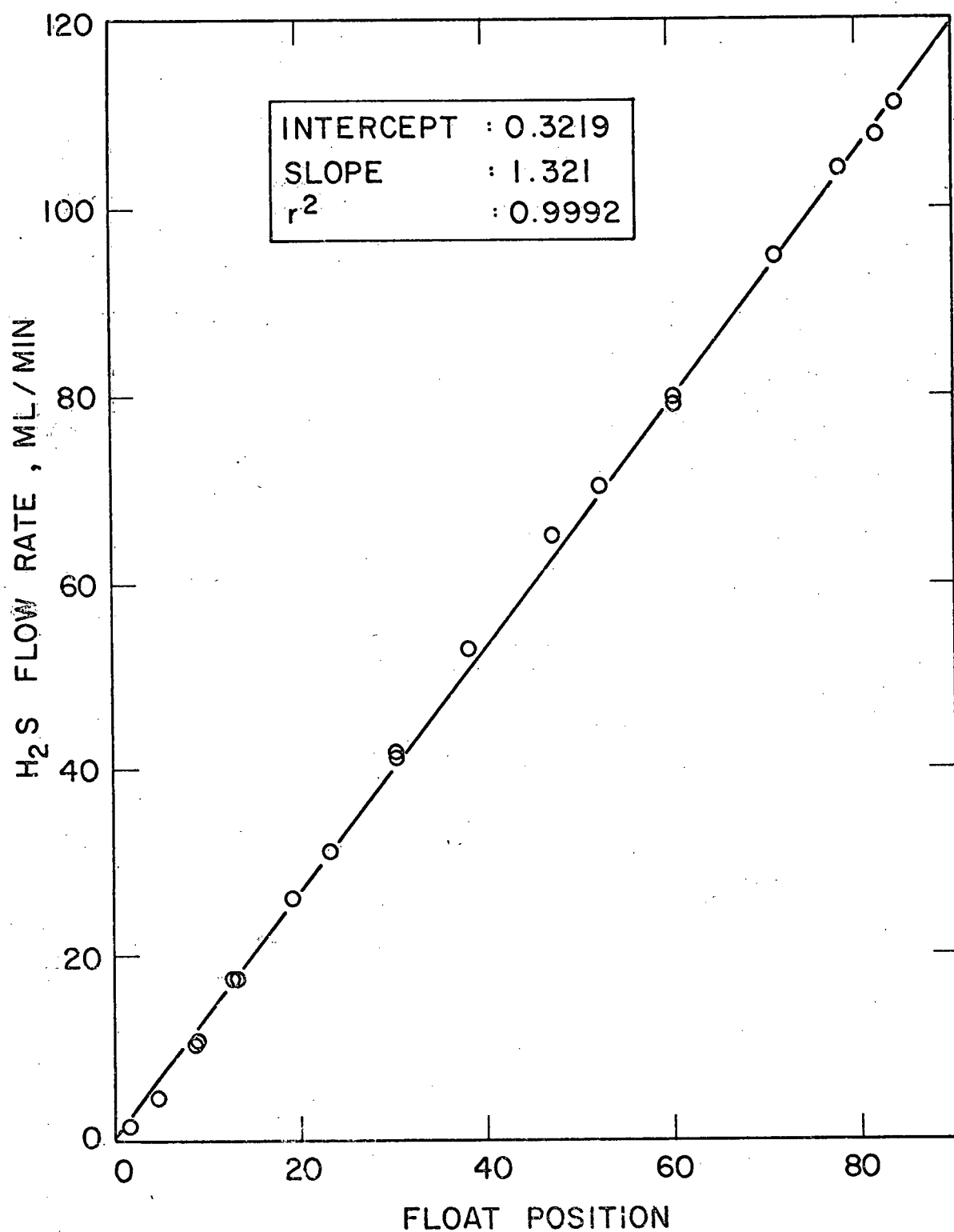


Figure C.6. Calibration of rotameter 2912A (Gilmont Model F-2000, size 10) for H₂S.

APPENDIX D
EXPERIMENTAL RESULTS

Table D.1 continued

Run Code	P A			Product Compositions (%)						Sulphur Yield(%)
	Flow	M.B.	Avg.	H ₂	H ₂ S	SO ₂	N ₂	H ₂ O	S ₂	
55		99.1		0.0	6.5	3.1	56.3	23.7	10.3	68.4
		98.7		0.0	5.7	2.6	56.1	24.6	11.0	72.5
		100.2		0.0	5.3	2.7	56.4	24.6	10.9	73.1
		100.9		0.0	6.0	3.2	56.6	23.8	10.3	69.2
		97.0		0.0	8.1	3.6	56.1	22.6	9.5	61.8
	99.1	100.5		0.0	6.7	3.4	56.7	23.3	9.9	66.3
	96.2	100.6		0.0	5.2	2.7	56.5	24.6	11.0	73.4
Mean, \bar{x}	97.7	99.6	98.7	0.0	6.2	3.0	56.4	23.9	10.4	69.2
100 σ/\bar{x}	2.1	1.4	-	0.0	16.2	12.7	0.4	3.2	5.6	6.1
57	117.2									
	120.6									
Mean, \bar{x}	118.9	121.1	120.0	0.0	3.4	4.5	60.0	22.9	9.2	70.0
100 σ/\bar{x}	2.0	-	-	-	-	-	-	-	-	-
74A	197.6	170.3		0.0	0.7	7.6	65.8	19.8	6.1	59.5
	205.2	160.1		0.0	0.7	6.8	64.7	20.8	7.0	64.8
Mean, \bar{x}	201.4	165.2	183.3	0.0	0.7	7.2	65.3	20.3	6.6	62.2
100 σ/\bar{x}	2.7	4.4	-	0.0	0.0	7.9	1.2	3.5	9.7	6.0

TABLE D.2

EXPERIMENTAL RESULTS OF HYDROGEN SULPHIDE OXIDATION
AT 900°K FOR VARIOUS P_A

Run Code	P_A			Product Compositions (%)						Sulphur Yield (%)
	Flow	M.B.	Avg.	H ₂	H ₂ S	SO ₂	N ₂	H ₂ O	S ₂	
83	-	-		2.1	96.8	-	-	-	1.1	2.1
	-	-		2.2	96.7	-	-	-	1.1	2.2
	-	-		2.1	96.9	-	-	-	1.0	2.1
	-	-		2.0	97.0	-	-	-	1.0	2.0
	-	-		1.9	97.2	-	-	-	0.9	1.9
	-	-		1.8	97.3	-	-	-	0.9	1.8
Mean, \bar{x}	-	-	-	2.0	97.0	-	-	-	1.0	2.0
100 σ/\bar{x}	-	-	-	7.3	0.2	-	-	-	8.9	7.3
66	45.9									
	45.9	49.7		0.2	23.8	0.4	42.8	21.9	10.8	47.2
	43.0	46.6		0.2	26.0	0.4	41.6	21.3	10.5	44.3
	48.7	50.1		0.2	23.5	0.4	43.0	22.0	10.9	47.7
Mean, \bar{x}	45.9	48.8	47.4	0.2	24.4	0.4	42.5	21.7	10.7	46.4
100 σ/\bar{x}	5.1	3.9	-	0.0	5.6	0.0	1.8	1.7	1.9	4.0
52	70.6	71.1		0.1	13.5	1.4	50.0	23.8	11.3	60.2
	56.8	74.9		0.1	13.4	2.2	51.1	22.8	10.4	57.1
	64.8	70.2		0.1	14.9	1.9	49.9	22.7	10.5	55.4
Mean, \bar{x}	64.1	72.1	68.1	0.1	13.9	1.8	50.3	23.1	10.7	57.6
100 σ/\bar{x}	10.8	3.5	-	0.0	6.0	22.0	1.3	2.6	4.6	4.2
50	-	73.4		0.1	12.5	1.5	50.6	24.0	11.3	61.8
	-	77.9		0.1	11.0	1.6	51.7	24.2	11.3	64.2
Mean, \bar{x}	-	75.7	-	0.1	11.8	1.6	51.2	24.1	11.3	63.0
100 σ/\bar{x}	-	4.2	-	0.0	9.0	4.6	1.5	0.6	0.0	2.7

Table D.2 continued

Run Code	P _A			Product Compositions (%)						Sulphur Yield (%)
	Flow	M.B.	Avg.	H ₂	H ₂ S	SO ₂	N ₂	H ₂ O	S ₂	
54		88.6		0.1	7.9	2.1	54.1	24.6	11.3	69.3
	95.7	86.5		0.1	9.5	2.6	53.8	23.5	10.5	63.5
	98.2	87.2		0.1	8.8	2.3	53.9	24.0	10.9	66.3
Mean, \bar{x}	97.0	87.4	92.2	0.1	8.7	2.3	53.9	24.0	10.9	66.4
100 σ/\bar{x}	1.8	1.2	-	0.0	9.2	10.8	0.3	2.3	3.7	4.4
57		123.1		0.0	4.1	5.1	60.4	22.0	8.4	64.8
		120.7		0.0	4.1	4.8	60.0	22.4	8.8	66.6
	117.2	123.5		0.0	3.8	5.0	60.4	22.2	8.6	66.1
	120.6	122.3		0.0	4.0	4.9	60.2	22.2	8.7	66.0
Mean, \bar{x}	118.9	122.4	120.7	0.0	4.0	5.0	60.3	22.2	8.6	65.9
100 σ/\bar{x}	2.0	1.0	-	0.0	3.5	2.6	0.3	0.7	2.0	1.2
93		130.3		0.0	3.6	5.6	61.4	21.4	7.9	63.3
	170.1	127.5		0.0	3.8	5.4	61.0	21.6	8.1	64.0
	170.1	126.2		0.0	3.7	5.2	60.8	21.9	8.3	65.1
	167.6	126.6		0.0	4.4	5.6	61.0	21.2	7.8	61.1
	167.6	125.4		0.0	4.3	5.5	60.8	21.4	8.0	61.9
Mean, \bar{x}	168.9	127.2	148.1	0.0	4.0	5.5	61.0	21.5	8.0	63.1
100 σ/\bar{x}	0.9	1.5	-	0.0	9.2	3.1	0.4	1.2	2.4	2.5
70	184.7									
	168.0	154.0		0.0	2.7	7.3	64.4	19.5	6.1	54.7
	168.0	164.5		0.0	3.1	8.4	65.6	18.1	4.8	45.7
Mean, \bar{x}	173.6	159.3	166.5	0.0	2.9	7.9	65.0	18.8	5.5	50.2
100 σ/\bar{x}	5.6	4.7	-	0.0	9.8	9.9	1.3	5.3	16.9	12.7

TABLE D.3

EXPERIMENTAL RESULTS OF HYDROGEN SULPHIDE OXIDATION
AT 1000°K FOR VARIOUS P_A

Run Code	P_A			Product Compositions (%)						Sulphur Yield(%)
	Flow	M.B.	Avg.	H ₂	H ₂ S	SO ₂	N ₂	H ₂ O	S ₂	
83	-	-		5.1	92.3	-	-	-	2.6	5.3
	-	-		5.2	92.3	-	-	-	2.6	5.3
	-	-		5.2	92.1	-	-	-	2.6	5.4
	-	-		5.1	92.4	-	-	-	2.5	5.2
	-	-		5.0	92.4	-	-	-	2.5	5.2
	-	-		5.2	92.3	-	-	-	2.6	5.3
	-	-		5.2	92.3	-	-	-	2.6	5.3
Mean, \bar{x}	-	-	-	5.1	92.3	-	-	-	2.6	5.3
100 σ/\bar{x}	-	-	-	1.6	0.1	-	-	-	2.0	1.4
63A	49.7									
	49.7									
Mean, \bar{x}	49.7	54.8	52.2	0.5	21.0	1.0	44.8	21.9	10.7	49.4
100 σ/\bar{x}	0.0	-	-	-	-	-	-	-	-	-
50	-	77.3		0.3	11.1	1.7	51.5	24.0	11.3	63.9
	-	71.9		0.3	12.9	1.4	50.2	23.9	11.4	61.3
	-	74.9		0.3	10.8	1.0	50.8	25.0	12.1	67.4
	-	70.9		0.4	12.8	1.2	49.8	24.2	11.7	62.5
	-	70.6		0.4	12.8	1.1	49.7	24.3	11.8	62.9
	-	70.6		0.4	12.8	1.1	49.7	24.3	11.8	62.9
Mean, \bar{x}	-	73.1	-	0.3	12.1	1.3	50.4	24.3	11.7	63.6
100 σ/\bar{x}	-	4.0	-	16.1	8.6	21.7	1.5	1.8	2.8	3.6
86		83.2		0.2	9.5	2.0	53.0	24.2	11.2	66.0
		83.6		0.2	9.1	1.9	53.0	24.4	11.4	67.3
		83.5		0.2	8.9	1.7	53.0	24.7	11.6	68.5
		85.5		0.1	8.4	1.8	53.4	24.8	11.5	69.2
	96.0	85.2		0.1	8.5	1.8	53.4	24.7	11.5	68.9
	96.0	85.8		0.1	8.0	1.7	52.5	25.1	11.7	70.9
	96.0	85.8		0.1	8.0	1.7	52.5	25.1	11.7	70.9
Mean, \bar{x}	96.0	84.5	90.3	0.2	8.7	1.8	53.2	24.7	11.5	68.5
100 σ/\bar{x}	0.0	1.4	-	36.5	6.2	6.4	0.5	1.3	1.5	2.5

Table D.3 continued

Run Code	P _A			Product Compositions (%)						Sulphur Yield(%)
	Flow	M.B.	Avg.	H ₂	H ₂ S	SO ₂	N ₂	H ₂ O	S ₂	
79	96.9	106.6		0.1	6.1	4.0	57.8	22.7	9.4	65.0
	96.9	105.3		0.1	5.8	3.7	57.5	23.1	9.7	67.0
Mean, \bar{x}	96.9	106.0	101.5	0.1	6.0	3.85	57.7	22.9	9.6	66.0
100 σ/\bar{x}	0.0	0.9	-	0.0	3.6	5.5	0.4	1.2	2.2	2.1
97		120.9		0.1	4.0	4.8	60.0	22.3	8.8	66.8
	123.8	118.3		0.0	3.8	4.4	59.5	23.0	9.3	69.6
	122.2	117.0		0.0	3.6	4.1	59.3	23.3	9.6	71.5
	120.7	120.4		0.0	3.1	4.3	59.8	23.3	9.5	71.9
Mean, \bar{x}	122.2	119.2	120.7	0.0	3.6	4.4	59.7	23.0	9.3	70.0
100 σ/\bar{x}	1.3	1.5	-	200.0	10.7	6.7	0.5	2.1	3.8	3.3
93		132.4		0.3	2.7	5.5	61.5	21.8	8.3	66.9
	170.1	129.3		0.3	2.9	5.3	61.1	22.0	8.5	67.5
	170.1	137.8		0.3	3.1	6.2	62.3	20.7	7.4	61.2
	167.6	132.9		0.3	3.2	5.8	61.7	21.3	7.9	63.8
	167.6	128.7		0.2	3.0	5.2	61.0	22.0	8.5	67.5
Mean, \bar{x}	168.9	132.2	150.6	0.3	3.0	5.6	61.5	21.6	8.1	65.4
100 σ/\bar{x}	0.9	2.7	-	16.0	3.4	7.3	0.8	2.6	5.8	4.3
74	-	152.0		0.1	1.4	6.6	63.9	20.8	7.2	64.3
	-	148.6		0.1	1.4	6.3	63.5	21.2	7.5	66.3
	-	158.4		0.1	1.5	7.1	64.6	20.1	6.5	60.2
	-	153.0		0.1	1.5	6.7	64.0	20.6	7.0	63.0
Mean, \bar{x}	-	153.0	-	0.1	1.5	6.7	64.0	20.7	7.1	63.5
100 σ/\bar{x}	-	2.7	-	0.0	6.9	4.9	0.7	2.2	6.0	4.0
72	200.1									
	197.1	183.1		0.1	0.4	8.3	66.9	18.9	5.4	55.2
	197.1	178.2		0.1	0.3	8.0	66.4	19.4	5.8	58.1
Mean, \bar{x}	198.1	180.7	189.4	0.1	0.4	8.2	66.7	19.2	5.6	56.7
100 σ/\bar{x}	0.9	1.9	-	0.0	20.2	2.6	0.5	1.8	5.1	3.6

TABLE D.4

EXPERIMENTAL RESULTS OF HYDROGEN SULPHIDE OXIDATION
AT 1100°K FOR VARIOUS P_A

Run Code	P_A			Product Compositions (%)						Sulphur Yield (%)
	Flow	M.B.	Avg.	H ₂	H ₂ S	SO ₂	N ₂	H ₂ O	S ₂	
83	-	-		9.8	85.3	-	-	-	4.9	10.3
	-	-		9.7	85.4	-	-	-	4.9	10.2
	-	-		9.5	85.7	-	-	-	4.8	10.0
	-	-		9.8	85.4	-	-	-	4.9	10.3
	-	-		9.6	85.7	-	-	-	4.8	10.0
Mean, \bar{x}	-	-	-	9.7	85.5	-	-	-	4.9	10.1
100 σ/\bar{x}	-	-	-	1.3	0.2	-	-	-	1.1	1.5
63A		53.8		0.9	19.8	0.2	44.2	23.1	11.9	54.3
		55.3		0.9	18.8	0.2	44.8	23.3	12.0	55.7
	49.7	57.7		0.8	17.8	0.4	45.6	23.4	11.9	56.7
	49.7	57.2		1.0	18.7	0.8	45.5	22.6	11.4	53.9
Mean, \bar{x}	49.7	56.0	52.9	0.9	18.8	0.4	45.0	23.1	11.8	55.2
100 σ/\bar{x}	0.0	3.2	-	9.1	4.4	7.1	1.5	1.5	2.3	2.3
48	70.9	78.1		1.1	10.1	1.8	51.5	23.8	11.6	66.0
	68.5	77.3		1.1	10.9	2.0	51.4	23.4	11.2	63.6
	74.4	78.5		1.1	9.9	1.7	51.6	24.1	11.7	66.9
Mean, \bar{x}	71.3	78.0	74.7	1.1	10.3	1.8	51.5	23.8	11.5	65.5
100 σ/\bar{x}	4.2	0.8	-	0.0	5.1	8.3	0.2	1.5	2.3	2.6
46		101.2		1.4	4.4	3.1	56.3	23.7	11.0	74.6
		99.0		1.5	4.2	2.7	55.8	24.3	11.5	77.0
		100.3		0.6	4.1	2.4	56.2	25.1	11.6	78.1
	99.1	99.8		0.6	4.2	2.3	56.1	25.2	11.7	78.3
	99.9	99.8		0.6	4.2	2.4	56.1	25.1	11.6	77.9
Mean, \bar{x}	99.5	100.0	99.8	0.9	4.2	2.6	56.1	24.7	11.5	77.2
100 σ/\bar{x}	0.6	0.8	-	49.7	2.6	12.7	0.3	2.7	2.4	2.0

Table D.4 continued

Run Code	P _A			Product Compositions (%)						Sulphur Yield(%)
	Flow	M.B.	Avg.	H ₂	H ₂ S	SO ₂	N ₂	H ₂ O	S ₂	
58	123.9									
	117.2	120.5		0.2	2.8	4.2	59.8	23.4	9.7	73.4
	123.9	126.0		0.3	3.6	5.2	60.7	21.8	8.4	65.7
Mean, \bar{x}	121.7	123.3	122.5	0.3	3.2	4.7	60.3	22.6	9.1	69.6
100 σ/\bar{x}	3.2	3.2	-	28.3	17.7	15.0	1.1	5.0	10.2	7.8
77		131.1		0.4	3.1	5.6	61.4	21.4	8.1	65.1
	115.7	128.3		0.4	3.0	5.3	61.0	21.9	8.5	67.1
	122.2	126.5		0.4	3.2	5.2	60.7	22.0	8.6	67.4
	120.6	123.7		0.4	3.2	4.9	60.3	22.3	8.9	68.7
Mean, \bar{x}	119.5	127.4	123.4	0.4	3.1	5.3	60.9	21.9	8.5	67.1
100 σ/\bar{x}	2.8	2.4	-	0.0	3.1	5.5	0.8	1.7	3.9	2.2
68		127.0		0.1	1.6	4.3	60.6	23.7	9.7	76.7
		124.3		0.2	2.0	4.2	60.2	23.6	9.7	75.6
	147.3	130.0		0.2	2.4	5.0	61.1	22.4	8.8	70.4
	141.1	130.4		0.2	2.5	5.2	61.2	22.2	8.7	69.3
Mean, \bar{x}	144.2	127.9	136.1	0.2	2.1	4.7	60.8	23.0	9.2	73.0
100 σ/\bar{x}	3.0	2.2	-	28.6	19.4	10.7	0.8	3.4	6.0	5.1
93		129.7		0.3	1.7	4.7	61.0	23.0	9.3	74.5
	170.1	125.5		0.3	1.6	4.2	60.3	23.7	9.9	77.3
	170.1	137.6		0.4	1.8	5.6	62.1	21.8	8.3	69.0
	167.6	139.7		0.4	1.9	5.9	62.4	21.4	8.0	67.3
	167.6	133.8		0.4	1.9	5.3	61.6	22.1	8.6	70.4
Mean, \bar{x}	168.9	133.3	151.1	0.4	1.8	5.1	61.5	22.4	8.8	71.7
100 σ/\bar{x}	0.9	4.3	-	15.2	7.3	13.4	1.4	4.2	8.8	5.7
72		162.5		0.4	0.8	7.2	64.9	20.0	6.6	62.1
	200.1	171.1		0.5	1.0	8.0	65.8	19.0	5.8	56.2
	197.1	165.3		0.5	0.9	7.6	65.2	19.6	6.2	59.5
	197.1	171.1		0.5	1.0	8.0	65.8	19.0	5.8	56.2
Mean, \bar{x}	198.1	167.5	182.8	0.5	0.9	7.7	65.4	19.4	6.1	58.5
100 σ/\bar{x}	0.9	2.6	-	10.5	10.4	5.0	0.7	2.5	6.3	4.9

TABLE D.5

EXPERIMENTAL RESULTS OF HYDROGEN SULPHIDE OXIDATION
AT 1200°K FOR VARIOUS P_A

Run Code	P_A			Product Compositions (%)						Sulphur Yield (%)
	Flow	M.B.	Avg.	H ₂	H ₂ S	SO ₂	N ₂	H ₂ O	S ₂	
84	-	-		12.4	81.3	-	-	-	6.2	13.3
	-	-		13.0	80.5	-	-	-	6.5	13.9
	-	-		13.3	80.1	-	-	-	6.6	14.2
Mean, \bar{x}	-	-	-	12.9	80.6	-	-	-	6.4	13.8
100 σ/\bar{x}	-	-	-	3.6	0.8	-	-	-	3.2	3.3
63		54.8		2.4	18.0	0.5	44.3	22.6	12.2	56.9
	47.3	54.7		2.4	18.2	0.5	44.2	22.5	12.2	56.7
	46.4	55.7		2.4	17.7	0.6	44.6	22.5	12.2	57.1
	44.9	51.1		2.7	19.8	0.4	42.8	22.1	12.2	54.8
Mean, \bar{x}	46.2	54.1	50.2	2.5	18.4	0.5	44.0	22.4	12.2	56.4
100 σ/\bar{x}	2.6	3.8	-	6.1	5.1	16.3	1.8	1.0	0.0	1.9
48		78.0		2.4	8.3	1.5	51.1	24.1	12.5	71.9
		77.0		2.5	8.7	1.5	50.9	24.0	12.5	70.9
		76.4		2.6	9.5	1.9	50.8	23.3	12.0	68.0
	70.9	75.7		2.6	9.6	1.8	50.6	23.4	12.1	68.0
	68.5	76.6		2.1	8.8	1.3	50.8	24.3	12.6	71.3
	74.4	75.8		2.2	8.9	1.2	50.6	24.4	12.7	71.5
Mean, \bar{x}	71.3	76.6	74.0	2.4	9.0	1.5	50.8	23.9	12.4	70.3
100 σ/\bar{x}	4.2	1.1	-	8.7	5.5	17.8	0.4	1.9	2.3	2.5
46		97.6		1.7	5.0	3.0	55.6	23.5	11.1	73.5
		96.8		1.8	4.9	2.9	55.4	23.7	11.3	74.3
		97.3		1.9	4.7	2.9	55.5	23.7	11.3	74.9
	99.1	97.6		1.8	4.4	2.8	55.5	24.0	11.5	76.3
	99.9	96.2		1.8	4.5	2.6	55.2	24.2	11.7	76.9
Mean, \bar{x}	99.5	97.1	98.3	1.8	4.7	2.8	55.4	23.8	11.4	75.2
100 σ/\bar{x}	0.6	0.6	-	3.9	5.4	5.3	0.3	1.2	2.0	1.9

Table D.5 continued

Run Code	P _A			Product Compositions (%)						Sulphur Yield(%)
	Flow	M.B.	Avg.	H ₂	H ₂ S	SO ₂	N ₂	H ₂ O	S ₂	
58		120.8		0.3	2.0	3.9	59.7	23.2	10.2	77.4
		119.9		1.5	2.6	4.7	59.4	22.3	9.5	72.3
	123.9	117.4		0.5	2.7	3.9	59.2	23.6	10.1	75.4
	117.2	122.2		0.5	3.1	4.7	60.0	22.5	9.2	70.1
	123.9	121.9		0.5	3.0	4.6	59.9	22.7	9.3	71.0
Mean, \bar{x}	121.7	120.4	121.1	0.7	2.7	4.4	59.6	22.9	9.7	73.2
100 σ/\bar{x}	3.2	1.6	-	72.3	16.1	9.7	0.6	2.3	4.8	4.2
68		129.9		0.2	1.7	4.7	61.0	23.1	9.3	74.5
		126.9		0.2	1.4	4.2	60.5	23.8	9.9	77.8
	147.3	128.7		0.2	1.6	4.5	60.8	23.4	9.5	75.9
	141.1	126.1		0.2	1.5	4.2	60.4	23.8	9.9	77.5
Mean, \bar{x}	144.2	127.9	136.1	0.2	1.6	4.4	60.7	23.5	9.8	76.4
100 σ/\bar{x}	3.0	1.3	-	0.0	8.3	5.6	0.5	1.4	3.1	2.0
72	201.1	152.5		0.2	0.6	6.3	63.8	21.4	7.7	69.0
	197.1	158.7		0.3	0.7	6.9	64.5	20.6	7.0	65.2
	197.1	157.8		0.3	0.7	6.8	64.4	20.7	7.1	65.5
Mean, \bar{x}	198.1	156.3	177.2	0.3	0.7	6.7	64.2	20.9	7.3	66.6
100 σ/\bar{x}	0.9	2.1	-	21.7	8.7	4.8	0.6	2.1	5.2	3.2

TABLE D.6

EXPERIMENTAL RESULTS OF HYDROGEN SULPHIDE OXIDATION
AT 1300°K FOR VARIOUS P_A

Run Code	P_A			Product Compositions (%)						Sulphur Yield(%)
	Flow	M.B.	Avg.	H ₂	H ₂ S	SO ₂	N ₂	H ₂ O	S ₂	
84	-	-		18.5	72.3	-	-	-	9.2	20.4
	-	-		20.9	68.7	-	-	-	10.4	23.3
	-	-		20.5	69.3	-	-	-	10.2	22.8
	-	-		18.5	72.3	-	-	-	9.2	20.3
	-	-		19.2	71.2	-	-	-	9.6	21.3
Mean, \bar{x}	-	-	-	19.5	70.8	-	-	-	9.7	21.6
100 σ/\bar{x}	-	-	-	5.8	2.4	-	-	-	5.7	6.4
63		55.5		3.1	16.2	0.2	44.3	23.1	13.0	61.2
		56.5		3.1	15.5	0.2	44.6	23.4	13.2	62.7
	47.3	50.6		3.9	18.8	0.4	42.4	21.8	12.7	57.1
	46.4	53.4		3.5	17.2	0.3	43.5	22.5	12.9	59.5
	44.9	51.9		3.9	17.8	0.3	42.9	22.2	12.9	58.7
Mean, \bar{x}	46.2	53.6	49.9	3.5	17.1	0.3	43.5	22.6	12.9	59.8
100 σ/\bar{x}	2.6	4.6	-	11.4	7.6	29.9	2.1	2.9	1.4	3.6
48		73.5		2.8	8.8	1.0	49.8	24.5	13.1	72.9
		75.0		2.6	7.9	0.8	50.2	25.0	13.4	75.4
		76.6		3.4	7.2	1.2	50.5	24.4	13.3	76.0
	70.9	75.0		3.7	7.7	1.3	50.0	24.1	13.3	74.7
	68.5	73.2		4.2	8.4	1.4	49.5	23.4	13.1	72.7
	74.4	73.5		4.1	8.1	1.3	49.6	23.7	13.2	73.8
Mean, \bar{x}	71.3	74.5	72.9	3.5	8.0	1.2	49.9	24.2	13.2	74.3
100 σ/\bar{x}	4.2	1.8	-	19.1	6.9	19.3	0.8	2.4	0.9	1.8
46	99.1	97.7		2.0	3.6	2.4	55.4	24.5	12.1	80.0
	99.9	97.0		2.6	3.9	2.8	55.2	23.7	11.8	77.8
Mean, \bar{x}	99.5	97.4	98.5	2.3	3.8	2.6	55.3	24.1	12.0	78.9
100 σ/\bar{x}	0.6	0.5	-	18.4	5.7	10.9	0.3	2.3	1.8	2.0

Table D.6 continued

Run Code	P _A			Product Compositions (%)						Sulphur Yield(%)
	Flow	M.B.	Avg.	H ₂	H ₂ S	SO ₂	N ₂	H ₂ O	S ₂	
58	123.9	120.1		0.6	2.1	4.0	59.5	23.7	10.2	77.1
	117.2	118.6		0.6	1.8	3.6	59.2	24.2	10.6	79.6
	123.9	118.0		0.7	2.0	3.7	59.1	24.0	10.5	78.7
Mean, \bar{x}	121.7	118.9	120.3	0.6	2.0	3.8	59.3	24.0	10.4	78.5
100 σ/\bar{x}	3.2	0.9	-	9.1	7.8	5.5	0.4	1.1	2.0	1.6
68		124.7		0.3	1.2	3.9	60.2	24.1	10.3	79.9
		124.3		0.3	1.2	3.9	60.1	24.2	10.3	80.1
	147.3	122.4		0.3	1.2	3.6	59.8	24.5	10.6	81.4
	141.1	127.0		0.3	1.5	4.3	60.5	23.5	9.8	77.0
Mean, \bar{x}	144.2	124.6	134.4	0.3	1.3	3.9	60.2	24.1	10.3	79.6
100 σ/\bar{x}	3.0	1.5	-	0.0	11.8	7.3	0.5	1.7	3.2	2.3
91		136.1		0.5	0.7	4.9	61.7	23.0	9.3	76.8
		131.6		0.5	0.8	4.5	61.1	23.5	9.7	78.5
	173.0	139.0		0.5	0.9	5.3	62.1	22.4	8.8	74.0
	177.8	137.4		0.2	1.0	5.1	62.0	22.8	9.0	74.7
	163.3	134.5		0.2	1.0	4.8	61.6	23.2	9.3	76.3
Mean, \bar{x}	171.4	135.7	153.6	0.4	0.9	4.9	61.7	23.0	9.2	76.1
100 σ/\bar{x}	4.3	2.1	-	43.2	14.8	6.2	0.6	1.8	3.7	2.3
72	200.1	157.2		0.4	0.7	6.8	64.3	20.7	7.2	65.8
	197.1	163.6		0.4	0.7	7.3	65.0	20.0	6.5	61.9
	197.1	155.0		0.4	0.7	6.6	64.1	20.9	7.3	66.8
Mean, \bar{x}	198.1	158.6	181.8	0.4	0.7	6.9	64.5	20.5	7.0	64.8
100 σ/\bar{x}	0.9	2.8	-	0.0	0.0	5.2	0.7	2.3	6.2	4.0

TABLE D.7

EXPERIMENTAL RESULTS OF HYDROGEN SULPHIDE OXIDATION
AT 1400°K FOR VARIOUS P_A

Run Code	P_A			Product Compositions (%)						Sulphur Yield(%)
	Flow	M.B.	Avg.	H ₂	H ₂ S	SO ₂	N ₂	H ₂ O	S ₂	
84	-	-		27.3	59.0	-	-	-	13.7	31.7
	-	-		27.0	59.5	-	-	-	13.5	31.2
	-	-		26.8	59.9	-	-	-	13.4	30.9
	-	-		26.0	61.0	-	-	-	13.0	29.8
	-	-		26.4	60.5	-	-	-	13.2	30.4
	-	-		26.6	60.1	-	-	-	13.3	30.7
Mean, \bar{x}	-	-	-	26.7	60.0	-	-	-	13.4	30.8
100 σ/\bar{x}	-	-	-	1.7	1.2	-	-	-	1.8	2.1
88A	46.4	67.2		4.6	8.4	0.3	47.6	24.7	14.5	76.9
	44.1	65.5		4.8	8.9	0.3	47.0	24.5	14.5	76.1
	45.2	65.9		4.8	8.6	0.2	47.1	24.6	14.6	76.7
	46.4	69.7		3.4	8.1	0.2	48.5	25.5	14.4	77.6
Mean, \bar{x}	45.5	67.1	56.3	4.4	8.5	0.3	47.6	24.6	14.5	76.8
100 σ/\bar{x}	2.4	2.8	-	23.7	4.0	23.1	1.4	0.4	0.6	0.8
95		61.6		5.6	10.6	0.5	45.8	23.3	14.2	71.7
	52.2	62.0		5.5	10.4	0.5	45.9	23.4	14.2	72.3
	49.9	62.3		5.4	10.3	0.4	46.0	23.6	14.3	72.8
	54.1	65.8		4.1	9.6	0.3	47.3	24.5	14.1	74.0
	53.4	65.8		4.0	9.6	0.3	47.3	24.6	14.2	74.1
Mean, \bar{x}	52.4	63.5	56.9	4.9	10.1	0.4	46.5	23.9	14.2	73.0
100 σ/\bar{x}	3.5	3.3	-	16.2	4.6	25.0	1.7	2.6	0.5	1.4
98		62.4		5.1	10.9	0.6	46.1	23.4	14.0	71.0
		62.7		5.1	10.6	0.5	46.2	23.5	14.0	71.6
		63.6		4.9	10.2	0.5	46.5	23.8	14.1	72.7
	50.3	69.1		4.1	8.7	0.7	48.3	24.3	13.9	74.6
	50.3	71.1		3.9	8.0	0.6	48.8	24.7	14.0	76.5
	48.7	70.1		4.1	7.8	0.5	48.5	24.9	14.3	77.5
	49.9	68.2		4.2	8.6	0.4	48.0	24.6	14.2	75.7
Mean, \bar{x}	49.8	66.7	58.3	4.5	9.3	0.5	47.5	24.2	14.1	74.2
100 σ/\bar{x}	1.5	5.6	-	11.7	13.8	18.0	2.5	2.5	1.0	3.4

Table D.7 continued

Run Code	P _A			Product Composition (%)						Sulphur Yield(%)
	Flow	M.B.	Avg.	H ₂	H ₂ S	SO ₂	N ₂	H ₂ O	S ₂	
90A		77.3		3.5	5.6	0.6	50.4	25.5	14.2	82.0
		76.9		3.7	5.4	0.6	50.3	25.6	14.4	82.7
	75.1	78.7		3.1	5.6	0.7	50.9	25.7	14.0	81.6
	74.0	78.8		2.9	5.9	0.8	51.0	25.6	13.9	80.6
	69.9	78.5		3.0	5.7	0.7	50.8	25.7	14.0	81.5
	65.8	80.1		2.5	5.9	0.8	51.4	25.7	13.7	80.2
Mean, \bar{x}	71.2	78.4	74.8	3.1	5.7	0.7	50.8	25.7	14.0	81.4
100 σ/\bar{x}	6.0	1.5	-	13.8	3.4	12.8	0.8	0.2	1.7	1.1
88B	101.0	89.8		1.7	4.5	1.5	53.8	25.7	12.9	81.3
	98.0	95.0		2.2	3.3	2.0	54.7	25.1	12.7	82.7
	87.4	93.9		2.1	3.4	1.8	54.5	25.3	12.8	83.1
Mean, \bar{x}	95.5	92.9	94.2	2.0	3.7	1.8	54.3	25.4	12.8	82.4
100 σ/\bar{x}	7.5	2.9	-	13.2	17.8	14.2	0.9	1.2	0.8	1.1
81C	93.1	101.8		0.8	3.5	2.4	56.4	25.1	11.8	79.9
	93.1	100.1		1.2	3.5	2.4	56.0	25.0	11.9	80.3
	88.1	102.2		1.8	3.8	3.1	56.3	23.7	11.2	76.5
Mean, \bar{x}	91.4	101.4	96.4	1.3	3.6	2.6	56.2	24.6	11.6	78.9
100 σ/\bar{x}	3.2	1.1	-	39.7	4.8	15.3	0.4	3.2	3.3	2.6
77		136.1		1.2	1.5	5.7	61.7	21.5	8.5	70.4
	115.7	132.7		1.1	1.4	5.3	61.2	22.0	8.9	72.8
	122.2	130.6		0.9	1.5	5.0	61.0	22.5	9.2	74.0
	120.6	128.2		0.8	1.3	4.6	60.6	23.0	9.6	76.3
Mean, \bar{x}	119.5	131.9	125.7	1.0	1.4	5.2	61.1	22.0	9.1	73.4
100 σ/\bar{x}	2.8	2.5	-	18.3	6.7	9.0	0.7	2.3	5.1	3.4

Table D.7 continued

Run Code	P _A			Product Compositions (%)						Sulphur Yield(%)
	Flow	M.B.	Avg.	H ₂	H ₂ S	SO ₂	N ₂	H ₂ O	S ₂	
91	173.0	140.2		0.7	0.7	5.4	62.2	22.2	8.7	74.1
	177.8	137.4		0.7	0.8	5.2	61.9	22.4	9.0	74.8
	163.3	132.8		0.5	0.8	4.6	61.3	23.3	9.6	77.9
Mean, \bar{x}	171.4	136.8	154.1	0.6	0.8	5.1	61.8	22.6	9.1	75.6
100 σ/\bar{x}	4.3	2.7	-	18.2	7.5	8.2	0.7	2.6	5.0	2.7
74	-	187.8		0.3	0.6	8.8	67.3	18.1	4.8	50.4
	-	201.9		0.4	0.6	9.7	68.4	17.0	3.9	42.7
	-	194.8		0.3	0.6	9.2	67.9	17.6	4.3	46.9
Mean, \bar{x}	-	194.8	-	0.3	0.6	9.2	67.9	17.6	4.3	46.7
100 σ/\bar{x}	-	3.6	-	17.3	0.0	4.9	0.8	3.1	10.4	8.3

TABLE D.8

EXPERIMENTAL RESULTS OF HYDROGEN SULPHIDE OXIDATION
AT 1500°K FOR VARIOUS P_A

Run Code	P_A			Product Compositions (%)						Sulphur Yield(%)
	Flow	M.B.	Avg.	H ₂	H ₂ S	SO ₂	N ₂	H ₂ O	S ₂	
84	-	-		32.0	52.0	-	-	-	16.0	38.1
	-	-		31.7	52.4	-	-	-	15.9	37.7
	-	-		32.0	52.0	-	-	-	16.0	38.1
	-	-		32.6	51.1	-	-	-	16.3	38.9
	-	-		32.5	51.2	-	-	-	16.3	38.8
	-	-		32.6	51.1	-	-	-	16.3	39.0
Mean, \bar{x}	-	-	-	32.2	51.6	-	-	-	16.1	38.4
100 σ/\bar{x}	-	-	-	1.2	1.1	-	-	-	1.2	1.4
88A		65.4		6.4	7.5	0.4	46.7	24.1	15.1	79.4
		67.6		6.0	6.5	0.2	47.3	24.7	15.2	81.9
	46.4	68.0		6.0	6.3	0.2	47.4	24.9	15.3	82.6
	44.1	66.2		6.5	7.0	0.4	46.8	24.2	15.2	80.5
	45.2	66.5		6.4	6.7	0.3	46.9	24.4	15.3	81.5
	46.4	64.8		7.1	6.7	0.2	46.3	24.1	15.5	81.7
Mean, \bar{x}	45.5	66.4	56.0	6.4	6.8	0.3	46.9	24.4	15.3	81.3
100 σ/\bar{x}	2.4	1.9	-	6.3	6.2	34.7	0.9	1.4	0.9	1.4
95		62.1		6.0	9.7	0.4	45.8	23.5	14.6	74.2
		62.8		5.8	9.4	0.4	46.1	23.7	14.6	74.8
	52.2	63.4		5.8	9.1	0.4	46.2	23.8	14.7	75.6
	49.9	63.7		5.7	9.2	0.4	46.3	23.8	14.5	75.0
	45.1	64.9		5.4	8.8	0.4	46.8	24.1	14.5	75.9
	53.4	65.2		5.4	8.5	0.3	46.8	24.2	14.7	76.8
Mean, \bar{x}	50.2	63.7	57.0	5.7	9.1	0.4	46.3	23.9	14.6	75.4
100 σ/\bar{x}	7.3	1.9	-	4.2	0.9	10.6	0.9	1.1	0.6	1.2

Table D.8 continued

Run Code	P _A			Product Compositions (%)						Sulphur Yield(%)
	Flow	M.B.	Avg.	H ₂	H ₂ S	SO ₂	N ₂	H ₂ O	S ₂	
98		62.8		6.7	9.0	0.6	45.9	23.2	14.7	75.4
		63.2		6.5	8.7	0.5	46.0	23.4	14.7	76.1
	50.3	63.8		6.4	8.5	0.5	46.2	23.7	14.8	76.8
	50.3	67.2		6.1	7.8	0.8	47.3	23.6	14.5	77.2
	48.7	67.0		6.0	7.8	0.7	47.3	23.7	14.5	77.4
	49.9	67.3		6.0	7.6	0.7	47.3	23.9	14.6	77.9
Mean, \bar{x}	49.8	65.2	57.5	6.3	8.2	0.6	46.7	23.6	14.6	76.8
100 σ/\bar{x}	1.5	3.3	-	4.7	7.0	19.1	1.5	1.1	0.8	1.2
90		80.1		3.9	4.3	0.7	51.0	25.7	14.4	85.3
		79.7		3.9	4.3	0.6	50.9	25.8	14.5	85.5
		78.3		4.2	4.6	0.7	50.5	25.5	14.5	84.5
		80.8		4.2	3.7	0.7	51.1	25.7	14.6	86.6
		80.6		4.2	3.3	0.5	51.0	26.1	14.9	88.5
		83.5		2.7	4.4	0.8	52.1	26.0	13.9	84.1
	75.1	81.9		3.1	4.4	0.8	51.6	25.9	14.2	84.5
	74.0	80.6		3.4	4.8	0.8	51.3	25.7	14.1	83.3
	69.9	83.5		3.4	3.9	0.9	51.9	25.8	14.2	85.6
	65.8	83.2		3.4	3.4	0.6	51.7	26.3	14.5	87.9
Mean, \bar{x}	71.2	81.2	76.2	3.6	4.1	0.7	51.3	25.9	14.4	85.6
100 σ/\bar{x}	6.0	2.2	-	14.3	12.4	16.9	1.0	0.9	2.0	1.9
81	93.1	103.6		1.6	2.8	2.7	56.5	24.6	11.7	80.8
	93.1	105.8		1.3	1.6	2.3	56.8	25.6	12.4	86.5
	88.1	104.6		1.2	1.3	1.9	56.6	26.3	12.8	88.7
Mean, \bar{x}	91.4	104.7	98.1	1.4	1.9	2.3	56.6	25.5	12.3	85.3
100 σ/\bar{x}	3.2	1.1	-	15.2	41.8	17.4	0.3	3.4	4.5	4.8
77		136.9		1.2	1.1	5.6	61.8	21.7	8.7	72.2
	115.7	134.2		1.2	1.0	5.3	61.4	22.0	9.0	74.0
	122.2	134.1		1.3	0.9	5.3	61.3	22.0	9.0	74.4
	120.6	130.4		1.3	0.9	4.9	60.8	22.6	9.5	76.7
Mean, \bar{x}	119.5	133.9	126.7	1.3	1.0	5.3	61.3	22.1	9.1	74.3
100 σ/\bar{x}	2.8	2.0	-	4.6	9.8	5.4	0.7	1.7	3.7	2.5

Table D.8 continued

Run Code	P _A			Product Compositions (%)						Sulphur Yield(%)
	Flow	M.B.	Avg.	H ₂	H ₂ S	SO ₂	N ₂	H ₂ O	S ₂	
91		150.8		0.8	0.9	6.5	63.5	20.7	7.5	67.1
	173.0	139.8		0.8	0.7	5.5	62.2	22.1	8.7	73.7
	177.8	154.4		0.8	0.9	6.9	64.0	20.3	7.2	64.9
	163.3	141.8		0.8	0.8	5.7	62.4	21.9	8.5	72.4
Mean, \bar{x}	171.4	146.7	159.1	0.8	0.8	6.2	63.0	21.3	8.0	69.5
100 σ/\bar{x}	4.3	4.8	-	0.0	11.6	10.7	1.4	4.2	9.2	6.0
74A		178.4		0.2	0.6	8.1	66.5	19.1	5.6	56.1
		170.6		0.2	0.5	7.6	65.7	19.8	6.2	60.3
		179.0		0.4	0.6	8.3	66.5	18.8	5.5	55.2
		173.5		0.4	0.6	7.9	66.0	19.2	5.9	58.0
		184.5		0.5	0.6	8.7	67.0	18.2	5.0	51.9
		177.1		0.5	0.6	8.2	66.3	18.8	5.5	55.5
Mean, \bar{x}	-	177.2	-	0.4	0.6	8.1	66.3	19.0	5.6	56.2
100 σ/\bar{x}	-	2.7	-	37.3	7.0	4.6	0.7	2.8	7.2	5.0

APPENDIX E
COMPUTER PROGRAMS

TABLE E.1
H₂S DISSOCIATION

```

$CREATE S23
$GET S23
$NUMBER
$$COMPILE TIME=500
COMPUTER PROGRAMME 1
CLAUS COMBUSTION CHAMBER EQUILIBRIA WITH 23 SPECIES CONTAINING C, H, N AND S
  DOUBLE PRECISION CPD
  REAL NSERR, N2EX, NSD, N5, N, NSNSD
  DIMENSION CPD(25), P(25,20), C(25,20), NCV(20)
  DATA NCPD/23/, NP/24/, NCPDP2/25/, NSNSD/1.0/, CSCSD/1.0/
  READ (5,100) (CPD(NC), NC=1,NCPDP2)
  READ (5,101) PERR, NSERR, HSERR, CSERR, N2EX, H2SEX, S2EX, CH4EX
  READ (5,102) ((C(NC,NT), NC=1,NCPD), NT=6,20)
  READ (5,103) NITERS, LOWT, KAOT, NFEEDES, NH3BYP, KWRT
  NTEMP = KAOT - LOWT + 1
  LOWTP7=LOWT+7
  LOWTP8=LOWT+8
  IF (NTEMP .LT. 9) LOWTP7=KAOT
  CALL TRAPS(0,0,9000)
  WRITE (6,104) NITERS, PERR, N2EX, LOWT, NSERR, H2SEX,
1  KAOT, HSERR, S2EX, NFEEDES, CSERR, CH4EX, NH3BYP
COMPUTER DOES NOT PRINT EQUILIBRIUM CONSTANTS IF KWRT .EQ. 0
  IF (KWRT .EQ. 0) GO TO 3
  WRITE (6,105)
  WRITE (6,106) (KT, KT=6,13)
  DO 1 NC=1,NCPD
1  WRITE (6,107) NC, CPD(NC), (C(NC,NT), NT=6,13)
  WRITE (6,108)
  WRITE (6,106) (KT, KT=14,20)
  DO 2 NC=1,NCPD
2  WRITE (6,107) NC, CPD(NC), (C(NC,NT), NT=14,20)
COMPOSITION OF THESE ARE GUESSED:      N2      H2S      S2      CH4
3  IF (NH3BYP .EQ. 0) READ (5,109) (P(2,NT),P(5,NT),P(10,NT),P(19,NT)) *DATA 20
1  , MAO, NT=LOWT,KAOT)
COMMENCE CH4 AND NH3 ITERATIONS
  DO 9 I=1,NFEEDES
  READ (5, 101) PCTNH3, PCTCH4
  WRITE(2, 101) PCTNH3, PCTCH4
COMPOSITION OF THESE ARE GUESSED:      N2      H2S      S2      CH4
  IF (NH3BYP .GE. 1) READ (5,109) (P(2,NT),P(5,NT),P(10,NT),P(19,NT)) *DATA -3
1  , MAO, NT=LOWT,KAOT)
COMPOSITION OF INITIAL MIXTURE IS FOUND--BASED ON PCTNH3 MOLES OF NH3, ET CETERA
  AH2S = 100.0 - PCTNH3 - PCTCH4
CALCULATE DESIRED RATIOS
  NSD = PCTNH3/AH2S
  HSD = (2.0*AH2S + 3.0*PCTNH3 + 4.0*PCTCH4) / AH2S
  CSD = PCTCH4/AH2S
COMMENCE TEMPERATURE ITERATIONS
  DO 8 NT=LOWT,KAOT
COMMENCE ITERATIONS TO OBTAIN CONVERGENCE AT GIVEN NH3+CH4 AND TEMPERATURE
  DO 7 NI=1,NITERS
  S2=P(10,NT)
  S5=S2**0.5
  N5 = P(2,NT)**0.5
  H2 = P(5,NT) / C(5,NT) / S5
  H5=H2**0.5
  P( 1,NT) = C( 1,NT) * N5 * H2**1.5
  P( 3,NT) = C( 3,NT) * H5

```

```

P( 4,NT) = H2
P( 6,NT) = C( 6,NT) * H2 * S2
P( 7,NT) = C( 7,NT) * S5 * H5
P( 8,NT) = C( 8,NT) * S5 * N5
P( 9,NT) = C( 9,NT) * S5
P(11,NT) = C(11,NT) * S2**1.5
P(12,NT) = C(12,NT) * S2**2
P(13,NT) = C(13,NT) * S2**2.5
P(14,NT) = C(14,NT) * S2**3
P(15,NT) = C(15,NT) * S2**3.5
P(16,NT) = C(16,NT) * S2**4
P(17,NT) = C(17,NT) * P( 1,NT) * P(19,NT) / H2**3
P(18,NT) = C(18,NT) * P(17,NT)**2 / H2
P(22,NT) = C(22,NT) * P(19,NT) * S5 / H2**2
P(23,NT) = C(23,NT) * P(22,NT) * S5
P(20,NT) = C(20,NT) * P(23,NT)**2 * H2 / S2**2
P(21,NT) = C(21,NT) * P(20,NT) * H2

COMPUTE TOTAL MOLES NITROGEN (N), HYDROGEN (H), SULPHUR (S) AND CARBON (CC)
N = P(1,NT) + 2.0*P(2,NT) + P(8,NT) + P(17,NT) + 2.0*P(18,NT)
H = 3.0*P(1,NT)+P(3,NT) + 2.0 * (P(4,NT)+P(5,NT)+P(6,NT))+P(7,NT) +
1 P(17,NT)+4.0*P(19,NT)+2.0*P(20,NT)+4.0*P(21,NT)
SLOST = P(5,NT)+2.0*P(6,NT)+P(7,NT)+P(8,NT)+P(22,NT)+2.0*P(23,NT)
SRECOV = P( 9,NT) + 2.0*P(10,NT) + 3.0*P(11,NT) + 4.0*P(12,NT) +
1 5.0*P(13,NT) + 6.0*P(14,NT) + 7.0*P(15,NT) + 8.0*P(16,NT)
S = SLOST + SRECOV
CC = P(17,NT) + 2.0*P(18,NT) + P(19,NT) + 2.0*P(20,NT) +
1 2.0*P(21,NT) + P(22,NT) + P(23,NT)

COMPUTE TOTAL PRESSURE
P(NP,NT) = 0.0
DO 6 NC=1,NCPD
6 P(NP,NT) = P(NP,NT) + P(NC,NT)
PTPTD=P(NP,NT)
IF (NSD .GT. 1.0E-06) NSNSD= N/S/NSD
IF (CSD .GT. 1.0E-06) CSCSD=CC/S/CSD
HSHSD= H/S/HSD
NCV(NT)=NI
IF (ABS(PTPTD-1.0) .GT. PERR) GO TO 61
IF (ABS(NSNSD-1.0) .GT. NSERR) GO TO 61
IF (ABS(HSHSD-1.0) .GT. HSERR) GO TO 61
IF (ABS(CSCSD-1.0) .GT. CSERR) GO TO 61
GO TO 75

COMPUTE NEW N2, H2S, S2 AND CH4
61 P( 2,NT) = P( 2,NT) * (PTPTD*NSNSD) ** N2EX
P( 5,NT) = P( 5,NT) * (PTPTD*HSHSD) **H2SEX
P(10,NT) = P(10,NT) * (PTPTD/HSHSD) ** S2EX
7 P(19,NT) = P(19,NT) * (PTPTD*CSCSD) **CH4EX

CONVERGENCE ITERATIONS END AT STATEMENT 7, TEMPERATURE AT 8 AND NFEEDES AT 9
75 WRITE (2,109) P(2,NT), P(5,NT), P(10,NT), P(19,NT), NI WRITE 2*
CALCULATE PERCENT RECOVERY
8 P(NCPDP2,NT) = SRECOV/S*100.0
WRITE (6,110) AN2S, PCTNH3, PCTCH4
WRITE (6,106) (KT, KT=LOWT,LOWTP7)
DO 83 NC=1,NCPDP2
83 WRITE (6,107) NC, CPD(NC), (P(NC,NT), NT= LOWT,LOWTP7)
WRITE (6,111) (NCV(NT), NT=LOWT, LOWTP7)
COMPUTER WRITES OUTPUT IN TWO SECTIONS IF NTEMP IS GREATER THAN 8
IF (NTEMP .LT. 9) GO TO 9
WRITE (6,108)

```

```

WRITE (6,106) (KT, KT=LOWTP8,KAOT)
DO 85 NC=1,NCPDP2
85 WRITE (6,107) NC, CPD(NC), (P(NC,NT), NT= LOWTP8,KAOT)
9 WRITE (6,111) (NCV(NT), NT=LOWTP8,KAOT)
WRITE (6,105)
STOP
100 FORMAT (10A8)
101 FORMAT (10F8.0)
102 FORMAT (1P4E20.8)
103 FORMAT (6I5)
104 FORMAT(' NITERS=', I5, 15X, ' PERR =', F10.3, 13X, ' N2EX =',
1 F7.3/ ' LOWT =', I3,'00', 15X, ' NSERR =', F10.3, 13X, ' H2SEX =',
2 F7.3/ ' HIGHT =', I3,'00', 15X, ' HSERR =', F10.3, 13X, ' S2EX =',
3 F7.3/ ' NPEDS=', I5, 15X, ' CSEER =', F10.3, 13X, ' CH4EX =',
4 F7.3/ ' NH3BYP=', I5)
105 FORMAT ('EQUILIBRIUM CONSTANTS FOR THE FORMATION OF COMPOUNDS'//)
106 FORMAT (' COMPOUND', 8(I11, '00 K'))
107 FORMAT (1H , I2, 1X, A8, (1P8E15.5))
108 FORMAT (//)
109 FORMAT (1PE15.7, 15X, 3E15.7, I5)
110 FORMAT (1H1, 10X, 'EQUILIBRIUM PARTIAL PRESSURES IN ATMOSPHERES ',
1'OF 23 COMPOUNDS PRODUCED FROM HYDROGEN SULPHIDE DISSOCIATION'/37X
2,'THE ACID GAS FEED CONTAINS', P6.1, ' % H2S,',
3 P5.1, ' % NH3 AND', P5.1, ' % CH4'/)
111 FORMAT (1H , ' ITERATIONS', 4X, I4, 7(11X, I4))
END

```

\$\$DATA

NH3	N2	H	H2	H2S	H2S2	SH	SN	S	S2
S3	S4	S5	S6	S7	S8	HCN	C2N2	CH4	C2H2
C2H4	CS	CS2	TOTAL	% YIELD					
0.001	0.001	0.001	0.001	-0.5	-0.5	-0.5	-0.5		

\$UNNUMBER

\$CREATE D23

\$GET D23

\$NUMBER

4.16273800E-02	1.00000000E 00	4.58864600E-17	2.31682100E-19
1.78501300E 05	4.30200000E 04	7.30341100E-07	2.06227600E-17
1.57395100E-16	1.00000000E 00	4.92304500E 00	1.46199700E 02
1.25130300E 05	6.17260800E 07	1.82596800E 09	1.57758500E 11
2.64267600E-11	1.30429600E-05	1.00000000E 00	5.40597400E-20
1.08633300E 09	2.22078400E-12	8.74355700E 10	9.38238900E-03
1.00000000E 00	2.50874600E-14	2.59746400E-16	1.42215700E 04
1.56400000E 03	7.24545500E-06	6.22555600E-15	7.74272100E-14
1.00000000E 00	9.92678100E-01	5.17212600E 00	4.02831500E 02
2.38653200E 04	1.57675500E 05	1.63128500E 06	6.16698200E-08
4.44312400E-05	1.00000000E 00	6.48061300E-17	5.87138900E 06
2.88050800E-09	5.51595700E 08	2.99851500E-03	1.00000000E 00
2.87781400E-12	5.12192100E-14	2.10270800E 03	1.31000000E 02
4.03865700E-05	4.52717600E-13	8.15645600E-12	1.00000000E 00
3.00051900E-01	4.28810400E-01	5.63423700E 00	6.94609800E 01
1.50721600E 02	2.99861800E 02	2.19395100E-05	1.13674800E-04
1.00000000E 00	1.29559600E-14	1.13982800E 05	6.45076600E-07
1.24682900E 07	1.21491400E-03	1.00000000E 00	1.16119300E-10
3.16529400E-12	4.71070500E 02	1.85200000E 01	1.53286100E-04
1.27101000E-11	3.06868300E-10	1.00000000E 00	1.18734700E-01
6.26114600E-02	2.09011000E-01	7.71857600E-01	7.10412900E-01
3.90628200E-01	2.20140300E-03	2.38960500E-04	1.00000000E 00
7.91374000E-13	5.21618700E 03	4.43958800E-05	6.57708100E 05

5.84712900E-04
 1.41555600E 02
 5.61691800E-09
 1.53069000E-02
 8.97550500E-02
 4.39243800E 02
 1.00000000E 00
 1.10400000E 00
 1.00000000E 00
 1.21213700E-03
 7.21415700E-04
 2.15141200E-02
 1.96115700E-07
 2.19801600E-03
 1.88379500E-02
 1.90636900E-05
 1.00000000E 00
 1.88389400E 03
 8.60745700E-08
 4.72730500E-08
 5.89338800E-04
 4.16356500E-08
 1.86826400E-08
 8.62130100E-05
 6.32032100E 00
 1.01252800E-05
 2.08943200E-05
 1.34426800E 03
 7.36714700E-01
 1.00000000E 00
 3.73900000E-02
 1.00000000E 00
 6.45227700E-07
 2.83190900E-03
 3.65025000E 01
 5.40765600E-05
 1.61594300E-02
 4.82209000E-03
 9.22392400E-09
 1.00000000E 00
 2.43446500E 01
 1.99948800E-05
 3.70657000E-06
 5.32818600E-05
 1.12903000E-11
 3.73411600E-06
 2.96152100E-05
 1.12271400E 00
 6.65079300E-04
 6.05226300E-07
 2.84605000E 05
 2.11724100E-02
 1.00000000E 00
 5.26599900E-03
 1.00000000E 00
 9.74672000E-09
 6.38268500E-03
 2.63662100E 03

1.00000000E 00
 3.91100000E 00
 1.00000000E 00
 2.18161900E-02
 4.37130600E-04
 1.32536000E-03
 2.56881900E-08
 1.06481900E-03
 3.10568500E-02
 3.26188000E-04
 1.00000000E 00
 9.25999600E 03
 1.26010700E-08
 1.01108800E-08
 1.39937200E-03
 8.11406700E-07
 2.83966200E-09
 1.24846200E-04
 1.15007600E 01
 2.38648400E-06
 7.29714500E-05
 2.10397500E 02
 2.52053100E 00
 1.00000000E 00
 7.27099700E-02
 1.00000000E 00
 2.76826900E-06
 2.15667600E-03
 8.47486500E 00
 1.75078000E-05
 1.08483900E-02
 6.32162300E-03
 4.13955800E-08
 1.00000000E 00
 5.78416100E 01
 6.59149000E-06
 1.52723800E-06
 8.63344600E-05
 5.84686300E-11
 1.27535800E-06
 3.68588900E-05
 1.60064600E 00
 2.80634900E-04
 1.24190400E-06
 9.47120000E 04
 4.39101600E-02
 1.00000000E 00
 7.92200100E-03
 1.00000000E 00
 2.30081400E-08
 5.38145000E-03
 1.08467600E 03
 7.89743100E-04
 4.16016900E-02
 2.55151600E-03
 2.82178900E-10
 1.00000000E 00
 3.17278200E 00

2.25432400E-09
 4.45121400E-04
 5.67152600E-02
 1.01790800E-02
 1.00000000E 00
 6.28695100E 04
 1.30559800E-09
 1.63446700E-09
 3.91529500E-03
 2.79277100E-05
 3.05872600E-10
 1.92058500E-04
 2.31327900E 01
 4.43379500E-07
 3.17781900E-04
 2.42555200E 01
 1.05857200E 01
 1.00000000E 00
 1.56599800E-01
 1.00000000E 00
 1.51082800E-05
 1.57869000E-03
 1.57050100E 00
 4.83533000E-06
 6.87248200E-03
 8.62468700E-03
 2.34229200E-07
 1.00000000E 00
 1.55905300E 02
 1.87912600E-06
 5.59675000E-07
 1.49753900E-04
 3.84822800E-10
 3.76196200E-07
 4.72354100E-05
 2.38998600E 00
 1.06376100E-04
 2.80760000E-06
 2.73654800E 04
 9.99176500E-02
 1.00000000E 00
 1.24999900E-02
 1.00000000E 00
 6.06850000E-08
 4.45109600E-03
 4.00998700E 02
 3.56426600E-04
 3.14476600E-02
 3.07867000E-03
 7.83902900E-10
 1.00000000E 00
 5.79164400E 00
 1.29837900E-04
 1.65051300E-05
 2.38312300E-05
 7.30105300E-13
 2.28135300E-05
 2.04416400E-05

8.65231900E-11
 1.83516200E-10
 1.35688700E-02
 2.00244200E-03
 2.10570300E-11
 3.19231300E-04
 5.27613000E 01
 6.07971600E-08
 1.83477600E-03
 1.89487100E 00
 5.76318900E 01
 1.00000000E 00
 3.83400000E-01
 1.00000000E 00
 1.11551600E-04
 1.10118900E-03
 2.19842000E-01
 1.09984900E-06
 4.06003300E-03
 1.23598900E-02
 1.76513000E-06
 1.00000000E 00
 4.91373200E 02
 4.48429300E-07
 1.77570400E-07
 2.82240300E-04
 3.34629700E-09
 9.35100900E-08
 6.24845200E-05
 3.76198000E 00
 3.54778000E-05
 7.13309500E-06
 6.71846000E 03
 2.53619600E-01
 1.00000000E 00
 2.08900000E-02
 1.00000000E 00
 1.92704100E-07
 3.59749300E-03
 1.30373900E 02
 1.46619000E-04
 2.29317800E-02
 3.80083100E-03
 2.48527700E-09
 1.00000000E 00
 1.13679500E 01
 5.36322600E-05
 8.15407300E-06
 3.47974700E-05
 2.65039800E-12
 9.70020200E-06
 2.43559900E-05
 8.16794200E-01
 1.44046000E-03
 3.19916500E-07
 7.61286800E 05
 1.10294100E-02
 1.00000000E 00

1.61847700E-03
5.35426500E-02
2.15615000E-03
1.13572900E-10
1.00000000E 00
1.84918400E 00

2.87799600E-04
3.11499600E-05
1.69909300E-05
2.31928600E-13
4.91821800E-05

6.14210000E-01
2.89144900E-03
1.81146500E-07
1.84275100E 06
6.13585800E-03

3.64600000E-03
1.00000000E 00
4.53513400E-09
7.44399000E-03
5.85400700E 03

\$UNNUMBER

TABLE E.2
H₂S OXIDATION

```

$CREATE S36
$GET S36
$NUMBER
$$COMPILE TIME=500
COMPUTER PROGRAMME 14
CLAUS COMBUSTION CHAMBER EQUILIBRIA WITH 36 SPECIES INCLUDING CARBON SPECIES
DOUBLE PRECISION CPD
REAL N5, N, NO, NONOD, NOERR, N2, N2EX, NOD
DIMENSION CPD(38), P(38,20), C(38,20), NCV(20)
DATA NCPD/36/, NP/37/, NCPDP2/38/, CSCSD/1./, NONOD/1./, R/1.0E10/
READ (5,100) (CPD(NC), NC=1,NCPDP2) *DATA A*
READ (5,101) PERR, NOERR, HSERR, HOERR, CSERR, N2EX, H2OEX, H2SEX, *DATA B*
1 S2EX, CO2EX
READ (5,102) ((C(NC,NT), NC=1,NCPD), NT=6,20) *DATA C*
READ (5,103) NITERS, LOWT, KAOT, NFEEDS, IARBYP, KWRT *DATA 11
NTEMP = KAOT - LOWT + 1
LOWTP7=LOWT+7
LOWTP8=LOWT+8
IF (NTEMP.LT. 9) LOWTP8=LOWT
CALL TRAPS(0,0,9000)
WRITE (6,104) NITERS, PERR, N2EX, LOWT, NOERR, H2OEX,
1 KAOT, HSERR, H2SEX, NFEEDS, HOERR, S2EX, IARBYP, CSERR, CO2EX
COMPUTER DOES NOT PRINT EQUILIBRIUM CONSTANTS IF KWRT.EQ. 0
IF (KWRT.EQ. 0) GO TO 3
WRITE (6,105) (KT, KT=6,13)
DO 1 NC=1,NCPD
1 WRITE (6,106) NC, CPD(NC), (C(NC,NT), NT=6,13)
WRITE (6,105) (KT, KT=14,20)
DO 2 NC=1,NCPD
2 WRITE (6,106) NC, CPD(NC), (C(NC,NT), NT=14,20)
3 IF (IARBYP.EQ. 0) READ (5,107) (P(3,NT), P(9,NT), P(10,NT), *DATA 20
1 P(19,NT), P(34,NT), MAO, NT=LOWT,KAOT)
COMMENCE NH3 AND CH4 ITERATIONS
DO 9 I=1,NFEEDS
READ (5, 101) PCTAIR, PCTNH3, PCTH2O, PCTCH4, PCTCO2 *DATA 32
WRITE(4, 101) PCTAIR, PCTNH3, PCTH2O, PCTCH4, PCTCO2 WRITE **
IF (PCTAIR.GT. 1.0E-06) R=200.0/PCTAIR
COMPOSITION OF N2, H2O, H2S, S2, CO2, IS GUESSED
IF (IARBYP.GE. 1) READ (5,107) (P(3,NT), P(9,NT), P(10,NT), *DATA -3
1 P(19,NT), P(34,NT), MAO, NT=LOWT,KAOT)
COMPOSITION OF INITIAL MIXTURE IS FOUND--BASED ON PCTCH4 MOLES OF CH4, ET CETERA
AH2S = 100.0 - PCTNH3 - PCTH2O - PCTCH4 - PCTCO2
AO2 = 0.005*AH2S*PCTAIR + 0.75*PCTNH3 + 2.0*PCTCH4
AN2 = 3.76*AO2
ATOTAL = 100.0 + AO2 + AN2
PN2 = AN2/ATOTAL
PO2 = AO2/ATOTAL
PH2S= AH2S/ATOTAL
PNH3=PCTNH3/ATOTAL
PH2O=PCTH2O/ATOTAL
PCH4=PCTCH4/ATOTAL
PCO2=PCTCO2/ATOTAL
CALCULATE DESIRED RATIOS
OXY = 2.0*PO2 + PH2O + 2.0*PCO2
NOD = (2.0*PN2 + PNH3)/OXY
SOD = PH2S/OXY
CSD = (PCH4+PCO2)/PH2S
HSD = (2.0*PH2S + 3.0*PNH3 + 2.0*PH2O + 4.0*PCH4) / PH2S

```

COMMENCE TEMPERATURE ITERATIONS

DO 8 NT=LOWT,KAOT

COMMENCE ITERATIONS TO OBTAIN CONVERGENCE AT GIVEN AIR AND TEMPERATURE

DO 7 NI=1,NITERS

N2 = P(3,NT)

N5=N2**0.5

S2=P(19,NT)

S5=S2**0.5

O2 =(C(5,NT) * P(9,NT) * S5 / P(10,NT)) **2

O5=O2**0.5

H2 = C(8,NT) * P(9,NT) / O5

H5=H2**0.5

P(1,NT) = C(1,NT) * N5 * H2**1.5

P(2,NT) = C(2,NT) * N5 * O5

P(4,NT) = C(4,NT) * O5

P(5,NT) = O2

P(6,NT) = C(6,NT) * O5 * H5

P(7,NT) = C(7,NT) * H5

P(8,NT) = H2

P(11,NT) = C(11,NT) * H2 * S2

P(12,NT) = C(12,NT) * S5 * H5

P(13,NT) = C(13,NT) * S5 * N5

P(14,NT) = C(14,NT) * S5 * O5

P(15,NT) = C(15,NT) * S5 * O2

P(16,NT) = C(16,NT) * S5 * O2**1.5

P(17,NT) = C(17,NT) * S2 * O5

P(18,NT) = C(18,NT) * S5

P(20,NT) = C(20,NT) * S2**1.5

P(21,NT) = C(21,NT) * S2**2

P(22,NT) = C(22,NT) * S2**2.5

P(23,NT) = C(23,NT) * S2**3

P(24,NT) = C(24,NT) * S2**3.5

P(25,NT) = C(25,NT) * S2**4

P(26,NT) = C(26,NT) / O2 * P(34,NT) * N5 * H5

P(27,NT) = C(27,NT) / H2 * P(26,NT)**2

P(36,NT) = C(36,NT) / P(9,NT)**2 * P(34,NT) * P(10,NT)**2

P(29,NT) = C(29,NT) / S2**2 * P(36,NT)**2 * H2

P(28,NT) = C(28,NT) * P(29,NT)**0.5 * H2**1.5

P(30,NT) = C(30,NT) * P(29,NT) * H2

P(31,NT) = C(31,NT) * P(30,NT) * O5

P(32,NT) = C(32,NT) / O5 * P(34,NT)

P(33,NT) = C(33,NT) / P(9,NT) * P(34,NT) * P(10,NT)

P(35,NT) = C(35,NT) / P(9,NT) * P(33,NT) * H2

COMPUTE TOTAL MOLES NITROGEN N, HYDROGEN H, OXYGEN O, SULPHUR S, AND CARBON CC

N = P(1,NT)+P(2,NT)+2.0*P(3,NT)+P(13,NT) + P(26,NT) + 2.0*P(27,NT)

H = 3.0*P(1,NT) + P(6,NT) + P(7,NT) + 2.0 * (P(8,NT) + P(9,NT) +

1 P(10,NT) + P(11,NT)) + P(12,NT) + P(26,NT) + 2.0*P(29,NT) +

2 4.0 * (P(28,NT) + P(30,NT) + P(31,NT))

O = P(2,NT) + P(4,NT) + 2.0*P(5,NT) + P(6,NT) + P(9,NT) +

1 P(14,NT) + 2.0*P(15,NT) + 3.0*P(16,NT) + P(17,NT) + P(31,NT) +

2 P(32,NT) + P(33,NT) + 2.0*P(34,NT)

SLOST = P(10,NT)+2.0*P(11,NT)+P(12,NT)+P(13,NT)+P(14,NT)+P(15,NT) +

1 P(16,NT)+2.0*P(17,NT)+P(33,NT)+P(35,NT) + 2.0*P(36,NT)

SRECOV = P(18,NT) + 2.0*P(19,NT) + 3.0*P(20,NT) + 4.0*P(21,NT) +

1 5.0*P(22,NT) + 6.0*P(23,NT) + 7.0*P(24,NT) + 8.0*P(25,NT)

S = SLOST + SRECOV

CC = P(26,NT)+2.0*P(27,NT)+P(28,NT) + 2.0 * (P(29,NT)+P(30,NT) +

1 P(31,NT)) + P(32,NT)+P(33,NT)+P(34,NT)+P(35,NT)+P(36,NT)

```

C
C
COMPUTE TOTAL PRESSURE
  P(NP,NT) = 0.0
  DO 6 NC=1,NCPD
6    P(NP,NT) = P(NP,NT) + P(NC,NT)
    PTPTD=P(NP,NT)
    IF (NOD .GT. 1.0E-08) NONOD= N/O/NOD
    HSHSD=H/S/HSD
    SOSOD=S/O/SOD
    IF (CSD .GT. 1.0E-08) CSCSD=CC/S/CSD
    NCV(NT)=NI
    IF (ABS(PTPTD-1.0) .GT. PERR) GO TO 61
    IF (ABS(NONOD-1.0) .GT. NOERR) GO TO 61
    IF (ABS(HSHSD-1.0) .GT. HSERR) GO TO 61
    IF (ABS(SOSOD-1.0) .GT. HOERR) GO TO 61
    IF (ABS(CSCSD-1.0) .GT. CSERR) GO TO 61
  GO TO 75

COMPUTE NEW N2, H2O, H2S, S2, CO2
61  P( 3,NT) = P( 3,NT) * (PTPTD*NONOD) ** N2EX
    P( 9,NT) = P( 9,NT) * PTPTD          ** H2OEX
    P(10,NT) = P(10,NT) * (PTPTD*HSHSD) ** H2SEX
    P(19,NT) = P(19,NT) * (PTPTD*SOSOD) ** S2EX
7   P(34,NT) = P(34,NT) * (PTPTD*CSCSD) ** CO2EX
CONVERGENCE ITERATIONS END AT STATEMENT 7, TEMPERATURE AT 8 AND NFEEDES AT 9
75  WRITE (4,107) P(3,NT), P(9,NT), P(10,NT), P(19,NT), P(34,NT), NI
CALCULATE PERCENT RECOVERY
8   P(NCPDP2,NT) = SRECOV/S*100.0
COMPUTER WRITES OUTPUT ON TWO PAGES IF NTEMP IS GREATER THAN 8
  IF (NTEMP .LT. 9) GO TO 84
  WRITE (6,108) NCPD, R, PCTAIR, PCTNH3, PCTH2O, PCTCH4, PCTCO2,
1   PH2S, P02, PN2, PNH3, PH2O, PCH4, PCO2, (KT, KT=LOWT,LOWTP7)
  DO 83 NC=1,NCPDP2
83  WRITE (6,106) NC, CPD(NC), (P(NC,NT), NT=LOWT,LOWTP7)
    WRITE (6,109) (NCV(NT), NT=LOWT,LOWTP7)
84  WRITE (6,108) NCPD, R, PCTAIR, PCTNH3, PCTH2O, PCTCH4, PCTCO2,
1   PH2S, P02, PN2, PNH3, PH2O, PCH4, PCO2, (KT, KT=LOWTP8,KAOT)
  DO 85 NC=1,NCPDP2
85  WRITE (6,106) NC, CPD(NC), (P(NC,NT), NT=LOWTP8,KAOT)
9   WRITE (6,109) (NCV(NT), NT=LOWTP8,KAOT)
    WRITE (6,105) KWRT
    STOP
100  FORMAT (10A8)
101  FORMAT (10F8.0)
102  FORMAT (1P4E20.8)
103  FORMAT (6I5)
104  FORMAT(' NITERS=', I5, 15X, ' PERR =', F10.3, 13X, ' N2EX =',
1    F7.3/ ' TLOW =', I3,'00', 15X, ' NOERR =', F10.3, 13X, ' H2OEX =',
2    F7.3/ ' THIGH =', I3,'00', 15X, ' HSERR =', F10.3, 13X, ' H2SEX =',
3    F7.3/ ' NFEEDES=', I5, 15X, ' HOERR =', F10.3, 13X, ' S2EX =',
4    F7.3/ ' IARBYP=', I5, 15X, ' CSERR =', F10.3, 13X, ' CO2EX =', F7.3/)
105  FORMAT (1H1, 28X, 'EQUILIBRIUM CONSTANTS FOR THE FORMATION OF COMPO
1UNDS'/// ' COMPOUND', 8(I11, '00 K'))
106  FORMAT (1H , I2, 1X, A8, (1P8E15.5))
107  FORMAT (1P5E15.7, I5)
108  FORMAT (1H1, 10X, 'EQUILIBRIUM PARTIAL PRESSURES IN ATMOSPHERES OF
1', I3, ' COMPOUNDS PRODUCED FROM HYDROGEN SULPHIDE COMBUSTION'/ 1H
20, 35X, 'H2S/O2 RATIO IS ', F8.3, ' (' , F5.1, ' % STOICHIOMETRIC AIR

```

```

3) '/ 31X, 'THE ACID GAS FEED CONTAINS', F5.1, ' % NH3', F5.1,
4 ' % H2O', F5.1, ' % CH4 AND', F5.1, ' % CO2'// 1H, 43X, 'CON
5 POSITION OF THE INITIAL MIXTURE'// 1H, 53X, 'H2S', 2PF8.3, ' %'/
6 1H, 53X, 'O2', F8.3, ' %'/ 1H, 53X, 'N2', F8.3, ' %'/
7 1H, 53X, 'NH3', F8.3, ' %'/ 1H, 53X, 'H2O', F8.3, ' %'/
8 1H, 53X, 'CH4', F8.3, ' %'/ 1H, 53X, 'CO2', F8.3, ' %'///
9 ' COMPOUND', 8(I11, '00 K'))
109 FORMAT (1H0, ' ITERATIONS', 4X, I4, 7(11X, I4))
END
$$DATA
NH3 NO N2 O O2 OH H H2 H2O H2S
H2S2 SH SN SO SO2 SO3 S2O S S2 S3
S4 S5 S6 S7 S8 HCN C2N2 CH4 C2H2 C2H4
C2H4O CO COS CO2 CS CS2 TOTAL % YIELD
0.001 0.001 0.001 0.001 0.001 -0.5 -0.5 -0.5 -0.5 -0.5
$UNNUMBER
$CREATE P1
$CREATE K36
$GET K36
$NUMBER
4.16273800E-02 6.15287900E-08 1.00000000E 00 2.65183500E-19
4.13566300E-14 2.45845500E-03 4.58864600E-17 2.31682100E-19
4.31625600E 18 1.78501300E 05 4.30200000E 04 7.30341100E-07
2.06227600E-17 1.95099000E 05 6.01277100E 27 2.53102200E 31
6.44970800E 12 1.57395100E-16 1.00000000E 00 4.92304500E 00
1.46199700E 02 1.25130300E 05 6.17260800E 07 1.82597000E 09
1.57758500E 11 4.29783200E-45 1.30429700E-05 2.21493700E 10
5.40597500E-20 1.08633400E 09 9.26735000E 04 8.14811300E-21
1.38865500E-03 1.00000000E 00 6.52103200E-10 4.43569700E-07
9.38238900E-03 8.18828300E-07 1.00000000E 00 3.53587700E-16
3.69405800E-12 7.57841300E-03 2.50874800E-14 2.59746400E-16
3.84990500E 15 1.42215700E 04 1.56400000E 03 7.24545700E-06
6.22555600E-15 3.72959100E 04 1.61092100E 23 4.64740600E 25
3.15320400E 10 7.74272100E-14 1.00000000E 00 9.92678100E-01
5.17212800E 00 4.02831500E 02 2.38653200E 04 1.57675500E 05
1.63128500E 06 1.59834200E-38 4.44312400E-05 7.81828100E 07
6.48061300E-17 5.87138900E 06 4.40074200E 03 2.74268300E-17
3.73537600E-03 1.00000000E 00 2.22011100E-08 3.21651400E-06
2.99851500E-03 5.70892000E-06 1.00000000E 00 7.88591700E-14
1.07699500E-10 1.75751400E-02 2.87781400E-12 5.12192100E-14
1.95238900E 13 2.10270900E 03 1.31000000E 02 4.03865700E-05
4.52717600E-13 1.07858000E 04 6.72882600E 19 2.33650000E 21
5.84836800E 08 8.15645600E-12 1.00000000E 00 3.00051900E-01
4.28810400E-01 5.63423700E 00 6.94609800E 01 1.50721600E 02
2.99861800E 02 1.34930900E-33 1.13674800E-04 1.09231100E 06
1.29559700E-14 1.13982800E 05 4.49515600E 02 1.20668900E-14
7.85576900E-03 1.00000000E 00 3.05324500E-07 1.42227000E-05
1.21491400E-03 2.58523900E-05 1.00000000E 00 5.32437800E-12
1.49106300E-09 3.37149900E-02 1.16110300E-10 3.16529400E-12
3.15926300E 11 4.71070500E 02 1.85200000E 01 1.53286100E-04
1.27101000E-11 4.10595300E 03 1.58254400E 17 1.06413800E 18
2.63109200E 07 3.06868300E-10 1.00000000E 00 1.18734700E-01
6.26114600E-02 2.09011000E-01 7.71857600E-01 7.10412900E-01
3.90628200E-01 9.15264100E-30 2.38960500E-04 3.84973500E 04
7.91374000E-13 5.21618700E 03 7.62276900E 01 1.36816400E-12
1.39822200E-02 1.00000000E 00 2.30229400E-06 4.49455100E-05
5.84712900E-04 8.65483700E-05 1.00000000E 00 1.55513100E-10
1.22478900E-08 5.66045400E-02 2.25432400E-09 8.65231900E-11

```

1.15575800E-10
 1.83516300E-10
 2.20435000E-06
 1.35688700E-02
 2.00244200E-03
 2.10570300E-11
 2.21531900E-02
 3.19231300E-04
 6.88858600E-08
 7.65932000E-08
 1.63446700E-09
 2.90805100E-05
 3.94529500E-03
 2.79277100E-05
 3.05872600E-10
 3.21942000E-02
 1.92058500E-04
 2.91498100E-07
 7.93582800E-07
 1.01108800E-08
 5.37249100E-04
 1.39937200E-03
 8.11406700E-07
 2.83966200E-09
 4.38679300E-02
 1.24846200E-04
 9.89923100E-07
 1.16178200E-07
 4.72730500E-08
 1.28801000E-04
 5.89338800E-04
 4.16356500E-08
 1.86826500E-09
 5.69517900E-02
 8.62130100E-05
 2.83423100E-06
 2.23000500E-06
 1.77570400E-07
 3.79494700E-03
 2.82240300E-04
 3.34629700E-09
 9.35100900E-08
 7.10269800E-02
 6.24845200E-05
 7.06926100E-06
 5.32161100E-05
 5.59675000E-07
 1.31776600E-03
 1.49753900E-04
 3.84822800E-10
 3.76196200E-07
 8.59531100E-02
 4.72354100E-05
 1.57536100E-05
 1.51710600E-05
 1.52723800E-06
 5.21609100E-02
 8.63344600E-05

1.41555600E-02
 1.89706400E-03
 5.61691800E-09
 1.53069000E-02
 1.06286400E-26
 4.39243800E-02
 1.00000000E-00
 2.32703600E-04
 8.63711800E-02
 5.27613000E-01
 1.00906200E-03
 6.07971600E-08
 1.83477600E-03
 3.41470500E-24
 5.76318900E-01
 1.00000000E-00
 5.30911400E-04
 1.22571400E-01
 2.31327900E-01
 5.96023300E-02
 4.43379500E-07
 3.17781900E-04
 4.19020900E-22
 1.05857200E-01
 1.00000000E-00
 1.06613500E-03
 1.64569600E-01
 1.15007600E-01
 3.81613500E-02
 2.38648400E-06
 7.29714500E-05
 2.45423900E-20
 2.52053200E-00
 1.00000000E-00
 1.93966800E-03
 2.11774700E-01
 6.32032100E-00
 2.60682800E-02
 1.01253000E-05
 2.08943200E-05
 8.03079900E-19
 7.36714700E-01
 1.00000000E-00
 3.25718100E-03
 2.63067000E-01
 3.76198000E-00
 1.87293700E-02
 3.54778000E-05
 7.13309500E-06
 1.65107700E-17
 2.53619700E-01
 1.00000000E-00
 5.12646500E-03
 3.18042200E-01
 2.38998600E-00
 1.40199400E-02
 1.06376100E-04
 2.80760000E-06

3.91100000E-00
 1.24940400E-15
 1.00000000E-00
 2.18161900E-02
 4.37130600E-04
 1.85222600E-01
 1.14334500E-05
 1.00000000E-00
 2.56881900E-08
 1.10400000E-00
 2.38533900E-13
 1.00000000E-00
 1.21213700E-03
 7.21415700E-04
 5.85025400E-00
 4.19449600E-05
 1.00000000E-00
 1.96115700E-07
 3.83400000E-01
 8.81250700E-11
 1.00000000E-00
 1.11551600E-04
 1.10118900E-03
 2.24661500E-00
 1.22717400E-04
 1.00000000E-00
 1.09984900E-06
 1.56599800E-01
 5.41212500E-10
 1.00000000E-00
 1.51082800E-05
 1.57869000E-03
 1.00309900E-00
 3.02378700E-04
 1.00000000E-00
 4.83533000E-06
 7.27099700E-02
 4.95858400E-09
 1.00000000E-00
 2.76826900E-06
 2.15667600E-03
 5.03824700E-01
 6.50546900E-04
 1.00000000E-00
 1.75078000E-05
 3.73900000E-02
 6.25870300E-08
 1.00000000E-00
 6.45227700E-07
 2.83190900E-03
 2.78321300E-01
 1.25734900E-03
 1.00000000E-00
 5.40765600E-05
 2.08900000E-02
 1.02289000E-08
 1.00000000E-00
 1.82704100E-07

4.45121400E-04
 2.27289900E-15
 5.67152600E-02
 1.01790800E-02
 2.61534500E-03
 5.99511500E-11
 1.12493700E-04
 2.47056900E-09
 1.30559800E-09
 1.06481900E-03
 1.49580900E-13
 3.10568500E-02
 3.26188000E-04
 2.87008000E-02
 1.31519500E-09
 2.37002500E-04
 2.48166700E-08
 1.26010700E-08
 2.19801600E-03
 2.28165000E-11
 1.88379500E-02
 1.90636900E-05
 4.53103900E-01
 1.71795300E-08
 4.38415200E-04
 1.75203700E-07
 8.60745700E-08
 4.06003300E-03
 6.65450900E-09
 1.23598900E-02
 1.76513000E-06
 9.48048900E-00
 1.50715300E-07
 7.35772700E-04
 9.37675500E-07
 4.48429300E-07
 6.87248200E-03
 3.22967800E-08
 8.62468700E-03
 2.34229200E-07
 2.47502100E-00
 9.66415400E-07
 1.13978300E-03
 4.01785100E-06
 1.87912600E-06
 1.08483900E-02
 2.35508000E-07
 6.32162300E-03
 4.13955800E-08
 7.72200200E-01
 4.82399300E-06
 1.66165900E-03
 1.43756500E-05
 6.59149200E-06
 1.61594300E-02
 2.38752300E-06
 4.82209000E-03
 9.22392400E-09

5.84686300E-11	2.32554500E-16	3.59749300E-03	2.78989900E-01
1.27535800E-06	9.99176500E-02	1.65901100E-01	1.9646100E-05
1.01342000E-01	1.00000000E 00	2.22888000E-03	2.30083700E-03
3.68588900E-05	7.64926800E-03	1.00000000E 00	4.42980200E-05
3.20048800E-05	3.75682400E-01	1.46619000E-04	1.99948800E-05
5.00127800E 04	1.60064800E 00	1.24999900E-02	2.29817800E-02
3.70657000E-06	1.08584100E 02	2.07125900E 07	3.17874000E 05.
2.30594100E 02	2.80634900E-04	1.00000000E 00	3.80083100E-03
5.32818600E-05	1.24190400E-06	6.06850000E-08	2.48527700E-09
1.12903000E-11	2.39950600E-15	4.45109600E-03	1.13521800E-01
3.73411600E-06	4.39101600E-02	1.05407500E-01	3.05892100E-03
1.17123400E-01	1.00000000E 00	3.67737300E-03	6.76654300E-05
2.96152100E-05	1.09202000E-02	1.00000000E 00	1.20626100E-04
6.02138700E-05	4.35266900E-01	3.56426600E-04	5.36322600E-05
1.86454800E 04	1.12271400E 00	7.92200100E-03	3.14476600E-02
8.15407500E-06	8.65446600E 01	5.01276800E 06	5.30677600E 04
1.11681300E 02	6.65079300E-04	1.00000000E 00	3.07867000E-03
3.47974700E-05	6.05226300E-07	2.30081400E-08	7.83902900E-10
2.65039800E-12	1.91082900E-14	5.38145000E-03	5.11100500E-02
9.70020200E-06	2.11724100E-02	7.05327300E-02	2.02793000E-04
1.33017100E-01	1.00000000E 00	5.72444800E-03	3.92802000E-03
2.46559900E-05	1.50085300E-02	1.00000000E 00	2.95756100E-04
1.06051400E-04	4.96284100E-01	7.89743100E-04	1.29838000E-04
7.70188600E 03	8.16794200E-01	5.26599900E-06	4.16016900E-02
1.65051300E-05	7.05893800E 01	1.40893300E 06	1.07191700E 04
5.83638100E 01	1.44046000E-03	1.00000000E 00	2.55151600E-03
2.38312300E-05	3.19916500E-07	9.74672000E-09	2.82178900E-10
7.30105300E-13	1.22279400E-13	6.38268500E-03	2.50273300E-02
2.28135300E-05	1.10294100E-02	4.93262100E-02	5.40447800E-04
1.49017500E-01	1.00000000E 00	8.47401000E-03	4.90517100E-03
2.04416400E-05	1.99918400E-02	1.00000000E 00	6.63443000E-04
1.76769500E-04	5.58761100E-01	1.61847700E-03	2.87799600E-04
3.47463700E 03	6.14210000E-01	3.64600000E-03	5.35426500E-02
3.11499600E-05	5.88051900E 01	4.50162300E 05	2.54650000E 03
3.25699900E 01	2.89144900E-03	1.00000000E 00	2.15615000E-03
1.69909300E-05	1.81146500E-07	4.53513400E-09	1.13572900E-10
2.31928600E-13	6.49944200E-13	7.44399000E-03	1.31722800E-02
4.91821800E-05	6.13585800E-03	3.58329300E-02	1.30320400E-03
1.64892000E-01	1.00000000E 00	1.20404600E-02	5.97735400E-03

\$NNNNUMBER
\$PUN *NATFIV SCARDS=S36+K36+D36 4=P1
\$LIST S36(LAST-8)
\$LIST K36(LAST)
\$LIST D36
\$SIGNOFF

TABLE E.3
CLAUS PLANT

```

$CREATE S28 SIZE=20P
$GET S28
$NUMBER
$$COMPILE
COMPUTER PROGRAMME 28 S
C*****
CLAUS FURNACE-CAT CONVERTER EQUILIBRIA WITH 36 SPECIES AND NUNITS-1 CONVERTERS *
CALCULATE ADIABATIC FLAME TEMPERATURE IN FURNACE AND IN CATALYTIC CONVERTERS *
COMPOUND NAMES ARE READ IN--H2S IS COMPOUND 10 *
C      0      1      2      3      4      5      6      7      8      9 *
C 0      NH3     NO      N2      O      O2      OH      H      H2     H2O *
C 1  H2S     H2S2    SH      SN      SO      SO2     SO3     S2O     S      S2 *
C 2  S3      S4      S5      S6      S7      S8      HCN     C2N2    CH4     C2H2 *
C 3  C2H4    C2H4O   CO      COS     CO2     CS       CS2     TOTAL *
CARDS IN FILE 'S' ARE:  HEATS OF FORMATION AT 298.15 K FOR 36 COMPOUNDS *
C                        ERR, EXPN2, EXPH2O, EXPH2S, EXPS2, EXPCO2 *
CARDS IN FILE 'A' ARE:  MCBRIDE COEFFICIENTS FOR 36 COMPOUNDS *
CARDS IN *SOURCE* ARE:  NFEEDS, NUNITS, NAFTI, NRRI, NEQMI, TERR *
C                        LIMIT, LOG, ISIMP, (STEP(I), I=1,4), EPS *
CARDS IN FILE 'P' ARE: *
CARD 1:  PCTAIR, PCTNH3, PCTH2O, PCTCH4, PCTCO2 *
CARD 2:  NUU, KREADP, KAO, TA, TE, TC, RR *
CARD 3:  P(3), P(9), P(10), P(19), P(34), (PRESSURES OF N2, H2O, H2S, S2, CO2) *
CARD 4:  FLAST, HSD, SOD, CSD, SLS *
CARDS 5, 6, 7 (FOR CATALYTIC CONVERTER #1): SIMILAR TO 2, 3, 4 (FOR FURNACE) *
COMPUTER PROGRAM COMPUTES UP TO 6 CAT CONVERTERS--ADD MORE SETS OF 3 CARDS EACH*
C*****
DOUBLE PRECISION CPD
REAL K, N, NO, NOD, NONOD, N2, N5
DIMENSION CPD(69), TEMPAP(7), ITES(4), BM(37), DM(37), PM(37),
1  A(36,2,7), B(36,2,7), X(4), STEP(4), K(36)
COMMON DHF(36), AM(37), CM(37), EM(37), P(41), C, H, N, O, S,
1  AC, AH, AN, AO, AS, CSD, HSD, NOD, SOD, SLS, EXPN2, EXPH2O,
2  EXPH2S, EXPS2, EXPCO2, RE, TERR, ADHF, OMRR, HTA, K, KWRT
C*****
COMPOUND NAMES, HEATS OF FORMATION, ERROR AND EXPONENTIALS AND ITER PARAMETERS
READ (5,1010) (CPD(NC), NC=1,69)
READ (5,1020) (DHF(NC), NC=1,36)
READ (5,1020) ERR, EXPN2, EXPH2O, EXPH2S, EXPS2, EXPCO2
READ (5,1030) (((A(NC,LH,J), J=1,7), LH=1,2), NC=1,36)
READ (5,1040) NFEEDS, NUNITS, NUWRT, NAFTI, NRRI, NEQMI, KWRT, TERR
READ (5,1045) LIMIT, LOG, IA, IB, (STEP(I), I=1,4), EPS
C*****
COMPUTER WRITES ERRORS AND EXPONENTS AND ITERATION PARAMETERS
WRITE (6,1050) ERR, EXPN2, EXPH2O, EXPH2S, EXPS2, EXPCO2,
1  NFEEDS, NUNITS, NAFTI, NRRI, NEQMI, TERR
C*****
CONVERT COEFFICIENTS OF EXPANSION FOR H TO GIVE IT THE SAME FORM AS THAT FOR CP
C      CPT/R = A1 + A2*T + A3 *T**2 + A4 *T**3 + A5 *T**4 + 0.0 *T**5
C      HT/R  = A6 + A1*T + A2/2*T**2 + A3/3*T**3 + A4/4*T**4 + A5/5*T**5
C      = B1 + B2*T + B3 *T**2 + B4 *T**3 + B5 *T**4 + B6 *T**5
C
DO 10 NC=1,36
DO 10 LH=1,2
B(NC,LH,1) = A(NC,LH,6)
B(NC,LH,2) = A(NC,LH,1)
B(NC,LH,3) = A(NC,LH,2)/2.0
B(NC,LH,4) = A(NC,LH,3)/3.0
B(NC,LH,5) = A(NC,LH,4)/4.0

```



```

      B(NC,LH,6) = A(NC,LH,5)/5.0
CONSTANT A6 IS SET TO ZERO SINCE CPT/R EXPANSION HAS NO T**5 TERM
CONSTANT B1 IS USED IN SUBROUTINE KP SINCE B1=A1 BEFORE A1 WAS SET EQUAL TO ZERO
10   A(NC,LH,6) = 0.0
      DO 130 NFDS=1,NFEEDS
COMPOSITION OF INITIAL MIXTURE IS FOUND--BASED ON 100 MOLES OF ACID GAS
      DO 20 NC=1,36
        AM(NC) = 0.0
        DM(NC) = 0.0
20   P (NC) = 0.0
      P(38)=0.0
      P(41)=0.0
C*****
COMPOSITION OF FEED TO FURNACE IS READ AT THE BEGINNING OF EACH FEED ITERATION
COMPUTER READS:      PCTAIR, PCTNH3, PCTH2O, PCTCH4, PCTCO2
      READ (5,1020) PCTAIR, AM( 1), AM( 9), AM(28), AM(34)
      WRITE(4,1020) PCTAIR, AM( 1), AM( 9), AM(28), AM(34)
C*****
      AM(10) = 100.0 - AM(1) - AM(9) - AM(28) - AM(34)
      AM( 5) = 0.005*AM(10)*PCTAIR + 0.75*AM(1) + 2.0*AM(28)
      AM( 3) = 3.76*AM(5)
      AM(37) = 100.0 + AM(3) + AM(5)
      PNH3 = AM( 1)/AM(37)
      PN2  = AM( 3)/AM(37)
      PO2  = AM( 5)/AM(37)
      PH2O = AM( 9)/AM(37)
      PH2S = AM(10)/AM(37)
      PCH4 = AM(28)/AM(37)
      PCO2 = AM(34)/AM(37)
      KUNITS=1
      KU=0
      IF (NAPTI .EQ. 1) KU=8
C*****
COMMENCE UNIT ITERATIONS BY READING GUESS OF APT, COMPOSITION AND ATOMIC RATIOS
      DO 130 NU=1,NUNITS
      IF (KUNITS .EQ. KU) STOP
CALCULATE VARIOUS RATIOS OF THE FOLLOWING ATOMS IN THE FEED STEAM: C, H, N, O, S
      AC = AM(26) + 2.0*AM(27) + AM(28) + 2.0*(AM(29)+AM(30)+AM(31)) +
1      AM(32) + AM(33) + AM(34) + AM(35) + AM(36)
      AH = 3.0*AM(1) + AM(6) + AM(7) + 2.0*(AM(8)+AM( 9)+AM(10)+AM(11))
1      + AM(12) + AM(26) + 2.0*AM(29) + 4.0*(AM(28)+AM(30)+AM(31))
      AN = AM(1) + AM(2) + 2.0*AM(3) + AM(13) + AM(26) + 2.0*AM(27)
      AO = AM( 2) + AM( 4) + 2.0*AM( 5) + AM( 6) + AM( 9) + AM(14) +
1 2.0*AM(15) + 3.0*AM(16) + AM(17) + AM(31) + AM(32) + AM(33) +
2 2.0*AM(34)
      AS = AM(10) + 2.0*AM(11) + AM(12) + AM(13) + AM(14) + AM(15) +
1      AM(16) + 2.0*AM(17) + AM(18) + 2.0*AM(19) + 3.0*AM(20) +
2 4.0*AM(21) + 5.0*AM(22) + 6.0*AM(23) + 7.0*AM(24) +
3 8.0*AM(25) + AM(33) + AM(35) + 2.0*AM(36)
      CSD = AC/AS
      HSD = AH/AS
      NOD = AN/AO
      SOD = AS/AO
      READ (5,1045) NUU, KREADP, KAO, IES, TA, TENEW, TC, RR
      READ (5,1060) P(3), P(9), P(10), P(19), P(34)
      IF (RR .GT. 1.0E-06) READ (5,1060) FLAST, HSD, SOD, CSD, SLS
C*****
      OMRR=1.0-RR

```

CALCULATE THE HEAT OF FORMATION OF THE REACTANTS OF STREAM A

ADHF = 0.0

DO 30 NC=1,36

30 ADHF = ADHF + AM(NC)*DHF(NC)

CALCULATE HEAT CONTENT OF STREAM A ENTERING FCE (NU=0) OR CAT CONVERTER (NU>0)

CALL CPH(AM, B, 298.15, HOA)

CALL CPH(AM, B, TA, HTA)

HTA=HTA-HOA

C*****
 COMMENCE ADIABATIC FLAME TEMP ITERATIONS FOR FURNACE OR CATALYTIC CONVERTERS *
 C*****
 CONVERGENCE CRITERIA IS INITIALLY SLACK--ONLY 9 OF THE 36 CPDS ARE CONSIDERED

ITERS(1)=0

ITERS(4)=0

35 ERROR=ERR

IF (KAO .EQ. 0) ERROR=10.0*ERR

DO 70 NF=1,NAFTI

ITERS(1)=ITERS(1)+1

TE=TENEW

CALL KP(TE, A, B, K)

CALCULATE EQUILIBRIUM COMPOSITIONS IN THE CATALYTIC CONVERTERS

DO 50 NRR=1,NERI

IF (IES .LE. 0) CALL EQM (NEQMI, KAO, ERR, JEQMI, X, SUMSQ, 1)

IF (IES .LT. 0) GO TO 45

IF (JEQMI .LT. NEQMI) GO TO 45

CALCULATE THE STARTING POINT FOR THE HILL-CLIMBING SUBROUTINE HOOKE

E=1.0E-06

X(1) = SQRT(P(3)) - E

X(2) = SQRT(P(9)) - E

X(3) = SQRT(P(10)) - E

X(4) = SQRT(P(19)) - E

WRITE (6,1090)

WRITE (6,1060) P(3), P(9), P(10), P(19), P(34)

WRITE (6,1060) X(1), X(2), X(3), X(4)

CALL HOOKE (Y, X, 4, LIMIT, STEP, LOG, EPS)

IF (Y .LT. 1.0E-02) GO TO 40

CALL HOOKE1(Y, X, 4, LIMIT, STEP, LOG, EPS)

40 CALL EQM (NEQMI, KAO, ERR, JEQMI, X, SUMSQ, 1)

45 ITERS(2)=NRR

ITERS(3)=JEQMI

ITERS(4)=ITERS(4)+ITERS(3)

CONVERGENCE MAY NOT HAVE BEEN OBTAINED FOR EQUILIBRIUM ITERS AT THIS TEMPERATURE
 CEASE FURTHER ITERATIONS BUT PRINT RESULT OBTAINED SO FAR

IF (ITERS(3) .GE. NEQMI) GO TO 55

CALCULATE MOLES OF C, H, N, O, S IN STREAM E OF FURNACE OR CATALYTIC CONVERTER

FC=0.0

DEN=4.0

KCONV=1

IF (C .LT. 1.0E-06) GO TO 46

FC = AC / OMRR / C

DEN=5.0

46 FH = AH / OMRR / H

FN = AN / OMRR / N

FO = AO / OMRR / O

PS = AS / (1.0-RR*SLS) / S

FAVG = (FC+FH+FN+FO+PS)/DEN

FAVGRR=FAVG*RR

CALCULATE MOLES OF EACH SPECIES IN STREAM E (EQUILIBRIUM) AND C (RECYCLE)

```

DO 47 NC=1,36
  EM(NC) = P(NC)*PAVG
47  CM(NC) = P(NC)*PAVGRR
CONDENSE ALL THE ELEMENTAL SULPHUR FROM STREAM C
DO 48 NC=18,25
48  CM(NC)=0.0
DO 49 NC=1,36
49  BM(NC) = AM(NC) + CM(NC)
CALCULATE RATIOS OF THE FOLLOWING ATOMS IN THE FEEDS TO EACH UNIT: C, H, N, O, S
  BC = BM(26) + 2.0*BM(27) + BM(28) + 2.0*(BM(29)+BM(30)+BM(31)) +
1    BM(32) + BM(33) + BM(34) + BM(35) + BM(36)
  BH = 3.0*BM(1) + BM(6) + BM(7) + 2.0*(BM(8)+BM(9)+BM(10)+BM(11))
1    + BM(12) + BM(26) + 2.0*BM(29) + 4.0*(BM(28)+BM(30)+BM(31))
  BN = BM(1) + BM(2) + 2.0*BM(3) + BM(13) + BM(26) + 2.0*BM(27)
  BO = BM(2) + BM(4) + 2.0*BM(5) + BM(6) + BM(9) + BM(14) +
1    2.0*BM(15) + 3.0*BM(16) + BM(17) + BM(31) + BM(32) + BM(33) +
2    2.0*BM(34)
  BS = BM(10) + 2.0*BM(11) + BM(12) + BM(13) + BM(14) + BM(15) +
1    BM(16) + 2.0*BM(17) + BM(18) + 2.0*BM(19) + 3.0*BM(20) +
2    4.0*BM(21) + 5.0*BM(22) + 6.0*BM(23) + 7.0*BM(24) +
3    8.0*BM(25) + BM(33) + BM(35) + 2.0*BM(36)
CALCULATE NEW GUESS OF RATIOS OF ATOMS
  BCSD=BC/BS
  BHSD=BH/BS
  BNOD=BN/BO
  BSOD=BS/BO
  FCSD=1.0
  IF (BCSD .GT. 1.0E-08) FCSD=BCSD/CSD
  IF (ABS(FCSD -1.0) .GT. ERR) GO TO 495
  IF (ABS(BHSD/HSD-1.0) .GT. ERR) GO TO 495
  IF (ABS(BNOD/NOD-1.0) .GT. ERR) GO TO 495
  IF (ABS(BSOD/SOD-1.0) .GT. ERR) GO TO 495
  GO TO 60
CALCULATE NEW DESIRED RATIOS IN STREAM B (ENTERING THE FURNACE)
495  CSD=BCSD
    HSD=BHSD
    NOD=BNOD
    SOD=BSOD
50  *****
CONVERGENCE HAS NOT BEEN OBTAINED FOR RECYCLE ITERATIONS AT THIS TEMPERATURE
CEASE FURTHER ITERATIONS IN ALL UNITS BUT PRINT RESULT OBTAINED SO FAR
55  KUNITS=0
CONVERGPD AT THE GIVEN RECYCLE RATIO AND TEMPERATURE
COMPUTE NEW GUESS OF THE ADIABATIC FLAME TEMPERATURE (AFT)
60  CALL AFT (TC, TE, A, B, NAFTI, TENEW, KCONV)
CURRENT VALUE OF TEMPERATURE IS WRITTEN
  IF (KCONV .EQ. 0) KUNITS=0
  IF (KUNITS .EQ. 0) GO TO 80
  IF (ABS(TE-TENEW) .LE. TERR) GO TO 65
70  CONTINUE
CHECK TO SEE IF ITERATING ON 9 COMPOUNDS (KAO=0) OR 36 COMPOUNDS (KAO=1)
65  IF (KAO .EQ. 1) GO TO 80
    KAO=1
    GO TO 35
*****
CONVERGENCE OBTAINED FOR APT ITERATIONS OR LAST APT ITERATION HAS BEEN REACHED *
CALCULATE TOTAL MOLES IN EACH STREAM
*****

```

```

80 DO 85 NC=18,25
85 DM(NC) = EM(NC)
   AM(37) = 0.0
   BM(37) = 0.0
   CM(37) = 0.0
   DM(37) = 0.0
   EM(37) = 0.0
   FM(37) = 0.0
   DO 90 NC=1,36
   FM(NC) = EM(NC) - DM(NC) - CM(NC)
   AM(37) = AM(37) + AM(NC)
   BM(37) = BM(37) + BM(NC)
   CM(37) = CM(37) + CM(NC)
   DM(37) = DM(37) + DM(NC)
   EM(37) = EM(37) + EM(NC)
90 FM(37) = FM(37) + FM(NC)
COMPUTE PERCENT RECOVERY, BASED ON EQUILIBRIUM AND ACID GAS STREAMS RESPECTIVELY
P(39) = P(38) / (1.0 - RR*(1.0-P(38)))
P(40) = P(39) * (1.0 - P(41))
P(41) = P(40) + P(41)
C*****
WRITE (4,1045) NU, KREADF, KAO, IES, TA, TE, TC, RR
WRITE (4,1060) P(3), P(9), P(10), P(19), P(34), NU
IF (RR .GT. 1.0E-06) WRITE (4,1060) NOD, HSD, SOD, CSD, SLS, NU
COMPUTER WRITES HEADINGS FOR EITHER FURNACE OR CATALYTIC CONVERTER RESULTS
IF (NU .LT. NUWRT) GO TO 115
IF (NU .EQ. 1) WRITE (6,1090) RR, PCTAIR, AM(1), AM(9), AM(28),
1 AM(34), PH2S, PNH3, PO2, PH2O, PN2, PCH4, PCO2
NUM1=NU-1
IF (NU .GT. 1) WRITE (6,1090) NUM1
WRITE (6,1100) TA, TE
DO 100 NC=1,37
100 WRITE (6,1110) NC, CPD(NC), P(NC), AM(NC), CM(NC), BM(NC), EM(NC),
1 DM(NC), FM(NC)
DO 110 NC=38,41
110 WRITE (6,1120) CPD(NC),CPD(NC+4),CPD(NC+8),CPD(NC+12),CPD(NC+16),
1 P(NC), CPD(NC+20), CPD(NC+24), CPD(NC+28), ITES(NC-37)
CHECK IF SULPHUR HAS CONDENSED--IF IT HAS, WRITE S PRESSURE AND S VAPOUR PRESS
C*****
115 PS=0.0
DO 120 NC=18,25
120 PS = PS + P(NC)
VP = 3.77978 + 1.91809E-06*TE*TE - 796.138/TE - 1883640.0/TE/TE
VP = EXP(VP)
IF (PS .GT. VP) WRITE (6,1130) PS, TE, VP
CHANGE NOTATION: STREAM F BECOMES STREAM A OF THE NEXT UNIT
DO 125 NC=1,36
125 AM(NC)=FM(NC)
130 CONTINUE
STOP
1010 FORMAT (10A8)
1020 FORMAT (8F10.4)
1030 FORMAT (20X, 3E20.8/ 4E20.8)
1040 FORMAT (7I5, F10.2)
1045 FORMAT (4I5, 5F10.2)
1050 FORMAT ('0 ERR EXPN2 EXPH2O EXPH2S EXPS2 EXP
1CO2'//, F10.3, 5F10.2//, '0 NFEDS NUNITS NAFTI NRRI
2 NEQMI TERR'//, I8, 3I10, I11, F10.2)

```

```

1060 FORMAT (1P5E15.7, I5)
1080 FORMAT ('1 EQUILIBRIUM PARTIAL PRESSURES IN ATMOSPHERES OF 36 COMP
1OUNDS PRODUCED FROM HYDROGEN SULPHIDE COMBUSTION WITH', 2PF5.1,
2 ' % RECYCLE'/// 1H , 37X, 'STOICHIOMETRIC AIR IS', 0PF6.1, ' %'/
3 14X, 'THE ACID GAS FEED CONTAINS', F5.1, ' % NH3', F5.1,
4 ' % H2O', F5.1, ' % CH4 AND', F5.1, ' % CO2'/// 1H , 34X, 'COM
5POSITION OF THE INITIAL MIXTURE'/ 1H , 34X, 'H2S', 2PF8.3, ' %',
6 8X, 'NH3', F8.3, ' %'/ 1H , 34X, 'O2', F8.3, ' %',
7 8X, 'H2O', F8.3, ' %'/ 1H , 34X, 'N2', F8.3, ' %',
8 8X, 'CH4', F8.3, ' %'/ 1H , 44X, 'CO2', F8.3, ' %'///)
1090 FORMAT ('1 EQUILIBRIUM PARTIAL PRESSURES IN ATMOSPHERES OF 36 COMP
1OUNDS PRODUCED IN CATALYTIC CONVERTER', I2////)
1100 FORMAT (' FEED TO THIS UNIT IS AT', F7.1, ' KELVIN'///,
1 ' COMPOUND', 8X, 'P(', F7.1, ') MOLES IN A MOLES I
2N C MOLES IN B MOLES IN E MOLES IN D MOLES IN F')
1110 FORMAT (1H , I2, 1X, A8, (1P7E15.4))
1120 FORMAT (1H , 4X, 5A8, 2PF8.4, ' %', 10X, 3A8, I5)
1130 FORMAT ('/' *****SULPHUR HAS CONDENSED*****SULPHUR PARTIAL PRESSURE
11S ', F8.4, ' VAPOUR PRESSURE OF S AT', F7.1, ' KELVIN IS', F9.4)
END
SUBROUTINE EQM (NEQMI, KAO, ERR, JEQMI, X, SUMSQ, I)
REAL K, N, NO, NOD, NONOD, N2, N5
DIMENSION A(36,2,7), B(36,2,7), K(36), X(4), SUMSQ(5)
COMMON DHP(36), AM(37), CM(37), EM(37), P(41), C, H, N, O, S,
1 AC, AH, AN, AO, AS, CSD, HSD, NOD, SOD, SLS, EXPN2, EXPH2O,
2 EXPH2S, EXPS2, EXPCO2, RR, TERR, ADHF, OMRR, HTA, K, KWRT
CSCSD=1.0
IF (NEQMI .NE. 1) GO TO 10
E=1.0E-06
P( 3) = (X(1)+E)**2
P( 9) = (X(2)+E)**2
P(10) = (X(3)+E)**2
P(19) = (X(4)+E)**2
10 DO 60 NI=1,NEQMI
N2 = P(3)
N5=N2**0.5
S2=P(19)
S5=P(19)**0.5
O2 = (K(5) * P(9) * S5 / P(10))**2
O5=O2**0.5
H2 = K(8) * P(9) / O5
H5=H2**0.5
P( 1) = K( 1) * N5 * H2**1.5
P( 2) = K( 2) * N5 * O5
P( 4) = K( 4) * O5
P( 5) = O2
P( 6) = K( 6) * O5 * H5
P( 7) = K( 7) * H5
P( 8) = H2
P(11) = K(11) * H2 * S2
P(12) = K(12) * S5 * H5
P(13) = K(13) * S5 * N5
P(14) = K(14) * S5 * O5
P(15) = K(15) * S5 * O2
P(16) = K(16) * S5 * O2**1.5
P(17) = K(17) * S2 * O5
P(18) = K(18) * S5
P(20) = K(20) * S2**1.5

```

```

P(21) = K(21) * S2**2
P(22) = K(22) * S2**2.5
P(23) = K(23) * S2**3
P(24) = K(24) * S2**3.5
P(25) = K(25) * S2**4
P(26) = K(26) / O2 * P(34) * N5 * H5
P(27) = K(27) / H2 * P(26)**2
P(36) = K(36) / P(9)**2 * P(34) * P(10)**2
P(29) = K(29) / S2**2 * P(36)**2 * H2
P(28) = K(28) * P(29)**0.5 * H2**1.5
P(30) = K(30) * P(29) * H2
P(31) = K(31) * P(30) * O5
P(32) = K(32) / O5 * P(34)
P(33) = K(33) / P(9) * P(34) * P(10)
P(35) = K(35) / P(9) * P(33) * H2

```

COMPUTE TOTAL MOLES CARBON C, HYDROGEN H, NITROGEN N, OXYGEN O, AND SULPHUR S

```

C = P(26) + 2.0*P(27) + P(28) + 2.0*(P(29)+P(30)+P(31)) + P(32) +
1 P(33) + P(34) + P(35) + P(36)
H = 3.0*P(1) + P(6) + P(7) + 2.0*(P(8)+P(9)+P(10)+P(11)) + P(12) +
1 P(26) + 2.0*P(29) + 4.0*(P(28)+P(30)+P(31))
N = P(1) + P(2) + 2.0*P(3) + P(13) + P(26) + 2.0*P(27)
O = P(2) + P(4) + 2.0*P(5) + P(6) + P(9) + P(14) + 2.0*P(15) +
1 3.0*P(16) + P(17) + P(31) + P(32) + P(33) + 2.0*P(34)
SLOST = P(10) + 2.0*P(11) + P(12) + P(13) + P(14) + P(15) +
1 P(16) + 2.0*P(17) + P(33) + P(35) + 2.0*P(36)
SRECOV = P(18) + 2.0*P(19) + 3.0*P(20) + 4.0*P(21) +
1 5.0*P(22) + 6.0*P(23) + 7.0*P(24) + 8.0*P(25)

```

COMPUTE TOTAL PRESSURE

```

P(37) = 0.0
DO 30 NC=1,36
30 P(37) = P(37) + P(NC)
PTPTD=P(37)
S = SLOST + SRECOV
SLS=SLOST/S
IF (CSD .GT. 1.0E-08) CSCSD=C/S/CSD
HSHSD=H/S/HSO
NONOD= N/O/NOD
SOSOD=S/O/SOD
JEQMI=NI
SUMSQ(I) = (PTPTD-1.0)**2 + (NONOD-1.0)**2 + (HSHSD-1.0)**2 +
1 (SOSOD-1.0)**2 + (CSCSD-1.0)**2
IF (NEQMI .EQ. 1) RETURN
IF (NI.EQ.NEQMI) WRITE(6,1) SUMSQ(I),PTPTD,NONOD,HSHSD,SOSOD,CSCSD
1 FORMAT (1P6E18.8)
IF (ABS(HSHSD-1.0) .GT. ERR) GO TO 50
IF (ABS(SOSOD-1.0) .GT. ERR) GO TO 50
IF (ABS(NONOD-1.0) .GT. ERR) GO TO 50
IF (ABS(PTPTD-1.0) .GT. ERR) GO TO 50
IF (ABS(CSCSD-1.0) .GT. ERR) GO TO 50

```

CALCULATE YIELD BASED ON STREAM E (COMPOSITION OF PRODUCTS AT EQUILIBRIUM)

```

P(38) = SRECOV/S
RETURN

```

COMPUTE NEW N2, H2O, H2S, S2, CO2

```

50 P(3) = P(3) * (PTPTD*NONOD)**EXPXN2
P(9) = P(9) * PTPTD **EXPXPH2O
P(10) = P(10) * (PTPTD*HSHSD)**EXPXPH2S
P(19) = P(19) * (PTPTD*SOSOD)**EXPXS2
60 P(34) = P(34) * (PTPTD*CSCSD)**EXPCO2

```

RETURN

END

SUBROUTINE KP(T, A, B, EQMK)

CALCULATE EQUILIBRIUM CONSTANTS, KP, FOR 36 SPECIES AT ANY TEMPERATURE, T KELVIN

C F(NC) IS FREE ENERGY OF FORMATION OF COMPOUND NC

C R(NC) IS FREE ENERGY OF THE REACTION THAT FORMS COMPOUND NC

CORRESPONDING EQUILIBRIUM CONSTANT AT TEMPERATURE, T IS GIVEN BY EQMK(NC)

REAL K, N, NO, NOD, NONOD, N2, N5

DIMENSION A(36,2,7), B(36,2,7), F(36), R(36), EQMK(36), H298(36), K(36)

COMMON DHP(36), AM(37), CM(37), EM(37), P(41), C, H, N, O, S,

1 AC, AH, AN, AO, AS, CSD, HSD, NOD, SOD, SLS, EXPN2, EXPH2O,

2 EXPH2S, EXPS2, EXPCO2, RR, TERR, ADHP, OMRR, HTA, K, KWRT

DATA KSKIP/0/

ALNT=ALOG(T)

TLNT=T*ALNT

LH=1

IF (T.GT. 1000.0) LH=2

CALCULATE FREE ENERGIES OF FORMATION DIVIDED BY R USING MCBRIDE'S COEFFICIENTS

IF (KSKIP.EQ. 1) GO TO 30

KSKIP=1

CALCULATE ENTHALPY AT 298.15 KELVIN FOR 36 COMPOUNDS

DO 20 NC=1,36

T0=298.15

T2=T0**2/2.0

T3=T0**3/3.0

T4=T0**4/4.0

T5=T0**5/5.0

CONSTANT B1 HAS BEEN SET EQUAL TO A6 IN THE MAIN PROGRAMME

20 H298(NC) = (A(NC,1,1)*T0 + A(NC,1,2)*T2 + A(NC,1,3)*T3 +
1 A(NC,1,4)*T4 + A(NC,1,5)*T5 + B(NC,1,1)) * 1.98726

30 T2=T/2.0

T3=T**2/6.0

T4=T**3/12.0

T5=T**4/20.0

RT=1.98726*T

DO 40 NC=1,36

40 F(NC) = A(NC,LH,1)*(1.0-ALNT) - A(NC,LH,2)*T2 - A(NC,LH,3)*T3 -
1A(NC,LH,4)*T4 - A(NC,LH,5)*T5 + B(NC,LH,1)/T - A(NC,LH,7) +
2 (1000.0*DHP(NC) - H298(NC)) / RT

COMPUTE FREE ENERGIES OF REACTION

FN2 = F(3)

FO2 = F(5)

PH2 = F(8)

PS2 = F(19)

FN = 0.5*FN2

FO = 0.5*FO2

PH = 0.5*PH2

PS = 0.5*PS2

R(1) = F(1) - FN - PH2*1.5

R(2) = F(2) - FN - FO

R(3) = 0.0

R(4) = F(4) - FO

R(5) = F(10) + FO - F(9) - PS

R(6) = F(6) - FO - PH

R(7) = F(7) - PH

R(8) = F(8) + FO - F(9)

R(9) = 0.0

R(10) = 0.0

```

R(11) = F(11) - PH2 - FS2
R(12) = F(12) - PS - PH
R(13) = F(13) - PS - PN
R(14) = F(14) - PS - FO
R(15) = F(15) - PS - FO2
R(16) = F(16) - PS - FO2*1.5
R(17) = F(17) - FS2 - FO
R(18) = F(18) - PS
R(19) = 0.0
R(20) = F(20) - 1.5*FS2
R(21) = F(21) - 2.0*FS2
R(22) = F(22) - 2.5*FS2
R(23) = F(23) - 3.0*FS2
R(24) = F(24) - 3.5*FS2
R(25) = F(25) - 4.0*FS2
R(26) = F(26) + FO2 - F(34) - PN - FH
R(27) = F(27) + PH2 - 2.0*F(26)
R(36) = F(36) + 2.0*F(9) - F(34) - 2.0*F(10)
R(29) = F(29) + 2.0*FS2 - 2.0*F(36) - PH2
R(28) = F(28) - 0.5*F(29) - 1.5*PH2
R(30) = F(30) - F(29) - PH2
R(31) = F(31) - F(30) - FO
R(32) = F(32) - F(34) + FO
R(33) = F(33) + F(9) - F(34) - F(10)
R(34) = 0.0
R(35) = F(35) + F(9) - F(33) - PH2
COMPUTE EQUILIBRIUM CONSTANTS FROM FREE ENERGY OF REACTION
DO 80 NC=1,36
80  EQMK(NC) = EXP(-R(NC))
RETURN
END
SUBROUTINE AFT (TC, TE, A, B, NAFTI, TENEW, KCONV)
CALCULATE ADIABATIC FLAME TEMPERATURE OF CLAUS FURNACE OR CATALYTIC CONVERTER
REAL K, N, NO, NOD, NONOD, N2, N5
DIMENSION A(36,2,7), B(36,2,7), K(36)
COMMON DHF(36), AM(37), CM(37), FM(37), P(41), C, H, N, O, S,
1  AC, AH, AN, AO, AS, CSD, HSD, NOD, SOD, SLS, EXPN2, EXPH2O,
2  EXPH2S, EXPS2, EXPCO2, RR, TERR, ADHF, OMER, HTA, K, KWRT
C*****
COMPOSITIONS OF STREAMS C AND E HAVE NOW BEEN CALCULATED FOR THIS TEMPERATURE *
CAN NOW FIND FLAME TEMPERATURE RESULTING FROM RECYCLE RATIO AND INITIAL COMP *
C*****
CALCULATE HEAT OF REACTION = ENTHALPY OF PRODUCTS - ENTHALPY OF REACTANTS
DHR=-ADHF
DO 50 NC=1,36
50  DHR = DHR + DHF(NC)*(EM(NC)-CM(NC))
DHR=DHR*1000.0
CALL CPH(CM, B, 298.15, HOC)
CALL CPH(EM, B, 298.15, HOE)
CALL CPH(CM, B, TC, HTC)
HTC = HTC - HOC
COMPUTE IMPROVED GUESS OF FLAME TEMPERATURE BY ITERATING AT CONSTANT COMPOSITION
TENEW=TE
DO 60 NDT=1,100
CALCULATE HEAT CONTENT AND HEAT CAPACITY FOR RECYCLE STREAM E
CALL CPH (EM, B, TENEW, HTE)
CALL CPH (EM, A, TENEW, CPTC)
HTE = HTE - HOE

```



```

CALCULATE TEMPERATURE DIFFERENCE FROM HTA + HTC - DHR = HTE + CPT*DT
DT = (HTA + HTC - DHR - HTE) / CPT
IF (NAFTI .EQ. 1) GO TO 65
TENEW=TENEW+DT
IF (ABS(DT) .LT. TERR) RETURN
60 CONTINUE
CONSTANT COMPOSITION ADIABATIC FLAME TEMPERATURE ITERATIONS HAVE NOT CONVERGED
65 KCONV=0
RETURN
END
SUBROUTINE CPH (XMOLES, A, T, HTX)
COMPUTES EITHER CP OR HT DEPENDING ON ARRAY A
C CPT/R = A1 + A2*T + A3 *T**2 + A4 *T**3 + A5 *T**4 + 0.0 *T**5
C HT/R = A6 + A1*T + A2/2*T**2 + A3/3*T**3 + A4/4*T**4 + A5/5*T**5
C = B1 + B2*T + B3 *T**2 + B4 *T**3 + B5 *T**4 + B6 *T**5
REAL K, N, NO, NOD, NONOD, N2, N5
DIMENSION A(36,2,7), XMOLES(36), HT(36), K(36)
COMMON DHF(36), AM(37), CM(37), EM(37), P(41), C, H, N, O, S,
1 AC, AH, AN, AO, AS, CSD, HSD, NOD, SOD, SLS, EXPN2, EXPH2O,
2 EXPH2S, EXPS2, EXPCO2, RR, TERR, ADHF, OMRR, HTA, K, KWRT
LH=1
IF (T .GT. 1000.0) LH=2
DO 10 NC=1,36
CALCULATE THE HEAT CONTENT OF EACH OF THE 36 SPECIES AT TEMPERATURE T
HT(NC) = A(NC,LH,1)
DO 10 J=2,6
10 HT(NC) = HT(NC) + A(NC,LH,J)*T**(J-1)
CALCULATE HEAT CONTENT OF STREAM X
HTX = 0.0
DO 20 NC=1,36
20 HTX = HTX + XMOLES(NC)*HT(NC)
HTX = HTX*1.98726
RETURN
END
SUBROUTINE RSP (Y, X, N, JRSP)
DIMENSION X(4), Y(N)
JRSP=JRSP+1
CALL EQN (1, 1, 0.001, JEQMI, X, Y, N)
RETURN
END
SUBROUTINE HOOKE (YO, X, N, NRSPI, DELTA, KWRT, EPS)
COMPUTES MINIMUM OF FCN USING ORDINARY HOOKE AND JEEVES METHOD (HJ)
CALLS SUBROUTINE RSP(Y, X, N, NRSP)
C Y VALUE OF FCN AFTER NTRL ITERATIONS
C X INITIAL STARTING POINT OF THE FCN TO BE MINIMIZED
C N NUMBER OF VARIABLES IN FCN TO BE MINIMIZED
C NRSPI MAXIMUM NUMBER OF FUNCTIONAL EVALUATIONS
C DELTA(I) INITIAL STEP SIZE IN THE I TH DIRECTION
CONSTANT KWRT SET AS FOLLOWS FOR OUTPUTS
C 1 AT BEGINNING AND END ONLY
C 0 AT END OF EACH PATTERN MOVE
C -1 AT END OF EACH TRIAL
C EPS MIN VALUE ANY DELTA(I) CAN HAVE--OTHERWISE PROGRAMME STOPS
C CARRIES OUT LOCAL SEARCHES EVEN IF PATTERN MOVE IS A FAILURE
DIMENSION X(N), DELTA(N), XINIT(5), Y(5), B(5,200), RHO(5), YO(1)
DO 10 I=1,N
10 RHO(I) = 0.5
WRITE (6,1000) (X(I), I=1,N)

```

```

DO 20 I=1,N
20  XINIT(I) = X(I)
    NT=1
    K=0
COMPUTE INITIAL RESPONSE
    NRSP=0
    CALL RSP(YO, X, 1, NRSP)
    NTRLS=NRSPI/N
    DO 200 NTRL=1,NTRLS
        IF (KWRT .LT. 1) WRITE (6,1010) NT, NRSP, YO(1), (X(I), I=1,N)
COMMENCE LOCAL EXPLORATION IN THE X1 DIRECTION
    X(1) = X(1) + DELTA(1)
    CALL RSP(Y, X, 1, NRSP)
    IF (Y(1) .LT. YO(1)) GO TO 30
    X(1) = X(1) - 2.0*DELTA(1)
    CALL RSP(Y, X, 1, NRSP)
    IF (Y(1) .LT. YO(1)) GO TO 30
    X(1) = X(1) + DELTA(1)
    Y(1) = YO(1)
COMMENCE LOCAL EXPLORATION IN THE X(I) DIRECTION
30  IF (KWRT .LT. 0) WRITE (6,1020) NRSP, Y(1), (X(I), I=1,N)
    IF (NRSP .GE. NRSPI) GO TO 210
    DO 50 I=2,N
        X(I) = X(I) + DELTA(I)
        CALL RSP(Y, X, I, NRSP)
        IF (Y(I) .LT. Y(I-1)) GO TO 40
        X(I) = X(I) - 2.0*DELTA(I)
        CALL RSP(Y, X, I, NRSP)
        IF (Y(I) .LT. Y(I-1)) GO TO 40
        X(I) = X(I) + DELTA(I)
        Y(I) = Y(I-1)
40  IF (KWRT .LT. 0) WRITE (6,1020) NRSP, Y(I), (X(J), J=1,N)
    IF (NRSP .GE. NRSPI) GO TO 210
50  CONTINUE
COMPUTE PATTERN MOVE
    NT=NT+1
    IF (K .GT. 0) GO TO 160
60  DO 70 I=1,N
70  B(I,NT) = X(I)
    IF (NT .GT. 2) GO TO 90
    DO 80 I=1,N
80  B(I,1) = XINIT(I)
90  DO 100 I = 1, N
100 X(I) = 2.0*B(I,NT) - B(I,NT-1)
CHECK TO SEE IF PATTERN MOVE HAS BEEN MADE
    DO 110 I=1,N
    IF (ABS(X(I) - B(I,NT)) .GT. 1.0E-03) GO TO 130
110 CONTINUE
CUT STEP SIZE IN HALF
    DO 120 I=1,N
    DELTA(I) = DELTA(I)*RHO(I)
    IF (DELTA(I) .LT. EPS) RETURN
120 CONTINUE
    WRITE (6,1030) (DELTA(I), I=1,N)
    GO TO 200
130 CALL RSP(YO, X, 1, NRSP)
    IF (YO(1) .LT. Y(N)) GO TO 150
    K=1

```

```

      YNOLD = Y(N)
      GO TO 200
150   K=-1
      GO TO 200
160   IF (Y(N) .LT. YNOLD) GO TO 60
      DO 180 I=1,N
180   B(I,NT) = B(I,NT-1)
      DO 190 I=1,N
190   X(I) = B(I,NT)
      YO(1) = YNOLD
      K=-1
200   CONTINUE
210   WRITE (6,1010) NT, NRSP, Y(1), (X(I), I=1,N)
      RETURN
1000  FORMAT (1H0, ' THE COORDINATES OF THE STARTING POINT ARE',
1     5F12.6/ (43X, 5F12.6))
1010  FORMAT (1H , 2I5, 1P6E16.7/, (27X, 5E16.7))
1020  FORMAT (1H , I10, 1P6E16.7/, (27X, 5E16.7))
1030  FORMAT (1P5E16.7)
      END
      SUBROUTINE HOOKE1 (YO, X, N, NRSP, DELTA, KWRT, EPS)
      COMPUTES MINIMUM OF FCN USING MODIFIED PERTURBATION METHOD
      DIMENSION X(N), XO(5), Y(5), YO(N), DELTA(N)
      NRSP=-1
      DO 40 NTRLS=1,4
      COMPUTE INITIAL FCN VALUE AND STEP SIZES AT START OF EACH SET OF N PERTURBATIONS
      DO 10 I=1,N
      XO(I)=X(I)
10    DELTA(I) = 0.005*X(I)
      DELTA(3)=0.1*X(3)
      CALL RSP(YO, XO, 1, NRSP)
      WRITE (6,1010) NRSP, NRSP, YO(1), (XO(J), J=1,N)
      DO 30 I=1,N
      DO 25 NXI=1,100
      X(I) = X(I) + DELTA(I)
      CALL RSP(Y, X, 1, NRSP)
      IF (KWRT .LT. 0) WRITE (6,1010) NXI, NRSP, Y(1), (X(J), J=1,N)
      IF (Y(1) .GE. YO(1)) GO TO 20
      YO(1)=Y(1)
      XO(I)=X(I)
      NXIO=NXI
      DELTA(I) = 2.0*DELTA(I)
      GO TO 25
20    X(I) = X(I) - DELTA(I)
      DELTA(I) = -0.5*DELTA(I)
      IF (ABS(DELTA(I)) .LT. EPS) GO TO 26
25    CONTINUE
26    Y(1)=YO(1)
      X(I)=XO(I)
30    IF (KWRT .LE. 0) WRITE (6,1010) NXIO, NRSP, Y(1), (X(J), J=1,N)
40    WRITE (6,1010) NXIO, NRSP, Y(1), (X(J), J=1,N)
      RETURN
1010  FORMAT (1H , 2I5, 1P6E16.7)
      END

```

\$\$\$DATA
 NH3 NO N2 O O2 OH H H2 H2O H2S
 H2S2 SH SN SO SO2 SO3 S2O S S2 S3
 S4 S5 S6 S7 S8 HCN C2N2 CH4 C2H2 C2H4

C2H4O	CO	COS	CO2	CS	CS2	TOTAL	YIELD	BAYIELD	BAYIELD	BA
YIELD OFSED ON ESED ON FSED ON F CLAUS PQUILIBRIED TO TEED TO CLANT INCUM COMPO						HIS UNITLAUS PLALUDING TSITION ONLY NT HIS UNITTOTAL PLLAST RECLAST EQ				
TOTAL EQAME	ITRYCLE	ITENILIBRIU	ITENILIBRIU	ITENILIBRIU	ITENILIBRIU	RATIONS	RATION	M ITER	M ITES	
-10.970	21.580	0.000	59.559	0.000	9.432	52.100	0.000			
-57.798	-4.880	3.830	34.600	63.000	1.640	-70.947	-94.590			
-13.500	66.680	30.840	33.810	34.840	26.140	24.360	27.170			
24.200	32.300	73.870	-17.895	54.190	12.540	-12.580	-26.417			
-33.080	-94.054	55.000	27.980							
0.001	-0.5	-0.5	-0.5	-0.5	-0.5	-0.5				

\$UNNUMBER

\$TRUNCATE S28

\$CRPATE A SIZE=5P

\$GET A

\$NUMBER

1 N1H3(G)	3.7716198E 00	-4.8621368E-04	9.8742257E-06
-9.5678898E-09	3.1313236E-12	-6.7280933E 03	1.4654049E 00
1 N1H3(G)	2.1493986E 00	6.4928521E-03	-2.2695193E-06
3.7393857E-10	-2.3605554E-14	-6.4019616E 03	9.2389071E 00
2 N1O1(G)	4.1469476E 00	-4.1197237E-03	9.6922467E-06
-7.8633639E-09	2.2309512E-12	9.7447894E 03	2.5694290E 00
2 N1O1(G)	3.1529360E 00	1.4059955E-03	-5.7078462E-07
1.0628209E-10	-7.3720783E-15	9.8522048E 03	6.9446465E 00
3 N2(G)	3.6916148E 00	-1.3332552E-03	2.6503100E-06
-9.7688341E-10	-9.9772234E-14	-1.0628336E 03	2.2874980E 00
3 N2(G)	2.8545761E 00	1.5976316E-03	-6.2566254E-07
1.1315849E-10	-7.6897070E-15	-8.9017445E 02	6.3902879E 00
4 O1(G)	3.0218894E 00	-2.1737249E-03	3.7542203E-06
-2.9947200E-09	9.0777547E-13	2.9137190E 04	2.6460076E 00
4 O1(G)	2.5372567E 00	-1.8422190E-05	-8.8017921E-09
5.9643621E-12	-5.5743608E-16	2.9230007E 04	4.9467942E 00
5 O2(G)	3.7189946E 00	-2.5167288E-03	8.5837353E-06
-8.2998716E-09	2.7082180E-12	-1.0576706E 03	3.9080704E 00
5 O2(G)	3.5975129E 00	7.8145603E-04	-2.2386670E-07
4.2490159E-11	-3.3460204E-15	-1.1927918E 03	3.7492659E 00
6 O1H1(G)	3.8234708E 00	-1.1187229E-03	1.2466819E-06
-2.1035896E-10	-5.2546551E-14	3.5852787E 03	5.8253029E-01
6 O1H1(G)	2.8895544E 00	9.9835061E-04	-2.1879904E-07
1.9802785E-11	-3.8452940E-16	3.8811792E 03	5.5597016E 00
7 H1(G)	2.5000000E 00	-0.	-0.
-0.	-0.	2.5470497E 04	-4.6001096E-01
7 H1(G)	2.5000000E 00	-0.	-0.
-0.	-0.	2.5470497E 04	-4.6001096E-01
8 H2(G)	2.8460849E 00	4.1932116E-03	-9.6119332E-06
9.5122662E-09	-3.3093421E-12	-9.6725372E 02	-1.4117850E 00
8 H2(G)	3.0436897E 00	6.1187110E-04	-7.3993551E-09
-2.0331907E-11	2.4593791E-15	-8.5491002E 02	-1.6481339E 00
9 H2O1(G)	4.1565016E 00	-1.7244334E-03	5.6982316E-06
-4.5930044E-09	1.4233654E-12	-3.0288770E 04	-6.8616246E-01
9 H2O1(G)	2.6707532E 00	3.0317115E-03	-8.5351570E-07
1.1790853E-10	-6.1973568E-15	-2.9888994E 04	6.8838391E 00
10 H2S1(G)	3.9163074E 00	-3.5188671E-04	4.2191312E-06
-2.7453665E-09	4.8584365E-13	-3.6095585E 03	2.3660042E 00
10 H2S1(G)	2.7657149E 00	4.0131914E-03	-1.5044898E-06
2.6807998E-10	-1.7967681E-14	-3.3859808E 03	7.9327186E 00
11 H2S2(G)	2.9838408D 00	1.8270295D-02	-3.3779430D-05
3.1916041D-08	-1.1334427D-11	-1.5049306D 04	1.0121993D 01
11 H2S2(G)	-4.0063758D 00	3.8259025D-02	-4.4842987D-05

	2.2766275D-08	-4.1196181D-12	-1.3521122D 04	4.5197966D 01
12 H1S1(G)	3.8324212E-09	4.2586855E 00	-1.2783317E-03	-8.3785906E-07
12 H1S1(G)	7.9044628E-11	-2.0252030E-12	1.7022862E 04	-3.5367303E-01
13 N1S1(G)	-9.5089130E-09	2.9882040E 00	1.3585811E-03	-4.7105835E-07
13 N1S1(G)	5.8053531E-11	-5.0575843E-15	1.7386935E 04	6.3482781E 00
14 S101(G)	-3.9518236E-09	4.0622151E 00	-2.8190179E-03	9.3158088E-06
14 S101(G)	6.3513293E-11	3.2843034E-12	3.0872668E 04	4.0612628E 00
15 S102(G)	-4.2206766E-09	3.8404466E 00	7.4574590E-04	-3.0578184E-07
15 S102(G)	1.6636523E-10	-4.0693848E-15	3.0785184E 04	4.4723207E 00
16 S103(G)	4.9787393E-09	3.1364326E 00	1.3080689E-03	2.1837364E-06
16 S103(G)	2.7322076E-10	1.6540306E-12	-3.4572672E 02	8.3570292E 00
17 S20(G)	7.6175958D-09	3.8116451E 00	7.8966107E-04	-3.2986127E-07
17 S20(G)	1.0656687D-10	-4.5139892E-15	-5.9599488E 02	4.5442232E 00
18 S1(G)	3.1382439E-09	3.2257132E 00	5.6551207E-03	-2.4970208E-07
18 S1(G)	-5.1868520E-11	2.1392733E-12	-3.6904476E 04	9.8177036E 00
19 S2(G)	6.5393276E-09	5.1982451E 00	2.0595095E-03	-8.6254450E-07
19 S2(G)	3.0368010E-11	-1.1847837E-14	-3.7541457E 04	-8.3059963E-01
20 S3(G)	3.6930520D-08	2.2848661E 00	1.6691404E-02	-1.4610560E-05
20 S3(G)	2.4455268D-11	-2.0664641E-13	-4.8841587E 04	1.3480117E 01
21 S4(G)	6.8491648D-08	7.0246624E 00	3.2795509E-03	-1.4202267E-06
21 S4(G)	4.9969144D-11	-1.9404513E-14	-5.0133303E 04	-1.0922853E 01
22 S5(G)	9.1984957D-08	2.9814487D 00	1.1177869D-02	-1.3450125D-05
22 S5(G)	6.7335992D-11	-1.6326458D-12	-8.0742255D 03	1.2316628D 01
23 S6(G)	1.0687417D-07	5.9047410D 00	1.2358188D-03	-5.4531390D-07
23 S6(G)	7.8730883D-11	-7.6705767D-15	-8.7753344D 03	-2.2896825D 00
24 S7(G)	1.1358385D-07	2.9137258E 00	3.1294061E-04	-2.6092508E-06
24 S7(G)	8.2012996D-11	-1.1708988E-12	3.2568272E 04	3.5681154E 00
25 S(8)	9.7442361D-08	2.9145770E 00	-5.6619390E-04	2.8497584E-07
25 S(8)	1.2118311D-10	3.2709932E-15	3.2604940E 04	3.7640850E 00
26 H101N1(G)		2.6999349E 00	6.2749549E-03	-9.2870775E-06
		-1.7802282E-12	1.4504935E 04	1.0534222E 01
		4.1896932E 00	3.8469704E-04	-1.5566633E-07
		-2.1795849E-15	1.4188133E 04	3.2930300E 00
		1.9945500D 00	2.2142854D-02	-4.1990531D-05
		-1.2163804D-11	1.5738152D 04	1.6000899D 01
		6.1926722D 00	8.2815064D-04	-1.3004522D-07
		-1.6931410D-15	1.5037963D 04	-3.3527720D 00
		1.4194155D 00	4.0145224D-02	-7.7553565D-05
		-2.2643419D-11	1.5894574D 04	2.0179984D 01
		9.0873363D 00	9.8431550D-04	-2.5876895D-07
		-3.5475839D-15	1.4614621D 04	-1.5120701D 01
		1.8897767D 00	5.3439612D-02	-1.0408885D-04
		-3.0426968D-11	1.0967167D 04	1.4282674D 01
		1.2164866D 01	9.1892483D-04	-3.4780612D-07
		-4.7932239D-15	9.2670434D 03	-3.3011300D 01
		3.1119561D 00	6.2103074D-02	-1.2103100D-04
		-3.5328000D-11	9.4447165D 03	1.0832292D 01
		1.5077601D 01	9.8626199D-04	-4.0678901D-07
		-5.6020931D-15	7.4637886D 03	-4.4250365D 01
		4.9778233D 00	6.6486125D-02	-1.2884774D-04
		-3.7491378D-11	1.0164422D 04	5.3569959D 00
		1.7773466D 01	1.2854026D-03	-4.2640406D-07
		-5.8018355D-15	8.0403715D 03	-5.3579567D 01
		8.1343806D 00	6.2010762D-02	-1.1457934D-04
		-3.1350711D-11	7.8307163D 03	-8.7973170D 00
		2.0746770D 01	1.4229802D-03	-6.2534047D-07
		-8.6368670D-15	5.5892652D 03	-6.7705210D 01
		2.1681150E 00	1.0728954E-02	-1.5088089E-05

1.1933018E-08	-3.7004453E-12	1.4682900E 04	9.2810199E 00
26 H101N1(G)	3.6538032E 00	3.4436455E-03	-1.2585128E-06
2.1691615E-10	-1.4296311E-14	1.4421804E 04	2.3726015E 00
27 C2N2(G)	3.4026925E 00	1.7756299E-02	-2.6860559E-05
2.1968412E-08	-7.0872074E-12	3.5550207E 04	5.4122791E 00
27 C2N2(G)	6.5024264E 00	4.0532184E-03	-1.6639966E-06
3.0947405E-10	-2.1482992E-14	3.4904749E 04	-9.4419093E 00
28 C1H4(G)	4.2497678E 00	-6.9126562E-03	3.1602134E-05
-2.9715432E-08	9.5103580E-12	-1.0186632E 04	-9.1754991E-01
28 C1H4(G)	1.1795744E 00	1.0950594E-02	-4.0622131E-06
7.1370281E-10	-4.7490353E-14	-9.8556627E 03	1.2505934E 01
29 C2H2(G)	7.9033340E-01	2.3466122E-02	-3.5541928E-05
2.7950550E-08	-8.4484125E-12	2.6254844E 04	1.4005228E 01
29 C2H2(G)	4.4965644E 00	5.2698321E-03	-1.8402668E-06
3.1054295E-10	-2.0004309E-14	2.5637191E 04	-3.1448152E 00
30 C2H4(G)	1.1202436E 00	1.3905716E-02	2.6568374E-06
-1.1560272E-08	5.2386929E-12	5.3328896E 03	1.5837760E 01
30 C2H4(G)	3.5023516E 00	1.1592101E-02	-4.4745225E-06
7.9452132E-10	-5.3235681E-14	4.4543960E 03	2.4667528E 00
-3.9768518D-08	9.7491815D-01	1.2001058D-02	2.4042816D-05
1.0582468D-09	1.6576402D-11	-7.0992211D 03	1.9331317D 01
32 C101(G)	4.3416262D 00	1.4234332D-02	-5.7342526D-06
-3.4737726E-09	-7.3375816D-14	-8.5337119D 03	-7.1698486D-01
32 C101(G)	3.7871332E 00	-2.1709526E-03	5.0757337E-06
1.1350336E-10	7.7216841E-13	-1.4363508E 04	2.6335459E 00
33 C101S1(G)	2.9511519E 00	1.5525567E-03	-6.1911411E-07
1.5062439E-08	-7.7892732E-15	-1.4231827E 04	6.5314450E 00
33 C101S1(G)	2.0885523E 00	1.4613989E-02	-2.0465884E-05
1.8787369E-10	-4.4468532E-12	-1.7624238E 04	1.2367372E 01
34 C102(G)	5.2068373E 00	2.4717661E-03	-1.0011287E-06
6.3459175E-09	-1.3103525E-14	-1.8327771E 04	-2.9133806E 00
34 C102(G)	2.1701000E 00	1.0378115E-02	-1.0733938E-05
2.4147446E-10	-1.6280701E-12	-4.8352602E 04	1.0664388E 01
35 C1S1(G)	4.4129266E 00	3.1922896E-03	-1.2978230E-06
-7.0858714E-09	-1.6742986E-14	-4.8944043E 04	-7.2875769E-01
35 C1S1(G)	3.3981992E 00	-5.8923594E-04	5.9449817E-06
7.4392024E-11	2.6157526E-12	2.6483370E 04	5.9195268E 00
36 C1S2(G)	3.6766152E 00	9.2679896E-04	-3.8873364E-07
1.0567832E-08	-5.2475514E-15	2.6292309E 04	3.9156151E 00
36 C1S2(G)	2.9174620E 00	1.2498700E-02	-1.6109132E-05
1.3744760E-10	-2.7944978E-12	1.2777076E 04	8.8763491E 00
	5.9491526E 00	1.7245610E-03	-7.2111106E-07
	-9.6838965E-15	1.2053749E 04	-6.2051076E 00

\$UNNUMBER
\$TRUNCATE A

TABLE E.4
MCBRIDE COEFFICIENTS

```

$CREATE S22
$GET S22
$NUMBER
$$COMPILE
COMPUTER PROGRAMME 22
CALCULATE SIMULTANEOUS LEAST SQUARES FIT OF CP, HT AND ST FOR H2S2, S2O, S2, S8,
C2H4O, WHICH YIELDS COEFFICIENTS OF MCBRIDE'S POWER SERIES
  REAL*8 T0, R, F, C43, A, T10, T20, T30, T40, T50, T60, T70, T80,
1  TM2, TM1, P, T02, T03, T04, T, T2, T3, T4, TT0, CP0, ST0, HT0,
2  TT, CP, ST, HT, D, B, Y, X, TE, DET, DFLCAT, DLOG
  DIMENSION LOWT(2), KAOT(2), F(10), A(10,10), TT(50), CP(50),
1  ST(50), HT(50), D(10), B(10,6), Y(10,6), X(7), TE(10,10),
2  IPERM(20)
  DATA NCPDS/3/, LOWT/3,10/, KACT/10,50/
  DATA F/1.0D-07, 1.0D-09, 1.0D-12, 1.0D-15, 1.0D-18,
1  1.0D-03, 1.0D-06, 1.0D-06, 1.0D-05, 1.0D-05/
  T0=1000.0
  R=1.98726
  C43=4.0/3.0
  DO 80 KT=1,2
  LOW=LOWT(KT)
  KAC=KAOT(KT)
  DO 20 I=1,10
  DO 20 J=1,10
20  A(I,J) = 0.0
  T10=0.0
  T20=0.0
  T30=0.0
  T40=0.0
  T50=0.0
  T60=0.0
  T70=0.0
  T80=0.0
  TM2=0.0
  TM1=0.0
  P =0.0
  T02=T0**2
  T03=T0**3
  T04=T0**4
  DO 40 NT=LOW,KAO
  T=DFLCAT(NT)*100.0
  T2=T**2
  T3=T**3
  T4=T**4
  A(1,1) = A(1,1) + 2.00 + (DLOG(T))**2
  A(2,1) = A(2,1) + (1.50 + DLOG(T)) *T
  A(3,1) = A(3,1) + (C43 + DLOG(T)/2.0)*T2
  A(4,1) = A(4,1) + (1.25 + DLOG(T)/3.0)*T3
  A(5,1) = A(5,1) + (1.20 + DLOG(T)/4.0)*T4
  A(6,1) = A(6,1) + 1.0/T
  A(7,1) = A(7,1) + DLOG(T)
  T10 = T10 + T
  T20 = T20 + T2
  T30 = T30 + T3
  T40 = T40 + T4
  T50 = T50 + T**5
  T60 = T60 + T**6

```

```

T70 = T70 + T**7
T80 = T80 + T**8
TM2 = TM2 + 1.0/T2
TM1 = TM1 + 1.0/T
P = P + 1.0
A(8,1) = 1.0
A(9,1) = 1.0
A(10,1) = DLOG(T0)
A(2,2) = 9.0/4.0*T20
A(3,2) = 5.0/3.0*T30
A(4,2) = 35.0/24.0*T40
A(5,2) = 27.0/20.0*T50
A(6,2) = P/2.0
A(7,2) = T10
A(8,2) = T0
A(9,2) = T0/2.0
A(10,2) = T0
A(3,3) = 49.0/36.0*T40
A(4,3) = 5.0/4.0*T50
A(5,3) = 143.0/120.0*T60
A(6,3) = T10/3.0
A(7,3) = T20/2.0
A(8,3) = T02
A(9,3) = T02/3.0
A(10,3) = T02/2.0
A(4,4) = 169.0/144.0*T60
A(5,4) = 17.0/15.0*T70
A(6,4) = T20/4.0
A(7,4) = T30/3.0
A(8,4) = T03
A(9,4) = T03/4.0
A(10,4) = T03/3.0
A(5,5) = 441.0/400.0*T80
A(6,5) = T30/5.0
A(7,5) = T40/4.0
A(8,5) = T04
A(9,5) = T04/5.0
A(10,5) = T04/4.0
A(6,6) = TM2
A(7,6) = 0.0
A(8,6) = 0.0
A(9,6) = 1.0/T0
A(10,6) = 0.0
A(7,7) = P
A(8,7) = 0.0
A(9,7) = 0.0
A(10,7) = 1.0
DO 30 I=8,10
DO 30 J=8,10
30 A(I,J) = 0.0
CALCULATE OTHER ELEMENTS OF SYMMETRIC MATRIX
DO 40 I=1,10
DO 40 J=1,10
40 A(I,J) = A(J,I)
COMPUTER WRITES MATRIX BEFORE INVERTING IT
WRITE (6,1000)
WRITE (6,1010) ((A(I,J), J=1,10), I=1,10)
WRITE (3,1010) ((A(I,J), J=1,10), I=1,10)
COMPUTER SCALES MATRIX BEFORE INVERTING IT
DO 45 I=1,10
DO 45 J=1,10
45 A(I,J) = A(I,J) * F(I)
WRITE (6,1010) ((A(I,J), J=1,10), I=1,10)
CALCULATE VECTOR D, WHICH IS A FUNCTION OF CP, HT AND ST
DO 65 NCPD=1,NCPDS
READ (5,1030) DHF298
WRITE (6,1030) DHF298
READ (5,1030) (TT(NT), CP(NT), ST(NT), HT(NT), NT=LOW, KAO)

```



```

WRITE(6,1030) (TT(NT), CP(NT), ST(NT), HT(NT), NT=LOW, KAO)
DO 55 I=1,10
D(I)=0.0
DO 60 NT=LOW, KAO
T=DFLOAT(NT)*100.0
CONVERT ENTHALPY FROM KILOCALORIES/MOLE TO CALORIES/MOLE AND DIVIDE BY TEMP
HT(NT) = (HT(NT)+DHF298) * 1000.0 / T
D(1) = D(1) + CP(NT) * HT(NT) + ST(NT)*DLOG(T)
D(2) = D(2) + (CP(NT) * HT(NT)/2.0 + ST(NT) ) * T
D(3) = D(3) + (CP(NT) * HT(NT)/3.0 + ST(NT)/2.0) * T**2
D(4) = D(4) + (CP(NT) * HT(NT)/4.0 + ST(NT)/3.0) * T**3
D(5) = D(5) + (CP(NT) * HT(NT)/5.0 + ST(NT)/4.0) * T**4
D(6) = D(6) + HT(NT)/T
60 D(7) = D(7) + ST(NT)
D(8) = CP(10)
D(9) = HT(10)
D(10) = ST(10)
COMPUTER DIVIDES D BY GAS CONSTANT R AND SCALES D IN SAME MANNER AS MATRIX A
DO 65 I=1,10
E(I,NCPD) = D(I)*F(I)/R
65 WRITE (6,1050) (D(I), I=1,10)
CALL SLE (10, 10, A, NCPDS, 10, B, Y, IPERM, 10, TE, DET, JEXP)
WRITE (6,1060) DET, JEXP
WRITE (6,1050) ((Y(I,NCPD), I=1,10), NCPD=1,NCPDS)
WRITE (4,1040) ((Y(I,NCPD), I=1,7), NCPD=1,NCPDS)
CHECK COEFFICIENTS OBTAINED BY WRITING CP, HT, AND ST, FROM 300 TO 1000 K
DO 80 NCPD=1,NCPDS
DO 70 I=1,7
70 X(I) = Y(I,NCPD)
T=298.15
T2=T**2
T3=T**3
T4=T**4
HT(2) = (X(1) + X(2)*T/2.0 + X(3)*T2/3.0 + X(4)*T3/4.0 +
1 X(5)*T4/5.0 + X(6)/T) * R * T
DO 80 NT=LOW, KAO
T = DFLOAT(NT)*100.0
T2=T**2
T3=T**3
T4=T**4
CP(NT) = X(1) + X(2)*T + X(3)*T2 + X(4)*T3 +
1 X(5)*T4
HT(NT) = X(1) + X(2)*T/2.0 + X(3)*T2/3.0 + X(4)*T3/4.0 +
1 X(5)*T4/5.0 + X(6)/T
ST(NT) = X(1)*DLOG(T) + X(2)*T + X(3)*T2/2.0 + X(4)*T3/3.0 +
1 X(5)*T4/4.0 + X(7)
CP(NT) = CP(NT)*R
CONVERT ENTHALPY FROM KILOCALORIES/MOLE TO CALORIES/MOLE
HT(NT) = HT(NT)*R*T/1000.0 - HT(2)/1000.0
ST(NT) = ST(NT)*R
80 WRITE (6,1030) T, CP(NT), ST(NT), HT(NT)
WRITE (6,1010) HT(2)
STOP
1000 FORMAT ('0')
1010 FORMAT (//(1P10D13.5))
1030 FORMAT (4F10.3)
1040 FORMAT (20X, 1P3E20.7/ 1P4E20.7)
1050 FORMAT (/ (1P5D26.16))
1060 FORMAT (D20.8, I5)
END
$$DATA
$UNNUMBER

```

APPENDIX F

ERROR ANALYSIS

The *maximum* errors, not the most probable ones are estimated in this appendix. Two rules were used in the estimation:

--When variables are added or subtracted, their *absolute* errors are added.

--When variables are multiplied or divided, their *percent* errors are added.

The absolute errors of directly measured variables were obtained from the specifications of instrument manufacturers. The other errors listed in Tables F1 and F2 were calculated from the following equations:

$$PA = 42(m_A x_A + b_A) / (m_{H_2S} x_{H_2S} + b_{H_2S}) \quad (F.1)$$

$$Q_i = m_i x_i + b_i \quad (F.2)$$

$$y_i = Q_i / (Q_i + Q_{N_2}) \quad (F.3)$$

where $i = H_2, H_2S$ or SO_2

The errors in the compositions, sulphur yield and PA by mass balance were estimated from Eqs. 4.12 to 4.21.

TABLE F.1

Estimate of errors in stoichiometric
air, PA, by flow meters (Run 77)

Variable	Typical Value	Absolute Error*	Percentage Error*
x_A	54.5	1	1.83
m_A	3.975	0.02	0.5
$m_A x_A$	216.64	5.05	2.33
b_A	-75.844	0.38	0.5
$m_A x_A + b_A$	140.796 ml/min	5.43 ml/min	3.86
42	42	0	0
$42(m_A x_A + b_A)$	5913.432	228.26	3.86
x_{H_2S}	36	1	2.78
m_{H_2S}	1.370	0.01	0.5
$m_{H_2S} x_{H_2S}$	49.32	1.62	3.28
b_{H_2S}	1.789	0.01	0.5
$m_{H_2S} x_{H_2S} + b_{H_2S}$	51.11 ml/min	1.63 ml/min	3.19
PA	115.70	8.16	7.05

* The errors may be positive or negative.

TABLE F.2

Estimates of errors in chemical
compositions and sulphur yield

Variable	Typical Value	Error	Percent Error
x_{H_2}	12.0	1	8.33
m_{H_2}	2.119	0.01	0.5
$m_{H_2} x_{H_2}$	25.43	2.25	8.83
b_{H_2}	-3.698	0.02	0.5
$Q_{H_2} = m_{H_2} x_{H_2} + b_{H_2}$	21.73 ml/min	2.27 ml/min	10.45
x_{H_2S}	48.20	1	2.07
m_{H_2S}	1.370	0.01	0.5
$m_{H_2S} x_{H_2S}$	66.03	1.70	2.57
b_{H_2S}	1.789	0.01	0.5
$Q_{H_2S} = m_{H_2S} x_{H_2S} + b_{H_2S}$	67.82 ml/min	1.71 ml/min	2.52
x_{SO_2}	47.4	1	2.11
m_{SO_2}	0.9427	0.005	0.5
$m_{SO_2} x_{SO_2}$	44.68	1.17	2.61
b_{SO_2}	5.262	0.03	0.5
$Q_{SO_2} = m_{SO_2} x_{SO_2} + b_{SO_2}$	49.95 ml/min	1.20 ml/min	2.40

TABLE F.2 Continued

Variable	Typical Value	Error	Percent Error
x_{N_2}	60.77	1	1.65
m_{N_2}	24.991	0.12	0.5
$m_{N_2} x_{N_2}$	1518.70	32.65	2.15
b_{N_2}	-213.403	1.07	0.5
$Q_{N_2} = m_{N_2} x_{N_2} + b_{N_2}$	1305.30 ml/min	33.68 ml/min	2.58
$(Q_{H_2} + Q_{N_2})$	1327.03 ml/min	35.96 ml/min	2.71
$y_{H_2} = Q_{H_2} / (Q_{H_2} + Q_{N_2})$	1.64 %	0.22 %	13.16
$(Q_{H_2S} + Q_{N_2})$	1373.12 ml/min	35.39 ml/min	2.58
$y_{H_2S} = Q_{H_2S} / (Q_{H_2S} + Q_{N_2})$	4.94 %	0.25 %	5.10
$(Q_{SO_2} + Q_{N_2})$	1355.25 ml/min	34.88 ml/min	2.57
$y_{SO_2} = Q_{SO_2} / (Q_{SO_2} + Q_{N_2})$	3.69 %	0.18 %	4.97

TABLE F.2 Continued

Variable	Typical Value	Absolute Error	Percent Error
$n_{H_2} = y_{H_2}$	0.5 moles	0.05 moles	10.45
$n_{H_2S} = y_{H_2S}$	4.7 moles	0.12 moles	2.52
$n_{SO_2} = y_{SO_2}$	7.1 moles	0.17 moles	2.40
$n_{N_2} = y_{N_2}$	87.7 moles	2.26 moles	2.58
$0.532 n_{N_2}$	46.66 moles	1.20 moles	2.58
$2n_{SO_2}$	14.20 moles	0.34 moles	2.40
$n_{H_2O} = 0.532n_{N_2} - 2n_{SO_2}$	32.46 moles	1.54 moles	4.75
$2n_{S_2} = n_{H_2} - n_{SO_2} + n_{H_2O}$	25.86 moles	1.76 moles	6.81
n_{S_2}	12.93 moles	0.88 moles	6.81
$n_T = n_{H_2} + n_{H_2S} + n_{SO_2} + n_{N_2} + n_{H_2O} + n_{S_2}$	145.39 moles	5.02 moles	3.45
P_{H_2}	0.0034 atm	0.0005 atm	13.90
P_{H_2S}	0.0323 atm	0.0019 atm	5.97
P_{SO_2}	0.0488 atm	0.0029 atm	5.85
P_{N_2}	0.6032 atm	0.0364 atm	6.03
P_{H_2O}	0.2233 atm	0.0194 atm	8.70
P_{S_2}	0.0889 atm	0.0091 atm	10.26

Variable	Typical Value	Error	Percent Error
$2n_{S_2}$	25.86 moles	1.76 moles	6.81
$(2n_{S_2} + n_{H_2S} + n_{SO_2})$	37.66 moles	2.05 moles	5.44
$Y = 200n_{S_2} / (2n_{S_2} + n_{H_2S} + n_{SO_2})$	68.67%	8.41%	12.25
Temperature	1200°C	12°C	1%