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THERMODYNAMIC ANALYSIS OF THE MODIFIED CLAUS PROCESS

University — Université

UNIVERSITY OF ALBERTA.

Degree for which thesis was presented — Grade pour lequel cette thèse fut présentée

MASTER OF SCIENCE

Year this degree conferred — Année d'obtention de ce grade

1982

Name of Supervisor — Nom du directeur de thèse

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THERMODYNAMIC ANALYSIS OF THE MODIFIED CLAUS PROCESS

by

TRUONG THI THU THUY

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE

DEPARTMENT OF CHEMICAL ENGINEERING

EDMONTON, ALBERTA
FALL 1982

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Supervisor

Date July 23, 1982

ABSTRACT

The predicted equilibrium conversion for H_2S/SO_2 system is less than the observed conversion. A sensitivity study of thermodynamic properties to establish which thermodynamic properties are most sensitive in the predictions of the equilibrium constant was carried out. It was found that thermodynamic properties of each species have to be changed by a large amount to predict the experimental conversion. Based on suggestion by Wakihara and Rau, sulfur vapor is assumed to be composed of the molecular species S_2, S_6, S_7 and S_8 in significant amounts alone. Equilibrium conversions for this assumed system were found to be very sensitive to changes in thermodynamic properties of H_2O, H_2S and S_2. When the thermodynamic properties of the species H_2S, SO_2, H_2O and sulfur are changed by the uncertainty values cited in the literature (±200 cal/mole for standard heat of formation, ±0.01 cal/mole-K for all standard entropy except, ±3.3 for S_6 and ±4.2 for S_7) the calculated conversion becomes larger then the observed conversion.

An alternative approach was examined by calculating an empirical equilibrium constant using proprietary experimental equilibrium data obtained at Lacq (France) for the overall reaction

$$2H_2S + SO_2 <=====> 3/x\ S_x + 2H_2O$$

The resulting equilibrium constant for the temperature range from 225°C to 370°C is given by

$$\ln K_p' = -17.885 + 15{,}466/T$$

which predicts both Cho's (32) and Tellier's (140) measured conversion within 10%. The only other model comparable but not identical in improved prediction, corresponds to $S_2-S_6-S_7-S_8$ species with data from Rau (126) for sulfur species and JANAF (74) for other species.

A graphical method for process calculations related to the modified Claus process was updated using thermodynamic properties for sulfur from Rau (126) and for other species in the equilibrium composition from JANAF (74). Calculations verify that for acid gas containing as lean as 60% H_2S, the method predicts reasonable equilibrium performance for catalytic converters.

ACKNOWLEDGEMENTS

The author wishes to express thanks to various individuals who have assisted in different ways in this research and in particular Dr. Dale [illegible] for his advice and guidance during the course of this study and also for his valuable discussions and help in the preparation of this thesis. Thanks are also due to Dr. Mather for his advice at the beginning of this research.

Thanks are also due to Neil McCulloch for his help in editing of this thesis.

The financial support of the University of Alberta is gratefully acknowledged.

Finally, the author is indebted to the family for their patience, understanding and support.

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1. INTRODUCTION

The modified Claus process is the standard process for converting hydrogen sulfide to elemental sulfur. The principal reactions in the Claus process are,

$$H_2S + 1.5\ O_2 \ \text{------>}\ SO_2 + H_2O \qquad (1.1)$$

$$2H_2S + SO_2 \ \text{<=====>}\ 3/\nu\ S_\nu + 2H_2O \qquad (1.2)$$

where ν is the average atomic number of sulfur vapor. Claus units usually consist of a reaction furnace and two or more catalytic converters. Each converter is preceded by a reheater and followed by a condenser. In the furnace, reaction (1.1) is carried out with sufficient air to obtain the stoichiometric ratio of H_2S/SO_2 for reaction (1.2). Reaction (1.2) occurs partly in the furnace (30 – 60%) and partly in the catalytic converters (40 – 70%). To maintain flame stability in the furnace, Claus units are operated in one of the following two methods :

1) once-through process (for 50 – 100% H_2S acid gas),

2) split-flow process (for 15 – 50% H_2S acid gas) (102).

In the second method two-thirds of acid gas bypasses the furnace, and none at all in the first.

Different aspects of the hydrogen sulfide and sulfur dioxide reaction have been studied extensively (mechanistic studies, catalyst effects...) together with important side reactions (COS/SO_2 reaction, COS/H_2O reaction...); however, the H_2S/SO_2 reaction also has a reverse reaction, S/H_2O, the importance of which varies with the operating temperature. The effect of the reverse rate of reactions on the global reaction and operating condition has not been investigated in detail. The objectives of this work are to study the limits of sulfur plant performance by a thermodynamic investigation of the H_2S/SO_2 system and to apply the results to a graphical method of prediction for sulfur plant performance.

1.1 Rationale

The thermodynamics of the Claus process have intrigued many chemists because the calculated equilibrium conversion has been found to be lower than the observed experimental conversion. Two reasons are proposed to account for this discrepancy; (a) an experimental error attributed to additional reaction after leaving the reactor and before the product stream is analyzed, (b) uncertainties associated with sulfur species and their thermodynamic properties. The problem of (a) has been eliminated by use of long reaction times enabling approach to experimental equilibrium from both reactants and from products; (b) cannot be eliminated since sulfur vapor is an unknown mixture of different homologous species.

Designing Claus plant reactors requires knowledge of kinetic data of both H_2S/SO_2 and sulfur association reactions . Lack of information on the rate of sulfur association and the reverse reaction S/H_2O has forced process engineers to turn to their own experience in operation or to thermodynamic calculations. Fortunately the calculated equilibrium conversion is lower than the observed value. As a result the practice of using the calculated equilibrium conversion in design or for predicting plant conversions has no serious effect except conservative prediction (41,43).

1.2 Previous Work

A detailed review of the earlier predictions of the thermodynamic equilibrium is given in section 2.2. Some investigators used the equilibrium constants of $H_2S/SO_2//S_2/H_2O$ reaction and of sulfur association reactions; others have used the thermodynamic properties to predict conversion. Their predicted values are always lower than the experimental conversion. It is noted that even though the sulfur thermodynamic data used are scattered, the calculated equilibrium conversions do not significantly differ from each other. However, the effect of each thermodynamic property on the magnitude of the predicted conversion can be evaluated using a sensitivity study.

1.3 Objectives

The purpose of this investigation is to study the discrepancy between predicted and actual equilibrium conversions in order to improve the equilibrium prediction for the H_2S/SO_2 system. In this study, only reactions(1.1) and (1.2) are considered to occur, i.e. the equilibrium mixture is composed of only H_2S, SO_2, H_2O, S_j (with j=1 to 8) and inerts. This is a reasonable assumption since Tellier's (140) and Cho's (32) conversion data (which are used as data for this study) are in the temperature range 400-700 K where other side reactions such as the formation of hydrogen, of hydrogen polysulfides... are insignificant. In the absence of knowledge of the rate of sulfur association, only the once-through process will be considered and association of sulfur atoms in the vapor phase is assumed to be fast. Because of the complexity of the problem, this thesis will be divided into three main chapters; Each deals with one aspect of the thermodynamics of H_2S/SO_2 system in a sulfur plant: sensitivity analysis of the thermodynamic properties, empirical equilibrium constant and the limit of the graphical method to predict Claus plant performance.

1.3.1 Sensitivity analysis of the effect of magnitude of thermodynamic properties of species on equilibrium conversion

Several authors have calculated the thermodynamic equilibrium conversion of H_2S/SO_2 system using thermodynamic properties from different sources, including distorted thermodynamic properties. However, it is difficult to isolate clearly the effect of each thermodynamic property on the equilibrium conversion. To evaluate the role of each thermodynamic property, it was decided to calculate the equilibrium conversion as a function of changes in thermodynamic properties, using the free energy minimization method. In particular the effects of enthalpy, entropy and heat of formation for H_2S, SO_2, H_2O and S_2, S_6, S_8 will be examined.

1.3.2 The equilibrium constant for H_2S/SO_2 system

An alternative approach to predicting equilibrium conversions is possible via the use of experimentally measured equilibrium conversions to generate equilibrium constants. This approach will be examined using certain proprietary experimental data provided by Aquitaine (20).

1.2.3 Graphical approach to Claus plant design

The extent of conversion of H_2S to elemental sulfur attainable under typical operating conditions in a modified Claus process has been a point of considered interest and discussion. In 1974, Della Lana, Cho and Liu (43) described an attempt to predict thermodynamic equilibrium conversion by relatively simple calculations involving a graphical method. The approximations made in determining the sequence of reaction paths will be examined. Some of these will be shown to be not of serious consequences.

2. LITERATURE REVIEW

There are many excellent reviews of the various academic schemes used for chemical equilibrium composition calculation. Those interested are referred to the literature reviews of Maadah (96) and McGregor (102) as a first step to a comprehensive understanding on the development of the free energy minimization method used in this thesis.

To provide background for subsequent chapters dealing with different aspects of the Claus process, this chapter will cover the process description, and previous work on conversion of H_2S/SO_2 system .

2.1 Claus process

The Claus process has been used extensively to reduce hydrogen sulfide to sulfur since 1898 (34). Increasing demand for natural gas will likely result in this process becoming even more important in the foreseeable future (116). This process has been modified since it was first used.

Originally, reduction was carried out in a single reactor with bauxite or iron ore as catalyst. Reaction temperature was controlled by the amount of feed gas (55). Since the oxidation of hydrogen sulfide to sulfur is highly exothermic, it was necessary that the feed rate be small. In 1937 Farbenindustrie (2) converted hydrogen sulfide to sulfur in two stages: (1) to sulfur dioxide, then (2) to elemental sulfur. Thus a lower temperature can be maintained in the second reactor (catalytic converter) resulting in higher overall conversion since reaction (1.2) is exothermic in this region.

Today, Claus plants usually consist of a furnace followed by three or four catalytic stages. Depending on the concentration of hydrogen sulfide in acid gas, two possible methods are used:

1) straight through process,
2) split-flow process. (102)

The straight through process is suitable for high hydrogen sulfide (>50%) and low hydrocarbon concentration gas (<1%). In this method air is admitted to the furnace to oxidize all hydrocarbons present and just one-third of hydrogen sulfide to sulfur dioxide in order to obtain stoichiometric ratio of H_2S/SO_2 for reaction (1.2).

The split-flow process is also suitable for high hydrocarbon acid gas since only one-third of the acid gas enters the reaction furnace. The amount of COS and CS_2 formed is lowered by about two-thirds, thus decreasing sulfur losses by sulfur/carbon reactions. The outlet gas from the furnace is then mixed with the remaining acid gas to feed to the first converter. To maintain flame stability in the furnace the split-flow method should have hydrogen sulfide concentration greater than approximately 20%.

Conversion can also be increased depending upon which reheat method is used to preheat converter feed gas. To decrease the amount of sulfur lost through entrainment in tailgas, indirect heat exchange is the best method, followed by use of inline burners, and lastly, by the hot gas bypass method. However, the latter two methods have advantage of lower capital investment and operation cost (63, 85). Sulfur recovery of up to 97.6% has been obtained in modified Claus plants with muffled furnace and heat exchangers (116). Modifications to Claus units since 1976 have been to the last converter involving continuous operation at a temperature lower than the sulfur dew point. Sulfur recovery has been improved to 99.5% (63).

2.2 Work done on the thermodynamic equilibrium conversion

Gamson and Elkins in 1953 (55) published calculations of thermodynamic conversion of H_2S/SO_2 system by applying the equilibrium constant method using the thermodynamic properties for sulfur species compiled by Kelley (79) from Preuner and Schupp 's (122) vapor pressure data. For the stoichiometric ratio of H_2S/air mixture, Gamson and Elkins assumed that sulfur exists only in the forms of S_2, S_6, S_8 over the temperature range 400-1600 K . They assumed the following reactions occurred in the system:

$$2H_2S + O_2 \longrightarrow 2H_2O + S_2 \qquad (2.1)$$

$$3S_2 \Longleftrightarrow S_6 \qquad (2.2)$$

$$4S_2 \Longleftrightarrow 4S_8 \qquad (2.3)$$

$$2H_2S + 3O_2 \Longleftrightarrow 2H_2O + 2SO_2 \qquad (2.4)$$

$$2H_2S + SO_2 \Longleftrightarrow 2H_2O + 1.5S_2 \qquad (2.5)$$

$$S_2 + 2O_2 \Longleftrightarrow 2SO_2 \qquad (2.6)$$

The direct oxidation by free oxygen molecules is very fast; therefore the conversion is only limited by the extent of reactions (2.2), (2.3) and (2.5).

Their calculated equilibrium conversion is below the experimental conversion. However their vapor pressure and thermodynamic data are out-dated. Preuner and Schupp's (122) data are scattered about 20% (Fig. 1). Kelley's (79) thermodynamic properties of reaction (2.2) and (2.3) have been revised many times since 1953.

Peter and Woy in 1960 (118) calculated the equilibrium constant of the overall Claus reaction from the known standard entropy, enthalpy and heat capacity of each component of the H_2S/SO_2 system, assuming only S_2 present. Even with this unrealistic assumption, their predicted equilibrium conversion is lower than observed values.

Munro and Masdin (1967) (104) used West and Menzies' (149) sulfur vapor pressure and the thermodynamic properties from JANAF, 1st ed. (1965) (73) to calculate equilibrium constants for reactions in the H_2S/SO_2 system (0.5% H_2S, 0.75% SO_2) assuming only S_2, S_6, S_8 are present over the temperature range 398-508 K. Their observed conversion is less than or equal to their predicted conversion for feed with less than 20% volume water vapor. The lowest space velocity used was 67 volumes of H_2S/volume cat.hr, thus experimental "equilibrium" conversion may not have been reached yet. Their thermodynamic properties and vapor pressure are similar to conditions described in chapter 4. They also observed that the conversion equilibrium is very sensitive to the free energy of species.

Erickson and Rosen (1968) (51) regarded Kelley's data (79) as inaccurate. They applied the free energy minimization method, with all possible species present in the equilibrium mixture; H_2S, SO_2, N_2, H_2O, H_2, O_2, S_2, S_4, S_6, S_8, H_2S_2, SO, SO_3 except HS, S_3, S_5, S_7, S_9 over the temperature range, 550-650 K. Under these conditions gases may be considered to behave ideally as shown by calculating [illegible]e fugacities. JANAF's thermodynamic properties (1965) (73) with Braune's equilibrium constants for S_4, S_6, S_8 from $S_2(g)$ (19) were used. Their calculated equilibrium compositions was reproduced in this work (chapter 4) wherein species other than S_2, S_6, S_8, H_2S, SO_2, H_2 are neglected in the equilibrium mixture from 400 to 1800 K. They did however consider S_4 to be significant. At 600 K, S_4 is more abundant than S_2 in their equilibrium mixture; this is due to Braune's equilibrium constants which emphasize the significance of S_4 over other thermodynamic data sources. (The higher the K_4 value, the ratio of partial pressure of S_4

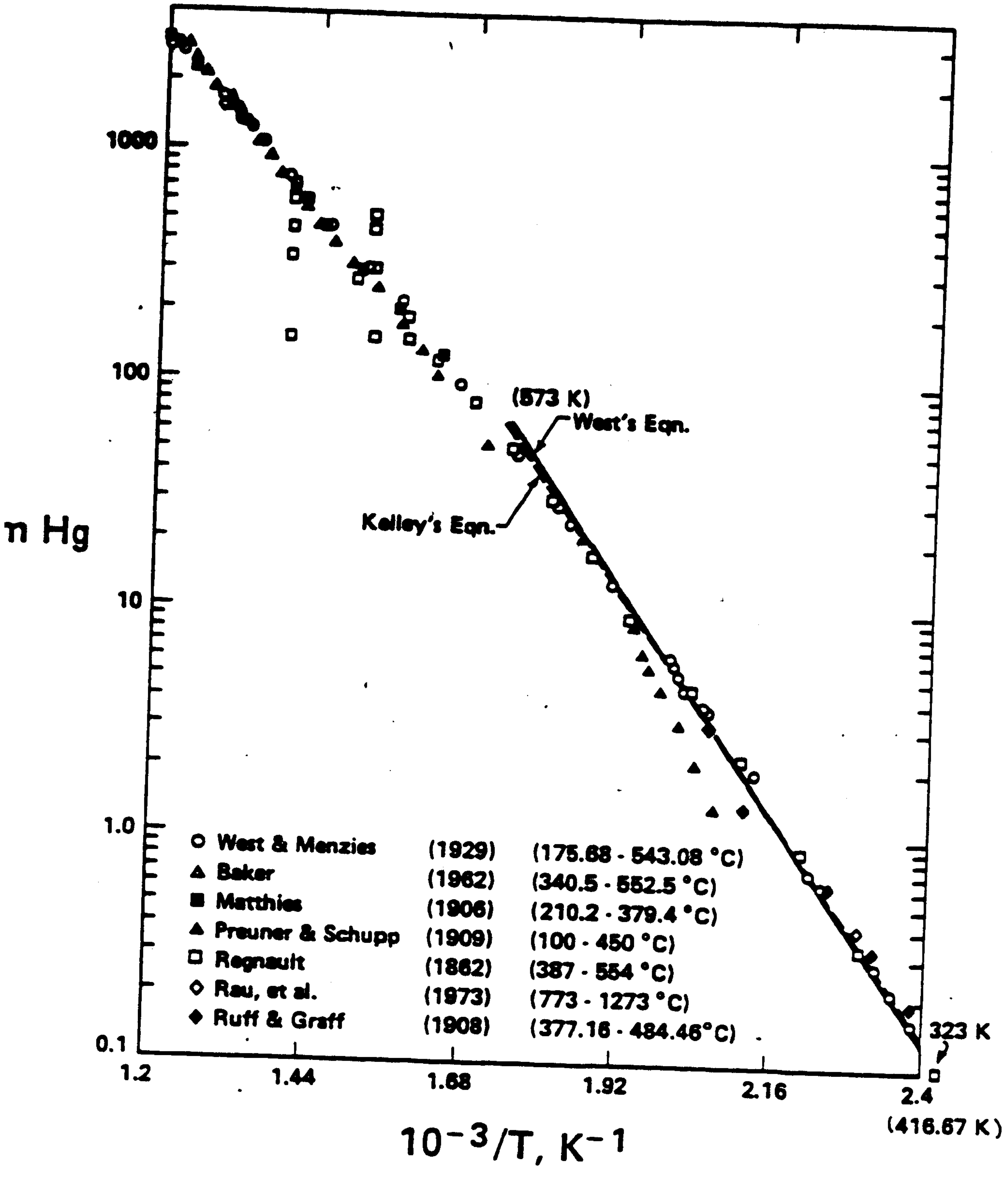


Fig. 1 Vapor Pressure Data

and the square of partial pressure of S_2, the more significant S_6 is in the equilibrium mixture.) The calculated sulfur yield thus differs only marginally from those of Gamson and Elkins (55).

Erickson and Rosen (51) used thermodynamic properties of H_2S, SO_2, H_2O, N_2, S_2 and S_8 from JANAF (1965) (73) and Berkowitz' (15) thermodynamic properties for S_6. Berkowitz et al. (14) used quantum mechanics to calculate the thermodynamic properties of S_6, applying the force field of $S_8(g)$ to $S_6(g)$. (The force field of a molecule is the magnetic forces generated by the attraction–repulsion and twisting forces in the molecule caused by atomic distances and angles.) The result agrees with their earlier prediction of S_6 thermodynamic properties using mass spectra of sulfur vapor. The second edition of JANAF (74) provides values for thermodynamic properties of S_8 in the direction of decreasing conversion (Fig. 2) in the catalytic region (<700 K.) However, Erickson and Rosen's thermodynamic conversion is lower than others who used 2nd ed. of JANAF tables (1971) for H_2S, SO_2, H_2O, N_2, S_2 and S_8 thermodynamic properties (104). They also estimated that the error in their Gibbs free energy value for S_6 and S_8 may be up to 10%.

Bennett and Meisen (10) calculated the equilibrium constants of reactions between H_2S and air assuming 40 species including free radicals present in the equilibrium mixture over temperature range 600–2000 K. In their calculations, only 25 species were found to have a concentration greater than 0.1 ppm: 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, S_j where j=1,2...8. Bennett and Meisen used the thermodynamic data taken from JANAF (1965) (73) and Detry's measurements for sulfur species and Mackle and O'Hare's free energy for H_2S_2 (97). Their equilibrium is between Gamson and Elkins's (55) and that of McGregor (102). They also noted a maximum conversion at 1700 K due to the existence of HS and SO, products of further oxidation of sulfur. The error in calculating the partial pressure in this work is $\pm 10^{-5}$atm, thus according to Bennett and Meisen's result only the following species need be considered in the range of temperature 400–1600 K: N_2, H_2S, SO_2, H_2, SO, SH, S_2O, H, S_2O, H_2S_2, S_j, j=2,3...8.

McGregor (102) and Liu (95) used the data by McBride et al (101) and Kelley's values (79) (i.e. Preuner and Schupp vapor pressure (122)) for S_6, S_8 assuming only S, S_2,

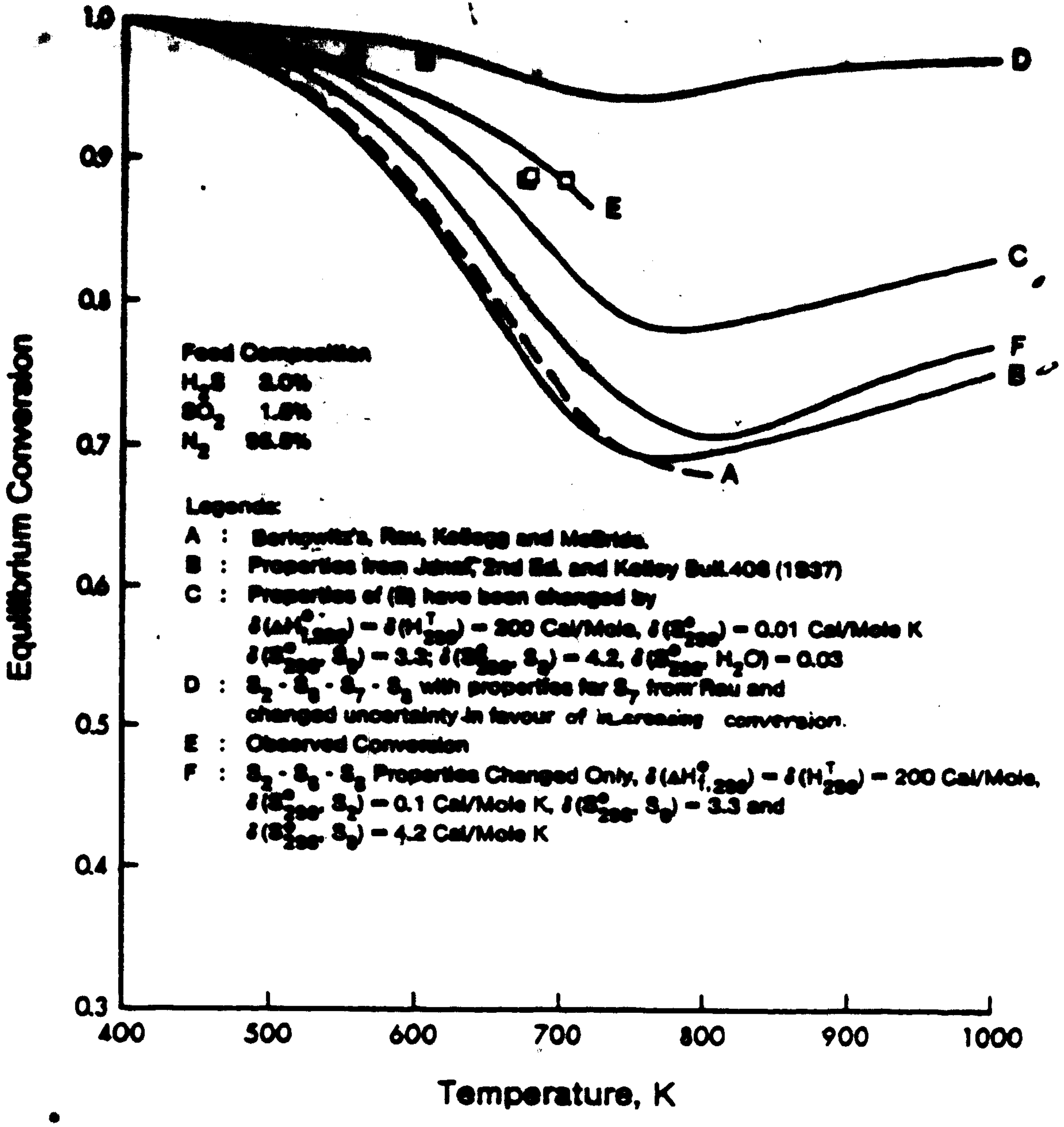


Fig. 2 Equilibrium Conversion Predicted from Different Sources.

S_7 and S_8 present in sulfur vapor over temperature range 400–1800 K for the H_2S/air system ,in stoichiometric ratio. The free energy minimization method was used. Both McGregor and Liu also took into account the formation of H_2 at high temperatures, as also included later by Bennett and Meisen (10), but ignored other oxidation products: SO, SH, S_2O, H_2S_2 and S_3, S_4, S_5 where partial pressures can be as high as 2.10^{-3}atm. Their predicted equilibrium conversions are slightly higher than those of both Gamson and Elkins (55) and Bennett and Meisen (10). Thermodynamic data used by McGregor and Liu is compatible with this work except for S_2 where JANAF (74) 2nd ed. is more recent. McGregor suggested the discrepancy may be partly caused by the assumption that all sulfur species are at equilibrium with each other. (This is not the case as shown later (Fig. 3)).

In Cho's (1975) (32) equilibrium study with γ-alumina (S-201) using 35 g catalyst in a 6 inch integral bed and a space velocity $4 hr^{-1}$, the conversion obtained is higher (by 6% to 20%) than that calculated, as shown in Fig. 3. Cho suggested the polymerization of sulfur in catalyst pores and non-equilibrated adsorption and desorption of sulfur as possible reasons. This polymerization has been observed as well by Dudzik (49) for zeolite. However, since each data point was obtained at steady state after 24 hours under the same conditions, unless the adsorption of sulfur is extremely slow the adsorption should be at equilibrium at the end of 24 hours. Furthermore, since the capacity of the catalyst to retain sulfur is very limited, Cho's reasons appear to be invalid ones. Thus the conversion should not be influenced by the sulfur adsorption-desorption.

Kerr in 1976 (84) used thermodynamic data from Berkowitz (1965) (14), Rau and Kutty (1974) (128), Kellogg (1971) (82) and McBride (101) to calculate the thermodynamic conversion for rich as well as lean acid gas (using a free energy minimization method) reacted with the stoichiometric amount of air. The equilibrium curve is superimposed on Fig. 3. The conversion is slightly better than McGregor's prediction.

The vapor pressure data of Rau and Kutty (128) is the most recent, is believed to be the most reliable, and is comparable to West and Menzies' results for high temperature and pressure, while McBride's source (101) is compatible with JANAF (74). Thus it is not surprising that a result using JANAF data is similar to McGregor's (102). Therefore sulfur thermodynamic data are taken from Rau for this study.

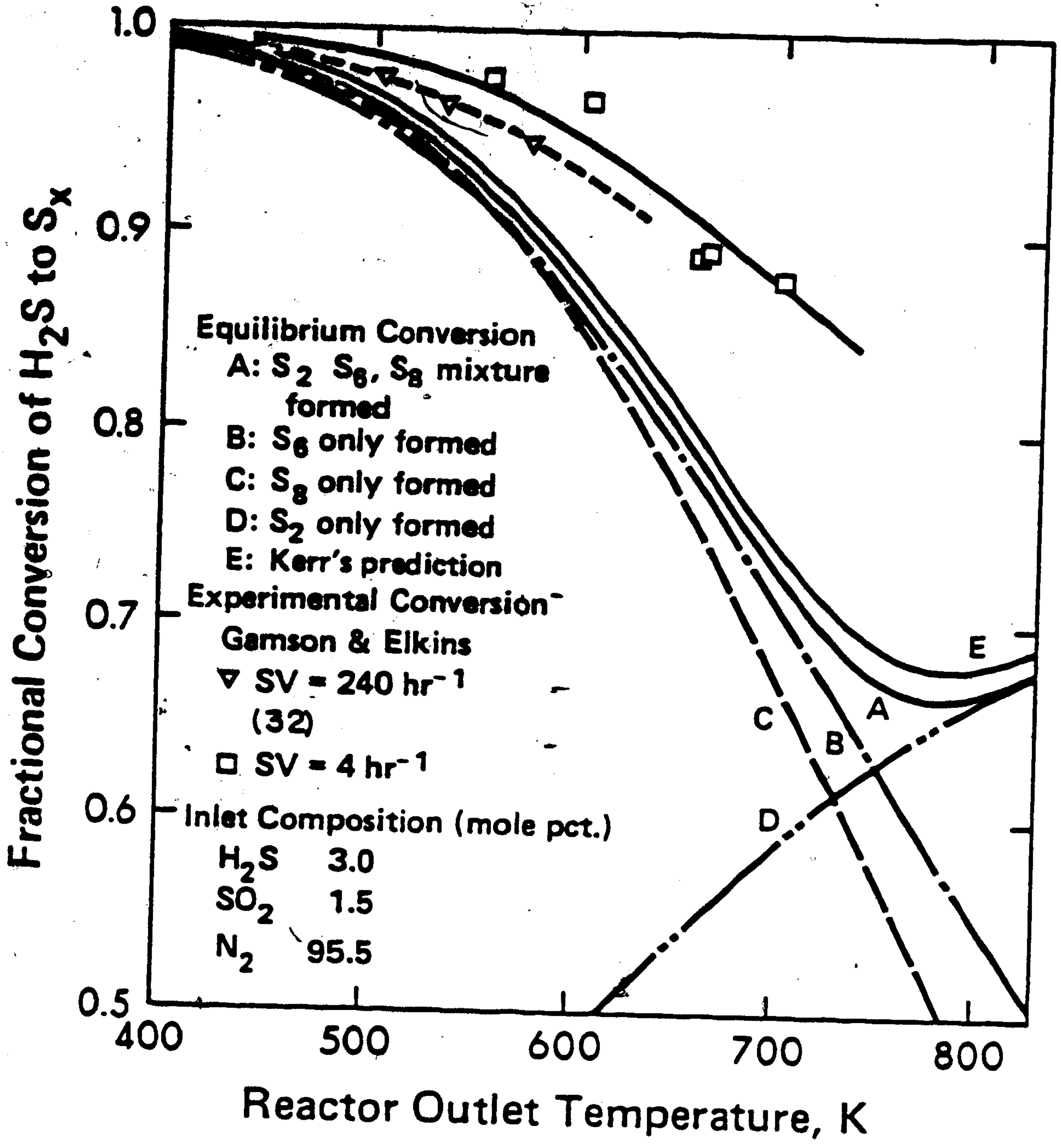


Fig. 3 Comparison between Predicted and Observed Conversion

3. THE FREE ENERGY MINIMIZATION PROGRAM

The free energy minimization program FREM used in this study has been written originally by McGregor (102) for his doctoral thesis. The program calculates the equilibrium composition of a chemical system by minimizing the total free energy of the system. The program has been modified to accomodate the following improvements over the original program:

1) The capability of calculating the equilibrium composition and conversion in the presence of liquid sulfur was added by introducing the constraint that the partial pressure of sulfur may never exceed the vapor pressure of sulfur for the given temperature.
2) The capability to calculate frozen dew point (dew point as a result of lowering the temperature only for a fixed composition) and equilibrium dew point (dew point at which all species have been re-equilibrated as a result of lowering the temperature) of the chemical system at equilibrium.

This chapter will briefly describe the theory and modification of FREM program.

FREM

FREM is the computer program that calculates the equilibrium composition of a chemical system from the input mole numbers and molar free energy of each species present in the initial and final composition. Lagrange multipliers are used to convert a minimization problem with constraints to a problem of solving a set of nonlinear equations using steepest descent iteration technique. The mathematical equations which are the basis of FREM are summarized in Appendix A.

The detailed description of both the mathematical procedure and the program are in Chapter 3 and Appendix B of McGregor's thesis(102).

FREMSULFUR: MODIFICATION OF FREM

During this study, the program was modified to calculate equilibrium composition of gas-liquid sulfur compound system with the constraint that the sulfur partial pressure may not exceed sulfur vapor pressure. This approach was used instead of thermodynamic properties of liquid sulfur and it assumed that the vapor pressure of pure sulfur is not influenced by presence of other components. The same principle can be used to extrapolate to other chemicals in the liquid phase when accurate thermodynamic properties are not available if they are not mixable.

The second modification is the calculation of frozen dew point and equilibrated dew point temperature of a sulfur-sulfur compound mixture after calculation of the equilibrium composition. The frozen dew point is the saturation temperature of sulfur in the mixture assuming the cooling process is so fast that the composition remains the same. The equilibrated dew point is the saturation temperature of sulfur in the mixture assuming the cooling process is slow enough for each species to reach equilibrium. This is accomplished through TDEW routine.

The third modification is changing the input data to accept molar free energy data in the form of standard heat of formation, standard enthalpy, standard entropy and least square coefficients of heat capacity functions.

Other modifications include changing variable dimensions for efficient use of storage during this sulfur system study. By changing dimensions the program can accomodate any number of species and any number of elements. The main problem then becomes the CPU time used. By minor modification certain features can be deleted when not needed e.g. dew point calculation, liquid sulfur at equilibrium calculation. To facilitate the analysis of effect of inerts and contaminants upon sour gas processing in a Claus plant, the programs for equilibrium calculation in the furnace and FREM are used separately.

ASSUMPTIONS

It is assumed that ideal gas equation of state PV=nRT is applicable. There are no solution effects, no interaction between species; only the main chemical reactions occur. The volume of the condensed phase is also neglected. It is believed that these assumptions will not affect the result much more than the error in thermodynamic data used to calculate conversions.

4. SENSITIVITY STUDY

4.1 Introduction

The main reactions in a Claus process are:

$$H_2S + 1.5O_2 \text{------>} SO_2 + H_2O \qquad (4.1)$$

$$H_2S + 0.5O_2 \text{------>} 1/\nu \; S_\nu + H_2O \qquad (4.2)$$

or combined to an overall reaction by eliminating oxygen,

$$2H_2S + SO_2 \text{<======>} 3/\nu \; S_\nu + 2H_2O \qquad (4.3)$$

where ν is the average atomic number of sulfur vapor.

Using reaction (4.3), predictions of equilibrium conversion (based upon selected thermodynamic properties published in literature) always seems to be lower than experimentally observed conversion.

Possible reasons for the discrepancy between predicted and observed conversions are:

1) effects which involved the reaction mechanism (surface chemistry) which purportedly shift the equilibrium limit toward increased conversion (39);
2) quality of thermodynamic data for H_2S, SO_2 and H_2O;
3) number of sulfur vapor (S_ν) species present, and quality of respective thermodynamic data.

4.2 Surface chemistry causing equilibrium discrepancy

From mechanistic studies of the Claus reaction, the discrepancy between the predicted and observed conversions may be a result of the non-equilibrium between the adsorbed and vapor sulfur species. This non-equilibrium can be caused by:

1) slow equilibration between sulfur species $S_2, S_3, \ldots S_8$ assuming the surface reaction on catalyst produces a single specie;
2) capillary condensation where no equilibration exists between S_2 formed on the surface and S_ν in the vapor phase. (39)

The earlier reason can be refuted by Fig. 3 where predicted conversions assuming only S_2, or S_6, or S_8 resulting in even lower conversion than when sulfur is a mixture of all three species.

4.3 Quality of thermodynamic data for H_2S, SO_2, and H_2O

In the free energy minimization method, each species contributes its free energy to the system free energy. This contribution is the product of the molar free energy and the stoichiometric number of moles of species. Therefore insignificant species have little effect on the resulting equilibrium conversion. By the same reasoning, inert species will not change the equilibrium conversion besides the dilution effect. As a result, only the thermodynamic properties of H_2S, SO_2 and $H_2O(g)$ will be surveyed in this section and those of the sulfur species in the next section as a basis for the study of the sensitivity of thermodynamic properties towards calculated equilibrium conversion.

4.3.1 Survey of the thermodynamic properties of H_2S, SO_2 and H_2O

A survey of eight different sources of thermodynamic properties from 1937 to 1971 reveals that the thermodynamic properties of H_2S, SO_2 and H_2O have been determined with the difference of only 115 cal/mole for standard heat of formation of H_2S, 0.47 cal/mole-K for standard entropy of H_2S, and 0.05 cal/mole-K for ideal heat capacity at 298 K of H_2S (Table 1). The same order of magnitude in the difference in cited values occurs for SO_2 and water vapor. Each of the cited values is within the uncertainty of the others (Table 2). The heat of formation is measured to the accuracy of ±150 cal/mole, the standard entropy ±0.01 cal/mole-K and ideal heat capacity to ±2.70 cal/mole-K.

4.3.2 Sensitivity of thermodynamic properties of H_2S, SO_2 and H_2O

Of the eight sources on Table 1, (78, 51, 105, 87, 79, 99, 73, 106) JANAF and McBride are the most recent, comprehensive sources. The thermodynamic properties for H_2S, SO_2 and H_2O from these sources are reasonably consistent with each other to within 2%. Since JANAF has a compilation table for S_8 and is the most recent (1974 addendum), it is used as a reference.

TABLE 1

THERMODYNAMIC PROPERTIES OF H2S, SO2 and H2O(g)

Source		H2S			SO2			H2O(g)		
		$\Delta H^0_{f,298}$ Kcal/mole	S^0_{298} cal/mole K	C^0_{p298} cal/mole K	$\Delta H^0_{f,298}$ Kcal/mole	S^0_{298} cal/mole K	C^0_{p298} cal/mole K	$\Delta H^0_{f,298}$ Kcal/mole	S^0_{298} cal/mole K	C^0_{p298} cal/mole K
Kelley, Bull 406	(1937)			8.14	-70.94		9.52			
Evans & Wagman	(1959)	20.24	49.57	8.19	-86.367	59.29	9.53			
NBS Cir. 500	(1952)	-4.815	49.15	8.19	-70.96	59.40	9.51	-57.7919	45.106	8.025
Kubaschewski	(1956)	-4.9	49.16	8.18	-70.95	59.25	9.54	-57.80	45.1	8.023
Kelley, Bull 477	(1950)		49.10			58.24			45.13	
McBride	(1963)	-4.820	49.163	8.183	-70.947	59.2967	9.529	-57.7979	45.106	8.025
NBS Tech-Note 270-3	(1968)	-4.93	49.16	8.18	-70.944	59.30	9.53	-57.796	45.104	8.025
Janaf, 2nd Ed.	(1971)	-4.88	49.151	8.172	-70.947	59.300	9.53	-57.7978	45.106	8.025

* Reference is S_1

TABLE 2

UNCERTAINTY OF THERMODYNAMIC PROPERTIES OF H2S, SO2 AND H2O(g)

Source		H2S			SO2			H2O(g)		
		$\Delta H^\circ_{f,298}$ cal/mole	S°_{298} cal/mole K	$C^\circ_{p,298}$ cal/mole K	$\Delta H^\circ_{f,298}$ cal/mole K	S°_{298} cal/mole K	$C^\circ_{p,298}$ cal/mole K	$\Delta H^\circ_{f,298}$ cal/mole K	S°_{298} cal/mole K	$C^\circ_{p,298}$ cal/mole K
Kelley, Bull 406	(1937)			2.7	* *		* *			
Evans & Wagman	(1959)	* *	* *	* *		* *	* *			
NBS Cir. 500	(1952)	* *	* *	* *	* *	* *	* *	* *	* *	* *
Kubaschewski	(1956)	100	0.1	1.5	100	0.1	1.5	10	0.03	1.5%
Kelley, Bull 477	(1950)		0.1			0.1			0.03	
McBride	(1963)	100	* *	* *	* *	* *	* *	* *	* *	* *
NBS Tech-Note 270-3	(1968)	* *	* *	* *	* *	* *	* *	* *	* *	* *
JANAF, 2nd Ed.	(1971)	150	0.1	* *	50	0.02	* *	* *	* *	* *

* * Uncertainty is not cited

In order to achieve a better understanding of the effect of the magnitude of the thermodynamic properties on calculated conversion, a sensitivity study was performed using the standard heats of formation, entropy and heat capacity of H_2S, SO_2, and water vapor. The effect of sulfur thermodynamic properties will be discussed in the next section.

The reference conversion is the conversion at a temperature using the thermodynamic properties from JANAF and Lee (73, 89) assuming sulfur exists as S_2, S_6 and S_8 only. The compositon of the initial mixture is 3%H_2S, 1.5%SO_2 and 95.5%N_2. For this composition, Cho's (32) experimental conversion at 700 K is 0.880, compared to the reference conversion of 0.687, 78% of Cho's experimental conversion.

4.3.2.1 Effect of standard heat of formation

For hydrogen sulfide, the standard heat of formation from JANAF (74) (the reference heat of formation for H_2S) is −4880 cal/mole. The uncertainty cited by JANAF is 150 cal/mole (Table 2). The range of heats of formation for H_2S is 0.97 to 1.02 of the reference value (Table 3); the lower value from Evans and Wagman (52) (146 cal/mole less than the reference value) and the higher value from more recent NBS, Circular No. 500 (107) (or an increase in absolute standard heat of formation of 97.6 cal/mole).

It is observed that the standard heat of formation of hydrogen sulfide should be larger for higher conversion (Fig. 4); since H_2S is a reactant, the larger its heat of formation, the larger the molar free energy, the smaller the number of moles in order to decrease the total system free energy.

Sensitivity analysis of the effect of standard heat of formation of hydrogen sulfide is studied by plotting the ratio of the standard heat of formation to the reference heat of formation vs the ratio of corresponding conversion and reference conversion (Fig. 5). The effect of standard heat of formation of hydrogen sulfide upon equilibrium conversion is approximately linear. At 0.97 of the reference standard heat of formation (the lowest cited value) the calculated conversion is 0.748 (85% of the experimental observed conversion). Therefore it is safe to conclude that standard heat of formation of hydrogen sulfide is not the prime reason for the discrepancy between calculated and observed conversion.

TABLE 3

RANGE OF THERMODYNAMIC PROPERTIES

OF H2S, SO2 AND H2O(g)

standard heat of formation				
specie	$\Delta H^{\circ}_{f,298}$ (cal/mole)	range	$\Delta(\Delta H^{\circ}_{f,298})$ (cal/mole)	
H2S	-4820	0.97 - 1.02	-145	+96.4
SO2	-70940	0.99 - 1.22	-709.4	+15,607
H2O	-57797.9	0.99 - 1.03	-578	+1734
standard entropy				
specie	S°_{298} (cal/mole-K)	range	$\Delta(S^{\circ}_{298})$ (cal/mole-K)	
H2S	49.151	1.00 - 1.008	-0.051	+0.419
SO2	59.300	0.999 - 1.001	-0.060	+0.100
H2O	45.106	1.00 - 1.000	-0.006	+0.024

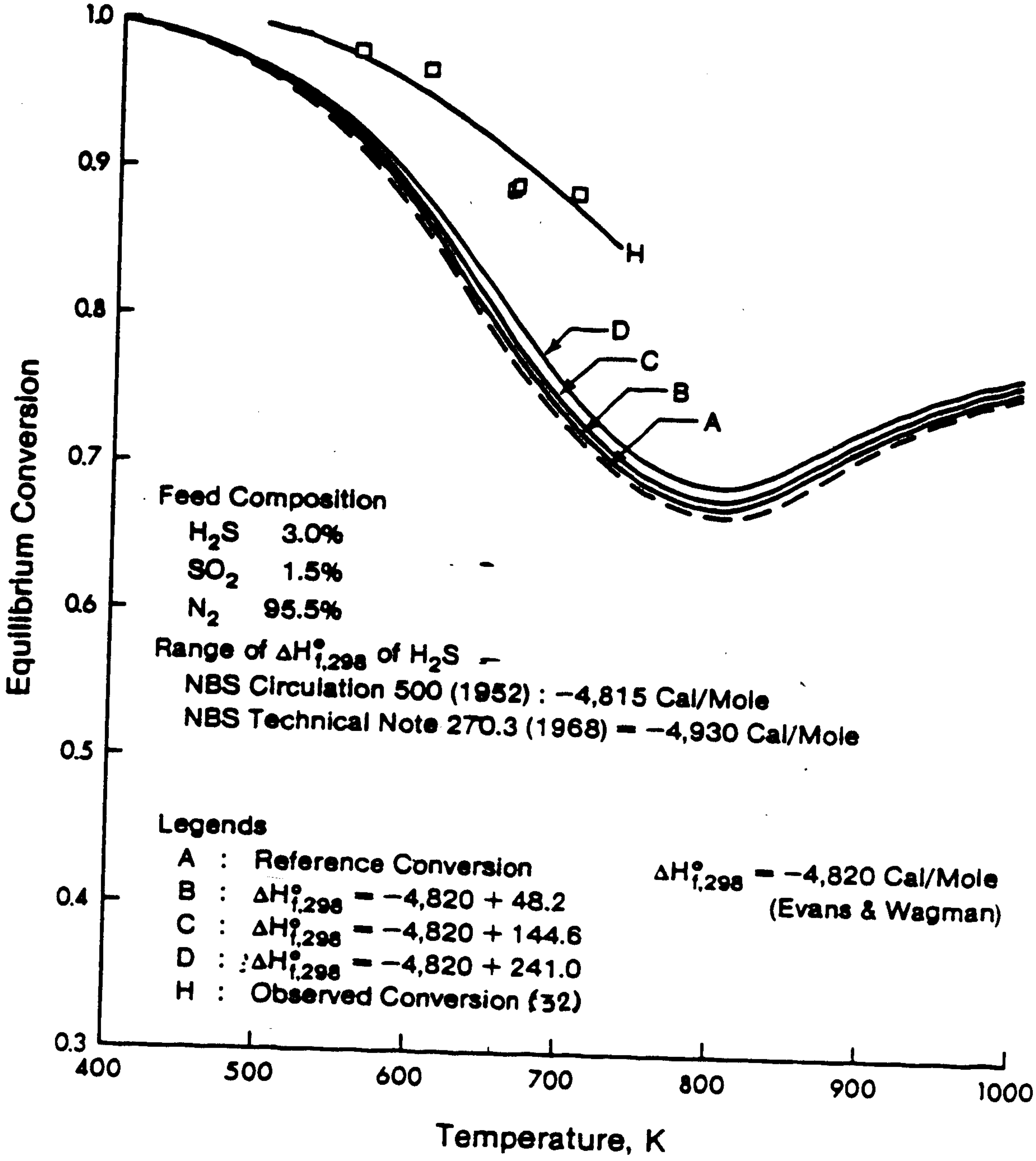


Fig. 4 Effect of $\Delta H^\circ_{f,298}$ of H_2S on Predicted Conversion.

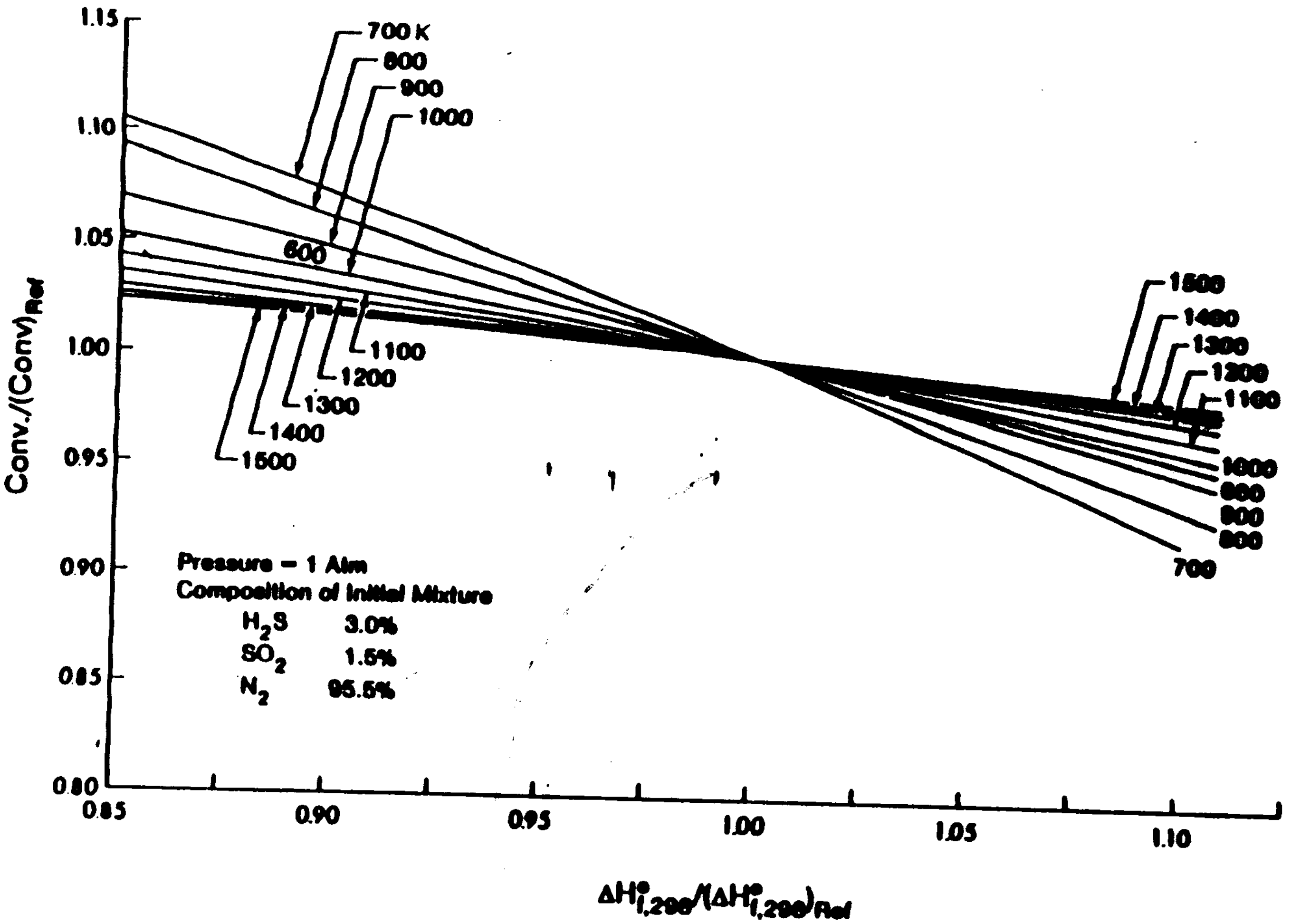


Fig. 5 Sensitivity Analysis $\Delta H^\circ_{f,298}$ of H_2S on Equilibrium Conversion.

The standard heat of formation for sulfur dioxide from JANAF is −70497 cal/mole ±50 cal/mole. The range of heat of formation for SO_2 is 0.99 to 1.22 of the JANAF value or a change of 709.4 cal/mole to −15607 cal/mole (Table 3). The lowest value is obtained from NBS, Circular 500 (107). The highest value (−86367 cal/mole) is from Evans and Wagman in 1952 (52) which was calculated from the heat of combustion of H_2S by Zeuner and Roth (153), the heat of formation of H_2S and of water vapor. Two other methods were used, the average value is reported. The uncertainty in this value is unknown and may be large.

Similiar to the effect of standard heat of formation of H_2S upon equilibrium conversion, the standard heat of formation of SO_2 should be smaller in absolute value for higher conversion (Fig. 6). Sensitivity analysis of the effect of standard heat of formation of sulfur dioxide is shown in Fig. 7. Similar effect to the effect of standard heat of formation of H_2S is observed. However due to the large negative value of sulfur dioxide standard heat of formation (−70497 cal/mole vs −4820 cal/mole for H_2S), the effect of sulfur dioxide heat of formation is more pronounced as shown on this kind of graph. At 93.8% reference standard heat of formation of SO_2, i.e. corresponding to a decrease of 4397 cal/mole. in standard heat of formation of sulfur dioxide, the conversion equals the actual observed conversion. Note that 4397 cal/mole decrease in the standard heat of formation of SO_2 is an unlikely error compared to the cited error of ±50 cal/mole and the classical method used to derive the reference standard heat of formation.

On the other hand, for water vapor, the smaller the standard heat of formation, the higher the calculated equilibrium conversion (Fig. 8) which would be expected. Since water vapor is a product of the reaction, the smaller the heat of formation (the larger the absolute value since standard heat of formation of water vapor is negative), the smaller the molar free energy; Thus the larger the number of moles of water vapor formed. Fig. 9 shows the effect of the standard heat of formation of water vapor on equilibrium conversion. The calculated conversion is equal to the observed conversion. when standard heat of formation of water vapor equals 1.041 reference value i.e. 2370 cal/mole increase in absolute value. Again this is an unlikely error compared to the range of literature value 0.99 to 1.03 of JANAF value (Table 3) i.e. corresponding to

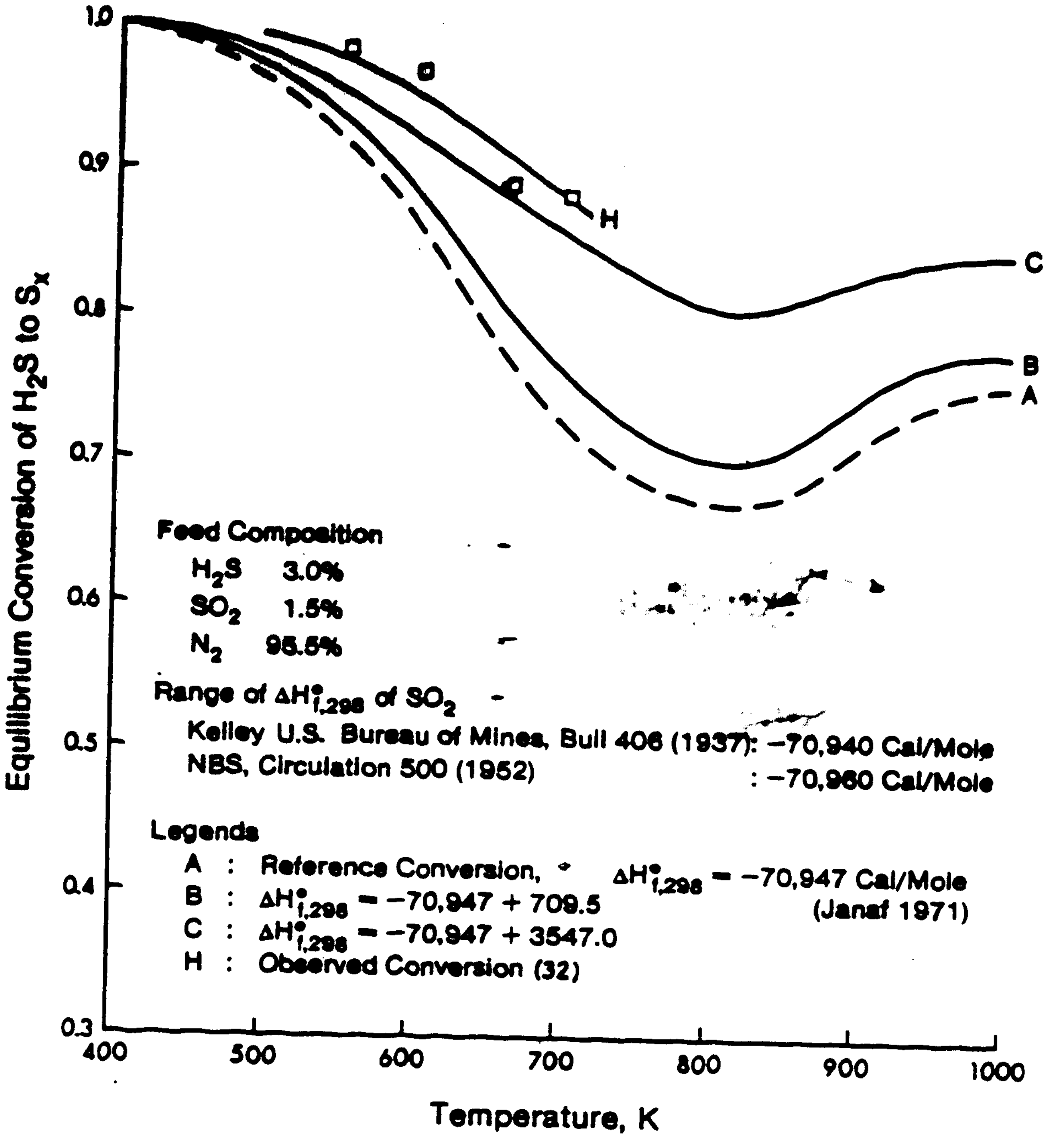


Fig. 6 Effect of $\Delta H^\circ_{f,298}$ of SO_2 on Predicted Conversion.

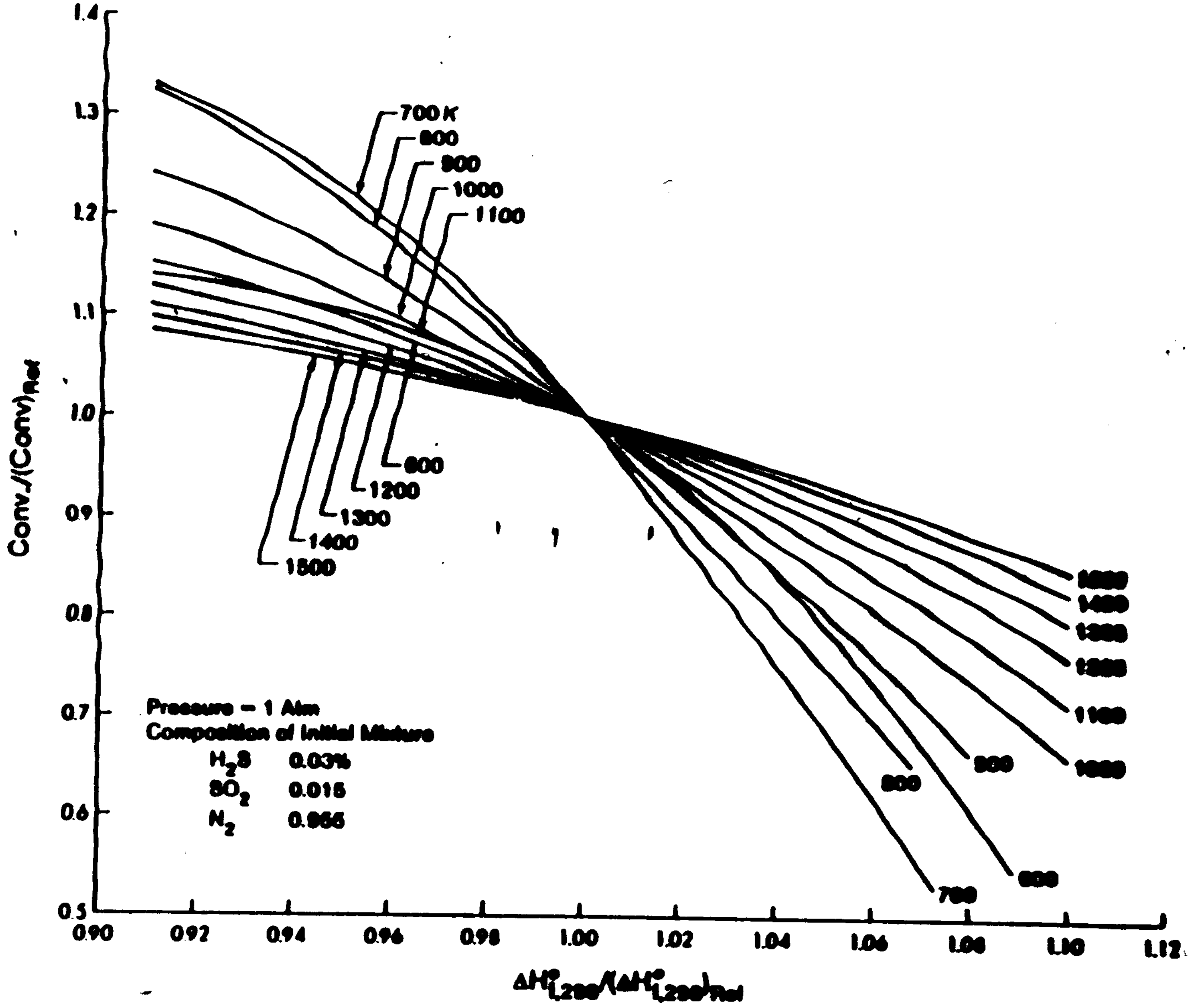


Fig. 7 Sensitivity Analysis of $\Delta H^{\circ}_{f,298}$ of SO_2 on Equilibrium Conversion.

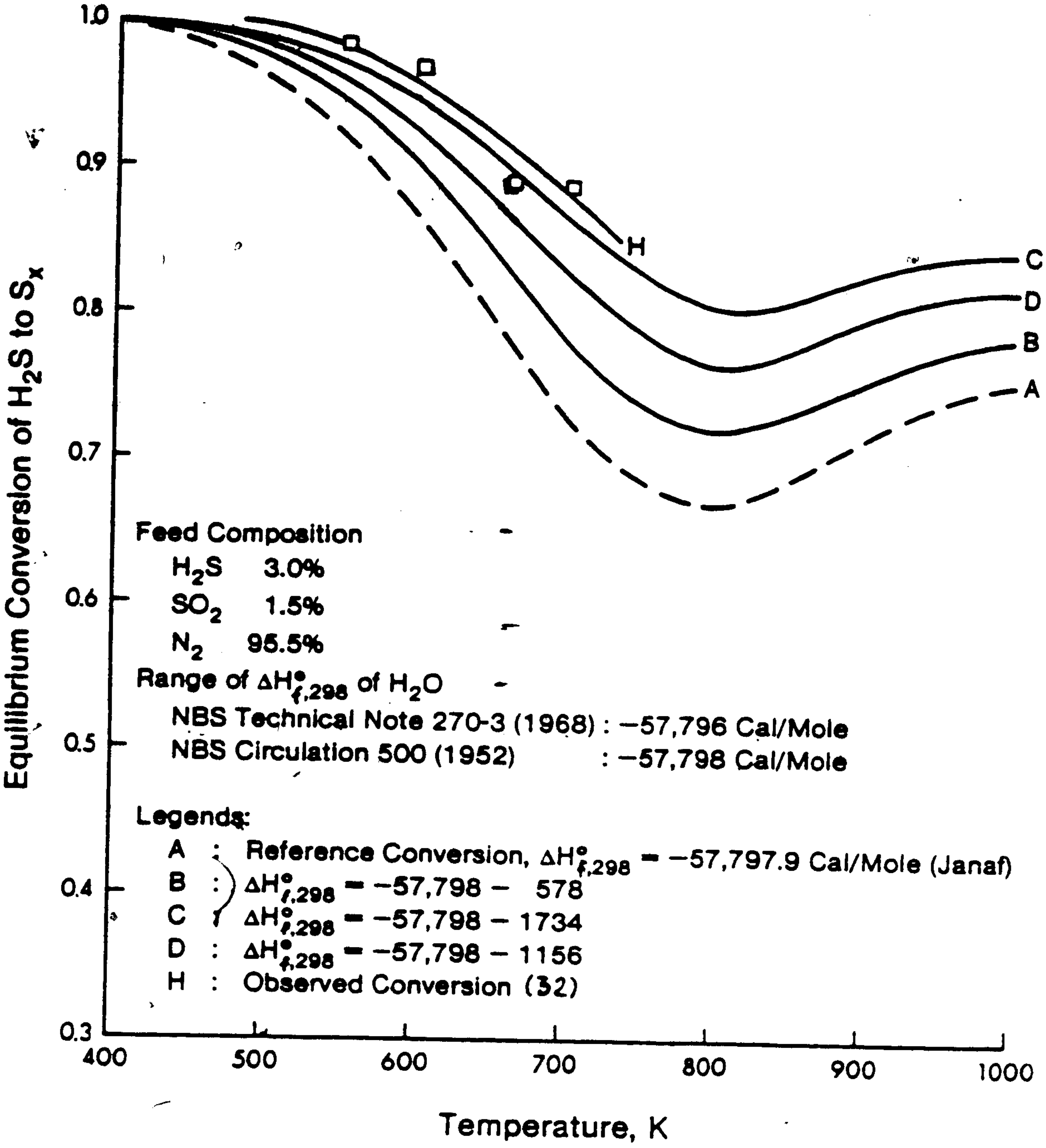


Fig. 8 Effect of $\Delta H^\circ_{f,298}$ of H_2O on Predicted Conversion.

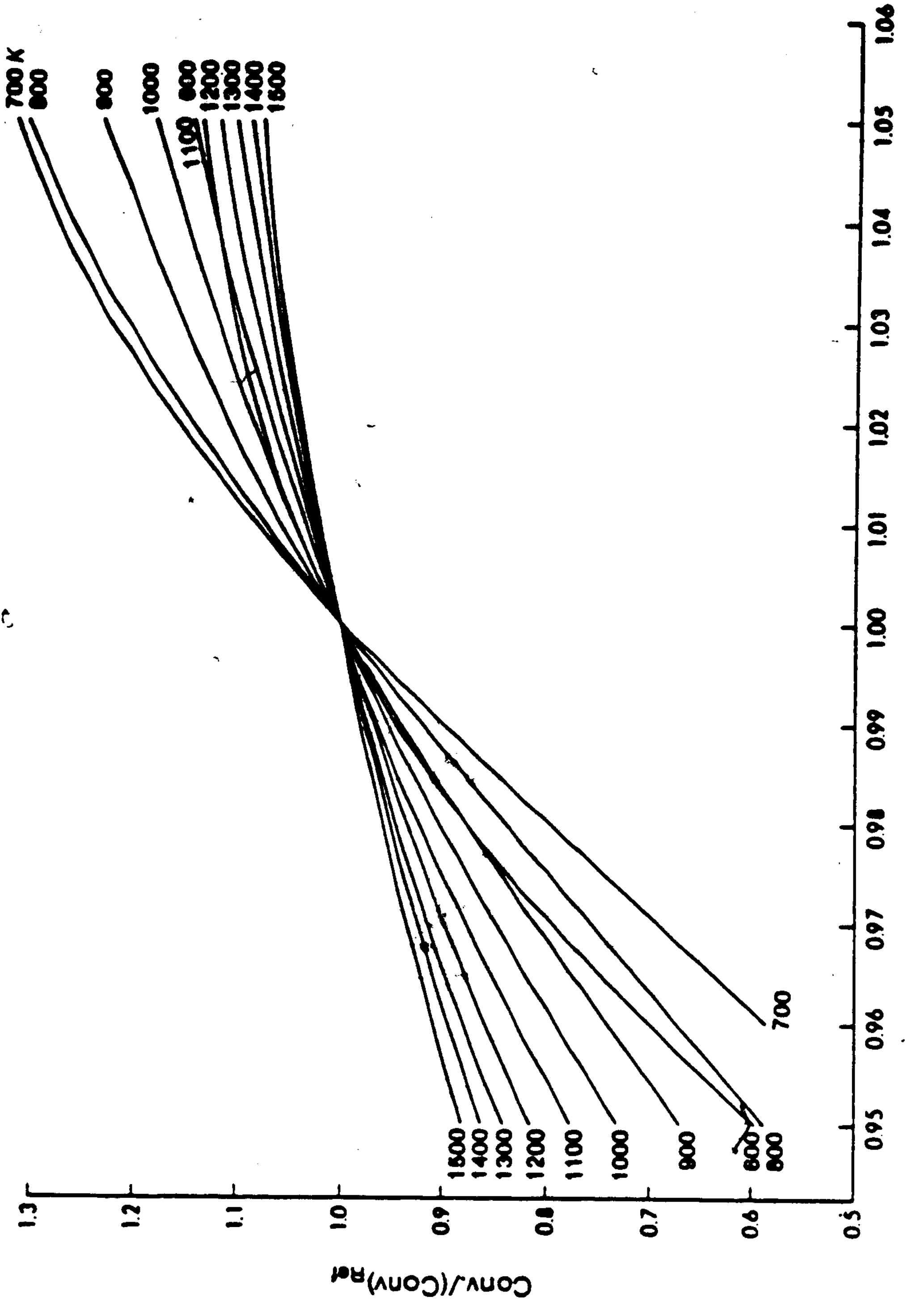


Fig. 9 Sensitivity Analysis of $\Delta H^\circ_{f,298}$ of H_2O on Equilibrium Conversion.

the difference in the cited values of +578 cal/mole to −1734 cal/mole from the reference value, as well as the cited uncertainty (±50 cal/mole) and the classical method used to derive at the reference standard heat of formation of water vapor. The lowest cited value (−51560 cal/mole) is from NBS, Circular 500 published in 1952 (107) and the highest value (−57800 cal/mole) is from Kubaschewski in 1967 (88) who gave as reference the same source (107). The most popular value −57797.9 cal/mole from JANAF (74) was used as reference standard heat of formation for water vapor. The influence of standard heat of formation of H_2S, SO_2 and water vapor on equilibrium conversation over the whole temperature range is illustrated in Fig. 10 where heat of formation for H_2S, SO_2 and water vapor is changed to the smallest cited value. Water is most sensitive to the equilibrium conversion.

4.3.2.2 Effect of standard entropy

Secondly the entropy of each species was varied; the same approach used with heats of formation was employed. A similar discussion results (Fig. 11) except that the effect of the entropy is more pronounced. In the calculation for free energy, F^0, the change in standard entropy S^0_{298} is not divided by temperature as is the change in standard heat of formation $\Delta H^0_{f,298}$:

$$F^0/RT = (\Delta H^0_{f,298})/RT - (S^0_T/R) \tag{4.4}$$

For hydrogen sulfide, the actual conversion is predicted if the molar standard entropy was 0.938 of the reference value or a decrease of 3.05 cal/mole-K (a large change compared to the uncertainty in the reference value of ±0.1 cal/mole) (Fig. 12). Again no sources cite as low a value as 46.10 cal/mole-K (i.e. 0.938 the reference value.) For water vapor, the standard molar entropy has to be 47.812 cal/mole-K or 1.06 of the reference value to predict the actual conversion, again an unlikely value (Fig. 13). For sulfur dioxide, the standard entropy should decrease even lower than 0.9 of the reference value to predict the observed equilibrium conversion (Fig. 14)

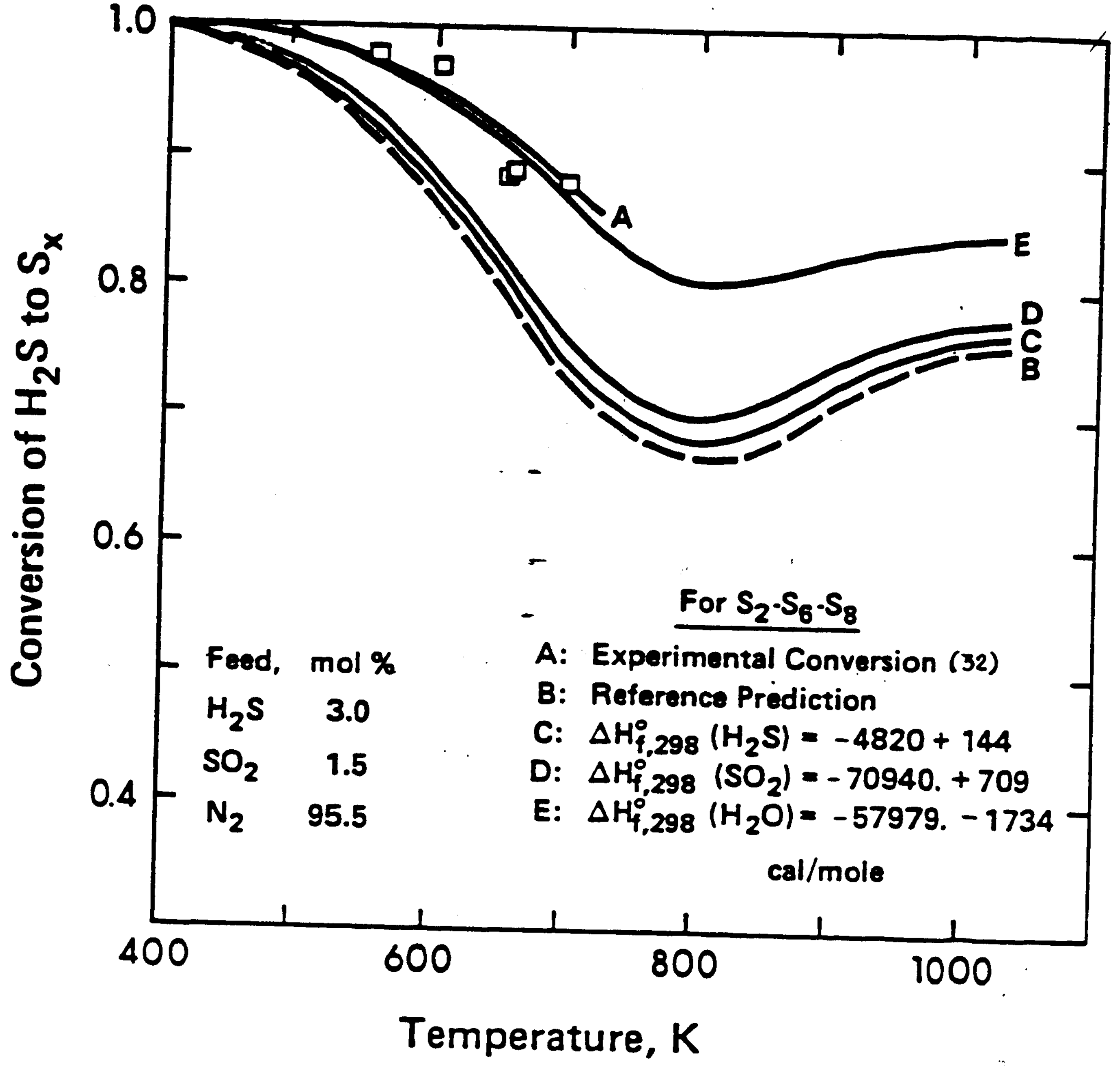


Fig. 10 Sensitivity Analysis of Standard Heat of Formation of H_2S, SO_2, H_2O

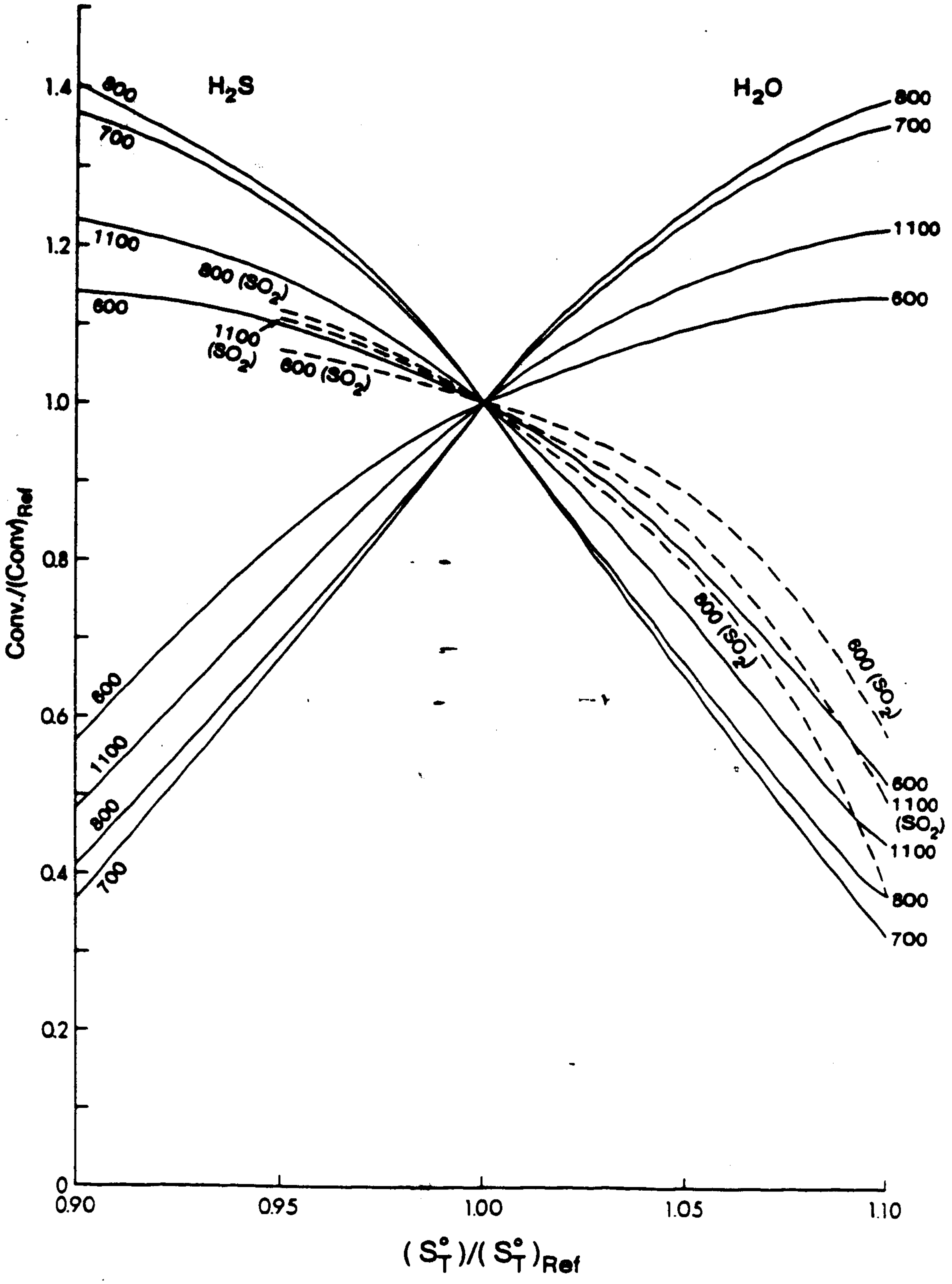


Fig. 11 Effect of Entropy of H_2S and of H_2O and SO_2

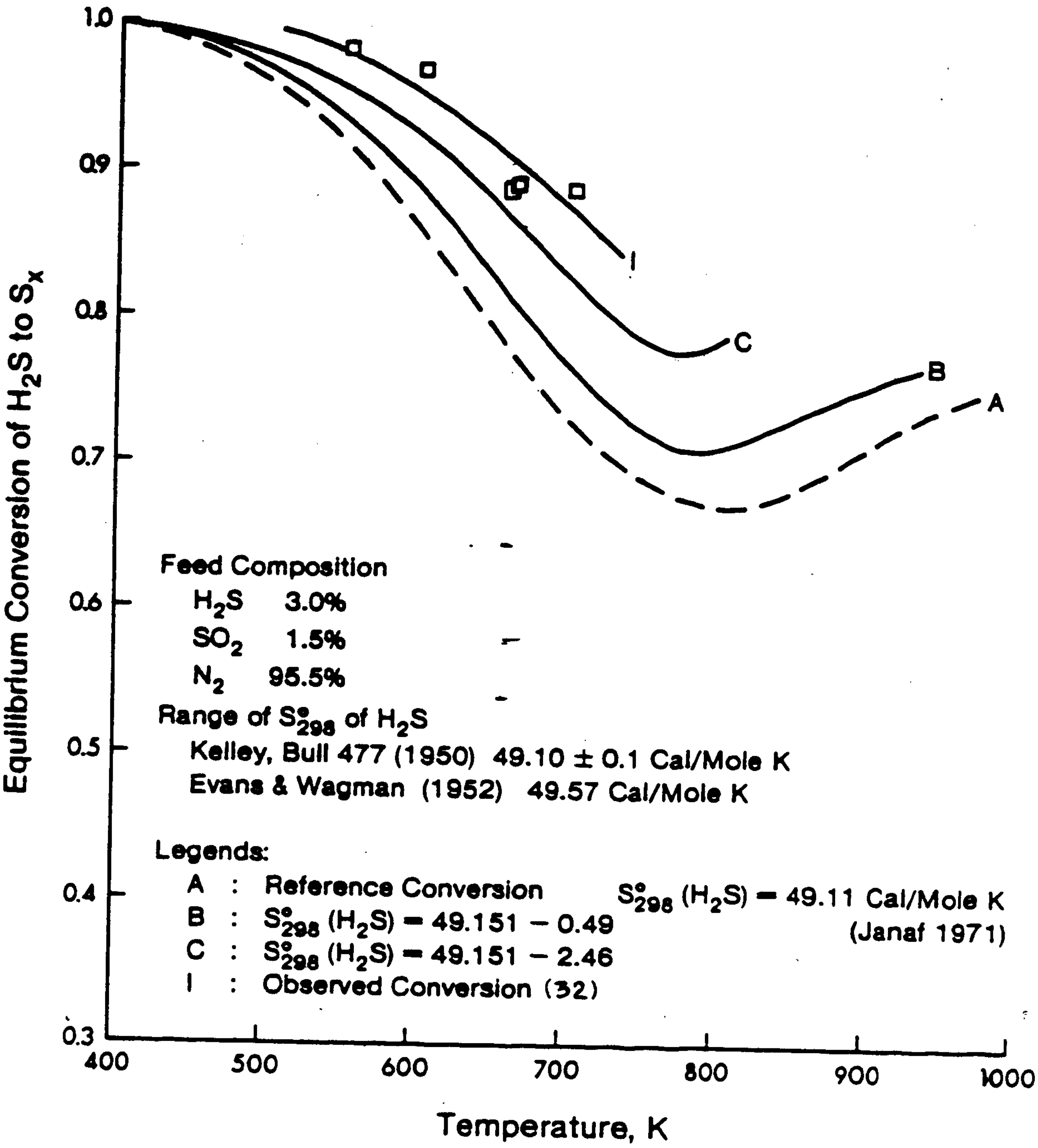


Fig. 12 Effect of S°_{298} of H_2S on Predicted Conversion.

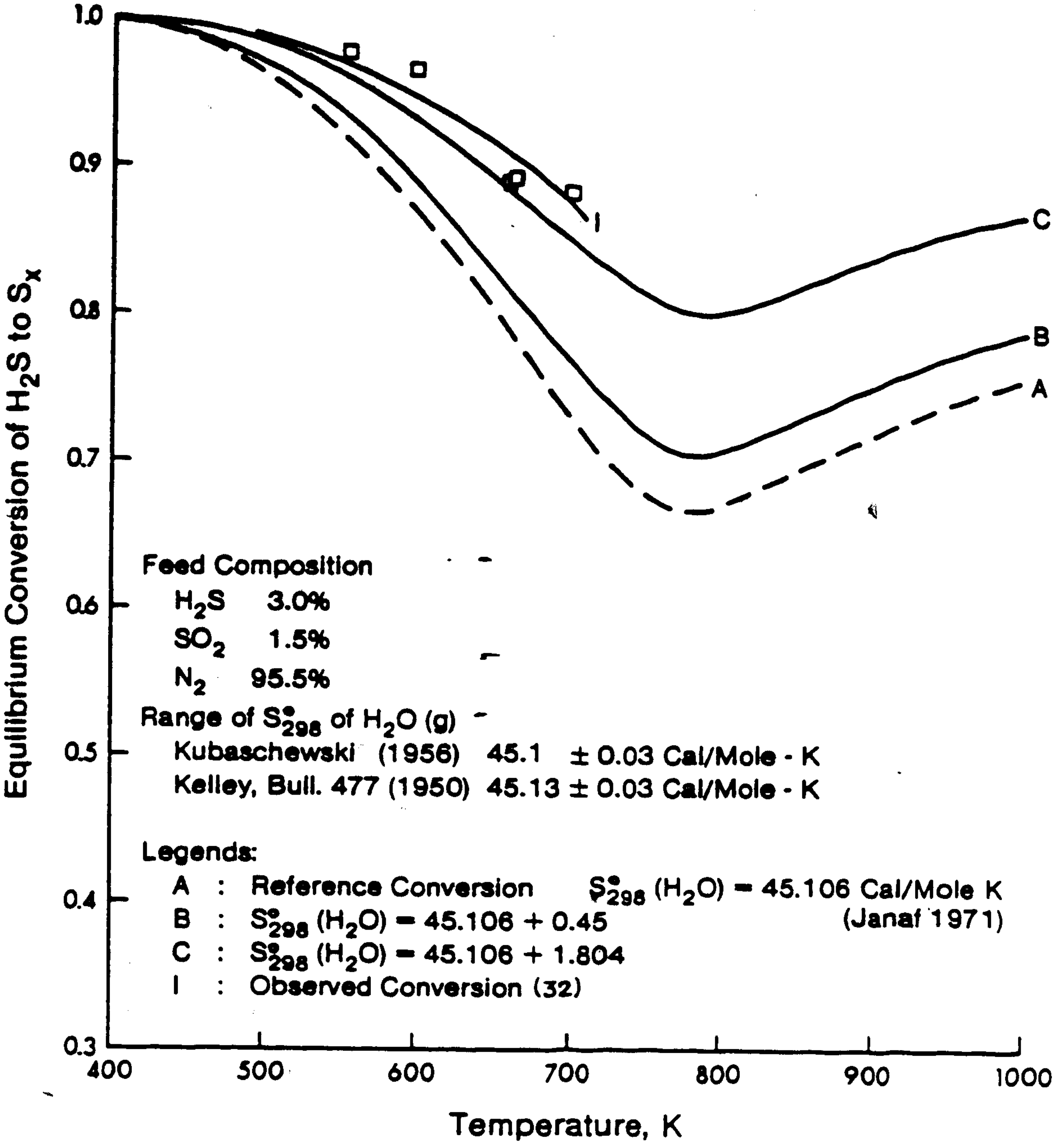


Fig. 13 Effect of S°_{298} of H_2O (g) on Predicted Conversion.

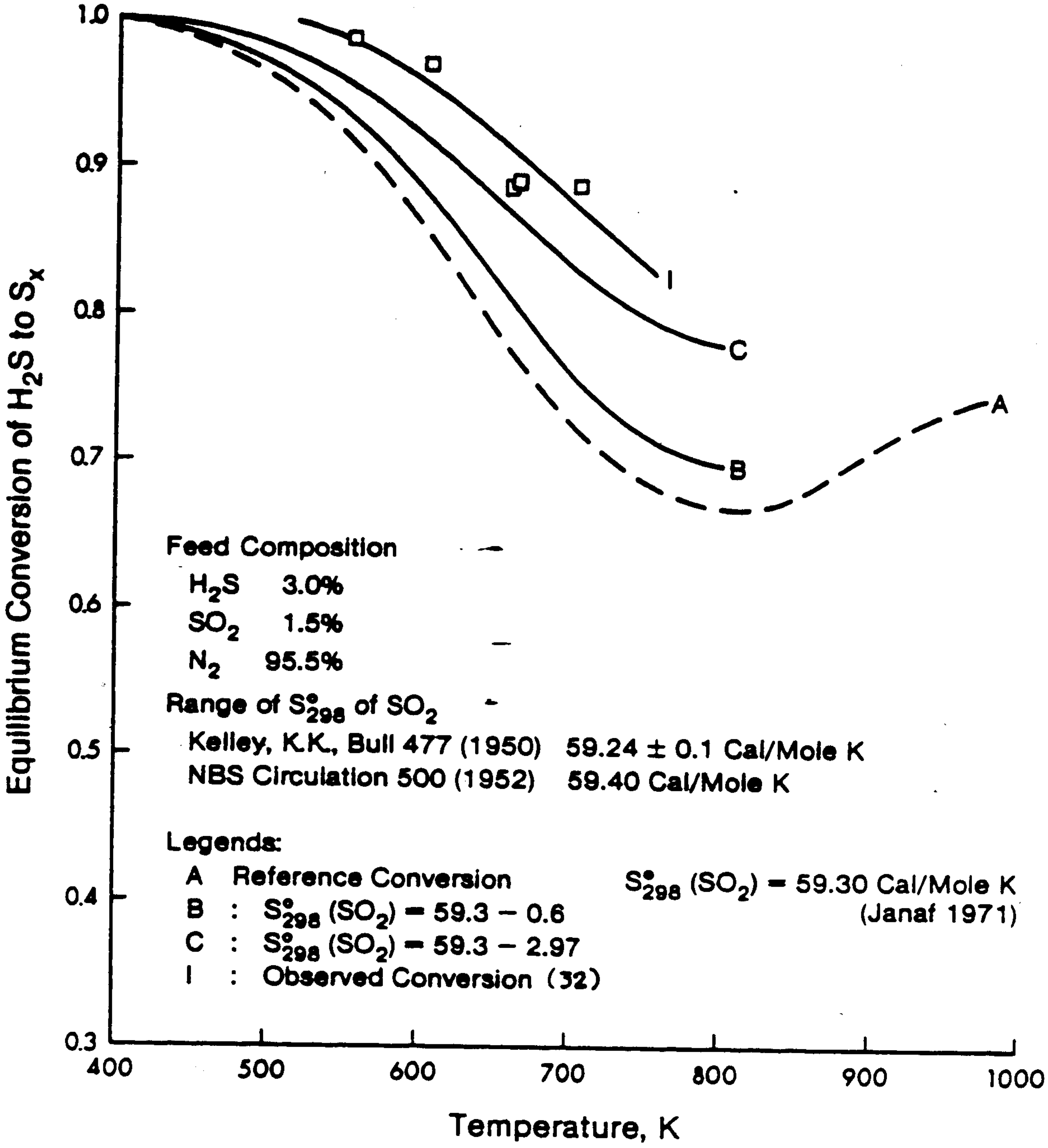


Fig. 14 Effect of S°_{298} of SO_2 on Predicted Conversion

4.3.3 Conclusion

Therefore to reconcile the observed equilibrium conversion, the thermodynamic properties of H_2S, SO_2 and $H_2O(g)$ need to be changed by rather large amounts resulting in values outside the expected range. From the survey, the thermodynamic properties of H_2S, SO_2 and $H_2O(g)$ have been well documented and determined with high accuracy through different methods. It is noted that the calculated equilibrium conversion is most sensitive to thermodynamic properties of water vapor. The sensitivity of sulfur properties will be investigated in the next section .

4.4 Sensitivity of sulfur thermodynamic properties

Sulfur vapor is known to be composed mostly of molecules of S_2 to S_8, existing in complex equilibrium whose composition changes with temperature and pressure. The thermodynamic properties of diatomic sulfur and octatomic sulfur have been determined with some accuracy at low pressure, using metallic sulfide vapor pressures. The second law of thermodynamics can be used with sulfur vapor pressure data to determine the thermodynamic properties of S_3 to S_7. However the accuracy depends on the rate of interconversion of sulfur species in the vapor phase. Both methods used to determine the thermodynamic properties of sulfur have their disadvantages. These result in large, difficult to estimate, uncertainties which may be the reason for the discrepancy between observed and calculated equilibrium conversion. Since sulfur vapor pressure data are the primary data used in determining sulfur thermodynamic properties, it is necessary to compare different sulfur vapor data before surveying the sulfur thermodynamic properties and their effects on equilibrium conversion.

4.4.1 Survey on sulfur vapor pressure

The role of sulfur vapor in resolving the discrepancy of equilibrium conversion of H_2S/SO_2 system is very crucial. It is as follows:

1) sulfur vapor pressures are used to determine the thermodynamic properties of sulfur species which will be used to calculate the equilibrium conversion. Therefore an inaccuracy in the measured vapor pressure will cause an error in calculated equilibrium conversion;

2) sulfur vapor pressure is used in the present free energy minimization method instead of the thermodynamic properties of liquid sulfur which itself is a complex mixture of different type of sulfur molecules;

3) thermodynamic properties of sulfur species obtained by other means than these should also describe the sulfur vapor composition.

Therefore a survey of sulfur vapor pressure will be described here. Many sets of vapor pressure data have been collected since Regnault (1862) (130). Table 4 summarizes this survey.

Baker (4) fitted his data over the range of 663−1073 K

$$\log P(\text{atm.}) = 6.00282 - 3584.42/T - 2.23934\times10^{-3}T + 1.14662\times10^{-6}T^2 \qquad (4.5)$$

Maximum percentage error = 2.00

Maximum deviation = 0.3 atm.

Above 1073 K, the following equation describes Rau's data(125):

$$\log Pr = -A(1-Tr)/Tr - 10^{-1.68(T_r-1)^2} \qquad (4.6)$$

$A = 16.25 - 73.85(Zc) + 90(Zc)^2$

$b = 1.80 - 6.20(Zc)$

$Zc = 0.263$

$Tc = 1313$ K

$Pc = 179.7$ atm.

At temperatures below 573 K where there is large deviation from one source to another, West and Menzies' (149) data are the most "consistent" data i.e. there is no obvious irregularity in ln P vs 1/T (Table 4 and Fig. 1). From 373−573 K, West suggested the equation for vapor pressure:

$$\log P(\text{atm}) = 6.04892 - 4087.8/T \qquad (4.7)$$

This equation is ± 10% error from experimental data.

Kelley (1935) (78) fitted these data for the entire range and derived a more complex equation,

$$\log P\ (\text{atm}) = -4940/T - 4.08\times10^{-3}T + 9.811 \qquad (4.8)$$

Again the equation describes data within 10% error. However Mathies' (1906) (100) data indicated a curve and deviated from West and Menzies' data at low temperatures (149).

TABLE 4

SURVEY ON SULFUR VAPOR PRESSURE

Researcher	Temp Range (K)	Date of Publication	Reference
West & Menzies	448.84 - 816.24	1929	(149)
Baker	613.66 - 825.66	1962	(4)
Mathies	483.36 - 652.56	1906	(99)
Rau	823.16 - 1273.16	1973	(126)
Regnault	660.16 - 827.16	1862	(130)
Berkowitz	623.16 - 373.16	1963	(14)
Fouretier	293.16 - 353.16	1944	(53)
Taillade	308.16 - 353.16	1944	(136)
Preuner & Schupp	317.16 - 393.16	1909	(122)

Preuner and Schupp's data deviate much from other sources at high temperatures (Fig. 1). As expected from the complexity of sulfur vapor species equilibrium the data are scattered in the intermediate range as illustrated in Fig. 1.

In the absence of a criterion to favor one set of data over another, the vapor pressure data were fitted by a least squares program.

At high temperatures, above 573 K, vapor pressure follows the Van't Hoff equation. The linear least square program yields the following coefficients (equal weight for each data point):

$$\log P(\text{mm Hg}) = -3518.93/T + 7.71284 \tag{4.9}$$

Variance = 0.001551

Standard deviation = 0.039389

Maximum percentage error = 3.45

Maximum deviation = 1.26 mm Hg

At low temperatures, below 573 K, the Biot equation gives a better fit than any straight line. The Rosenbrock method was used to minimize the variance:

$$\log P\ (\text{mm Hg}) = 6.46543 - 7.63591(0.9983)^{t+20} - 6.936946(0.9908)^{t+20} \tag{4.10}$$

where temperature t is in degree Celsius.

Variance = 0.0056

Maximum deviation = 1.43 mm Hg

Maximum percentage deviation = 4.8%

4.4.2 Survey on simplified models for sulfur vapor pressure

Sulfur vapor is a complex mixture of homologous species. Neither the composition nor the identification of the species have been determined with certainty. Since there is a lack of concrete data, many researchers have used a simplified model. Preuner and Schupp were the first to introduce a model composed of S_2, S_6, and S_8 for the range of temperatures 300-800°C and pressure 7.5-1182 mm Hg. Later Braun et al. (19) disregarded this model and introduced S_4 into the vapor. Their reasoning is based on the agreement with the Van't Hoff equation of the temperature dependency of the equilibrium constants for the formation of the S_i from diatomic sulfur. This argument will be tested here by using the Rosenbrock method of data fitting, and criterion of minimum standard deviation of sulfur average atomic number to obtain the best model, which in turn will be used to calculate the equilibrium conversion of H_2S/SO_2 system.

The test is done as follows: the percentage deviation of average atomic number is calculated using Braun's original equilibrium constants for the association of S_2 to S_4, S_6, S_8. The percentage deviation is calculated using Braun's original equilibrium constants for the association of S_2 to S_4, S_6, S_8. The percentage deviation is 0.1 to 22.48%. The fitting is better at low temperature isotherms than higher temperature ones.This deviation is much larger than the error cited in the paper as attributed to experimental error (2%). The Rosenbrock hill climbing technique is then used to find more accurate equilibrium constants using the same sulfur vapor model $S_2-S_4-S_6-S_8$.

The objective function is

$$\Phi = \sum_i^n (\nu_{exp} - \nu_{cal})^2/N \tag{4.11}$$

where

$$\nu_{cal} = \frac{(2Ns_2+4Ns_4+6Ns_6+8Ns_8)}{Ns_2+Ns_4+Ns_6+Ns_8}$$

but $Ns_2/\sum_i^n Ns_i = P_2/\pi$

$Ns_4/\sum_i^n Ns_i = P_4/\pi$

however from reaction $2S_2=S_4$, $K_4=P_4/P_2^2$

therefore $Ns_4/\sum_i^n Ns_i = P_2^2K_4/\pi$

Similar for Ns_6 and Ns_8:

$$Ns_6/\sum_i^n Ns_i = P_2^3K_6/\pi$$

$$Ns_8/\sum_i^n Ns_i = P_2^4K_8/\pi$$

therefore

$$\nu_{cal} = (2P_2 + 4P_2^2K_4 + 6P_2^3K_6 + 8P_2^4K_8)/\pi \tag{4.12}$$

N = total data points

ν_{cal}= calculated average atomic number

ν_{exp}=experimental average atomic number

ν_{exp} can be calculated from average molecular weight of sulfur vapor which derived from measured density:

ν_{exp}=average sulfur molecular weight/ atomic weight of sulfur

π = total pressure in atm. from experiment

P_2 = partial pressure of S_2 in atm. obtained from the following equation

$$P_2 + P_2^2K_4 + P_2^3K_6 + P_2^4K_8 = \pi \qquad (4.13)$$

which is a derivation of Dalton's law: total pressure is the sum of the partial pressures

$$P_2 + P_4 + P_6 + P_8 = \pi$$

and the definitions of K_4, K_6, K_8 are employed.

Since equilibrium constants are functions of temperature, each isotherm was fitted separately. Table 5 shows the final K values, their variances, their average deviation, and the relative compositions of S_2, S_4, S_6 and S_8.

The resulting values of K_6, K_8 as fitted do not follow the Van't Hoff equation (Fig. 15). The reasons for this might be:

1) Heats of vaporization of S_4, S_6 and S_8 are not constant as assumed in Van't Hoff equation.

2) Other sulfur species occur in significant amounts e.g. S_7 (31).

The original assumption of sulfur vapor being composed of S_2, S_6 and S_8 is used with Preuner and Schupp's equilibrium constants (122) as the initial guess for Rosenbrock fitting of K_2, K_4, K_6, K_8 at various temperatures. The resulting equilibrium constants fit the straight line of Van't Hoff equation better (standard deviation is 3.2%) (Table 6)

$\log K_6 = -14525.33/4.58\,T + 21.888$,std. dev. = 2.32% (4.14)

$\log K_8 = -21617.65/T + 33.294$,std. dev. = 3.33% (4.15)

thus Braun's argument for the inclusion of S_4 is invalid as shown in Fig. 15.

Table 6 gives the values of equilibrium constants and the goodness of fit for 12 isotherms from Braun's data. Again the log K vs 1/T curves were not straight lines (Fig. 15.) Log K_6 seems to follow two straight lines, one for high temperatures and one for low temperatures. The goodness of fit of the K values from the 6 lower isotherms from the linear least square model is less than for the previous model.

It is concluded that for Braun's data on vapor pressure of sulfur (19), neither model is the better. At low temperatures (<900 K, substmospheric pressure) where S_4 is insignificant compared to the S_6, the S_2−S_6−S_8 model is adequate. Therefore in the next section only the thermodynamic properties of S_2, S_6 and S_8 are surveyed and the sulfur vapor will be considered to consist of S_2, S_6 and S_8.

TABLE 5

EQUILIBRIUM CONSTANTS USING ROSENBROCK METHOD

T (K)	K4	K6	K8	J	Variance	%	Relative Composition
623.16	0.42	0.24	0.13	7.05	$1.11 \cdot 10^{-3}$ (±0.03)	0.03 - 0.79	P8 > P6 > P4 > P2
673.16	2.17	2.54	6.21	6.768	$1.6 \cdot 10^{-3}$ (±0.04)	0.6 - 1.18	P8 > P6 > P4 > P2
773.16	$1.04 \cdot 10^{4}$	$7.13 \cdot 10^{3}$	$5.05 \cdot 10^{4}$	5.287	$8.70 \cdot 10^{-4}$ (±0.03)	0.09 - 1.48	P2 > P6 > P8 > P4
823.16	$2.32 \cdot 10^{2}$	$8.50 \cdot 10^{4}$	$1.93 \cdot 10^{6}$	4.30	$9.17 \cdot 10^{-4}$ (±0.03)	0.09 - 2.06	P2 > P6 > P8 > P4
873.16	$6.31 \cdot 10^{2}$	$1.02 \cdot 10^{5}$	$4.87 \cdot 10^{7}$	3.39	$1.79 \cdot 10^{-3}$ (±0.04)	0.03 - 2.09	P2 > P6 > P8 > P4
923.16	$1.66 \cdot 10^{5}$	$7.33 \cdot 10^{5}$	$8.65 \cdot 10^{9}$	2.69	$7.88 \cdot 10^{-4}$ (±0.03)	0.18 - 1.85	P2 > P4 > P6 > P8
1023.16	$6.59 \cdot 10^{3}$	$2.29 \cdot 10^{7}$	$1.17 \cdot 10^{11}$	2.14	$1.48 \cdot 10^{-4}$ (±0.01)	0.09 - 1.43	P2 > P4 > P6 > P8
1078.16	$1.20 \cdot 10^{4}$	$9.89 \cdot 10^{7}$	$9.71 \cdot 10^{11}$	2.08	$2.05 \cdot 10^{-4}$ (±0.01)	2.06 - 1.32	P2 > P4 > P6 > P8
1123.16	$2.06 \cdot 10^{4}$	$3.74 \cdot 10^{8}$	$6.65 \cdot 10^{12}$	2.05	$2.21 \cdot 10^{-4}$ (±0.01)	0.15 - 1.28	P2 > P4 > P6 > P8
1273.16	$9.51 \cdot 10^{4}$	$1.08 \cdot 10^{10}$	$8.64 \cdot 10^{12}$	2.01	$9.18 \cdot 10^{-4}$ (±0.01)	0.07 - 0.82	P2 > P4 > P6 > P8

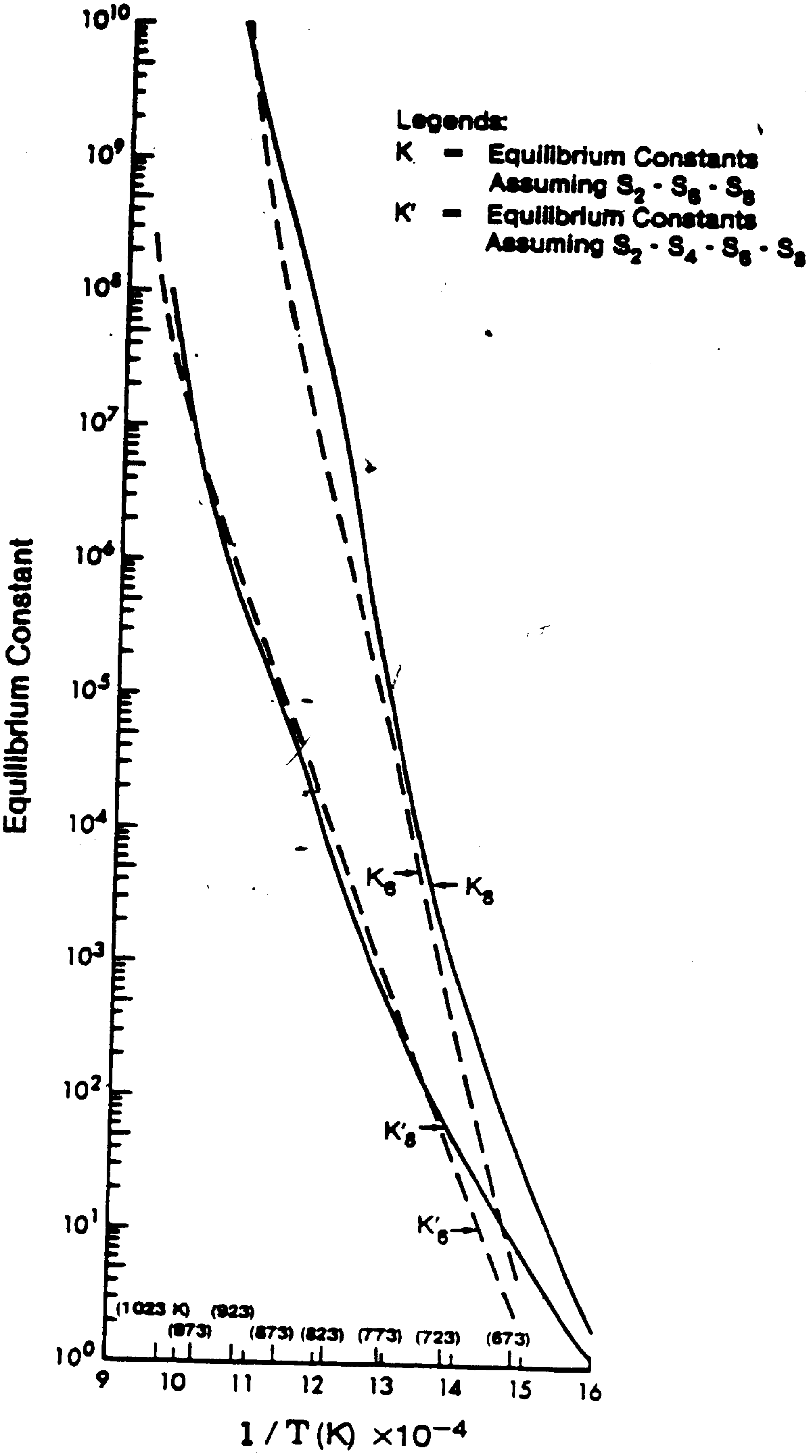


Fig. 15 K from Rosenbrock Fitting Method of Braun's Data.

TABLE 6

FITNESS OF BRAUN'S VAPOR PRESSURE

USING PREUNER's K VALUES

T	K6	K8	Ɔ	Variance	%	Relative Composition
623.16	0.037	3.8	7.05	$1.15 \cdot 10^{-2}$ (±0.14)	11.68 - 17.24	P6 > P8 > P2
673.16	2.0	14.7	6.768	$5.24 \cdot 10^{-2}$ (±0.22)	0.21 - 3.66	P6 > P8 > P2
723.16	70.0	$2.88 \cdot 10^{3}$	6.17	$7.46 \cdot 10^{-2}$ (±0.26)	3.30 - 5.22	P6 > P8 > P2
773.16	$1.35 \cdot 10^{3}$	$2.37 \cdot 10^{5}$	5.287	$1.10 \cdot 10^{-2}$ (±0.04)	4.54 - 10.77	P6 > P8 > P2
823.16	$1.8 \cdot 10^{4}$	$1.14 \cdot 10^{7}$	4.30	0.16 (±0.39)	5.48 - 15.71	P6 > P2 > P8
873.16	$1.7 \cdot 10^{5}$	$3.22 \cdot 10^{8}$	3.39	0.15 (±0.37)	6.70 - 13.21	P2 > P6 > P8
923.16	$1.35 \cdot 10^{6}$	$6.93 \cdot 10^{9}$	2.69	0.14 (±0.26)	7.16 - 14.83	P2 > P6 > P8
973.16	$9.17 \cdot 10^{6}$	$1.203 \cdot 10^{10}$	2.27	$5.28 \cdot 10^{-1}$ (±0.22)	4.46 - 12.79	P2 > P6 > P8
1023.16	$4.92 \cdot 10^{7}$	$1.834 \cdot 10^{12}$	2.14	$1.95 \cdot 10^{-2}$ (±0.13)	3.32 - 9.22	P2 > P6 > P8
1073.16	$2.25 \cdot 10^{8}$	$1.413 \cdot 10^{13}$	2.08	$7.02 \cdot 10^{-3}$ (±0.08)	2.33 - 5.57	P2 > P6 > P8
1123.16	$9 \cdot 10^{8}$	$1.1 \cdot 10^{14}$	2.05	$3.30 \cdot 10^{-3}$ (±0.05)	1.93 - 3.29	P2 > P6 > P8
1273.16	$3.01 \cdot 10^{10}$	$2.063 \cdot 10^{16}$	2.01	$1.32 \cdot 10^{-4}$ (±0.01)	0.001 - 0.99	P2 > P6 > P8

4.4.3 Survey on the thermodynamic properties of sulfur species

In the following review the thermodynamic properties of each species will be considered separately for easy comparison of the merits of each source. Consistency is taken care of by choosing ideal gases and rhombic sulfur at 298.16 K as the reference states.

There are two methods of calculating the thermodynamic properties of sulfur species,i.e. (1) by mass spectroscopy and (2) by vapor pressure measurement.

The mass spectrometer ionizes each sulfur species at a very low pressure (about 0.001 atm.) and the thermodynamic properties are determined by extrapolation to atmospheric pressure. Besides this questionable extrapolation, the problem is complicated by the fact that both the determination of the charged fragments of homologous species S_4, S_5, S_6, S_7, S_8 as well as of true vapor equilibrium are unreliable.

In the second method sulfur vapor pressure is measured as a function of temperature. Models for sulfur vapor pressure are assumed. The most prevalent models are $S_2-S_6-S_8$, $S_2-S_4-S_6-S_8$ and S_2 to S_8. Either the second or third law of thermodynamics is then used to determine the corresponding thermodynamic properties for each species. The accuracy of this method depends on the reality of the model and the accuracy of the measured vapor pressure over the whole temperature range, which is difficult to satisfy, especially in the intermediate region 555-717 K, as shown in Fig. 1.

The standard entropy at 298 K and the heat capacity are usually calculated from the same spectroscopic data; therefore the data sources and method of calculation will not be repeated in the heat capacity section.

A large discrepancy occurs between the reported thermodynamic properties of sulfur species from different sources in the literature (Table 7) (79, 52, 64, 76, 14, 46, 108, 74, 126). As expected the uncertainty is also higher than those of H_2S, SO_2, and water vapor discussed in previous sections (Table 8). Attempts have been made to follow through the assumptions and sources of primary data or other experimental heat data. The values will be chosen on the soundness of assumptions and the most accurate data available, not on the effect of each value on the equilibrium conversion of H_2S/SO_2 to sulfur.

TABLE 7

THERMODYNAMIC PROPERTIES OF S2; S6; S8

Source		S2			S6			S8		
		$\Delta H^\circ_{f,298}$ Kcal/mole	S°_{298} cal/mole K	$C^\circ_{p,298}$ cal/mole K	$\Delta H^\circ_{f,298}$ Kcal/mole	S°_{298} cal/mole K	$C^\circ_{p,298}$ cal/mole K	$\Delta H^\circ_{f,298}$ Kcal/mole	S°_{298} cal/mole K	$C^\circ_{p,298}$ cal/mole K
Kelley, Bull 406	(1937)	31.02		8.015	27.780		26.79	27.09		38.06
Evans & Wagman	(1952)	30.84	54.51	7.760						
Guthrie	(1944)							24.25	102.76	37.18
Kubaschewski	(1956)	31.02	54.4	7.730	27.45	89.8		30.0	112.5	
Kelley, Bull 584	(1960)			7.760						37.18
Kelley, Bull 477	(1950)		54.4			92			109.	
McBride	(1963)	30.84	54.51	7.760						
Berkowitz	(1967)				24.36	84.6	26.67			
Detry	(1967)	30.86	59.69		24.86					
NBS Tech-Note 270-3	(1968)	30.68	54.51	7.760	24.50			24.45	102.98	37.39
JANAF, 2nd Ed.	(1971)	30.84	54.51	7.760				24.20	102.823	37.296
Rau et al	(1973)	31.20	54.40	7.730	24.36	84.6	26.67	24.32	102.76	37.18
CODADA	(1975)	30.71	54.56							

TABLE 8

UNCERTAINTY OF THERMODYNAMIC PROPERTIES OF S2, S6, S8

Source		S2			S6			S8		
		$\Delta H^\circ_{f,298}$ cal/mole	S°_{298} cal/mole K	$C^\circ_{p,298}$ cal/mole K	$\Delta H^\circ_{f,298}$ cal/mole K	S°_{298} cal/mole K	$C^\circ_{p,298}$ cal/mole K	$\Delta H^\circ_{f,298}$ cal/mole K	S°_{298} cal/mole K	$C^\circ_{p,298}$ cal/mole K
Kelley, Bull 406	(1937)	*	*	1	*			*		*
Evans & Wagman	(1952)	150	* *	1						
Guthrie	(1944)							* *	* *	* *
Kubaschewski	(1956)	1000	0.1	1	2000	*		5000	1.0	
Kelley, Bull 584	(1960)			* *						0.1
Kelley, Bull 477	(1950)		0.1			*			*	
McBride	(1963)	150	0.1	1						
Berkowitz	(1967)				* *	* *	* *			
Detry	(1967)	350	* *		* *					
NBS Tech-Note 270-3	(1968)	* *	* *	* *	* *			* *	* *	* *
JANAF, 2nd Ed.	(1971)	200	* *	* *				150	* *	
Rau et al	(1973)	50	0.1	1	* *	* *	* *	* *	* *	* *
CODADA	(1976)	70	0.01	* *						

* Uncertainty is large but difficult to estimate

* * Uncertainty is not cited

After having confidence in the best thermodynamic data used, the reference conversion will be calculated and the effect of each sulfur thermodynamic property on equilibrium conversion will be studied.

4.4.3.1 Heat of formation of $S_2(g)$

The heat of formation of S_2 varies from 30.68 kcal/mole reported by the NBS (1968) (108) to 31.2 kcal/mole reported by Rau (1973) (126), the difference is 0.52 kcal/mole (Table 7).

The earliest report on the properties of diatomic sulfur available is Kelley's (79) compilation of the heat capacity of S_2 from Godnev and Sverdin's (60, 61)) data. The heat of formation from S(rh) was then obtained with additional information from the heat of reaction

$$H_2S + I_2(s) = 2HI + S(rh) \tag{4.16}$$

$$2H_2 + S_2 = 2H_2S \tag{4.17}$$

$$S_2 + 2O_2 = 2SO_2 \tag{4.18}$$

Data were taken from Preüner (121), Randall and Bichowsky (124), Preuner and Schupp (122) for the first reaction. The obtained values agree, within experimental error, with Kelly's latter values derived from the sulfur vapor equilibrium composition at the boiling point. The standard heat of formation of S_2 is thus obtained as 31.2 kcal/mole. In this source, sulfur vapor was assumed to be present in S_2-S_6-S_8 only.

Evans and Wagman (52) calculated the heat of formation of S_2 from reaction (4.18) using again the data of Preuner (121), Preuner and Schupp (122), and Randall and Bichowsky (124). The average heat of dissociation of H_2S is 19.53±0.02 kcal/mole, the heat of formation of H_2S at 298 K is -4.82±0.10 kcal/mole as calculated earlier. The resulting heat of formation of $S_2(g)$ from rhombic sulfur is 30.84±0.15 kcal/mole.

JANAF (74), using the third law method with heat of dissociation of $S_2(g)$ as 101.5 kcal/mole, arrived at the same value as Evans and Wagman (52). They also used the second law with $\Delta H^\circ_{f,298}(H_2S)=-4.88\pm0.15$ kcal/mole. Since the results obtained from the third law method are less susceptible to experimental error and the heat of dissociation of $S_2(g)$ is considered established after Brewer's work (22), the JANAF value 30.84±0.20 kcal/mole is used as reference in this work.

After above works, NBS (108) has published a value for $\Delta H^\circ_{f,298}$ of 30.74± kcal/mole, within accuracy of the reference value. This value was obtained by the third law method, with the partial pressure of S_2 over sulfur as reported by Berkowitz et al (15) and $\Delta H^\circ_{f,298}(H_2S)$ from Lewis and Randall (93), Kapustinskii and Shamovskii (76), Thomsen (139) and Zeumer and Roth (153).

Rau et al (126) used thermodynamic properties of S_2, S_6, and S_8 calculated by Berkowitz et al (15), Kubaschewski (88) and Evans and Wagman (52) to fit their experimental measurement of sulfur vapor at high temperature and pressure. To account for the thermodynamic properties of S_3, S_4, S_5, S_7, they assumed the vibrational heat capacity of sulfur species to be a linear function of the atomic number of the species and also equality of the fugacities and compressibilities. They found that the heat of formation of S_2 at 298 K should be revised to 31.20±0.05 kcal/mole.

Due to the complexity of sulfur vapor and the uncertainty in the thermodynamic properties of S_3 to S_7, the data of Kelley (79), Evans (52), NBS (108), and Rau (126) for standard heat of formation the above will be considered only as a range of possible values .

4.4.3.2 Heat of formation of $S_6(g)$

The heat of formation of S_6 ranges from 21.212 to 27.78 kcal/mole; the latter being the earliest reported value, the former the most recent.

Kelley (79) assumed the heat capacity of reaction $6S_8=8S_6$ to be 2 cal/mole S_6, for the reaction $4S_2 = S_8$ to be 6 cal/mole S_8, and $\Delta H^\circ_{f,298}(S_2) = 31.020$ kcal/mole. He determined the heat of formation of $S_6(g)$ from rhombic sulfur to be 27.78 kcal/mole, a revised value from Lewis and Randall's (93) earlier work of 22.6 kcal/mole.

Detry (46) used the mass spectroscopy method with a Knudsen cell in conjunction with West and Menzies' (149) vapor pressure data to arrive at a value of 24.8±2.7 kcal/mole at 400 K. This agrees with the results of Berkowitz and Marquart's (14) study of the sulfur vapor equilibrium composition at low temperature and pressure using HgS as the source of vapor. Berkowitz and Marquart's also reported the heat of reaction of $0.75S_8=S_6(g)$ at 400 K to be 6.2 kcal/mole, using the heat of formation of S_2 and S_8 from Evans and Wagman (52) and Guthrie et al (64) respectively. Using that Berkowitz calculated the heat of formation at 400 K of S_6 as 24.46 kcal/mole.

The NBS (108) in 1968 reported a new value of 24.50 kcal/mole. Kubaschewski (88) used the same method as Kelley's (79) but instead of the assumption of constant heat capacities for the sulfur association reactions, he used Braune et al's (19) dissociation constants of sulfur vapor,and arrived at 27.45±2.0 kcal/mole for heat of formation of $S_6(g)$ compared to Kelley's value of 27.78 kcal/mole. As with other values reported by this author, the uncertainty is too large for practical use.

Braune et al (19) described the sulfur vapor as a mixture of $S_2-S_4-S_6-S_8$. Applying the second law of thermodynamics they found the heat of formation from $S_2(g)$ to be 28.4, 63.71 and 92.18 kcal/mole for S_4, S_6, S_8, respectively, and the heat of reaction $0.75S_8(g)=S_6(g)$ to be 5.43 kcals/mole (298 K). Detry's (46) and Berkowitz' (14) value using mass spectrometry is 6.2 kcal/mole at 400 K. Earlier Preuner and Schupp (122) noted that only consideration of the species $S_2-S_6-S_8$ is adequate to describe sulfur vapor, and proposed the heat of formation of S_6 and S_8 from S_2 as 67.1 and 99.6 kcal/mole, respectively, and the heat of reaction $0.75S_8=S_6$ as 7.63 kcal/mole (298 K). As Braune (19) and Kelm and Kilian (83) mentioned in their articles, the Preuner and Schupp 's (122) vapor pressure data is scattered (10%); thus the latter values are more prone to error.

Rau et al (126) used Detry's (46) value 24.56 kcal/mole in fitting their sulfur vapor density at high temperature and pressure using all sulfur species S_2 to S_8. They found no modification to be necessary.

In trying to resolve the discrepancy between the predicted and observed conversion in the plant at Lacq (France) for the input stream compositon 3%H_2S, 1.5%SO_2, 28%H_2O and 67.5%N_2 at 503-593 K, using only $S_2-S_4-S_6-S_8$ species and with Rau's (126) values for S_2 and S_8, Tellier and his associates (140) arrived at a heat of formation for S_6 of 22.36 kcal/mole, much lower than any other reported values. Using the same conversion data, Leibovici (90) preferred considering all sulfur species from 2 to 8 and in addition assumed a linear function of heat capacity with respect to atomic number of sulfur species. The heat of formation of S_6 was revised to 21.212 kcal/mole in order to achieve the experimental conversion.

Due to the wide range of values reported for the heat of formation of S_6 and the assumptions involved in each value and/or the reliability of the experimental results (as in the case of mass spectrometry) the old value from Kelley (79) will still be used as the reference value.

4.4.3.3 Heat of formation of S_8

There is a range of 5.8 kcal/mole for heat of formation of octatomic sulfur between the lowest value reported in JANAF (74) which is 24.20 kcal/mole and the highest value by Kubaschewski (88) which is 30.0 kcal/mole.

Kelley (79) assumed the heat capacity of the reaction $4S_2=S_8$ to be 6 cal/mole and using their value of 31.02 for $\Delta H^{\circ}_{f,298}(S_2)$ to obtain the heat of formation of S_8, 27.09 kcal/mole.

In Bulletin 584 (1960) (81) reported heat capacity of S_2 and S_8 as

$$C_p(S_8) = 42.54 + 1.04 * 10^{-3}T - 5.04 * 10^{5}T^{-2} \tag{4.19}$$

$$C_p(S_2) = 8.72 + 0.16 * 10^{-3}T -0.90 * 10^{5}T^{-2} \tag{4.20}$$

that is

$$C_p(4S_2=S_8) = -7.66 - 4.0 * 10^{-4}T + 1.44 * 10^{5}T^{-2} \tag{4.21}$$

Evaluating this last equation at 298 K and 1000 K, the heat capacity for the reaction $4S_2=S_8$ are 6.16 cal/mole and 7.92 cal/mole respectively. However no attempt was made to account for this temperature dependence of heat capacity since the new values will not differ significantly from 27.09 kcal/mole, the difference being well within experimental error.

Guthrie et al (64) calculated the heat of formation of S_8 from the partial pressure of S_8 over sulfur using the vapor pressure data of West and Menzies (149), Fouretier (53), Taillade (136), Newman (109) and Bradley (18). Vapor pressure data were obtained by various methods, for example,, the piston method, to gas entrainment, and Knudsen diffusion. He also used Eastman and McGavock's (50) calorimetric data for rhombic sulfur, and Braune's (19) equilibrium constants for the reaction $0.75S_8(g)=S_6(g)$. The average heat of formation of S_8 is 24.23±0.05 kcal/mole. As Rau (126) pointed out, this value is in error due to the error in calculation and suggested 24.35 kcal/mole as the correct value.

Detry (1967) (46) calculated the partial pressure of S_8 in a subatmospheric system using mass spectrometry with a Knudsen cell and West and Menzies' saturated vapor pressure (149) to arrive at a value of 26.0±2.7 kcal/mole.

JANAF (74) applied both the second and the third law methods to the ,at that time, seven most recent sources of vapor pressure data (109, 18, 98, 149, 74, 136, 23) resulting in a heat of sublimation of S_1 of 24.20±0.15 kcal/mole, with a correction for the presence of S_6 in the gas phase.

NBS (108) in 1968 published technical note 270-3, where the heat of formation of S_1 at 298 K was recorded as 24.45 kcal/mole. No information on the uncertainty or the method of calculation was given.

Kubaschewski (88) obtained a value with large uncertainty 30.0±5.0 kcal/mole from Braune's (19) vapor pressure data using the second law method. The error is much too large for practical application.

In addition to Kubaschewski's (88) and Kelley's (79) suggested values, others are 24.05 to 24.45, within experimental error. JANAF (74) applied the third law method which is insensitive to error in vapor pressure as compared to second law method applied by Kelley (79). This source also included more recent vapor pressure data of Magee (1955) (98) and Briske et al (1960) (23) before the availability of Rau's vapor pressure data (1973) (126). JANAF (74) also gives better agreement between predicted and observed conversions than when data from Guthrie (64) or Kelley (79) are used. Thus 24.20 was chosen as the reference value.

4.4.3.4 Standard entropy of $S_2(g)$

The discussion on standard entropy of sulfur species will be easier to follow if Table 9 is using as a guide. Kelley (80) obtained a value for the standard entropy of $S_2(g)$ at 298 K of 54.40±0.10 cal/mole-K using Herzberg's (68) vibrational frequency of 723 cm^{-1} and Badger's (1) interpretation of spectroscopic data for $S_2(g)$; bond distance of 1.840 Å, principal moment of inertia of 90 * 10^{-40} g-cm^2/molecule, and quantum weight of lowest energy state. The same value of standard entropy was calculated by Cross (38).

Evans and Wagman (52) corrected the isotopic composition for Herzberg's (68) rotational and vibrational constants of $S_2(g)$ resulting in 54.51 cal/mole-K. The NBS (108) technical note 270-3 (1968) agrees with this value, as does JANAF (74) (1971). However the CODATA (1975) (36) group combined the efforts of the NBS (108) and the Institute for High Temperature of the Academy of Sciences USSR and recommended a value of 54.000 cal/mole using Herzberg's spectroscopic data including that of Barrow, duParcq

TABLE 9.

SUMMARY OF SPECTROSCOPIC DATA FOR SULFUR SPECIES

Source of Therm. Prop.	Source of primary data	Values of primary data	Values of calculated therm. prop.	Note
Kelley (79)	Badger	d = 1.84 Å J = 90. 10^{-40} gcm2/molecule W = 728 cm^{-1} quantum wt = 3	S^{0}_{298} (S2) = 54.00±0.01 cal/mole-K	Neglecting nuclear spin
Evans & Wagman (52)	Hertzberg	We = 724.62 cm^{-1} WeXe = 2.844 cm^{-1} σ = 2 triplet electronic ground state	S^{0}_{298} (S2) = 54.51 cal/mole-K Cp_{298} (S2) = 7.76 cal/mole-K	Neglecting nuclear spin
CODATA (36)	Hezberg Barrow Rock & Du Parq Barrow & Du Parq	spectra of species	S^{0}_{298} (S2) = 54.001	Neglecting nuclear spin TE 298 - 2000 K
Berkowitz and Chupka (15)	Berkowitz & Marquart calculated from normal coordinate analysis similar to S8	mass spectra of S6 vibrational frequency of S6 from IR and Raman spectra	S^{0}_{298} (S6) = 84.6 cal/mole K Cp (S6) = $31.58+0.12.10^{-3}T-4.4.10^{5}/T^{2}$	
JANAF (74)			S^{0}_{298} (S2) = 54.51 ± 0.1 Cp_{298} (S2) = 7.76 S^{0}_{298} (S8) = 37.296 Cp (S8) = $43.323 + 0.209 . 10^{-3} T - 5.44 . 10^{6}\ T^{2}$	Neglecting nuclear spin TE 298 - 2000 K
NBS (107)			S^{0}_{298} (S2) = 54.51 S^{0}_{298} (S8) = 37.39	Neglecting nuclear spin

and Ricks (7) and Barrow and duParcq (6).

Tellier proposed that the old value of 54.40 cal/mole-K of Kelley (80) was correct in the determination of the equilibrium conversion of H_2S/SO_2 system using all S_2 to S_8 species. This value is within the range of uncertainty of JANAF (74) value.

As is customary, all authors have neglected the nuclear spin contribution which is a reasonable assumption, as Evans and Wagman (52) pointed out. All authors also use spectroscopic data as the basis for their calculations. With the recent changes in interpretation of spectra and better equipment, the JANAF's value will be used as the reference. Note that the values obtained as far back as 1935 (54.41±0.1 (78)) are not much different from the most recent source with isotopic species being accounted for (JANAF (74) 54.51 cal/mole).

4.4.3.5 Standard entropy of $S_6(g)$

Kelley (80) (1950) used Preuner and Schupp's (122) equilibrium data and entropy of S_2 ($S^\circ_{298}(S_2)$ = 54.40± 0.10 cal/mole-K) to estimate $S^\circ_{298}(S_6(g))$ = 92.0 cal/mole-K. The probable error is large but difficult to estimate.

Berkowitz and Chupka (15) reassigned the vibrational frequency of S_6 from IR and Raman spectra to include complete polarization for a solution of S_6. They then used the normal coordinate analysis of the force field similar to S_8 (due to the similar structures of S_8 and S_6). From mass spectrometric data (14), the standard entropy is 84.6 cal/mole-K agreeing with their previous calculation using heats of reaction from mass spectra (14).

Kubaschewski (88) (1956) recalculated Kelley's (79) value using more recent vapor pressure data from Braune (19). The value obtained is 89.8 cal/mole-K, lower than Kelley ([illegible]) but higher than the later value of Berkowitz (15) (1967).

Tellier (140) suggested that a value of 86.71 cal/mole-K predicted the equilibrium conversion obtained at CRL Laboratory when only S_2-S_4-S_6-S_8 were assumed present. Using the same data, Leibovici (90) of the same Laboratory adjusted all the sulfur thermodynamic properties from S_3 to S_7 and arrived at 82.914 cal/mole-K for $S^\circ_{298}(S_6)$.

Due to the large differences in entropy value for $S_6(g)$, and the inaccuracy of each value is large, without any further proof of any value is better than the old value from Kelley of 92. cal/mole-K, Kelley's value will be used in this work.

4.4.3.6 Standard entropy of $S_8(g)$

Similar to the calculation for $S_6(g)$, Kelley (80) (1950) estimated the absolute entropy of $S_8(g)$ at 298 K to be 109.0 cal/mole-K from Preuner and Schupp's (122) vapor density.

Kubaschewski (88) recalculated the standard entropy of $S_8(g)$ using the more recent vapor density data of Braune et al (19) and arrived at 112.5 cal/mole-K. The error in these values is undoubtedly large but difficult to estimate due to the method of calculation.

Guthrie (64) reassigned the vibrational assignments of S_8 from Raman and IR spectroscopy to give better consistency with the vapor pressure data than Bernstein and Powling's (12) assignments. The rigid rotator, harmonic oscillator approximation was used to compute the thermodynamic function for S_8. Translational and rotational contributions to the entropy of $S_8(g)$ were calculated from the equations of Wagman (146). The vibrational contributions were calculated from the vibrational assignment. The entropy for the temperature range 273-1000 K was calculated. $S^\circ_{298}(S_8)$ from this, is 102.76 cal/mole-K. From these thermodynamic properties, the equilibrium constant for $4S_2 = S_8(g)$ was calculated and compared with the interpretation of vapor density of Preuner and Schupp (122) and Braune et al (19). The result is still unsatisfactory. The author suggested the inconsistency arises from the interpretation of vapor density data.

NBS (108) (1968) published technical note 270-3 from their data and assigned a slightly different value, 102.98 cal/mole-K

JANAF (74) used the most recent assignments from Scott, McCullough, and Kruse (132) who took into account the inclusion of torsional forces. The molecular structure, bond distance and angle were taken from Donohue et al (48). The results are consistent with the spectra and thermodynamic data of S_8. As a result, $S_{2}98(S_8)$ is slightly higher than Guthrie's value (102.823 cal/mole-K).

On the other hand, Tellier and Leibovici, in attempting to predict equilibrium conversion for $H_2S/SO_2/H_2O/S_x$ /N_2 system, arrived at values of 102.76 or 99.785 when only S_2-S_4-S_6-S_8 were present in the vapor or S_2 to S_8 were present, respectively. The second value is much lower than any value obtained by thermodynamic methods.

Detry (46) (1967) used mass spectroscopy to measure the entropy of reaction, $S_8(g)=4S_2(g)$ at 460–625 K (110.2±4.2 cal/mole–K) and arrived at 126.8±4.2 cal/mole–K for $S^\circ_{298}(S_8)$ which agrees with the JANAF result (124.97 cal/mole–K)

Values from Kelley (79) and Kubaschewski (88) are disregarded due to the large error associated which is difficult to estimate. Guthrie's (64) calculation depends on the vibrational assignment of IR and Raman bands. Since then many authors have assigned new values to respond to the accuracy of new spectroscopic techniques. Scott and McCullough's (132) value is the most recent obtained and JANAF's values are still in use in recent handbooks (5, 148). For these reasons, the JANAF (74) value was again chosen as the reference value.

4.4.3.7 Heat capacity of S_2

Evans and Wagman (52) used a statistical method with the same spectroscopic molecular constants as for entropy and used Wagman's equation (146) to calculate $C_p(S_2)$ over the temperature range, 100–1500 K, obtaining $C^\circ_{p,298}(S_2)$ = 7.76.

Kelley (80) in the compilation of heat capacity in Bull 584 (1950) selected as the best value up to that time,

$C_p = 8.72 + 0.16 * 10^{-2}T - 0.9 * 10^{5}T^{-2}$ (±1%, T ∈ 298–3000 K) (4.22)

That is, $C_{p,298}$ = 8.185 cal/mole–K, a revised value from the earlier compilation,

$C_p = 8.54 + 0.28 * 10^{-3}T - 0.79 * 10^{5}T^{-2}$ (T ∈ 298–2000 K) (4.23)

or $C_{p,298}$ = 7.735 cal/mole–K. NBS (108) in technical note 270–3 again gave the value of $C_{p,298}$ = 7.76 cal/mole–K, as the best value up to 1968.

JANAF (74) using the molecular constants from Herzberg (68) and modified for natural isotopic abundances, arrived at $C_{p,298}(S_2)$ = 7.76, again the same as Evans and Wagman's (52).

Due to the consistency between JANAF (74) and NBS (108) and Evans and Wagman (52), the JANAF value will be used as the reference.

4.4.3.8 Heat capacity of S_6

The only experimental source of heat capacity obtained for S_6 is from Berkowitz and Schupka (15) (1967), from their reassigned vibrational assignment for IR and Raman spectra of Engel sulfur vapor

$$C_p = 31.580 + 0.120 * 10^{-3}T - 4.400 * 10^{5}T^{-2} \qquad (4.24)$$

or C_{p298} = 26.67 cal/mole-K. Earlier, Kelley (79) assumed the heat capacity of reaction of $0.75S_8=S_6$ to be 2. cal/mole-K and

$$C_p(S_2) = 7.75 + 0.888 * 10^{-3}T \pm 0.16 \ (300-1500\ K) \qquad (4.25)$$

and

C_p = 6 cal/mole-K for $4S_2=S_8$

therefore

$$C_p(S_8) = 37.00 + 3.552 * 10^{-3}T \pm 0.64 \qquad (300-1500\ K) \qquad (4.26)$$

or

$$C_p(S_6) = 28.00 + 2.664 * 10^{-3}T \pm 0.64 \qquad (300-1500\ K) \qquad (4.27)$$

i.e. $C_{p298}(S_6)$ = 28.79 cal/mole-K which is much different from Berkowitz' value (15).

Rau(126) assumed that the vibrational heat capacity of sulfur species is a linear function of atomic number. Selecting the heat capacities of S_2 and S_8 from Evans and Wagman's work (52) and Guthrie's (64) respectively, he then added the rotational and translational contributions. The heat capacity of S_6 was calculated to be

$$C_p(S_6) = 31.58 - 0.120 * 10^{-3}T - 4.400 * 10^{5}T^{-2} \qquad (4.28)$$

or C_{p298} = 26.67 cal/mole-K

Similarly Leibovici (90) assumed the total heat capacity of each species rather than the vibrational heat capacity to be a linear function of the atomic number of the species. Then

$$C_p(S_6) = 31.3212 + 0.943083 * 10^{-3}T - 0.276206 * 10^{-6}T^2$$
$$- 0.44157 * 10^{6}T^{-2} \qquad (4.29)$$

i.e. C_{p298} = 26.21 cal/mole-K. This value, when used with their set of equations, predicts their experimental equilibrium conversion.

Since the accuracy of each source cannot be determined, the original value of Kelley (79) is used as the reference, though this will affect the entropy and sensible enthalpy dramatically, especially for temperatures far from 298 K, due to the second term in the integral ($0.9431T^2/2$).

4.4.3.9 Heat capacity of S_8

As mentioned in previous section, Kelley (79), due to the lack of heat capacity data in the 30's, suggested

$$C_p(S_8) = 37.00 + 3.552 * 10^{-3}T \pm 0.64 \quad (300-1500\ K) \tag{4.30}$$

or $C_{p,298} = 38.06$ cal/mole-K

From spectroscopic studies, Guthrie (64) calculated

$$C_p(S_8) = 42.670 + 0.86 * 10^{-3}T - 5.11 * 10^{5}T^{-2} \tag{4.31}$$

or $C_{p,298} = 37.17$

In a comprehensive comparison of heat capacity data from all sources available up to 1960, Kelley (81) recommended

$$C_p(S_8) = 42.54 + 1.04 * 10^{-3}T - 5.04 * 10^{5}T^{-3} \tag{4.32}$$

as the best value, $C_{p,298} = 37.18$ cal/mole-K. This equation described Guthrie's results to within 1%.

JANAF (74) used the most recent assignment for vibrational frequency and molecular constants, $C_{p,298}(S_8) = 37.296$ cal/mole-K. Barin and Knackle (5) fitted their table to the equation:

$$C_p = 43.323 + 0.283 * 10^{-3}T - 5.44 * 10^{-6}T^{2} \quad (\pm 1\%,\ 298-2000\ K) \tag{4.33}$$

NBS (108) technical note 270-3 (1968) recommended a slightly higher value of 37.39 cal/mole-K at 298 K.

Leibovici (90) suggested

$$C_p = 42.7613 + 0.110011 * 10^{-2}T - 0.33032 * 10^{-6}T^{2} - 0.51449 * 10^{6}T^{-2} \tag{4.34}$$

or $C_{p,298} = 37.27$ cal/mole-K

in his thermodynamic properties adjustment in order to predict experimental conversion.

Again JANAF (74) which employs both statistical methods using the latest spectroscopic data and molecular constants, will be used as reference due to the reliability of method and data.

4.4.3.10 Conclusion

In conclusion, JANAF (74) will be used as the primary source of thermodynamic properties to be used in this work, except for S_6 where Kelley's (79) value will be used due to the convenience of equation form over the range of interested temperatures.

The reasons for choosing these sources are: most recent, most comprehensive and best available data, as well as reliable methods when enough spectroscopic data are available. The consistency of Kelley (79) and JANAF (74) source has been checked. The reference state is S(rh) at 298.16K and gases at 298.16K since only water vapor is present in this study.

Table 10 shows the thermodynamic data to be used in the FREM program to calculate the reference equilibrium conversion.

4.4.4 Sensitivity of thermodynamic properties of sulfur species

From the survey it was found that the state functions of the different sulfur species are not known to an adequate accuracy because of the methods used (sec. 4.4.3). To assist in the future determination of the thermodynamic equilibrium conversions for H_2S/SO_2 system, it is important to study the effect of each thermodynamic property on calculated conversion. Thus a sensitivity study was also done on the thermodynamic properties of sulfur species. The reference conversion is the same as that mentioned in sec. 4.3.2.

4.4.4.1 Effect of standard heat of formation

The same result as the effect of standard heat of formation for H_2S occurs for sulfur species. Because the sulfur heat of formation is positive and sulfur is a product of the reaction, a decrease in the heat of formation is necessary to increase the calculated conversion. At the limit of the cited values, the calculated conversion is still lower than the actual conversion as shown on Table 10 and Figs. 16,17,18. For example, from Table 10, the lowest cited value for standard heat of formation of S_2 is 160 cal/mole less than the reference value of 30.84 kcal/mole, the equilibrium conversion corresponding to this value of standard heat of formation of S_2 is shown between line A and B lower than line H for observed conversion. From Table 10, the lowest cited value for standard heat of formation for S_6 is 5568 cal/mole less than the cited value of 27.780 kcal/mole or 22.21 kcal/mole. From Fig. 17 line D corresponds to standard heat of formation of S_6 of 25.88 kcal/mole and line I for standard heat of formation for S_6 of 24.36 kcal/mole. Comparing location of these two lines D and I with line H for observed conversion, it is clear that with standard heat of formation of S_6 of 22.21 kcal/mole, equilibrium

TABLE 10

RANGE OF SULFUR THERMODYNAMIC PROPERTIES

Standard heat of formation			
Species	$\Delta H^{\circ}_{f,298}$ Kcal/mole	Range	$\Delta(\Delta H^{\circ}_{f,298})$ Cal/mole
S2	30.84	0.995 - 1.1012	160 - 360
[illegible]	27.780	0.7996 - 1	5,568 - 0
[illegible]	24.20	0.8137 - 1.1194	4,507 - 2,890
Standard Entropy			
Species	S°_{298} Cal/mole K	Range	(S°_{298}) cal/mole K
S2	54.51	0.958 - 1.095	0.11 - 5.18
S6	84.6	1.0 - 1.0875	0.0 - 7.4
S8	102.828	0.97 - 1.06007	3.038 - 6.177

Note: Unit for standard heat of formation Kcal/mole
Unit for standard entropy Cal/mole-K

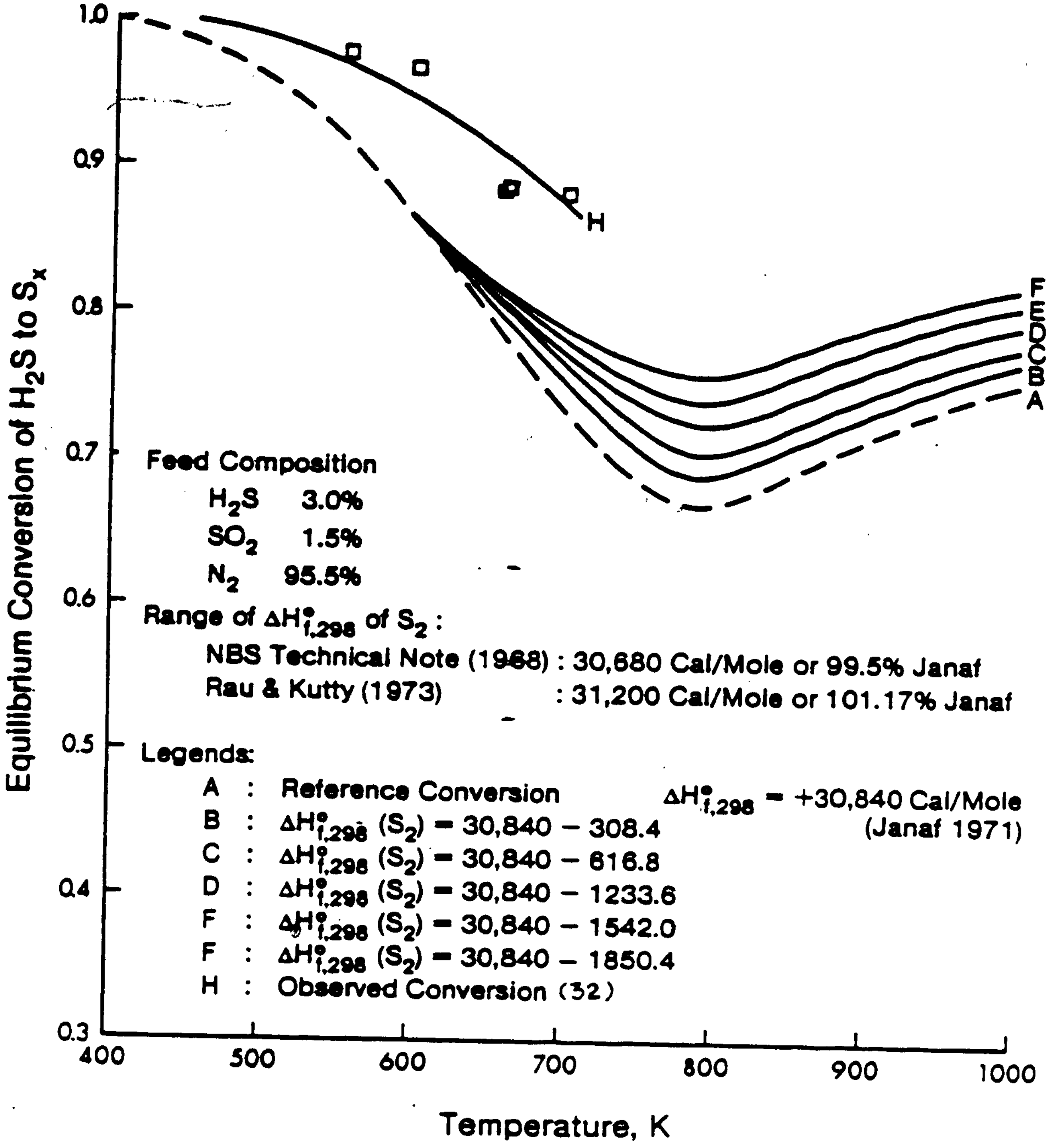


Fig.16 Effect of $\Delta H^\circ_{f,298}$ of S_2 on Predicted Conversion

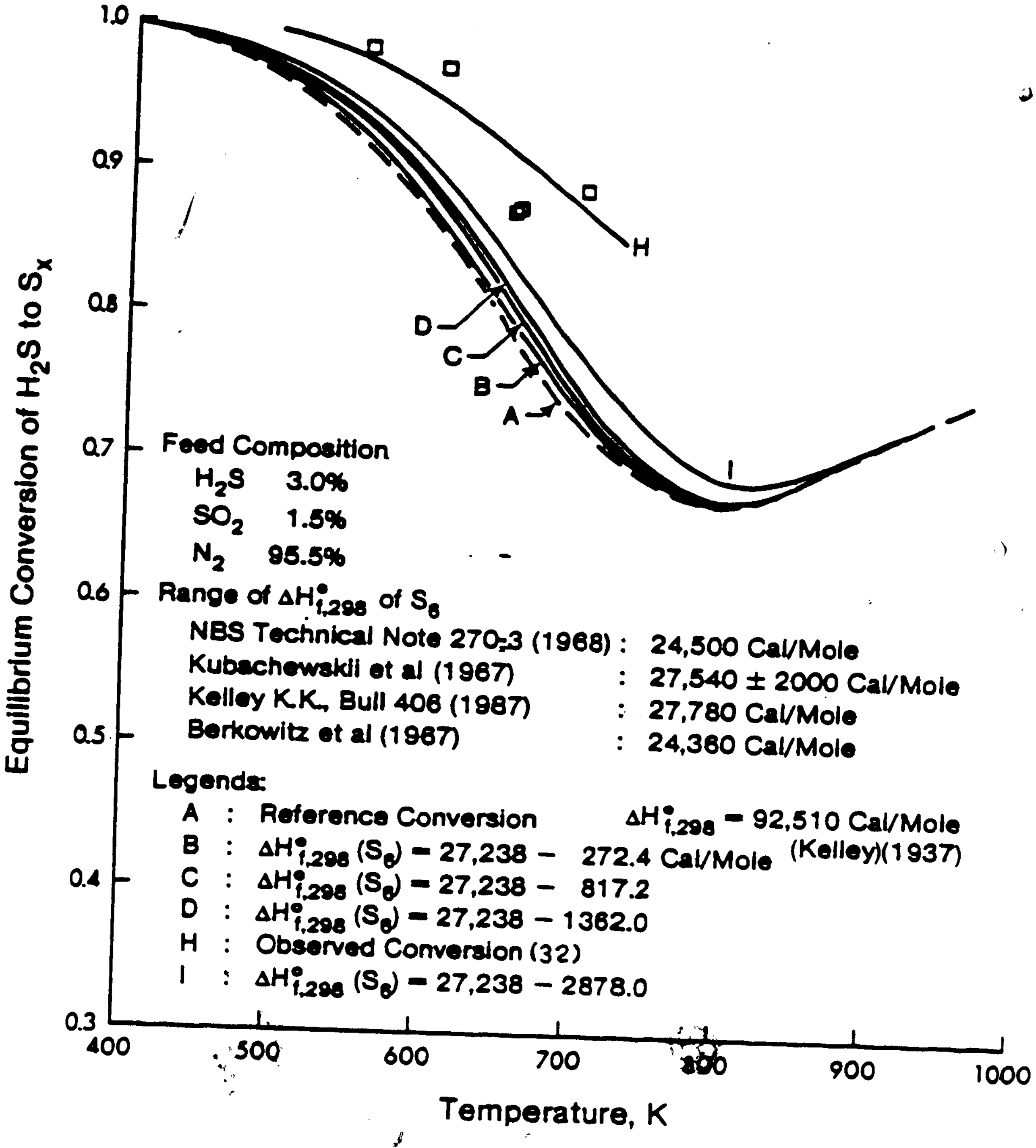


Fig. 17 Effect of $\Delta H^{\circ}_{f,298}$ of S_8 on Predicted Conversion

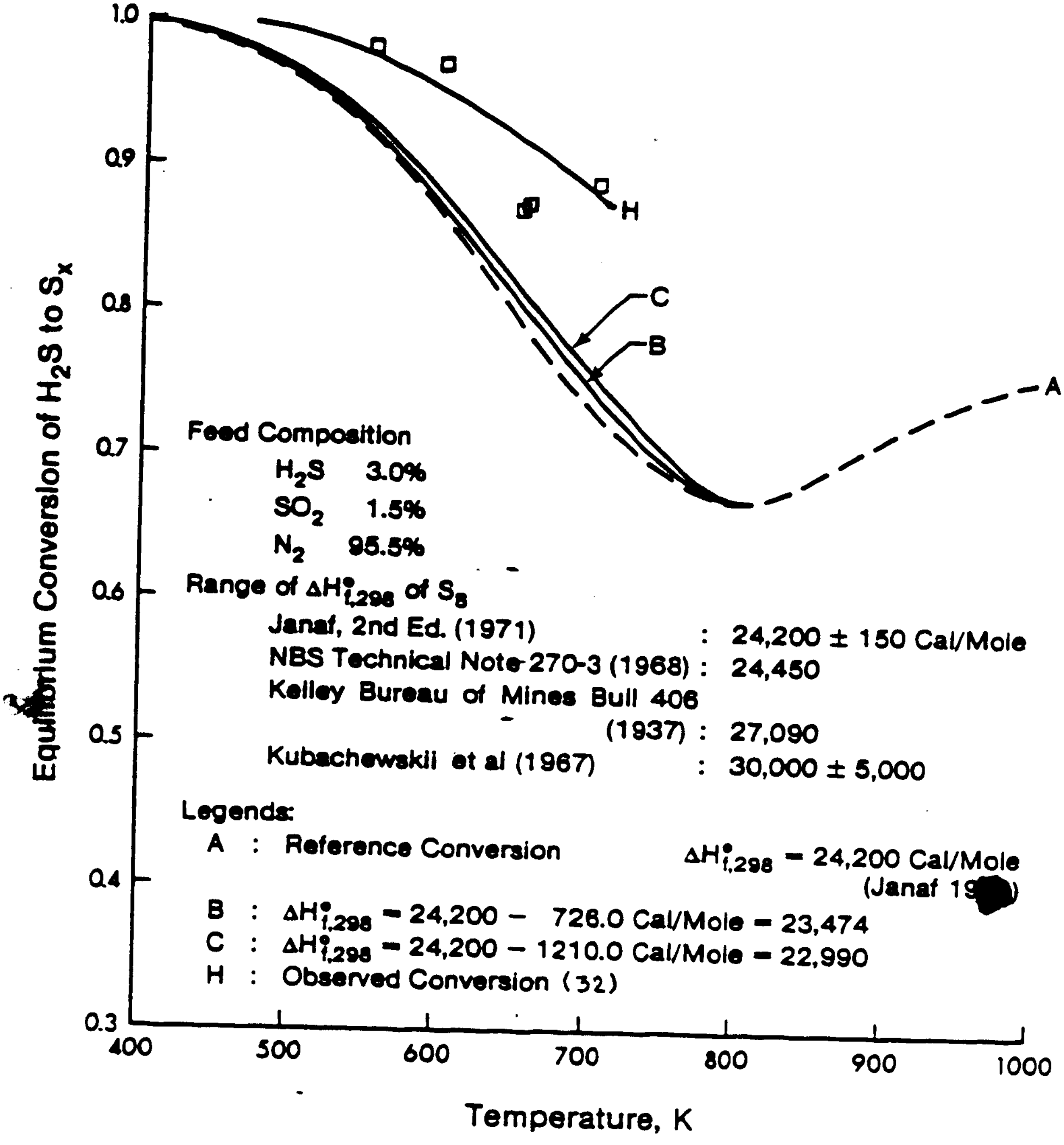


Fig. 18 Effect of $\Delta H^\circ_{f,298}$ of S_8 on Predicted Conversion.

conversion still cannot be predicted. From Table 10, the lowest cited value for standard heat of formation for S_8 is 4507 cal/mole less than the cited value of 24.20 kcal/mole or 19.693 kcal/mole. From Fig. 18, line C corresponds to standard heat of formation of S_8 of 22.99 kcal/mole. Comparing line A and C for standard heat of formation of S_8 of 24.20 kcal/mole and 22.99 kcal/mole, respectively, and line H for observed conversion. It is clear that even if standard heat of formation of S_8 is actually lower to 19.693 kcal/mole, equilibrium conversion still can not be predicted. This lowest value of standard heat of formation of S_8 is from Kubaschewski (88),a very unreliable source of data as mentioned in section 4.4.3. From Fig. 19 it is found that the conversion is 0.804 actual conversion at 0.9935 of the reference standard heat of formation or a decrease of 200 cal/mole in diatomic sulfur heat of formation. This is lower than the lowest cited value of 30.68 kcal/mole. For octatomic sulfur, the conversion is 0.88 of the actual conversion at 0.814 of the reference standard heat of formation, a decrease of 4507 cal/mole from Leibovici value of 19.693 kcal/mole. For hexatomic sulfur at 0.800 of the reference standard heat of formation, a decrease of 5568 cal/mole from Kelley's value of 27.78 kcal/mole the conversion is 1.13 reference conversion or 88% actual conversion for 700 K. It is also noted from Fig. 21 that the effect of standard heat of formation of S_6 on equilibrium conversion at 500 K, 900 K and 1000 K are almost exactly the same. This phenomenon is expected since S_6 is the species causing the equilibrium conversion to be minimum at 700 K where S_6 occurs in highest concentration. As temperature decreases or increases from 700 K, the effect of S_6 is diminished as amount of S_6 decreases. At 500 K, 900 K, and 1000 K, amount of S_6 in the equilibrium coposition is the same thus standard heat of formation having the same effect on the equilibrium conversion at these temperature. It is observed that the effect of diatomic sulfur heat of formation is quadratic while octatomic sulfur effect is linear. However at about 600 K, diatomic sulfur has no significant effect on conversion, since the mole fraction of S_2 in the equilibrium sulfur vapor is very small. For the same reason the effect of hexatomic sulfur heat of formation is the same at 500 K, 900 K and 1000 K.

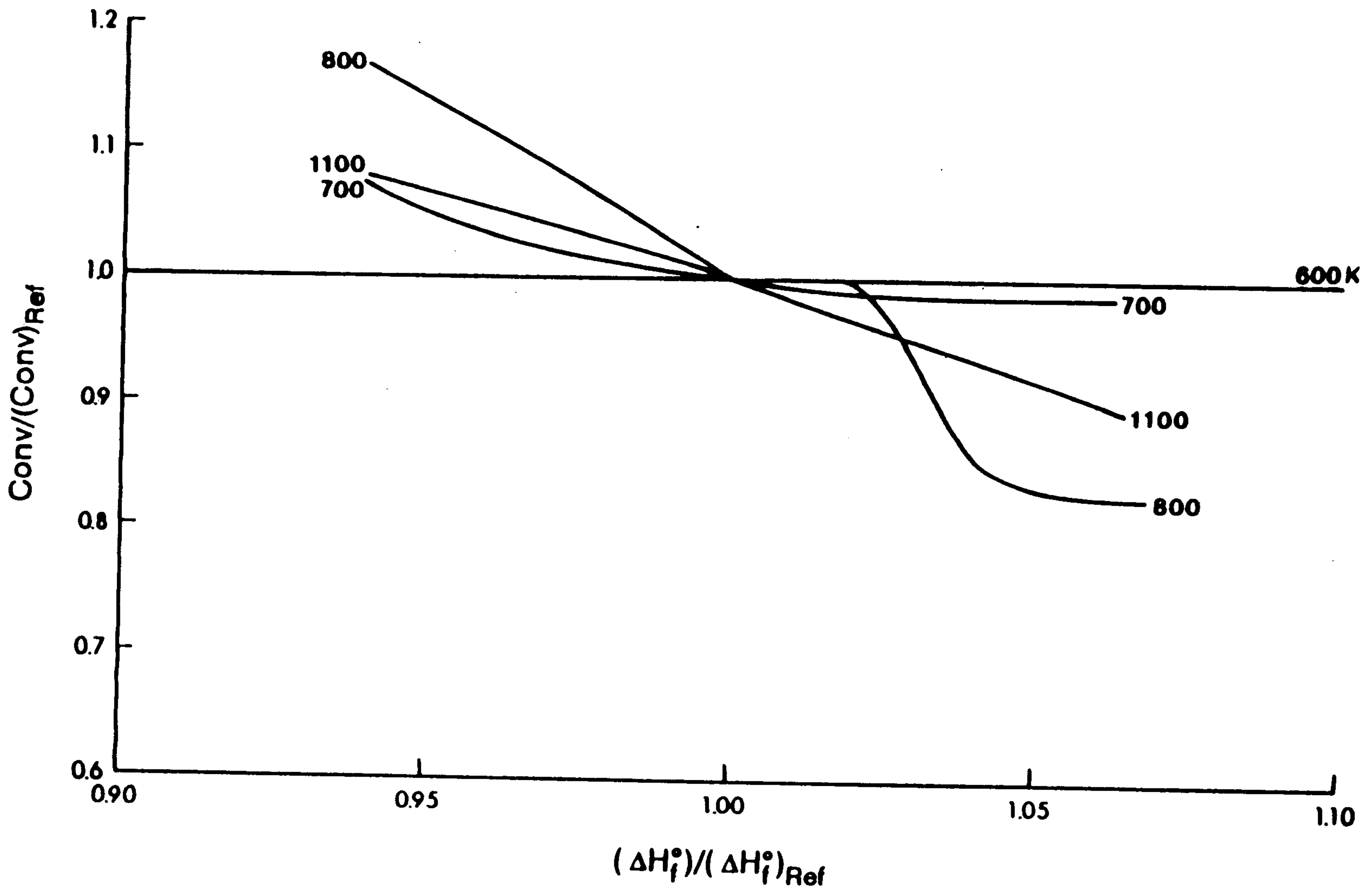


Fig. 19 Effect of $\Delta H^\circ_{f,298}$ of S_2 on Equilibrium Conversion.

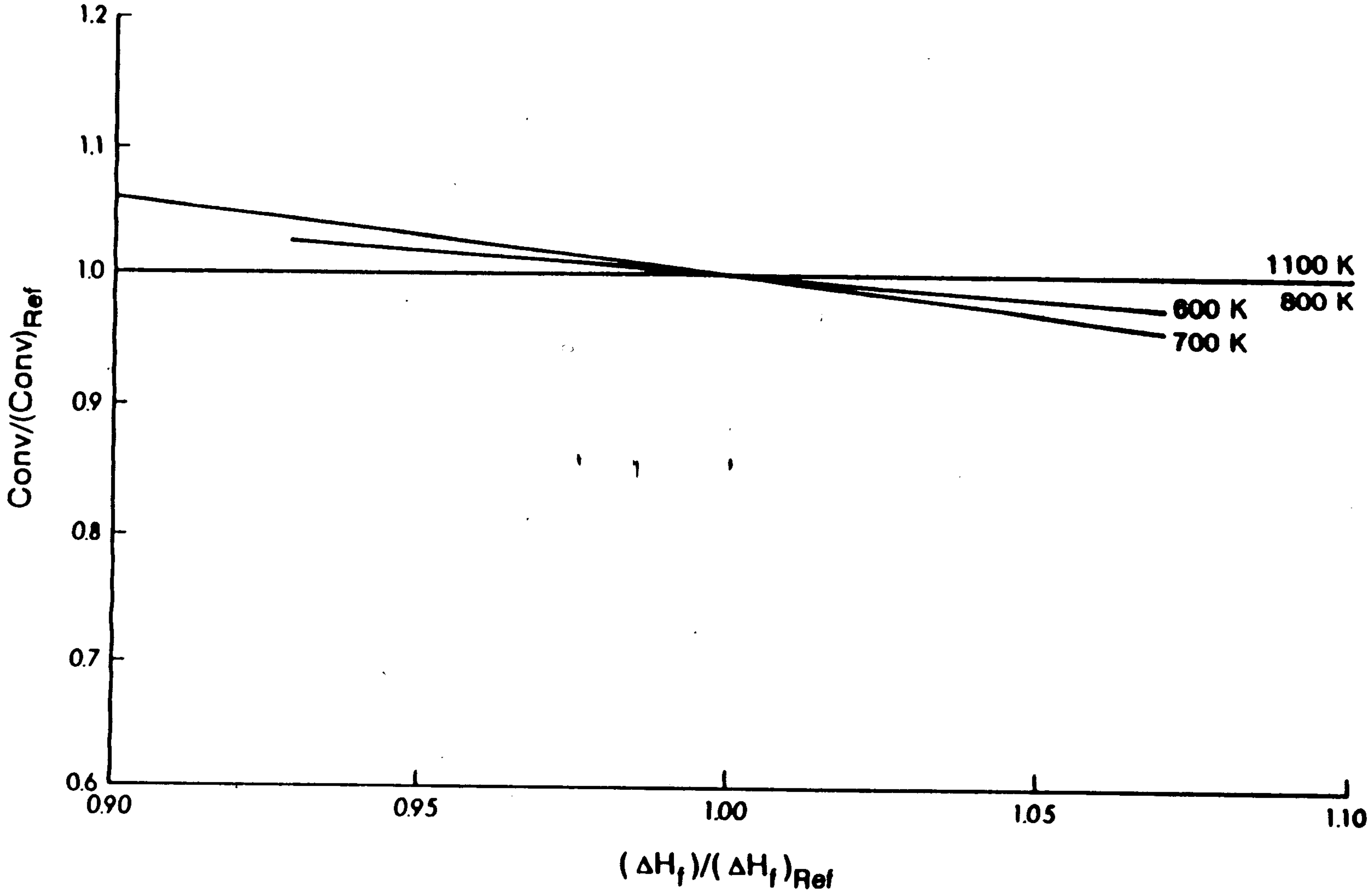


Fig. 20 Sensitivity Analysis of $\Delta H^\circ_{f,298}$ of S_8 on Equilibrium Conversion.

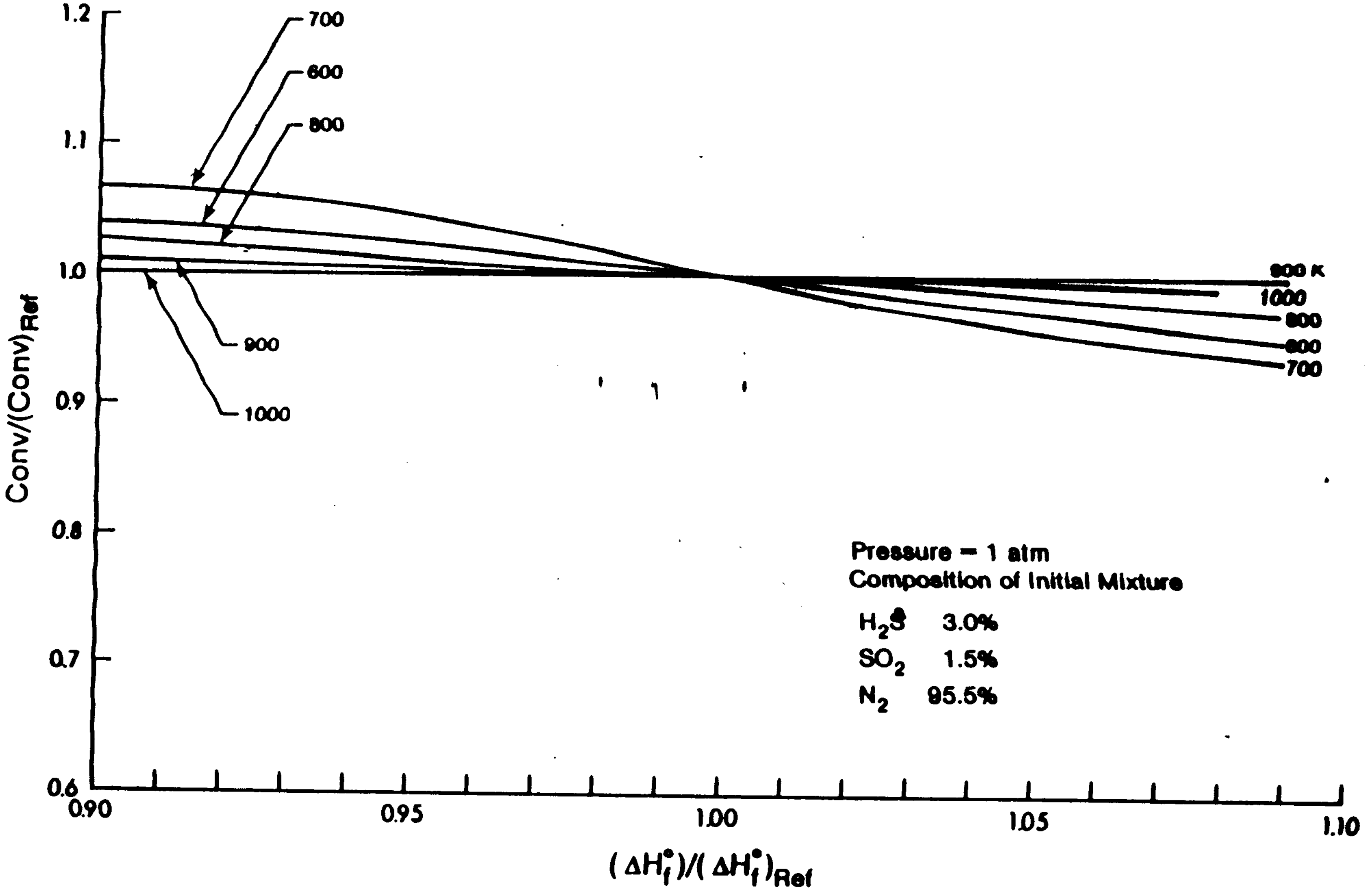


Fig. 21 Sensitivity Analysis of $\Delta H^\circ_{f,298}$ of S_6

4.4.4.2 Effect of standard entropy

At the highest cited value of standard entropy of diatomic sulfur 59.6 cal/mole-K from Detry (46), the calculated conversion is 0.976 of the actual conversion (Fig. 22). Fig. 23 shows the effect of 2.18 cal/mole-K increase in standard entropy of S_2 over the whole temperature range 500 to 1000 K. This constitutes 5.18 cal/mole-K increase which is much above the 0.1 cal/mole-K uncertainty in JANAF source. For octatomic sulfur at the highest cited value of 109 cal/mole-K from Kelley (1960), the calculated conversion is 0.89 of the actual conversion, corresponding to an increase of 6.177 cal/mole-K (Fig. 24). Fig. 25 shows the effect of 4.2 cal/mole-K increase on the standard entropy of S_8 over the temperature range 500 to 1000 K. The reference standard entropy of S_6 is the lowest cited value (Table 10) However the uncertainty for standard entropy of S_6 is not defined. From Fig. 26, the actual conversion (1.28 of the actual conversion) can be predicted if the standard entropy of S_6 is 0.75 the reference standard entropy of S_6 or 63.45 cal/mole-K, a decrease of 21.15 cal/mole-K, an unlikely value. Fig. 27 shows the effect of 3.30 cal/mole-K of increase of st[illegible]py of S_6 on equilibrium conversion over the whole temperature range 500 to 1000 K. Below 600 K, the entropy of S_6 does not affect the conversion while that of octatomic sulfur is more pronounced. This is as expected from the temperature dependence of sulfur species.

4.4.5 Conclusion

Comparing the effect of S_8 and S_2, H_2S, SO_2 and H_2O at 10% deviation from standard heat of formation reference value, the ratio of conversion is highest for H_2O followed by SO_2, S_2, H_2S and S_8 (1.54, 1.34, 1.23, 1.07, and 1.06). While considering the effect of standard entropy, H_2S is the most sensitive, and then $H_2O(g)$, S_2, S_8, and SO_2 (1.37, 1.30, 1.25, 1.25, and 1.10). Though the calculated conversion is the most sensitive to water vapor properties, from the survey of thermodynamic properties, water vapor properties have been determined accurately by several methods from different reactions. It is concluded that the heat of formation of S_2 should be determined more accurately than that of S_8 since equilibrium conversion is more sensitive to the heat of formation of S_2 than the heat of formation of S_8, while the accuracy of standard entropy values of S_2

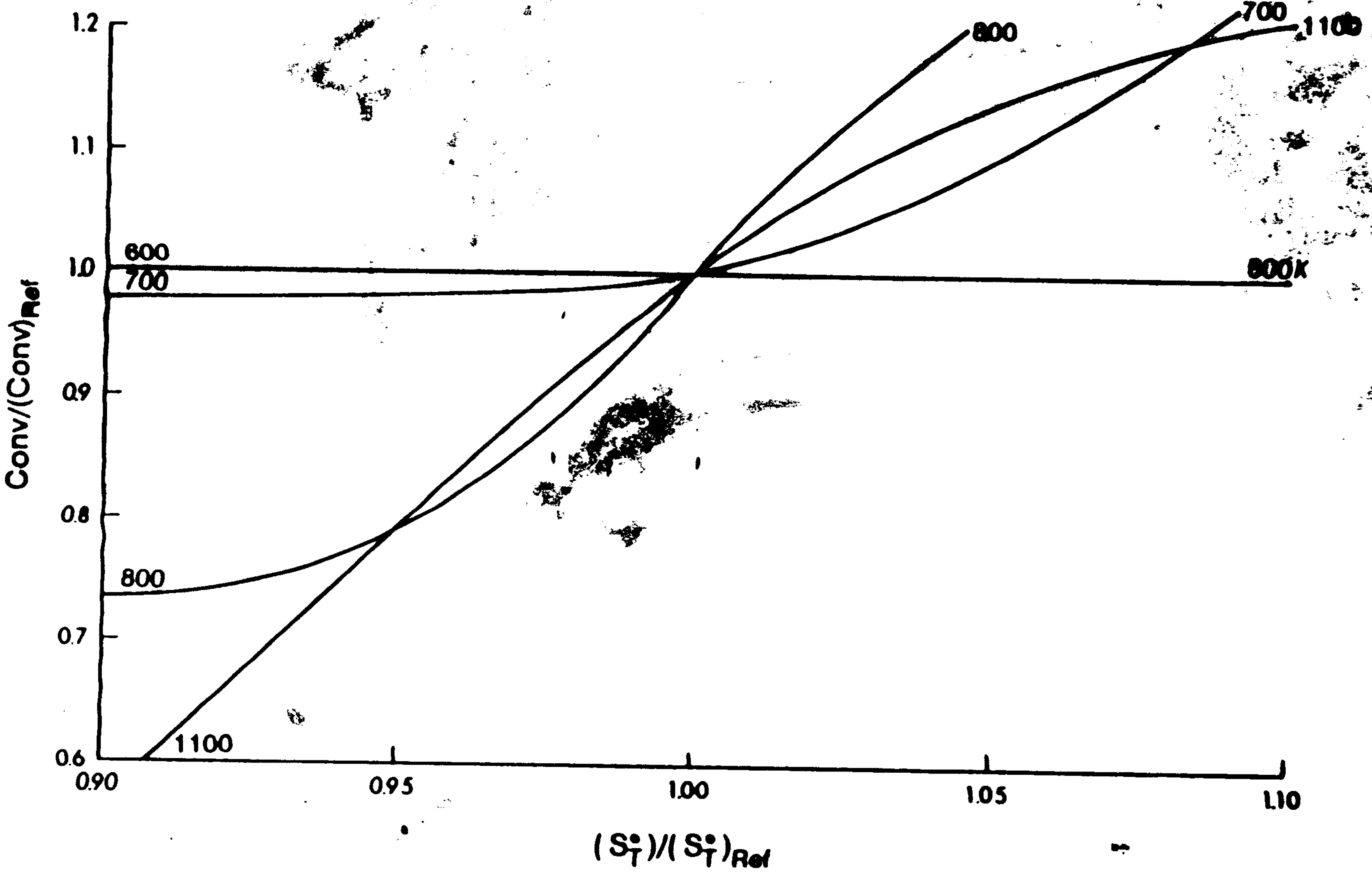


Fig. 22 Sensitivity Analysis of Standard Entropy for S_2

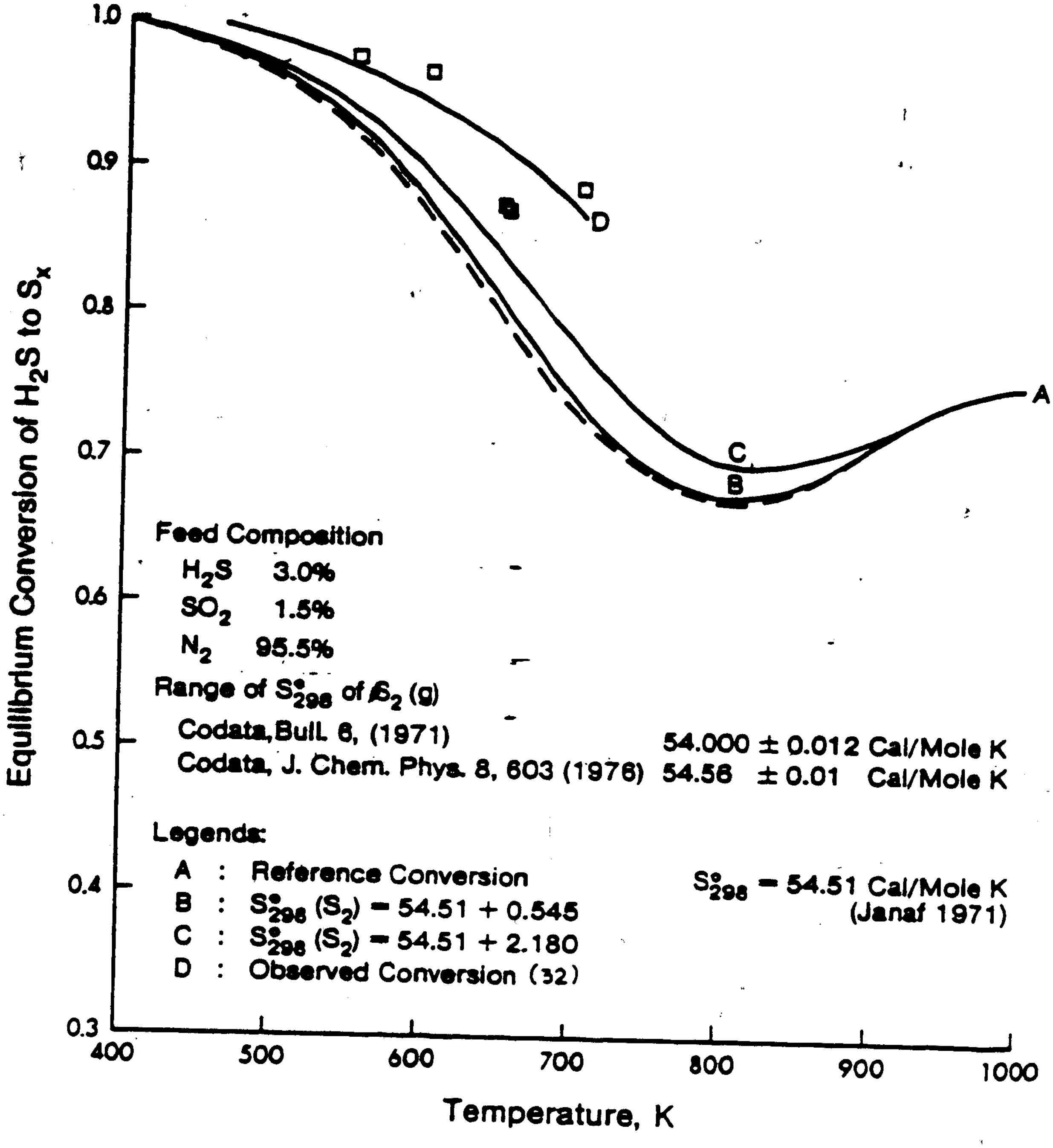


Fig. 23 Effect of S°_{298} of S_2 on Predicted Conversion.

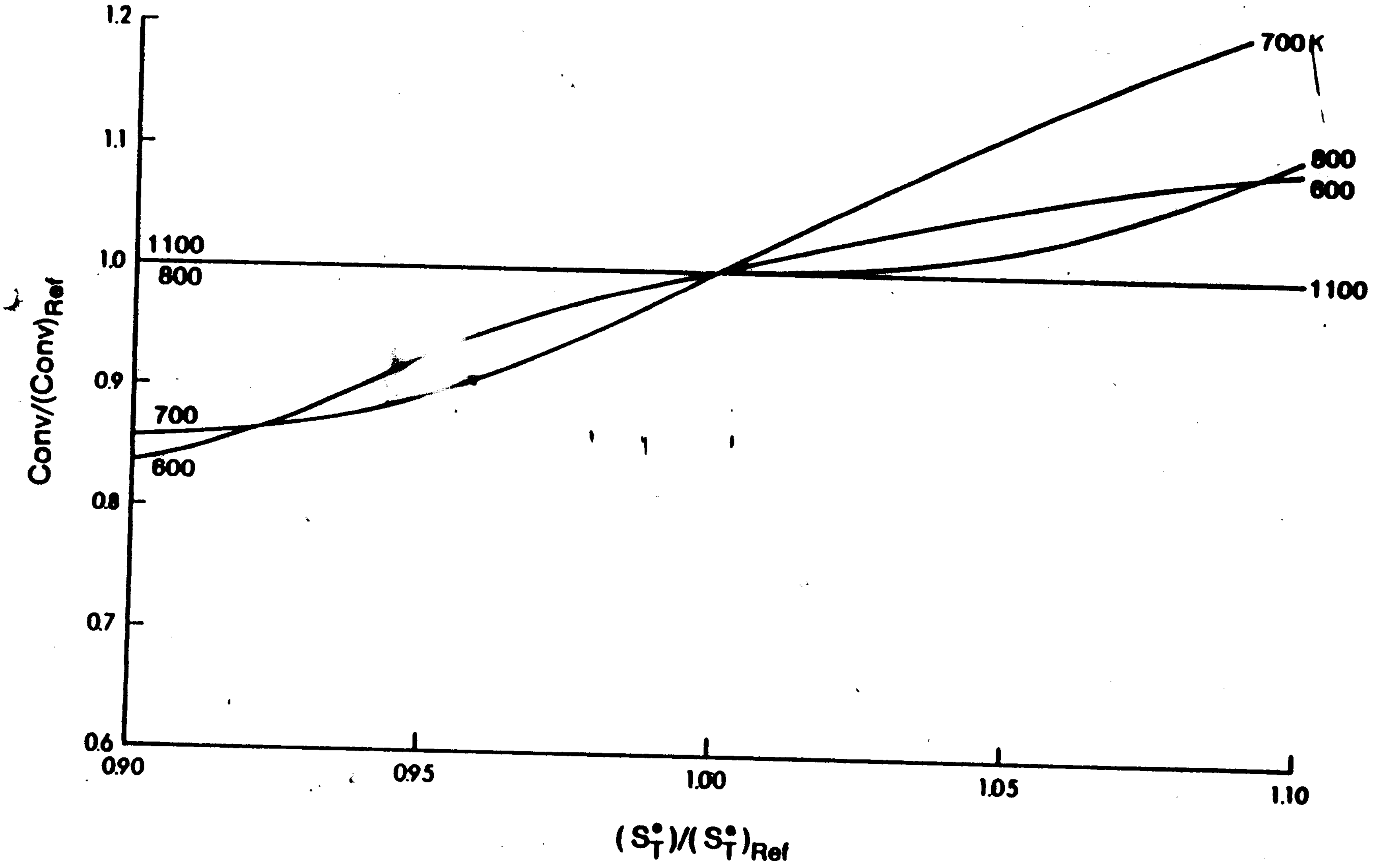


Fig.24 Sensitivity Analysis of Standard Entropy of S_8

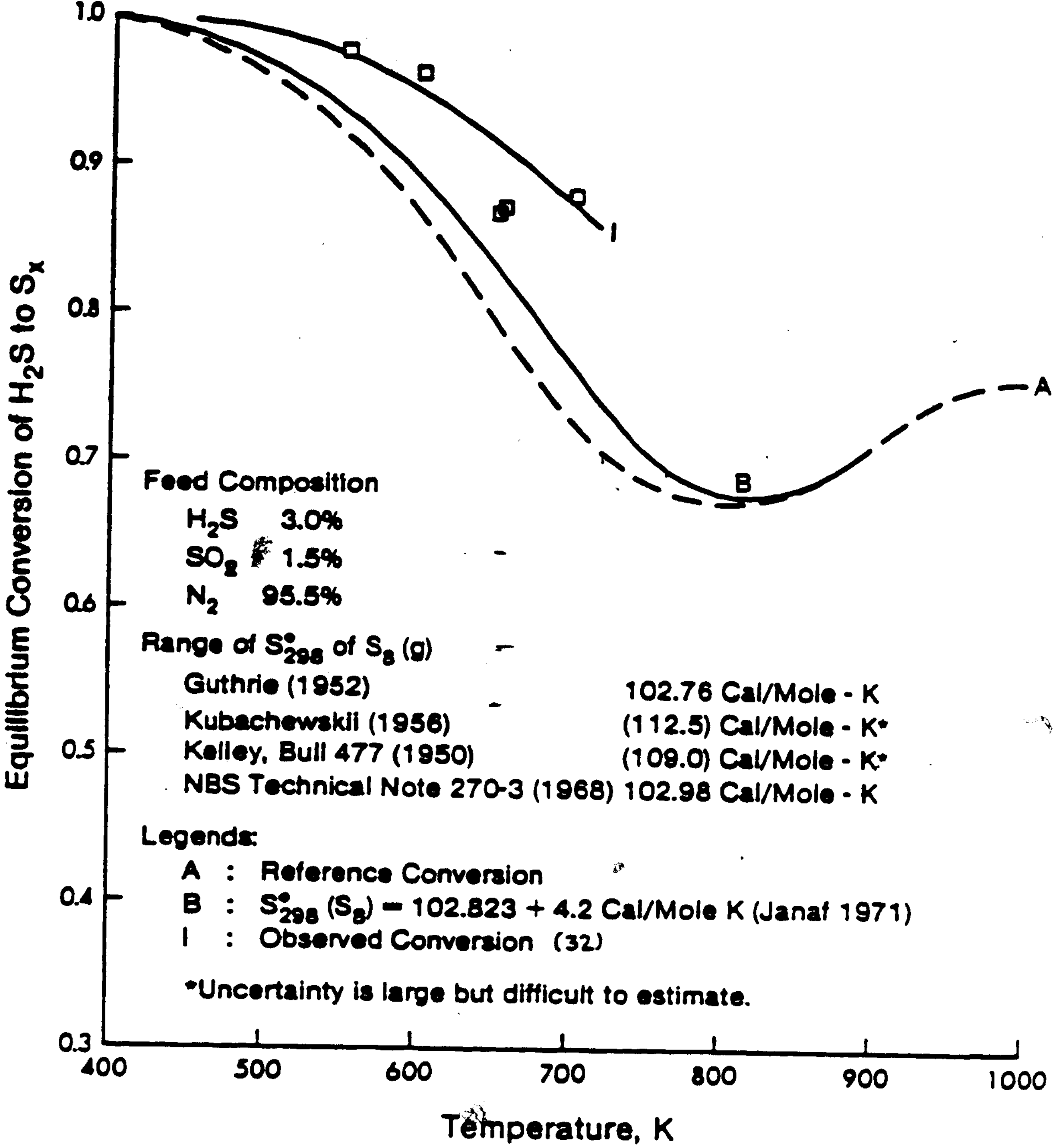


Fig. 25 Effect of S°_{298} of S_8 on Predicted Conversion

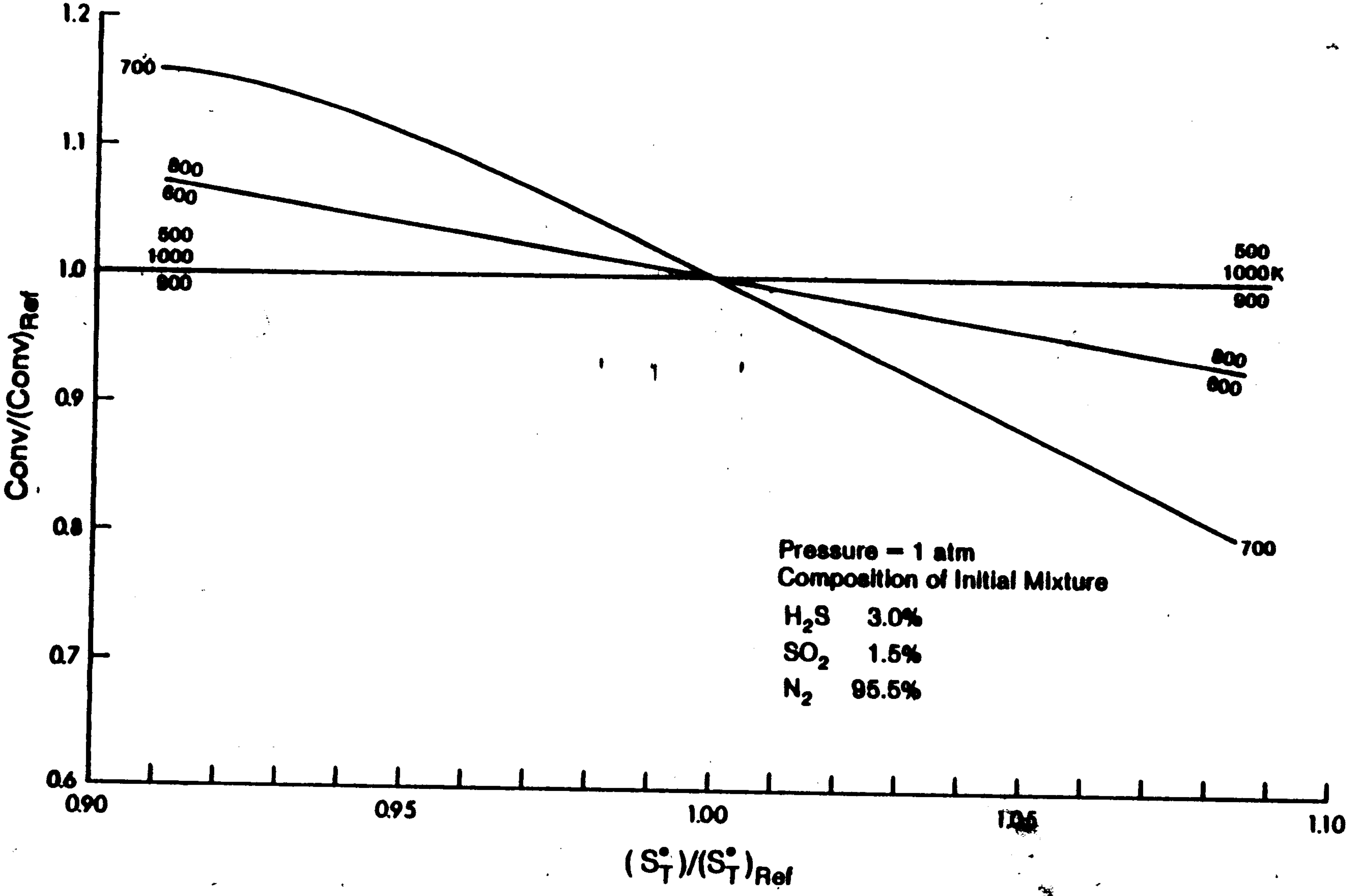


Fig. 26 Sensitivity Analysis of Standard Entropy of S_8

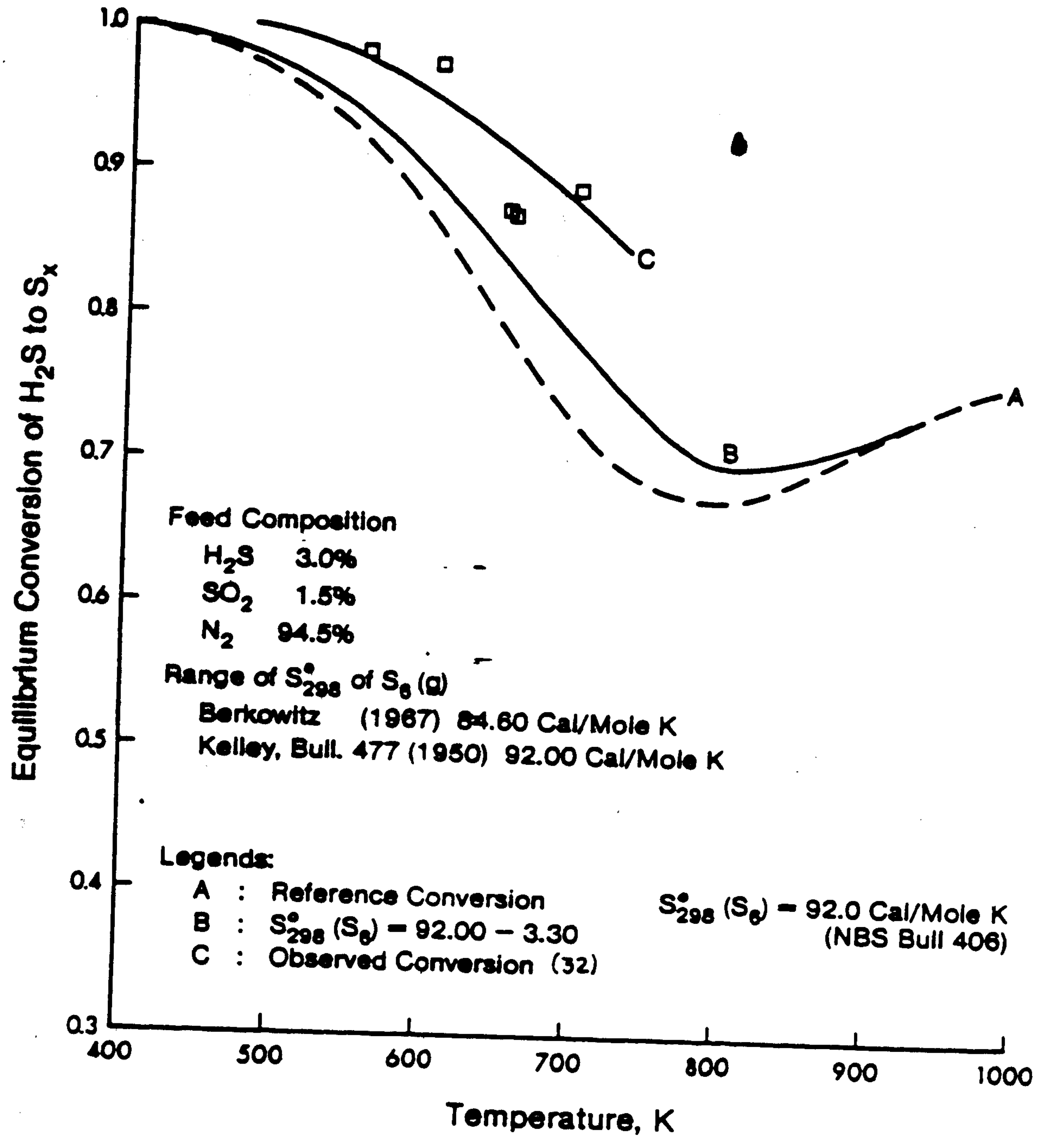


Fig. 27 Effect of S°_{298} of S_8 on Predicted Conversion.

and S_8 is not responsible for the effect on equilibrium conversion since large changes are needed to bring about the small change in equilibrium conversions.

Again the thermodynamic properties of sulfur species have to be modified to ridiculous values outside the cited range and accuracy to predict the observed equilibrium conversion. It is concluded that more than one thermodynamic property of any species or of several species at least need to be changed to reconcile the discrepancy. This is reasonable and to be expected for consistency, since most standard entropies and heat capacities were calculated from the spectra. If the standard entropy is not correct, the molar heat capacity will also not be correct, which will in turn, affect the sensible enthalpy. The effect of heat capacity C°_p on absolute entropy S_{298} and sensible enthalpy H^T_{298} can be determined readily, but a complicated correlation exists between standard entropy S°_{298} and heat capacity at the reference temperature C°_{p298} which are functions of ϵ_i and p_i, the energy level and the probability of the corresponding energy level.

4.5 Synergism

To preserve the validity of thermodynamic properties of species, the properties of species will be modified first of all by the uncertainty cited, then the new model of sulfur vapor will be determined in order to predict the equilibrium conversion for H_2S/SO_2 system before investigation into distorting the sulfur thermodynamic properties.

The uncertainty of each thermodynamic property is listed in Tables 2 and 8. The thermodynamic properties were changed in the direction of increased conversion. In this way, the consistency of thermodynamic properties is preserved and the thermodynamic data sources are still valid. When all heats of formation were changed by 200 cal/mole in the favorable direction, the conversion at 700 K is 0.788 or 90% observed conversion, assuming only H_2S, SO_2, H_2O, S_2, S_6, S_8 and N_2 in the product. When values of S°_{298} were also changed by 0.1 cal/mole-K, and 3.3 for hexatomic sulfur, 4.2 for entropy of octatomic sulfur then the predicted conversion is 0.830 i.e. 94.3% of observed conversion. The effect of changing the standard heats of formation, sensible enthalpies and standard entropies by the degree of uncertainty results in conversion of 0.865 i.e. 98.3% of observed conversion. Fig. 2 shows the equilibrium conversion obtained from adjustment using the inaccuracy of thermodynamic properties. Line B is the reference conversion using the cited values of thermodynamic properties from different sources. Comparing A and B the changes in equilibrium conversion due to the use of different thermodynamic properties sources only can improve the equilibrium conversion slightly, insignificant compared to the discrepancy of the observed conversion (line E) and the calculated conversion. Line C shows the equilibrium conversion resulting by changing the standard heat of formation by 200 cal/mole for all species including S_2 but not S_6 and S_8, the cited uncertainty, in the direction of increased equilibrium conversion and the standard entropy of species by 0.01 cal/mole-K, except for S_6 and S_8 and H_2O(g), where standard entropy is changed by 3.3, 4.3 and 0.03 cal/mole-K, respectively, according to the cited uncertainties (14) The equilibrium conversion shown by line C is still below the observed conversion (line E) except at the minimum conversion around 720 K.

The next significant species, S_7, suggested by Rau (126) and Wakihara (147) is then included in the sulfur model: $S_2-S_6-S_7-S_8$. Using Rau's thermodynamic properties for S_7, the unmodified conversion is lower than the observed conversion. With the thermodynamic properties modified towards the favorable direction by an amount equal to the uncertainty , the predicted conversion is higher than the conversion observed by Cho (32).

Line D in Fig. 2 shows the equilibrium conversion when S_7 is included in the sulfur vapor and all the thermodynamic properties are changed by the uncertainty (as line C) in the direction of increased equilibrium conversion. The predicted equilibrium shown by line D is higher than the observed conversion (line E). However minimum conversion occurs at 750 K instead of 720 K. This may be due to incorrect sulfur vapor distribution in this region (600 to 800 K)

Line F shows equilibrium conversion when only the thermodynamic properties of sulfur species are changed by the uncertainty. Comparing line F and C, the difference is due to the effect of the uncertainty of the thermodynamic properties of H_2S, SO_2, and H_2O(g). The calculation of K_1 based upon a particular model of sulfur vapor will contain partial pressure terms for each molecular species of sulfur. Therefore, care should be taken when thermodynamic properties of sulfur species are used to predict equilibrium conversion. They should be used together as a set with the corresponding sulfur vapor model.

It should be noted that the possibility of all the thermodynamic properties simultaneously having maximum uncertainty in the favorable conversion direction is unlikely. In addition the sulfur vapor distribution will be altered as shown in Fig. 28 and 29. This alteration of sulfur vapor distribution results in minimum conversion occurring at 750 K instead of 760 K (line D and B of Fig. 2) The resulting thermodynamic properties are given in Table 11. Line D on Fig. 30 illustrates the predicted conversion using these thermodynamic properties. For the same reason the usefulness of thermodynamic properties in Table 11 should be tested in other reaction systems which involve sulfur vapor. Since the thermodynamic properties have not been greatly distorted, it is reasonable to expect that they will predict equilibrium in any other systems, in addition to for the lean H_2S/SO_2 system.

The sensitivity analysis of available thermodynamic properties for the H_2S/SO_2 system concluded that the $S_2-S_6-S_8$ model cannot predict the chemical equilibria adequately without distorting the thermodynamic properties of sulfur species by a large amount. However when using properties for $S_2-S_6-S_7-S_8$ the equilibrium conversion is more satisfactorily with the slight adjustment of the thermodynamic properties of species within the accuracy cited. When better experimental sulfur vapor distribution measurements become available, the entropies of S_6, S_7, and S_8 will be determined more accurately. With these improved data a more complex model for predicting chemical equilibria of H_2S/SO_2 system and between sulfur vapor molecular species may be developed. Note that the entropies of S_6 and S_8 were changed by an unusually large value of 3.3 and 4.2 cal/mole-K, respectively, while attempting to predict equilibrium by distorting thermodynamic data.

4.6 Testing the model of sulfur vapor pressure data

Sulfur vapor pressure is the primary measured property used to determine the thermodynamic properties of sulfur species, using a reasonable sulfur model deduced from mass spectrometry. In the sensitivity study the thermodynamic properties of sulfur are determined from the equilibrium conversions of the H_2S/SO_2 system. To be valuable in calculation for systems besides H_2S/SO_2, the resulting sulfur properties must be compatible with the physical evidence of sulfur vapor composition. This section will

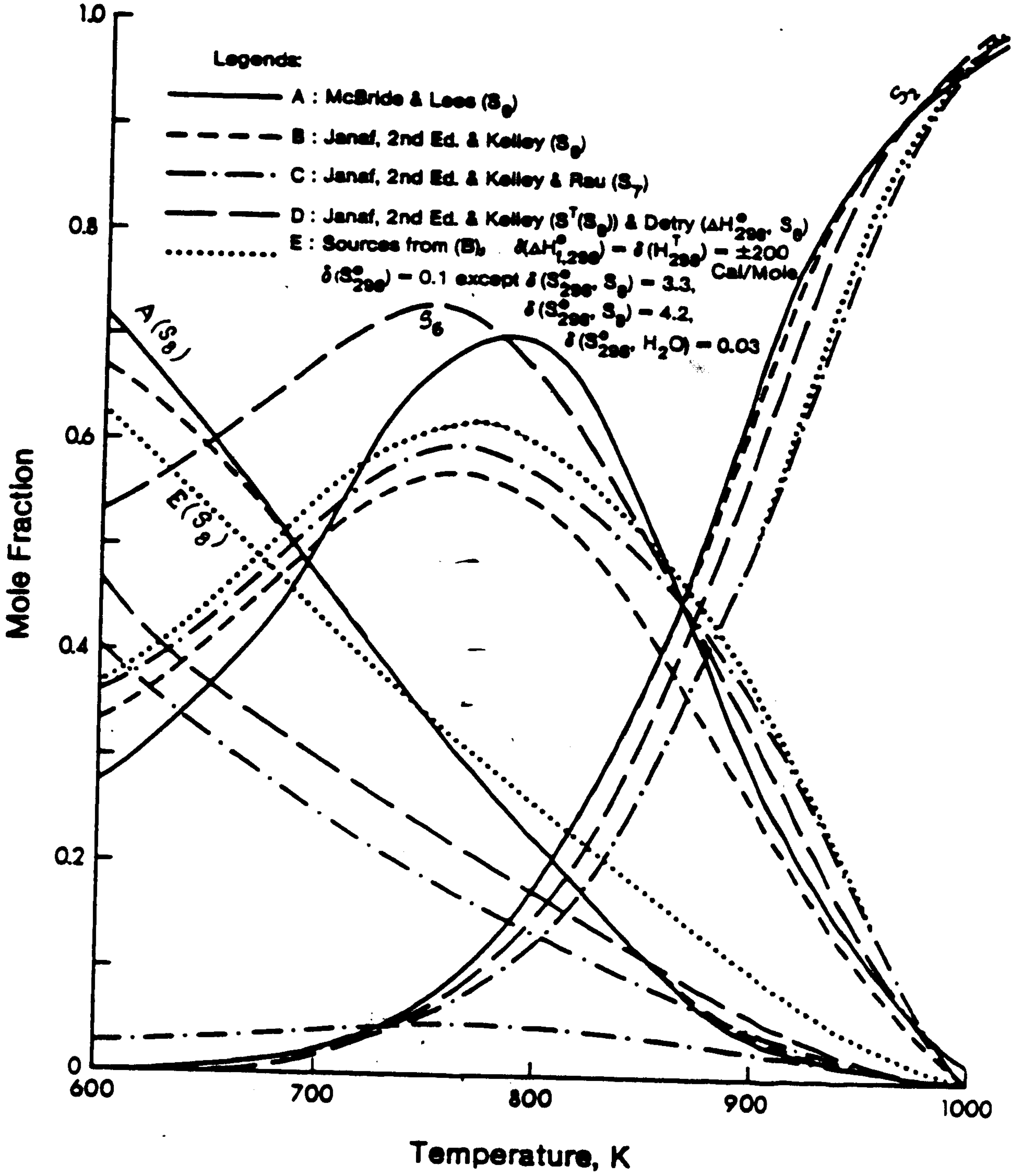


Fig. 28 Sulfur Vapor Distribution for Different Thermodynamic Sources.

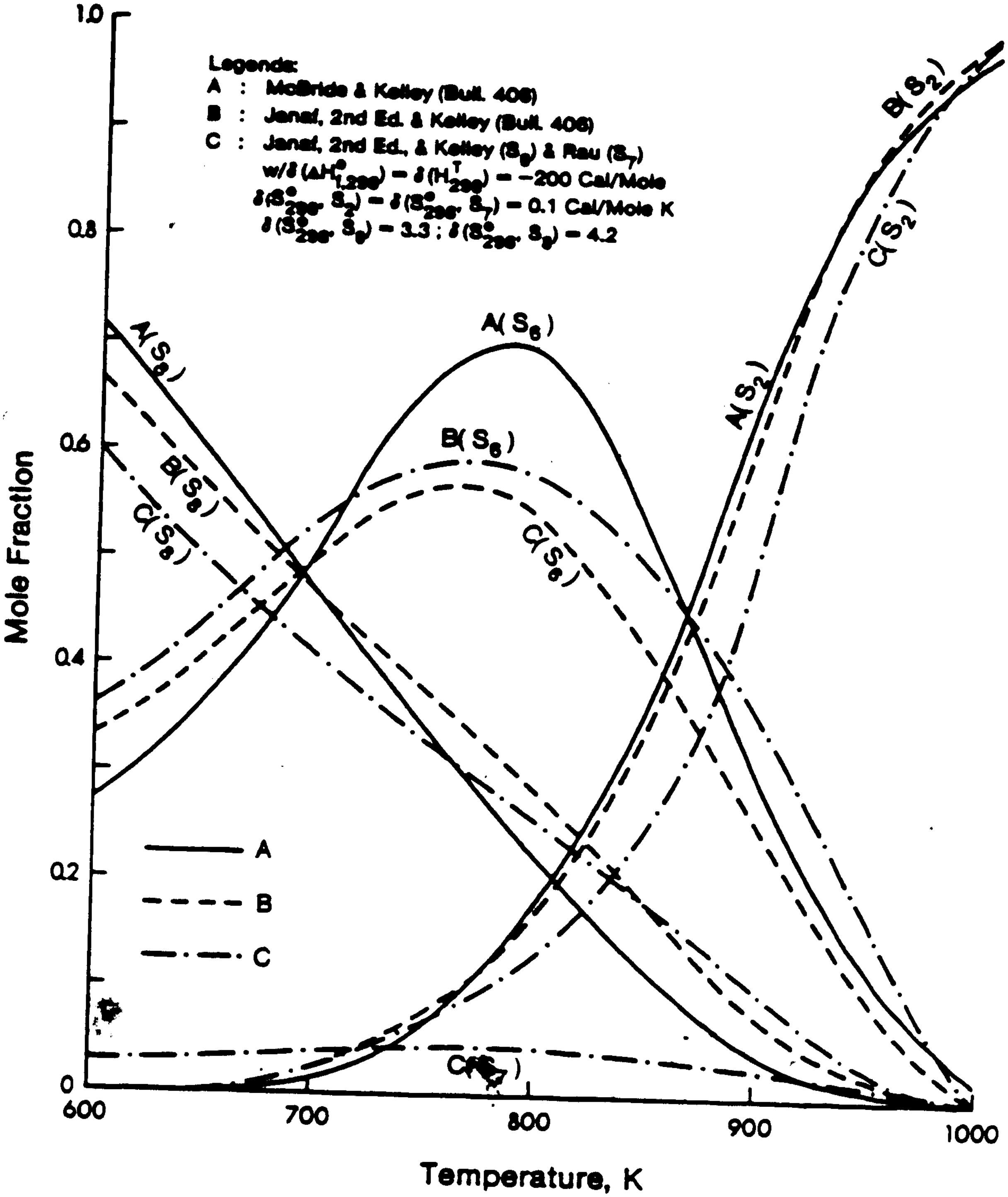


Fig. 29 Sulfur Vapor Distribution of Distorted Sulfur Properties

TABLE 11

DISTORTED THERMODYNAMIC PROPERTIES AT 700 K

Species	Standard Heat of formation (cal/mole)	Entropy (cal/mole K)	Sensible Enthalpy (cal/mole)
H2S	-5,020	56.560	3380
SO2	-70,747	58.450	4233
H2O	-57,988	42.349	3590
S2	30,640	61.664	3147
S6	27,780	84.60	
S7	26,970	97.41	
S8	24,000	141.493	16167

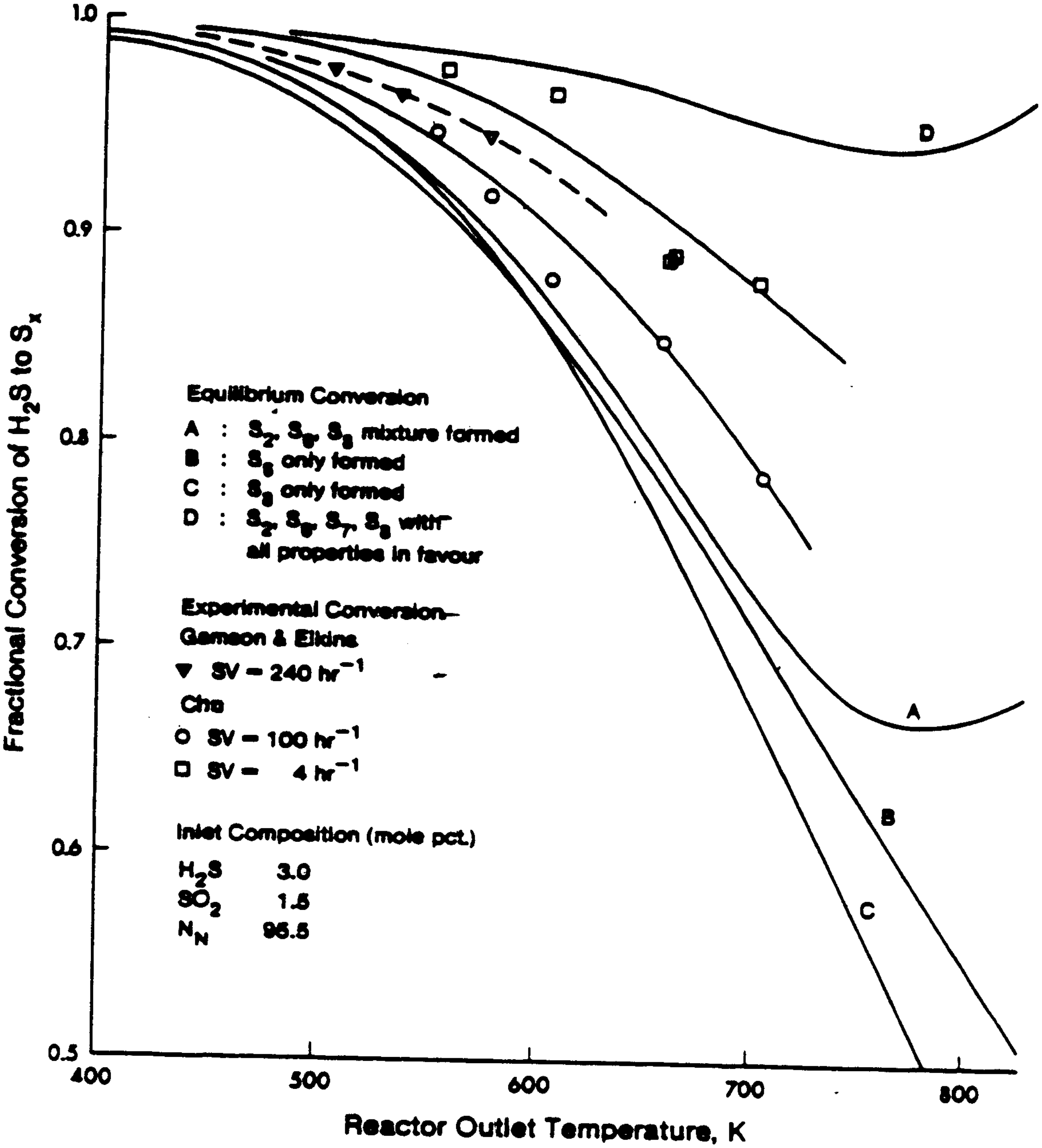


Fig. 30 Comparison between Present Predicted and Experimental Conversions.

study the resulting sulfur vapor distribution due to the distortion of sulfur thermodynamic properties from the sensitivity analysis.

Braune's vapor pressure data (19) at subatmospheric pressure were fitted to their suggested model S_2-S_4-S_6-S_8. Their values of K_i's do not fit their experimental data well (20%, a larger than experimental error.) The Rosenbrock hill climbing method is then used to find a better K_i's at each temperature for their experimental data, the percentage standard deviation is only 5% compaired to 20% for Braun's equilibrium constants. The Rosenbrock method is also used to find better K_i's for sulfur vapor model S_2-S_6-S_8. The resulting ln K_i vs 1/T has about the same curvature as if only S_2-S_6-S_8 existed significantly (Fig. 15). This is expected from the results obtained from mass spectroscopy by Berkowitz et al. (14) and later by Detry et al. (46), where S_4 is found to be the least significant species in sulfur vapor at low pressure after S_9 and S_{10}. Therefore S_4 was not included in the sulfur vapor model used in this study for sensitivity analysis of thermodynamic properties. It is also not included in any calculation used in Chapter 6 in calculating the equilibrium conversion.

Wakihara et al. (147) used Rau's thermodynamic properties for all sulfur species (126) to find the significance of each species in Braune's (19) range of temperatures and pressures and to test the reliability of Rau's data. They concluded that S_7 is significant enough to be included in subatmospheric sulfur vapor pressure in the range 350-1000°C. The plots of ln K_i vs 1/T are linear, suggesting that Rau's data are consistent and thus reliable. As an extension of this work, Rau's data were also used to calculate partial pressures of each species for atmospheric and higher vapor pressures using a program supplied by Rau. It is noted that at low temperatures S_7 is significant even at atmospheric pressure. Futhermore, S_3 is significant in the high temperature and pressure region and S_4 is insignificant (mole fraction less than 0.001) over the whole range of temperatures and pressures. Rau used Detry's mass spectra for determination of the composition of sulfur species for his vapor data. Therefore the result obtained on the significance of S_7 and S_3 at low and high temperature ranges is the consequence of the accuracy of Detry's mass spectra data. Chao (31) also conceded that S_7 is significant in sulfur vapor as well as liquid sulfur. Therefore a new model of sulfur vapor is adopted S_2-S_6-S_7-S_8.

When S_7 was added to the sulfur vapor model S_2-S_6-S_7-S_8 using Rau's (126) thermodynamic data for S_7, the conversion increased only slightly. However with the presence of S_7, the conversion seems to be very sensitive to the input thermodynamic properties. If standard heat of formation and sensible enthalpies of all species are changed by 200 cal/mole and the entropy of all species are changed by 0.01 cal/mole-K, except 3.3 cal/mole-K for S_6, 4.2 cal/mole-K for S_8, and 0.03 cal/mole-K for H2O(g), the predicted conversion is higher than those observed by Cho (32) and Gamson and Elkins (55). This set of data were then used to calculate the sulfur vapor distribution at 1 atm. which was compared to other work (Fig. 29). The result is S_6 becomes more important than accounted for in previous calculation.

Since with the addition of S_7 the conversion is improved, it is reasonable to include all other species to assess the effect of the heretofore neglected species on conversion. Unfortunately when Rau's (126) thermodynamic properties for S_i i=2 to 8, were used in conjunction with JANAF (74) values for H_2S, SO_2, H_2O, the resulting conversion is lower than the present referenced conversion (at 700 K, 0.722 vs 0.728). Thus Rau's values of thermodynamic properties for S_2 to S_8 (126) are not applicable to low temperature, low pressure range. Another experimental study of the type done by Rau (126) should to be done for low temperature, low pressure range to find out the new equations for thermodynamic properties of sulfur species. For the sulfur system, Tegman and Erickson (140) noticed there is an inconsistency between Rau (126) and JANAF (74) values. This inconsistency may or may not be accounted for by the drop in equilibrium conversion. Tegman (140) also noticed the large deviation from ideality of sulfur vapor above 600 K. Since a large amount of inert N_2 was used in this study, the partial pressure of sulfur vapor is very low, thus the ideal gas law still holds for this work, as a check on fugacity confirms.

The improved model, S_2-S_6-S_7-S_8, was used mainly in predicting yield in the converter temperature range, 400-700 K. Since no data are available on equilibrium conversion at high temperature, the accuracy of this model at high temperature cannot be checked.

4.7 Conclusions and recommendations

The simplified models for sulfur vapor used to date cannot predict the equilibrium conversion of H_2S/SO_2 system without distorting the thermodynamic properties by large amounts. In light of Wakihara's interpritation of Rau's data that S_7 is an important species, a new model was created, S_2–S_6–S_7–S_8. This new model described the equilibrium conversion for lean acid gas (less than 10% H_2S) at low temperatures (<700 K) using the cited thermodynamic properties and corresponding uncertainty. From the sensitivity study it is suggested that the thermodynamic properties of S_2 need to be determined with more accuracy than those of S_8 since equilibrium conversion is more sensitive to the change in thermodynamic properties of S_2

For the model to be comprehensive S_3 and S_5 need to be added for rich acid gas or for high temperature. To arrive at a sulfur model valid over the entire temperature range of 400–1600 K, more data on sulfur vapor pressure as a function of temperature and pressure for the intermediate region(700–1000 K), between the West and Menzies' condition and Rau's condition, are necessary. This will determine the significance of each sulfur species as a function of temperature and sulfur pressure, and the sulfur thermodynamic properties.

5. EQUILIBRIUM CONSTANT FOR H_2S/SO_2 MIXTURE

5.1 Introduction

A sensitivity analysis was performed on the H_2S/SO_2 reaction by systematically varying the standard heat of formation, sensible enthalpy and the standard entropy of each species in the mixture as well as each molecular species in the model of sulfur, $S_2-S_6-S_7-S_8$. Experimental equilibrium conversions obtained by Cho were used as the standard for comparison when evaluating the effect of each thermodynamic property on the predicted equilibrium conversion. This sensitivity analysis has generated some useful information on the effect of thermodynamic properties on the equilibrium conversion. However the degree of error inherent in the measured properties remained uncertain as shown in the following explanation. Knowing the relative effect of thermodynamic properties of each species on equilibrium conversion, one can attempt to predict the equilibrium conversion with as minimal as possible changes in the values of the standard heat of formation, sensible enthalpy and the standard entropy for each component. However the thermodynamic properties (e.g. standard heat of formation, sensible enthalpy, standard entropy...) are determined from physical data (e.g. spectra, vapor pressure...) using quantum theory, and thermodynamic principles and rules. There are two types of error in the value of a thermodynamic property obtained from reference sources: error in measuring experimental quantities and error in the method used to calculate thermodynamic properties from the above experimental data. The second type of error is not cited with the values of standard enthalpy, standard entropy, and other thermodynamic properties, may be large. The first type of error may often be small with the present advances in measurement devices. For the second type of error, unless a different method is used to arrive at the same result, the error is almost unkown.

To illustrate, using the $S_2-S_6-S_8$ model,

$$2H_2S + SO_2 = 3/2\ S_2 + 2H_2O \qquad (5.1)$$

$$3S_2 = S_6 \qquad (5.2)$$

$$4S_2 = S_8 \qquad (5.3)$$

K_ps for each of the three reactions would be required to define the equilibrium composition of this system. However, if the equilibrium mixture is approximated by one overall reaction of the form of equation (5.4),

$$2H_2S + SO_2 = 3/\nu \ S_{\nu} + 2H_2O \qquad (5.4)$$

an approximate K_p' may be defined,

$$K_p' = [P(H_2O)^2 \times Ps^{3/\nu}]/[P(H_2S)^2 \times P(SO_2)] \qquad (5.5)$$

where $Ps = \sum_{i}^{8} Ps_i$

and ν = average atomic number for sulfur vapor

To calculate the correct K_ps, measurement of $Ps_1, \ldots, Ps_8$ at equilibrium would be required. At present, such measurements are not possible.

5.2 Assumption used in the determination of an equilibrium constant

Using equation (5.4), the number of g-atom of sulfur vapor may be determined. Ps can be determined if the amount of each S_i could be measured. This might be done experimentally by using mass spectrometry to determine partial pressures of each S_i. However fragmentation of sulfur ions in the mass spectrometer will create much uncertainty about the accuracy of sulfur distribution (likely equivalent to that in the determination of the thermodynamic properties). The resulting equilibrium constant, supposedly K_p', would likely predict equilibrium conversions with no better accuracy than those from using the present thermodynamic properties.

The average atomic number of sulfur is a function of both the temperature and the partial pressure of sulfur, and can be estimated from vaporization of pure sulfur. Such data have been obtained by Preuner and Schupp (122) for low pressure range and Rau (128) for high pressure ranges. The data from the first two sources (illustrated in Fig. 31) for the low pressure range are not accurate enough, e.g. 20% deviation at 450°C, 50 mm Hg, as pointed out by Braune (19). This results in considerable uncertainty concerning the values of average atomic number of sulfur at various temperatures and pressures in the low pressure range.

In the sensitivity analysis, variation in the magnitude of thermodynamic properties equivalent to errors of the first kind were examined. Calculated equilibrium conversions were found to be less than observed conversions for those conditions assuming a sulfur vapor model, S_2-S_6-S_8. Published values of standard entropy at 298K for octatomic sulfur cited an inaccuracy of the order of magnitude of 0.1 cal/mole K. On the other

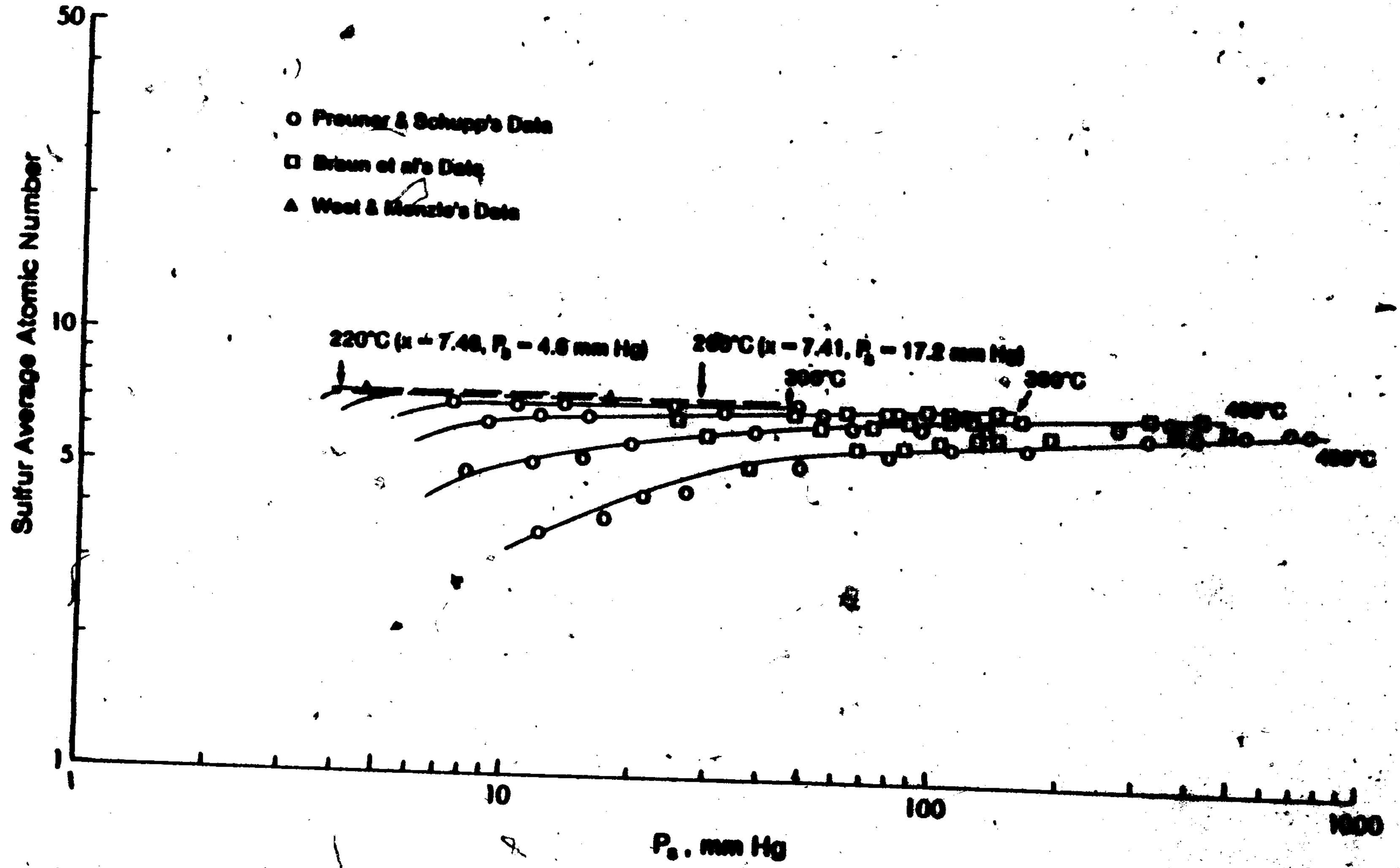


Fig. 31 Sulfur Average Atomic Number vs. Sulfur Pressure (Superheated)

hand, adjustment as large as 4.2 cal/mole K were required to increase the equilibrium predicted, but still with deficiency. Even greater uncertainty in the entropy of heptatomic sulfur existed. Upon modifying the sulfur model to include S_7, minor improvement in predicted conversions resulted. However, when the thermodynamic properties of S_7 were adjusted, comparable to an error of the first kind, then the resulting predictions exceeded observed conversions. As a result, it would seem that the lack of knowledge concerning S_7 – errors of both first and second types being involved – is the primary source of discrepancy between predicted and observed conversion.

If there is no effect of other species upon the sulfur distribution, then, at each temperature the sulfur average atomic number will be nearly constant for the range of data used. Since there is only 1.5 to 10% H_2S and stoichiometric ratio of H_2S to SO_2 in the initial mixture with the bulk inert nitrogen, the partial pressure of each species will be small in the equilibrium mixture (5 to 100 mm Hg as shown in Table 12.) Then, no change in average atomic number of sulfur when sulfur partial pressure changes between 5 to 100 mm Hg is observed at 225°C, less than 0.3 at 270°C, less than 1.1 at 320°C, and less than 2.60 at 320°C (Table 13). As a result the assumption of average atomic number of sulfur as a function of temperature only does not have significant effect on equilibrium conversion for mixture with low H_2S/SO_2 initial composition.

From Fig. 31, at low sulfur pressure (<20mm Hg), the average sulfur atomic number is dependent upon temperature and sulfur pressure. At higher sulfur pressure, the data tend to converge to a constant value for the average sulfur atomic number at all temperatures and pressures, somewhere between 7 and 8.

If a given experimental equilibrium conversion was obtained for reaction (5.4) at a specified temperature and pressure, Fig. 31 could provide an additional condition to be satisfied. If an arbitrary value is assumed for sulfur pressure, the average sulfur atomic number may be obtained directly from the graph. Knowing sulfur pressure and the total pressure for the system, the partial pressures for the other components can be easily calculated, enabling K_γ' to be calculated as per equation (5.5). Different assumed values for sulfur pressure Ps should lead to different K_γ'.

If a similar experiment starting with a different initial composition is treated in the same way, another set of K_γ' versus γ results. The intersection of these two curves

TABLE 12

SULFUR PARTIAL PRESSURE IN EQUILIBRIUM COMPOSITION USING RAU & JANAF THERMODYNAMIC PROPERTIES

Temperature (K)	Temperature (C)	*Predicted Equilibrium Conversion	Average sulfur atomic number	Sulfur Partial Pressure mm Hg.
500	227	0.9817	7.404	5.7
600	327	0.9161	7.06	30.12
700	427	0.9117	5.88	30.92
800	527	0.7068	3.14	42.38
1000	627	0.7261	2.04	65.97

NOTE: Inlet Composition
3% H_2S
1.5% SO_2
95.5% N_2

TABLE 13

EXPERIMENTAL SULFUR AVERAGE ATOMIC NUMBER

Pe T(°C)	5 mm Hg.	30 mm Hg.	100 mm Hg.	$\Delta\bar{Z}$
220	7.46	7.46	7.46	0.00
260	7.41	7.41	7.41	0.00
300	7.00	7.10	7.30	0.30
350	6.10	6.80	7.20	1.10
400	4.20	6.10	6.80	2.60
450	2.30	5.10	5.80	3.50

should provide values of ϑ and K_γ' which satisfy both experiments. Extending this approach to more than two experiments would be very useful if a common convergence to K_γ' could be obtained. This procedure was tested using equilibrium composition data provided by Aquitaine (90).

Results from this method indicated no common solution could be obtained when 3 or more such plots of K_γ' vs ϑ were compared. On the surface either the data represented by Fig. 31 or the equilibrium compositions determined experimentally, or both, may contain substantial error. Reference to Fig. 31 shows that the actual Ps values likely to be encountered are at partial pressures less than 10 mm Hg. This region had little or no data determined experimentally. In the absence of data, another approach was introduced to force these $K_\gamma' - \vartheta$ graphs to converge to a near-common solution.

For any arbitrary ϑ, a value of K_γ' can still be calculated, since Ps may also be determined once ϑ is specified. When there are more than two experimental conversions, the convergence is not very clear (Figs. 33, 34, and 35), knowledge of sulfur association as well as effect of species on equilibrium is used to determine the pseudo-equilibrium constant K_γ'. The values of K_γ' so estimated at the four temperatures corresponding to Figs. 32 to 35 are listed in Table 14. As the result of this approach, the average atomic number of sulfur is not a function of sulfur partial pressure for equilibrium data predicted (Fig. 36).

Additional justification for this approach was obtained by using the Van't Hoff equation to test the temperature dependency of K_γ' so calculated.

$$\ln K_\gamma' = A/T + B \qquad (5.6)$$

where A and B are constants.

To summarize, the equilibrium constant for H_2S/SO_2 mixture was calculated in this chapter using the following assumptions:

1) Pseudo equilibrium constant K_γ' determined by Eq. (5.5) is assumed to be a function of temperature only like the true equilibrium constant, K_γ of the overall reaction (5.4)
2) $\ln K_\gamma'$ is a linear function of $1/T$
3) Sulfur average atomic number is a function of temperature only.

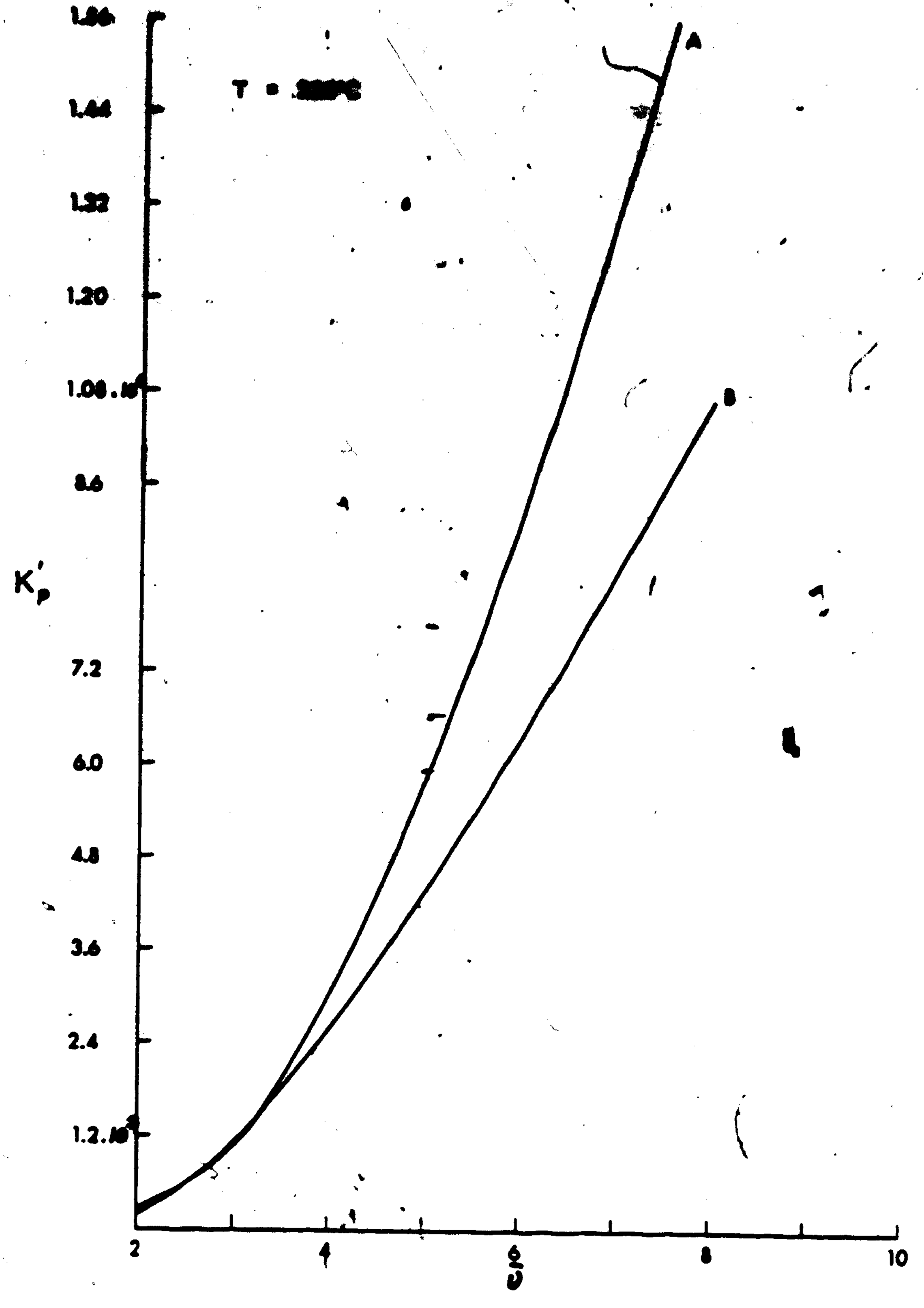
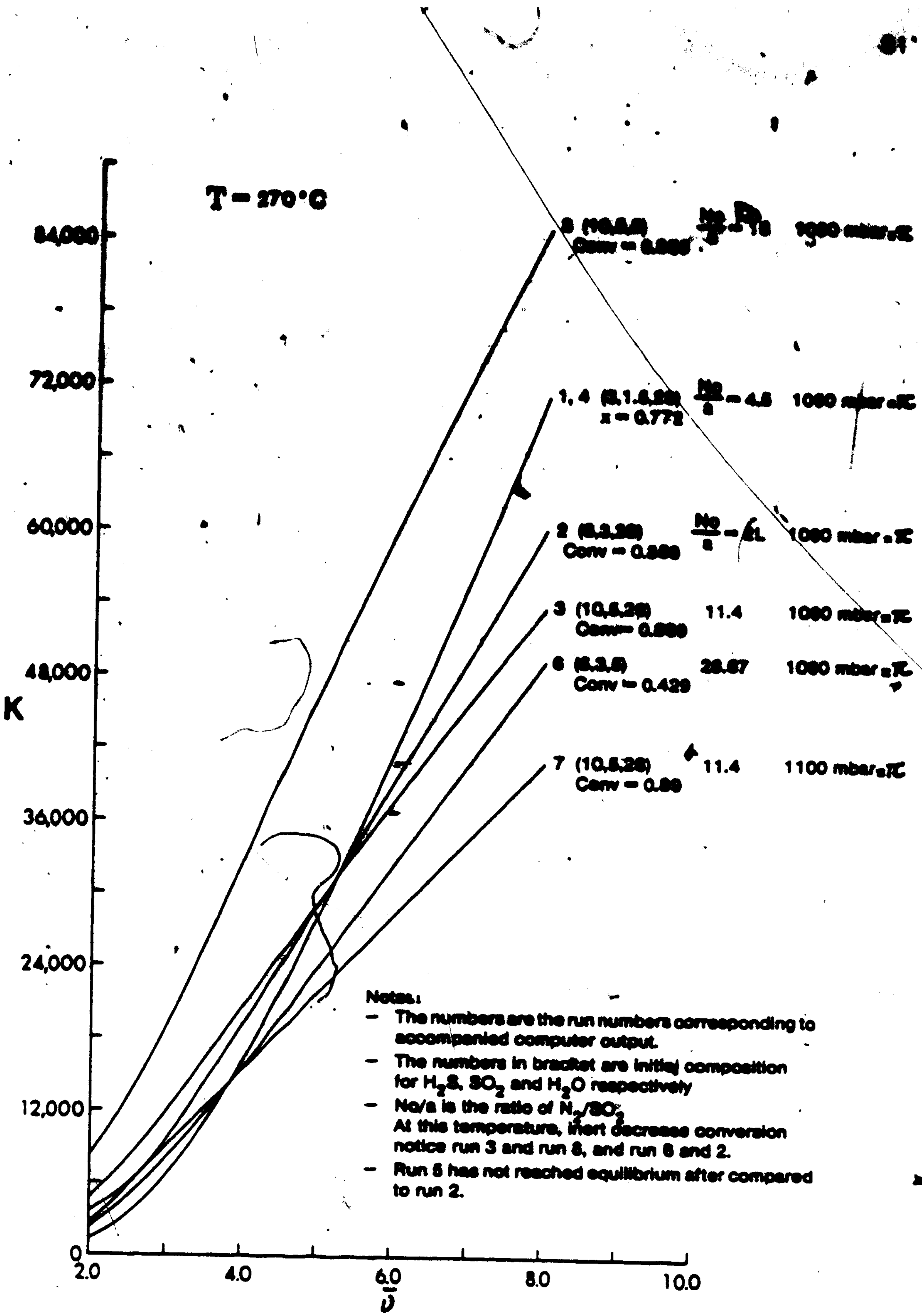


Fig. 32 Determination of Equilibrium Constant at 225°C



Notes:

- The numbers are the run numbers corresponding to accompanied computer output.
- The numbers in bracket are initial composition for H_2S, SO_2 and H_2O respectively
- Na/a is the ratio of N_2/SO_2
  At this temperature, inert decrease conversion notice run 3 and run 8, and run 6 and 2.
- Run 5 has not reached equilibrium after compared to run 2.

Fig. 33 Determination of Equilibrium Constant at 270°C

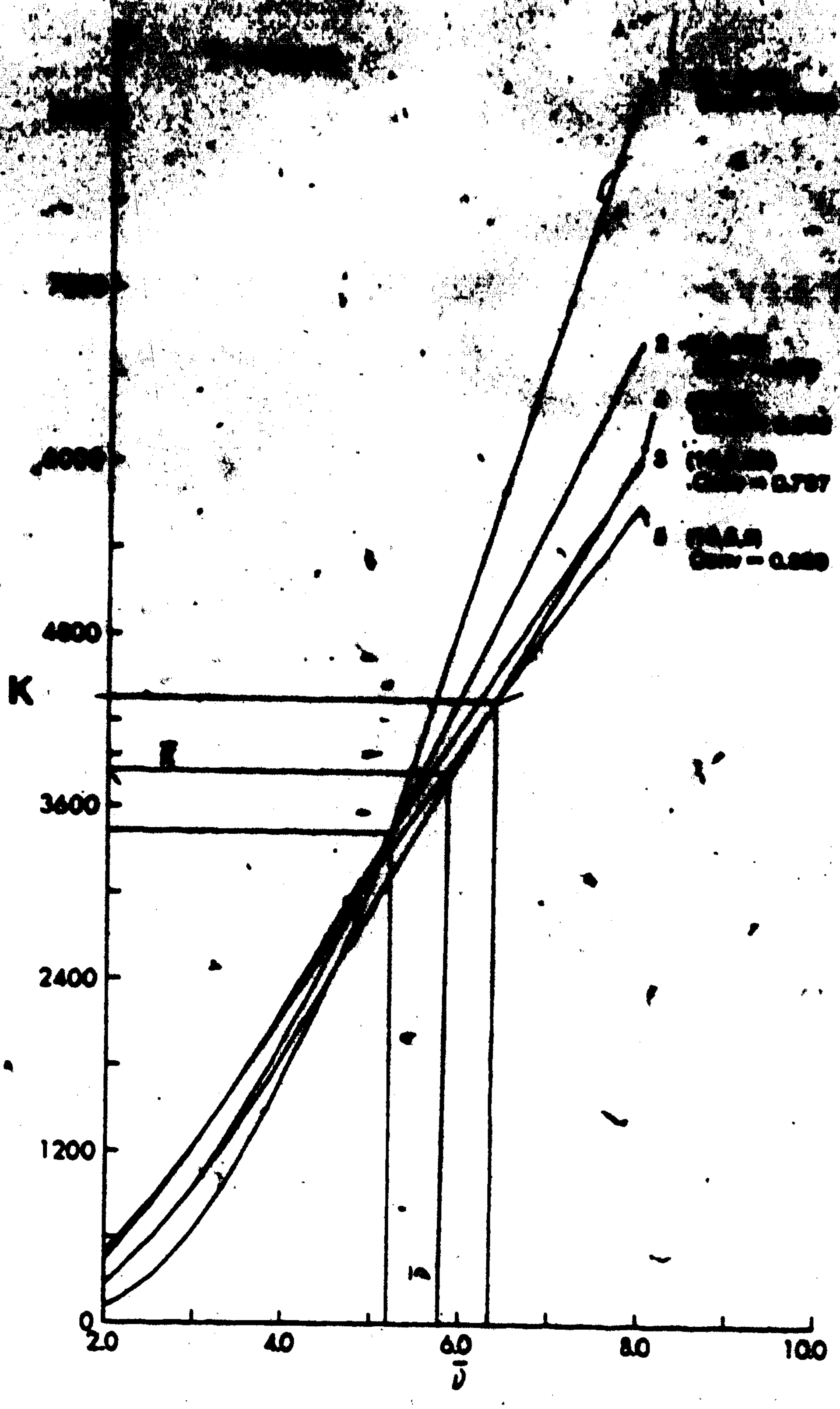


Fig. 34 Determination of Equilibrium Constant at 320°C

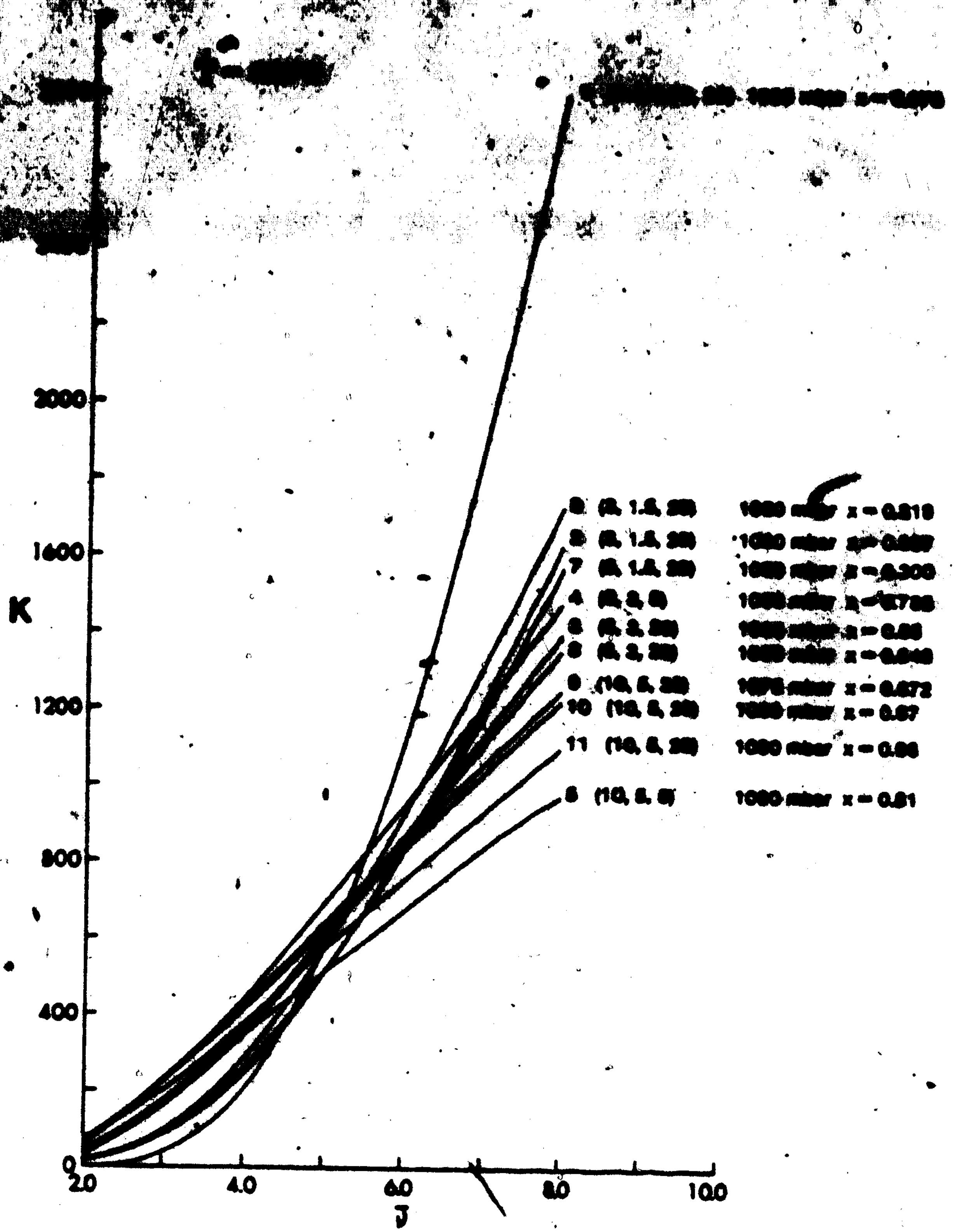


Fig. 38 Determination of Equilibrium Constant at 370°C

[illegible]

T(°C)	[illegible]	[illegible]
[illegible]	1.5 . 10	[illegible]
[illegible]	2.27 . 10	[illegible]
[illegible]	[illegible] . 10	5.3[illegible]
[illegible]	[illegible] . 10	4.7[illegible]

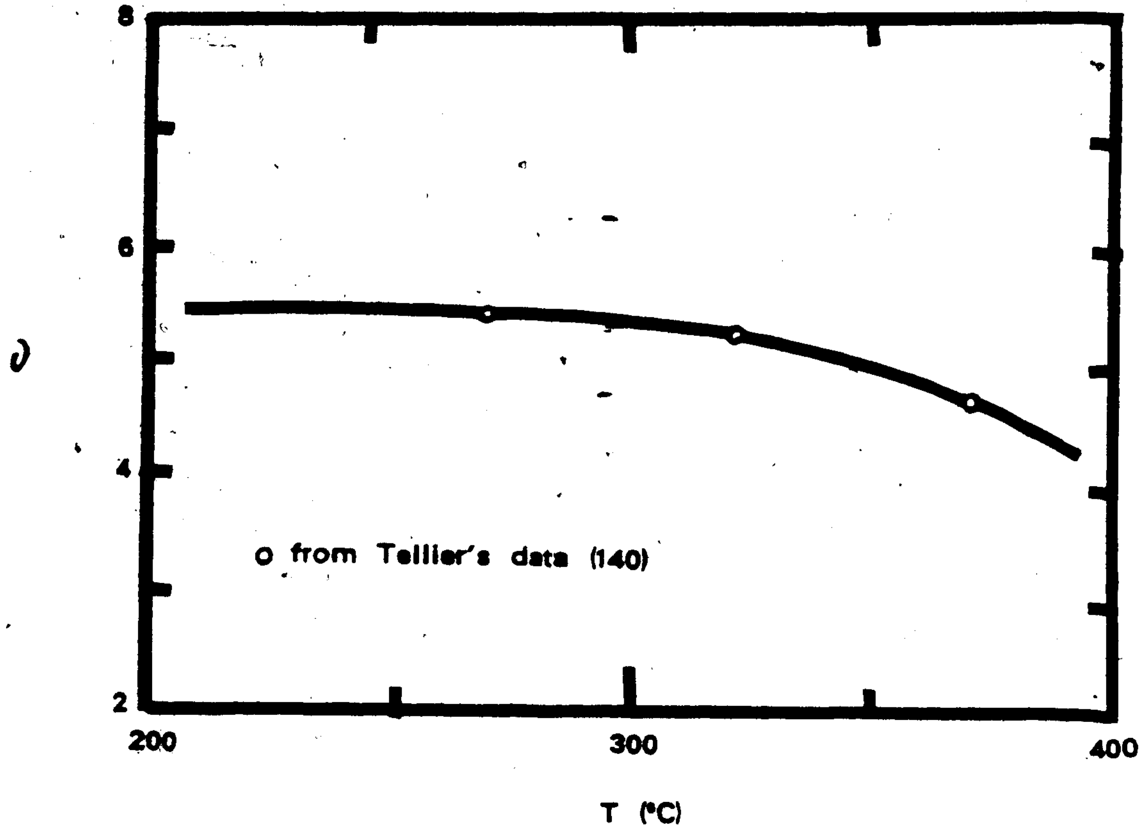


Fig. 36 Sulfur Average Atomic Number to be used with Pseudo-equilibrium Constant expressed by Eq. (5.7)

5.3 Result

In Fig. 32 for 225°C isotherms, the two curves intersect at the average atomic number of sulfur of 3.28 and equilibrium constant of 150,000.

In Fig. 33 for 270°C isotherms, the curves 6 and 8 (the number indicates the order of the data point for each isotherm) for 5% initial water concentration do not intersect with each other. Therefore only the runs with 28% initial water concentration were used. The convergence appears sharp at 5.4 average atomic number of sulfur and 32,700 for the equilibrium constant. Run 5 has been discarded since comparison with run 2 shows that equilibrium has not been reached. Curve 7 has not been used in determining the equilibrium constant at 270°C since comparison with run 3 also shows that equilibrium was not reached. In run 3, the total pressure of 1090 mbar is slightly lower than the pressure 1100 mbar of run 7. The corresponding conversions were 0.899 and 0.890, respectively.

In Fig. 34 for 320°C isotherms, curves for runs with 28% H_2O initial composition converge to an average atomic number of sulfur of 5.3 and the equilibrium constant of 3360. On the other hand, curves for runs with 5% H_2O initial composition converge to an average atomic number of sulfur of 6.31 and an equilibrium constant of 4190. Convergence clearly occurs at two different equilibrium constants and two different average atomic numbers of sulfur, with the assumption that the sulfur average atomic number and equilibrium constant are both unique functions of temperature, one should expect only one average atomic number of sulfur and one equilibrium constant for each temperature. The average value for each of the coordinates of the two convergence points is used as the value for the equilibrium constant (3775) and the average atomic number (5.81) at 320°C.

In Fig. 35 for 370°C isotherms, the curves 4 and 5 for the runs with 5% initial water composition do not intersect. Runs 1, 3, 6, 8 and 9 for 28% initial water composition converge at an average atomic number of sulfur of 5.06 and equilibrium constant of 746. Runs 10 and 11 were not shown, comparison with run 9 shows that equilibrium has not been reached. Similarly, runs 2 and 7 were deleted after comparison with run 6.

The results are summarized in Table 14. The linear plot of equation (5.6), the Van't Hoff equation, was determined using the least square program LLS and values from Table 14. The result is shown in Fig. 37, with constants,

$$\ln K_{\gamma}' = -17.885 + 15466/T \qquad (5.7)$$

The program LLS is documented in Appendix B. Table 15 lists the values of K_{γ}' obtained in the preceding Fig. 32 to 35, and compares these values to those predicted using equation (5.7) In Fig. 37, the vertical lines indicate the spread in value for the equilibrium constant obtained from the intersection of the curves for each temperature isotherm. Fig. 38 compares the predicted equilibrium constants with the corresponding intersection values at the four temperatures. The K_{γ}' predicted using equation (5.7) were used to calculate theoretical conversions for the H_2S/SO_2 reaction at the conditions shown in Fig. 32 to 35. A comparison between the predictions and the conversions cited earlier is shown in Fig. 38. The predicted conversions are within 3% of the actual conversion, Table 16 shows that the equilibrium constant described by equation (5.7) generates values which are within 10% of Cho's experimental conversions but on the low side.

5.4 Discussion

The specific argument for the assumptions on the calculation of pseudo-equilibrium constant will be discussed in this section.

5.4.1 Discussion on the average atomic number of sulfur

If there is no effect of other species upon the sulfur distribution, then, at each temperature the sulfur average atomic number will be nearly constant for the range of data used. Since there is only 1.5 to 10% H_2S and stoichiometric ratio of $2H_2S$ to $1SO_2$ in the initial mixture with the bulk inert nitrogen, the partial pressure of each species will be small in the equilibrium mixture (5 to 100 mm Hg as shown in Table 12.) Then no change in the average atomic number of sulfur is observed at 225°C, when sulfur partial pressure changes between 5 to 100 mm Hg, less than 0.3 at 270°C, less than 1.1 at 320°C, and less than 2.60 at 370°C (Table 13). As a result the effect on equilibrium conversion of the assumption of average atomic number of sulfur as a function of

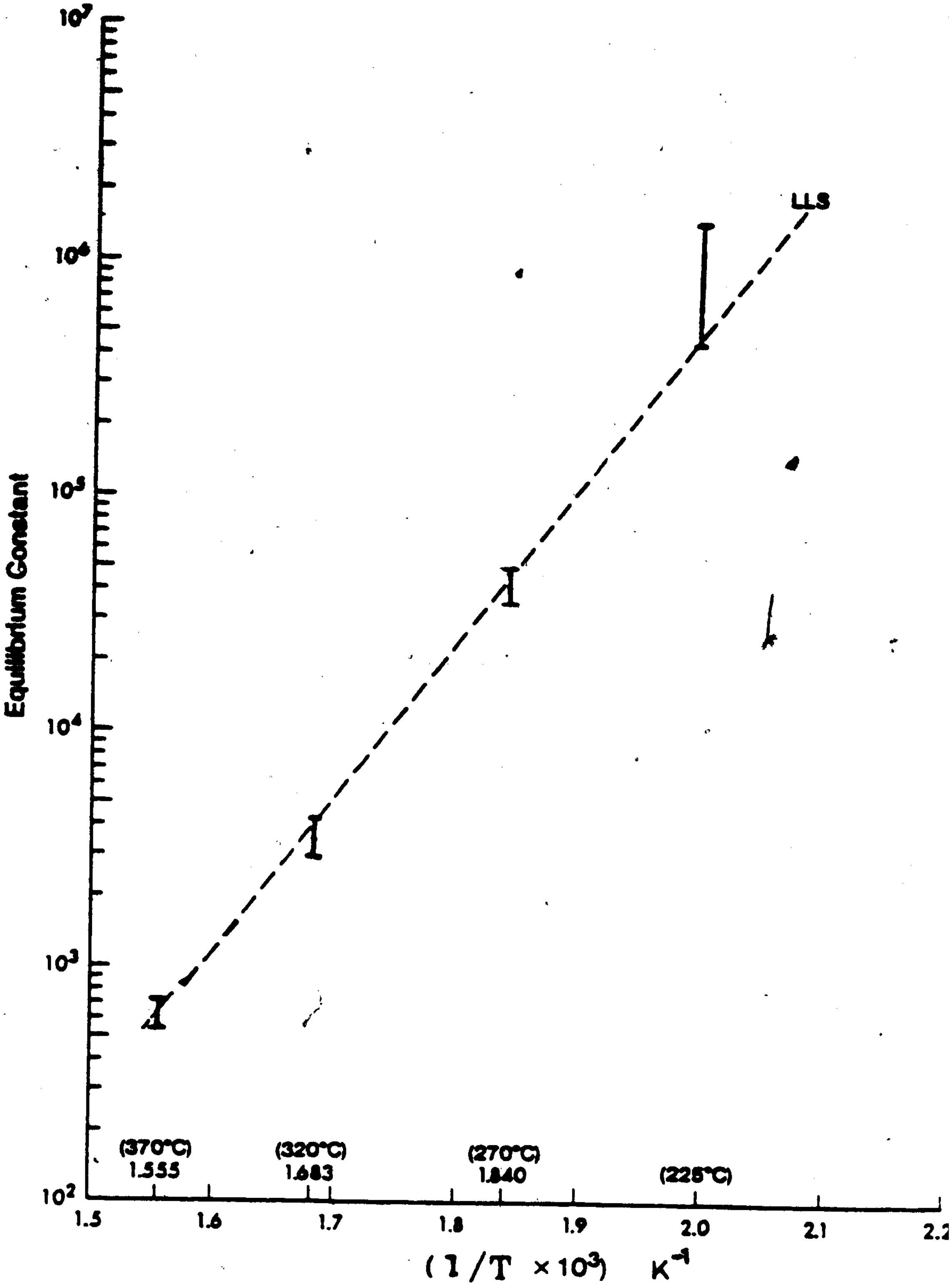


Fig. 37 Linear Least Square of Equilibrium Constants.

TABLE 15

LINEAR LEAST SQUARE EQUILIBRIUM CONSTANTS FOR H2S/SO2 REACTIONS

T(°C)	K_p's from plots	K_p'(LLS)
225	$6.00 \cdot 10^5$	$5.196 \cdot 10^5$
270	$3.27 \cdot 10^4$	$3.87 \cdot 10^4$
320	$3.36 \cdot 10^3$	$3.608 \cdot 10^3$
370	$5.35 \cdot 10^2$	$4.743 \cdot 10^2$

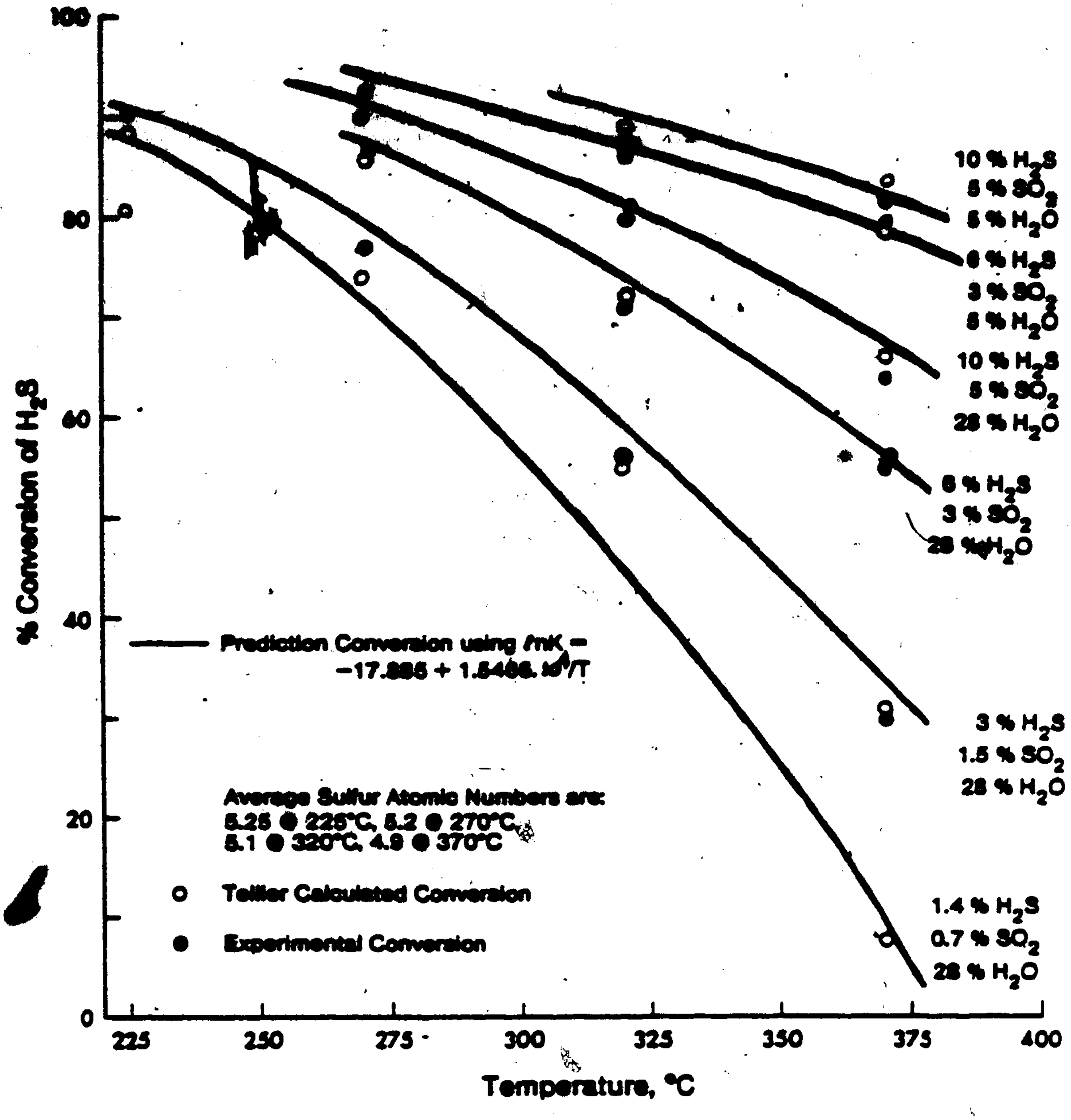


Fig. 38 Comparison between Actual Conversion and Predicted Conversion Using Linear Least Square Equilibrium Constant.

TABLE 16

PREDICTION OF CHO'S DATA (32)

T(K)	%H2S	%SO2	Ptot mm Hg.	Xcal	Xact	% DEV.
702	3.10	1.5	738.56	80.95	88.0	-8.01
555	3.18	1.61	734.05	94.67	98.0	-3.4
604	3.20	1.58	737.85	88.50	97.0	-8.76
658	3.18	1.63	738.72	82.67	89.0	-7.11
660	3.16	1.57	741.25	81.70	89.0	-8.20

temperature only is not significant for mixtures with low total mole fraction of H_2S and SO_2.

5.4.2 Van't Hoff assumption

In the determination of the equilibrium constants, the Van't Hoff equation was used as the criterion. However, the Van't Hoff equation as used herein is only applicable for a temperature range where the heat of reaction is constant. This condition may not be fulfilled for the H_2S/SO_2 system due to the associated reactions of sulfur. When the heat of reaction is not constant, the equilibrium constant can be expressed in the form,

$$R \ln K_p = C - \Delta H_0/T + \sum_i^n n_i (a_i \ln T + b_i T/2 + c_i T^2/6) \qquad (5.8)$$

With known heat capacities, there are twelve coefficients C, ΔH_0, n_i, i=H_2S, SO_2, H_2O and S_j, j=2 to 8, or at the minimum six coefficients if Eq. (5.4) was used.

Using equation (5.7) at four temperatures does not provide a sufficient number of equations to solve for the unknown 6 to 12 coefficients. In the absence of the above, the heat of reaction was assumed to remain constant.

5.4.3 Convergence of K_p vs sulfur average atomic number

It is well known that as temperature increases, sulfur vapor molecules dissociate: the higher the temperature, the smaller the average atomic number. Futhermore, under stoichiometric conditions the higher the H_2S concentration, the higher the conversion, and hence a higher sulfur partial pressure. Therefore, using Fig. 31, one would anticipate an increasing sulfur average atomic number with increasing H_2S concentration. On the other hand, increasing the amount of water decreases both the sulfur partial pressure and the extent of reaction. Therefore sulfur average atomic number would be expected to decrease with an increase in water initial concentration.

However at 270°C, Fig. 33 shows that for the runs of 5% initial water composition, the curve for 6%H_2S is always lower than the curve for 10%H_2S i.e. $\bar{\nu}$ (6%H_2S)> $\bar{\nu}$ (10%H_2S) contrary to the analysis in the preceding paragraph. An explanation is offered that run 6 may not have attained equilibrium conversion. If analytical error were present, then run 8 would be high in conversion or run 6 low in conversion. As mentioned in the previous section, these two runs were not used in the determination of the equilibrium constant. However, the equilibrium constant predicts the actual conversion for these cases within 1.7%.

In Fig. 34, for 320°C, the same problem occurs at the convergence point of runs 4 and 5. Nonetheless the predicted conversions show in Fig. 38 are within 71% of the actual conversion.

For both 270° and 320°C isotherms, for runs with 28% initial water concentration, the curves converge to a single point in each case. Correspondingly the prediction for these two isotherms was better than for the other two isotherms, 225° and 370°C.

At 225°C (Fig. 32) the convergence point is at a very low average atomic number, ϑ =3.28; less than the average atomic number found for 270°C. Since this is contrary to experimental evidence, the sulfur average atomic number at 225°C was determined by extrapolating ϑ vs T on Fig. 36 based upon the first two temperatures 320°C and 370°C. Using these value of ϑ, so determined, the only data available at 225°C are those shown in Fig. 32. In using Fig. 32 to predict K_p' at the given ϑ, the average of the two possible values of K_p' was used. The predicted conversion was within 1.91% of the actual conversion (Table 17).

At 370°C the common convergence also was not clearly established (Fig. 35), but the conjecture about the magnitude of the average atomic number is satisfied. The prediction is within 3% except for runs number 7 and 8 (5.46%).

This analysis results in predictions which are better than Tellier's prediction (140) for Aquitaine's data (90). Cho's equilibrium conversion (32) is predicted within 10% on the low side (Table 16).

5.4.4 Comparision with superheated vapor pressure

Sulfur partial pressure and the average atomic number are then used to compare with Braun's (19) and Preuner and Schupp's data (122) on superheated vapor pressures. For the 270°C, 320°C and 370°C isotherms, Table 17 shows that the pressure of sulfur is much higher than the corresponding pressure of pure sulfur for the average atomic number from Fig. 31. As a result of the values of the actual average atomic number being higher , Fig. 32 to 35 would give values of the equilibrium constant higher than the chosen values. Consequently the assumption that ϑ = f(T) alone is not valid. Using equation

TABLE 17

DEVIATION OF PREDICTED EQUILIBRIUM CONVERSION

T(°C)	DEV (TELLIER'S)	DEV (PRESENT PREDICTION)	∂	Ps (Calculated) mm Hg.	∂ From Fig. 31
225	$3.2 * 10^{-3}$	$1.43 * 10^{-4}$	4.9	-	2.2 to 5.0
270	$8.0 * 10^{-5}$	$1.08 * 10^{-4}$	5.1	6.2 to 24.6	7.5 to 7.5
320	$9.0 * 10^{-5}$	$1.03 * 10^{-5}$	5.2	3.7 to 19.8	6.0 to 6.5
370	$9.66 * 10^{-4}$	$2.33 * 10^{-4}$	5.25	5.0 to 45.2	5.5 to 6.5
All Runs	$3.82 * 10^{-4}$	$1.44 * 10^{-4}$			

(5.7) and the corresponding values of ϑ from Fig. 31 to predict equilibrium conversions at the 0% H_2O initial concentration conditions reported by Cho (32), the agreement attained at temperatures below 500 K is suprisingly good, within 10%.

5.4.3 Conclusion

The predictions of equilibrium conversions using the equilibrium constant method are comparable to those obtained by adjusting thermodynamic properties according to their cited uncertainties. At high conversion, prediction using equilibrium constant is better; at low conversion, prediction using thermodynamic properties is better. Since equilibrium constant data are not available, the reader is necessarily resorted to the thermodynamic properties approach.

6. ANALYSIS OF CLAUS PLANTS

6.1 Introduction

The extent of conversion of H_2S to elemental sulfur attainable under typical operating conditions in a modified Claus process plant has been a point of considerable interest and discussion. In 1974, Dalla Lana, Cho and Liu (44) described an attempt to predict thermodynamic equilibrium conversions by relatively simple calculations involving graphical methods. The utility of a simple method lies in its ease of use by operators or process engineers to predict equilibrium limits for process stages or to make comparisons with actual plant performance. Subsequently, additional improvements have been added to the method and it is the purpose of this section to upgrade the method further and to illustrate this approach. In essence, the 1974 report purported to show that detailed calculations for 100% H_2S acid gas could within limitations be applied to acid gases of lower H_2S content. The basis for the method lay in regarding partially converted 100% H_2S acid gas, after removal of the elemental sulfur produced, as an acid gas of lower H_2S content. To the extent that thermodynamic specific heats for the gaseous mixtures are not changing significantly with composition, the graphical method provides some reasonable predictions.

6.2 Deficiency of the graphical method

6.2.1 Equilibrium curves

The usefulness of the graphical method depends on the reliability of the family of calculated equilibrium conversion curves. The discrepancies between calculated and observed conversion could not be ignored. Fig. 3 illustrates this discrepancy.

Fig. 3 also illustrates how uncertainties regarding the mean molecular weight of sulfur vapor greatly affect the thermodynamic equilibrium conversion which were predicted. This is the fundamental problem in applying thermodynamic properties available for the various species, S_2, S_3,...,S_7, S_8. In such a case free energy data calculated using experimental equilibrium conversion would likely provide the safest route. By using

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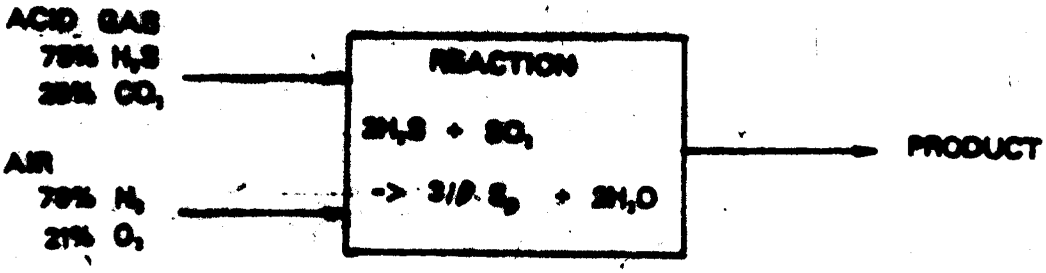
Example 1

Consider the problem of determining the partial pressures of each reactant and product in the following chemical reaction situation:



Air is added in stoichiometric amount to oxidize 50% of the H_2S to elemental sulfur.

Component	*Moles in feed*	*Moles in product*
H_2S	3	1.5
CO_2	1	1
O_2	0.75	0
N_2	2.82	2.82
H_2O	0	1.5
S	0	*(1.5/ν)*
	TOTAL	6.82 + (1.5/ν)

To calculate partial pressures simply via Dalton's Law,

$$P_i = (N_i/N_p)P_t \qquad (6.2)$$

N_p, the total moles of product is needed. Since

$$N_p = 6.82 + (1.5/\nu) \qquad (6.3)$$

Therefore, P_i, depend on an unknown quantity, ν.

Using [illegible] (6.7) for equilibrium constants, the predicted equilibrium [illegible] [illegible] the [illegible] shown in Fig. 3. The results are given by the [illegible] line in [illegible]. At low temperatures, sulfur occurs mainly as S_8, whereas at temperatures above 500 to [illegible] S_8 gradually [illegible]. In this intermediate region, the uncertainties in the average atomic number of sulfur may become large resulting in the increasing discrepancy.

[illegible] [illegible] free energy minimization method predicts on the low [illegible] also below the equilibrium constant experimental method. Under these circumstances, the safest approach seemed to lie in using the best thermodynamic data and try to optimize an unsatisfactory situation. Irrespective of the thermodynamic data used, one sees that predictions of equilibrium conversions will be generally conservative, i.e. on the low side.

Since the equilibrium measurements at Lacq (France) remain proprietary information, use of their data to upgrade the graphical mehtod would not be publishable. Hence thermodynamic properties for H_2S, SO_2, H_2O, N_2 and S(g) were taken from the JANAF tables (74), while those for S_2 to S_8 species, respectively, were taken from values published by Rau, et.al (128).

6.2.2 Assumptions for acid gas with less than 100% H_2S

In this section, questions concerning assumptions involved in the method for acid gas with less than 100% H_2S and their reliability will be reviewed briefly.

An obvious error, probably the main weakness in the graphical approach, originates when an acid gas of less than 100% H_2S content is regarded as a "partially reacted acid gas" from which sulfur product has been removed. The family of equilibrium curves are based upon an initial 100% H_2S acid gas in which both water and sulfur were formed after air was added but only the sulfur product has been removed. This error is illustrated in Example 2.

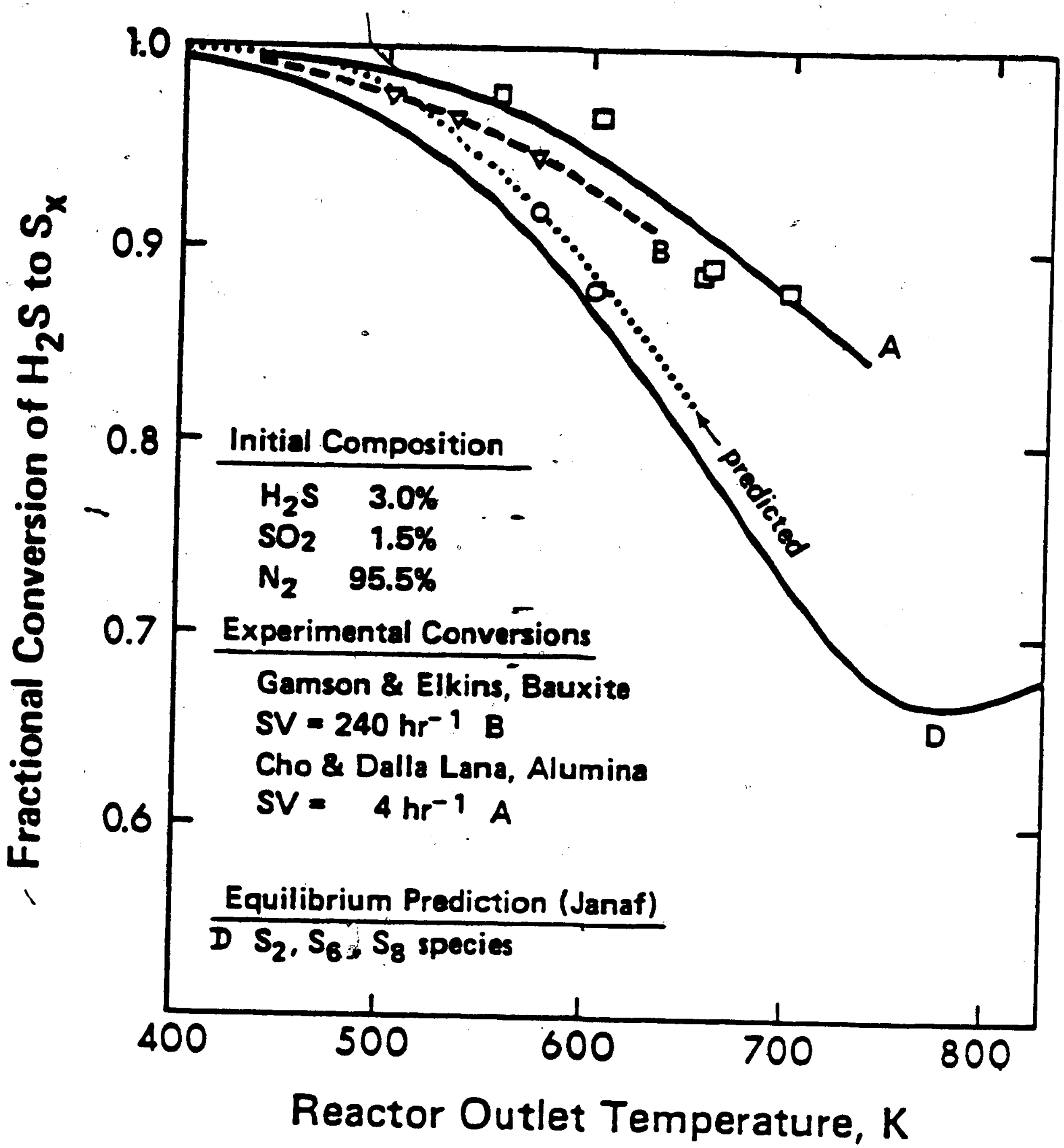


Fig. 39 Prediction of Conversions Using Rau, et al. Based Thermodynamic Properties.

Example 2

Consider acid gas with 30% CO_2 Basis : 100 moles acid gas

After oxidation reaction:	H_2S	+ 1.5 O_2	+ N_2 ----->	SO_2	+ H_2O	+ N_2	+ CO_2	(6.4)
Initial (moles)	70	35	132				30	
After reaction (moles)	47			23	23	132	30	
Mole fraction (%)	18.4			9.0	9.0	51.8	11.7	

Consider acid gas with 100% H_2S and remove 30% sulfur content of feed

	H_2S	+ 1.5O_2	+ N_2 ----->	SO_2	+ H_2O	+ N_2	(6.5)
Initial (moles)	100	50	188				
After reaction (moles)	66.7			33.3	33.3	188	

After removing 30% sulfur content of feed (i.e. 30 moles of atomic sulfur), since H_2S and SO_2 are always at stoichiometric ratio, the composition of "furnace gas" after 30% sulfur removal is:

H_2S = 66.7(0.7) = 46.7 moles (16.0%)
SO_2 = 33.3(0.7) = 23.3 moles (8.0%)
H_2O = 33.3 moles (11.4%)
N_2 = 188 moles (6.5%)

Comparing these mole fractions with mole fractions of products of oxidation for acid gas with 30% CO_2 as shown under in equation (6.4), the assumption results in the larger amount of water in product stream and larger inert due to larger air requirement. In the furnace these two driving forces (effect of water and effect of inert) are opposite. The result is not significant. However in the converter, the two driving forces enhance each other. The result is a smaller equilibrium conversion than that obtained without this assumption. This assumption may be eliminated by calculating thermodynamic equilibrium conversions for acid gases of different H_2S content, i.e. a complete set of curves such as those in Fig. 40 is generated for each acid gas of different H_2S content. This question is evaluated in sec. 6.4.

Acidgas constituents are primarily H_2S, CO_2, N_2 and small amounts of other impurities including water vapor. Since the major diluents, CO_2 and N_2, are essentially unreactive gases in the catalytic converter temperature range, their main influence upon thermodynamic equilibria occurs to the extent that dilution affects equilibria via

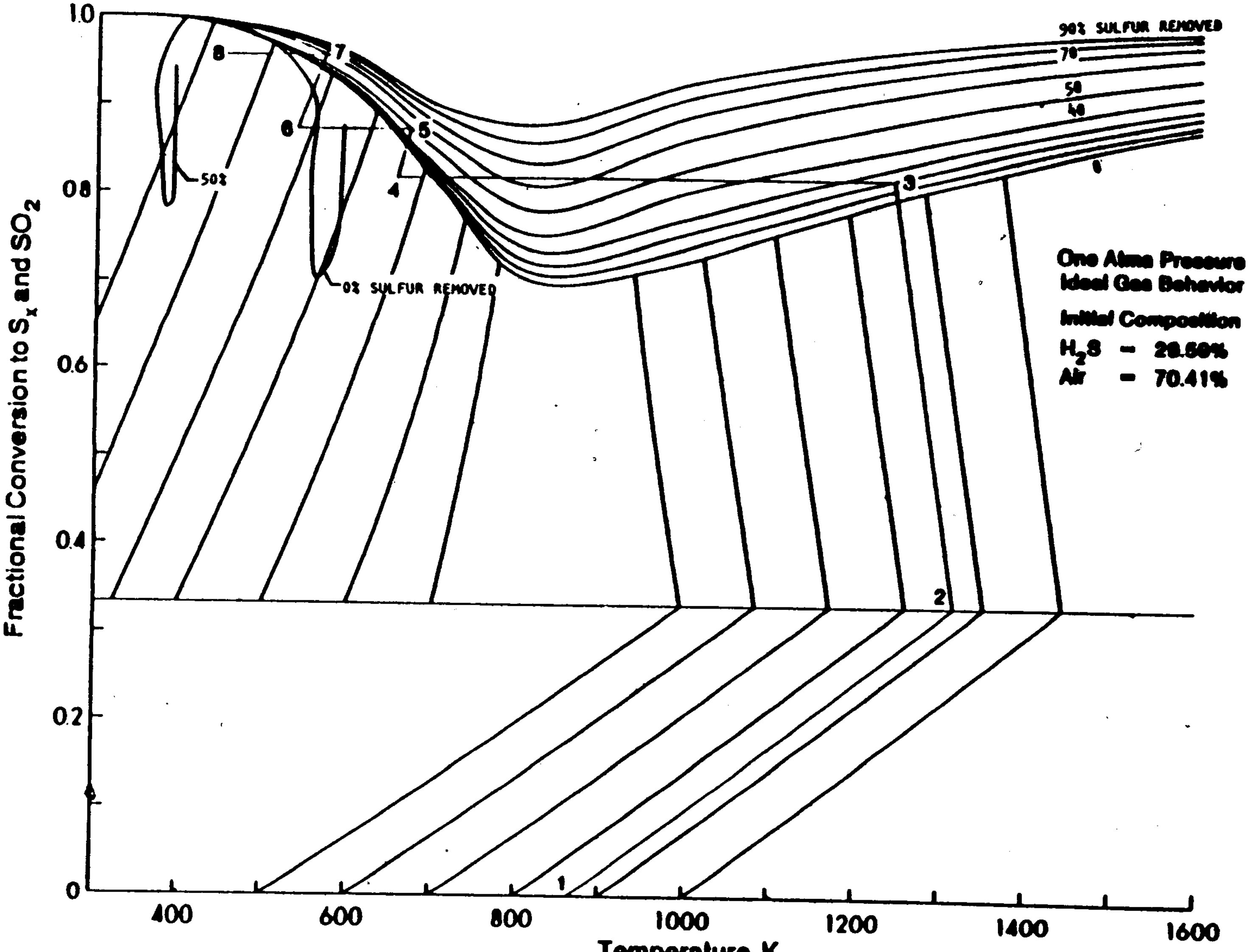


Fig. 40 Graphical Method for Equilibrium Stage Design in Claus Process.

Le Chatelier's principle. This introduces some error into the calculations but this error is believed to be small. The amount and type of diluent also affects the adiabatic reaction path because their slopes, dX/dT, are dependent upon the heat capacity of the gases. Earlier calculations (44) indicated that this effect is minor for the various gases involved.

All reaction paths shown in the figures are developed on the basis of equilibration of sulfur species, S_1, ..., S_8, at all temperatures. This problem of whether sulfur vapor equilibrates is not expected to be influential at furnace temperatures where sulfur occurs primarily as diatomic sulfur, and near catalytic converter temperatures where S_D approaches S_8. In the waste heat boilers after the front-end furnace, reaction path 3-4, it is not known whether the homogeneous reaction rate is rapid enough for equilibration of sulfur vapor molecular species or even further reaction of H_2S with SO_2 or S_D with H_2O (reverse Claus reaction)? The horizontal reaction path 3-4 may be interpreted differently. Point 3 corresponds to a particular equilibrium value for S_D . Cooling at constant conversion (i.e. without further chemical reaction) could maintain this S_D . If on the other hand, homogeneous chemical reaction proceeds while cooling, then the value of S_D will be somewhat higher depending upon the extent of equilibration possible.

The final point to be considered arises from the condensation of sulfur when a stream is cooled to the sulfur vapor dew point temperature. Since the vapor pressure of liquid sulfur will be a function of the temperature but the partial pressure of sulfur is dependent on the molecular species present in the vapor phase, the range of dew points possible are bracketed by the two values predicted theoretically. These dew points correspond to the quench compositions with and without equilibration of sulfur species at the conversion described by path 3-4. The two envelopes shown on Fig. 40 represent dew point situations for the 0% and the 50% sulfur removal curves as indicated. If cooling after a reaction stage proceeds to the envelope, condensation of sulfur vapor may occur. In tracing horizontal reaction paths, the lower dew point is probably the more realistic one to use because the sulfur vapor generally lies in the vicinity of S_8 at these low temperatures.

By assuming all liquid sulfur is removed from condensers, the condensation envelopes can be used to determine the amount of liquid sulfur removed from the condensers assuming either:

1) no further reactions in the cooling devices (quench situation); in this case the right branches of the envelopes is used
2) sulfur equilibration in the cooling devices (equilibration during cooling); the left branches are used
3) partial sulfur equilibration in the heating devices; estimated by comparing the condenser outlet point position with relative distance to each branch of the envelope.

If cooling occurs with H_2S/SO_2 reaction and sulfur vapor equilibration, the path 3-4 will fall along the equilibrium curve to some point where the reaction ceases. At this state the sulfur is quenched at that local value of S_y. Invariably, this state will be at a lower conversion than that attained in the furnace.

6.3 Use of graphical reaction paths to predict equilibrium conversions

Fig. 40 shows the reaction path approach described in the original report (44). While this plot is somewhat approximate, it will be used to describe the method. Table 18 summarizes the interpretation for each section of the reaction path shown in Fig. 40.

To illustrate the method, Example 3 analyzes a hypothetical modified Claus plant with two catalytic converters as depicted in Fig. 41.

Example 3

A flow of 7.50 MMSCFD (measured at 14.65 psia and 60°F) of acid gas with the composition (in mol per cent),

$H_2S = 81.37$

$CO_2 = 18.31$

$CH_4 = 0.32$

is to be processed in a modified Claus plant for recovery of elemental sulfur. Adiabatic combustion of this acid gas with the stoichiometric amount of air required to burn one-third of the sulfur and all carbon and hydrogen is expected to reach a maximum temperature of 2152°F. The combustion gases are then cooled successively to 1695°F and to 1215°F in two sections of a waste-heat boiler (heat exchanger). Further cooling of this hot gas is achieved by heat exchange (indirect) with the inlet gases to the first and second stage catalytic converters. This hot gas is finally cooled to 375°F and flows to

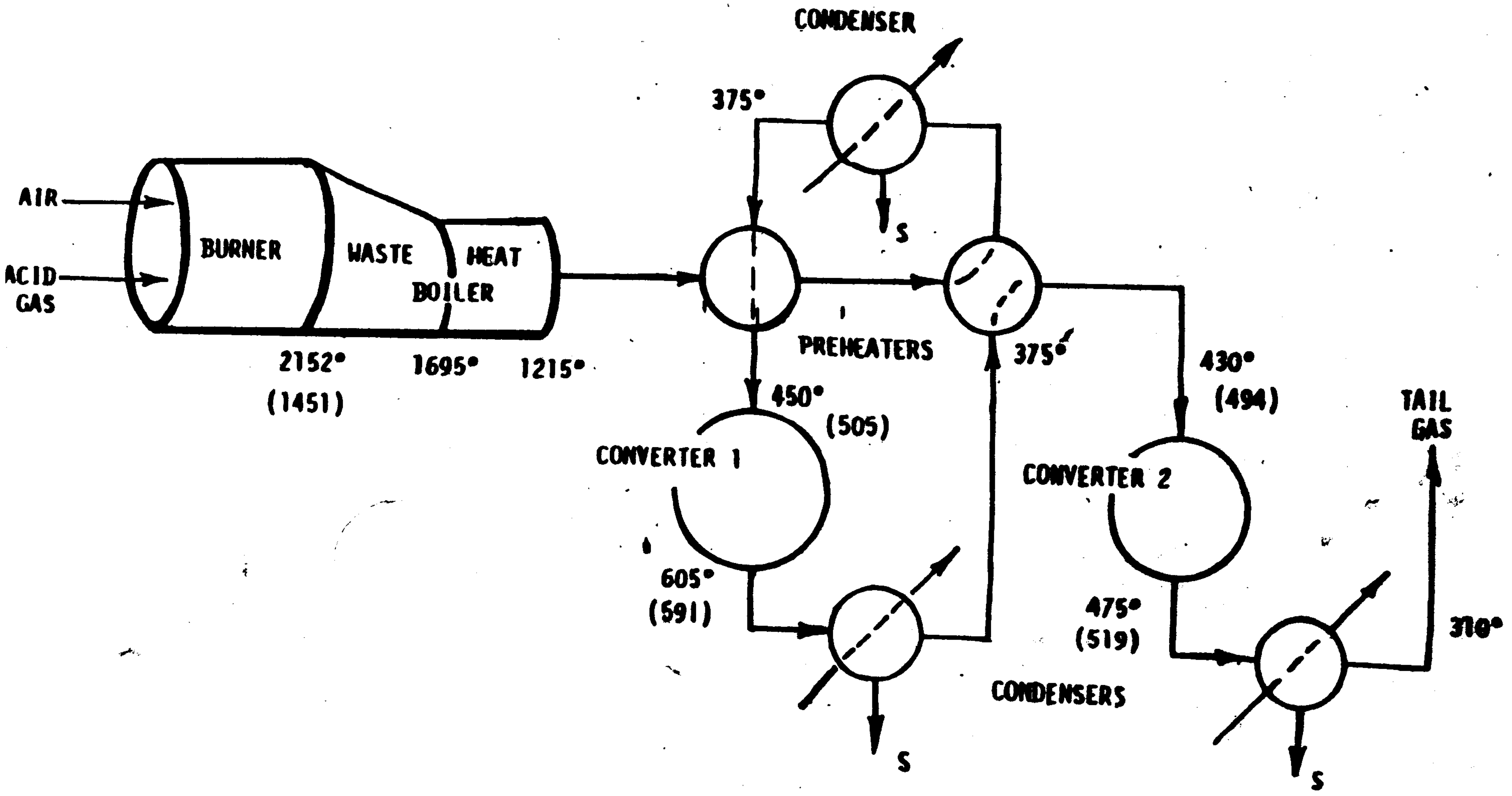


Fig. 41 Flowsheet for Example 3

TABLE 18

USE OF REACTION PATHS TO DEFINE EQUILIBRIUM CONVERSIONS WITHIN CLAUS PLANTS

Reaction Path	Description	Chemical Reaction
1 - 2	Acidgas combustion in front-end furnace (rapid reaction)	$H_2S + 3/2\ O_2$ $\rightarrow SO_2 + H_2O$ (1)
2 - 3	Acidgas conversion to sulphur in front-end furnace (slow reaction)	$2H_2S + SO_2$ $\rightarrow 3/8\ S_8 + 2H_2O$ (2)
3 - 4	Furnace products cooling in waste-heat boiler	No net reaction assumed
4 - 5	Catalytic conversion of cooled furnace products to elemental sulphur in 1st stage converter	Reaction (2)

Reaction step (1) is assumed to proceed to completion and reaction step (2) to thermodynamic equilibrium composition.

the sulfur separator where liquid sulfur is removed. (At 375°F, the sulfur vapor which remains uncondensed may be neglected.) The gas is then reheated to 450°F (via the indirect heat exchanger), enters the first stage converter and leaves at 605°F. After cooling to 375°F, sulfur removal, and reheating to 430°F, the stream enters the second stage converter and leaves at 475°F. This stream then enters the final sulfur condenser where it is cooled to 310°F. Liquid sulfur is removed and the resulting tailgas is incinerated at 1200°F.

The above conditions are represented on the flowsheet shown in Fig. 41. The temperatures shown in brackets have been converted from °F to K to accommodate the reaction path diagram scale.

Use the following data and the reaction path diagram to estimate the following :

1) the "fractional conversion of H_2S to S and SO_2 " which would be anticipated for the temperatures listed in the above process description;
2) the "fractional conversion of H_2S to S and SO_2" which would be predicted for this process using a furnace temperature of 1252°F and adiabatic reaction paths.
3) on the basis of 1), how many tons of elemental sulfur would be produced daily? What % recovery of sulfur does this production rate yield?

Data

PV = RT, R= 10.7 (psia)(cu. ft.)/(lb mol)(°R)

Composition of air is 79% N_2 and 21% O_2.

Atomic weights:

H = 1.008	S = 32.07	O = 16.00
N = 14.010	C = 12.01	

Mean specific heat of any gas mixture over the temperature range, 60°F to 1300°F, estimated at 10 BTU/(lb mol)(°F).

One lb mole is equivalent to 359 cu. ft. at 32°F and 14,7 psia.

Reactions involved are:

$H_2S + 1,5\ O_2 \text{ ---> } H_2O + SO_2$

$2H_2S + SO_2 \text{ <---> } 1.5\ S_2 + 2H_2O$

$4S_2 \text{ <---> } S_8$

Molecular species of sulfur may be assumed to be entirely S_2 at 2152°F and entirely S_8 at lower temperatures.

SOLUTION(Using Fig. 42 and 43)

(a) *Basis:* 100 moles of H_2S in hypothetical acid gas (100%H_2S)

1) *Feed details*

%H_2S in acid gas = 81.37

Use of Fig. 42 (or 43), "Fractional conversion of H_2S to S_p and SO_2" implies 100% acid gas as basis.

Thus, convert 81.37% acid gas to 100% basis via,

$x = (H_2S in - H_2S out)/H_2S in = (100 - 81.37)/100 = 0.1867$

2) *Front-end furnace*

Assume conversion at max. temp. (≈1451 K) is quenched when stream cooled

(X,T)out = (0.86, 1451), located on 18.7% sulfur removed curve " of Fig. 40

3) *First-stage converter*

Assuming no reaction occurs in the condenser the conversion at the inlet of first stage converter is 0.86 . Therefore,

(X,T)in = (0.86,505)

(X,T)out = (? ,591)

After removal of sulfur produced in furnace,

H_2S unreacted = 100 − 86 = 14

SO_2 unreacted = $(H_2S)/2$ = 7

Total unreacted S 21

which locates equilibrium point on "79% sulfur removed curve"

(X,T)out = (0.943,591)

4) *Second-stage converter*

(X,T)in = (0.943,494)

(X,T)out = (? ,519)

After condensing and removing sulfur from 1st stage,

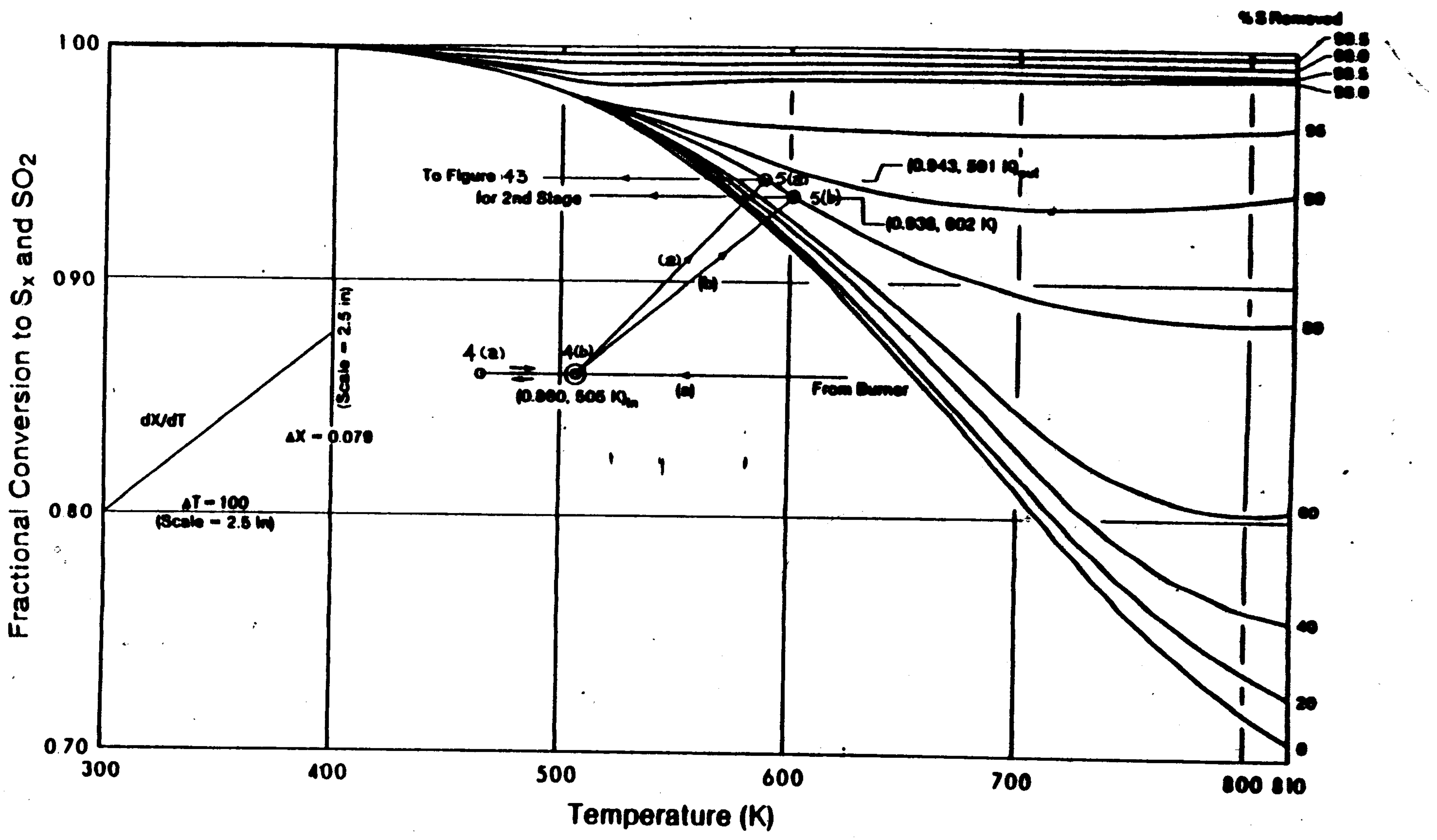


Fig. 42 Solution to Example 3 (1st Stage Converter)

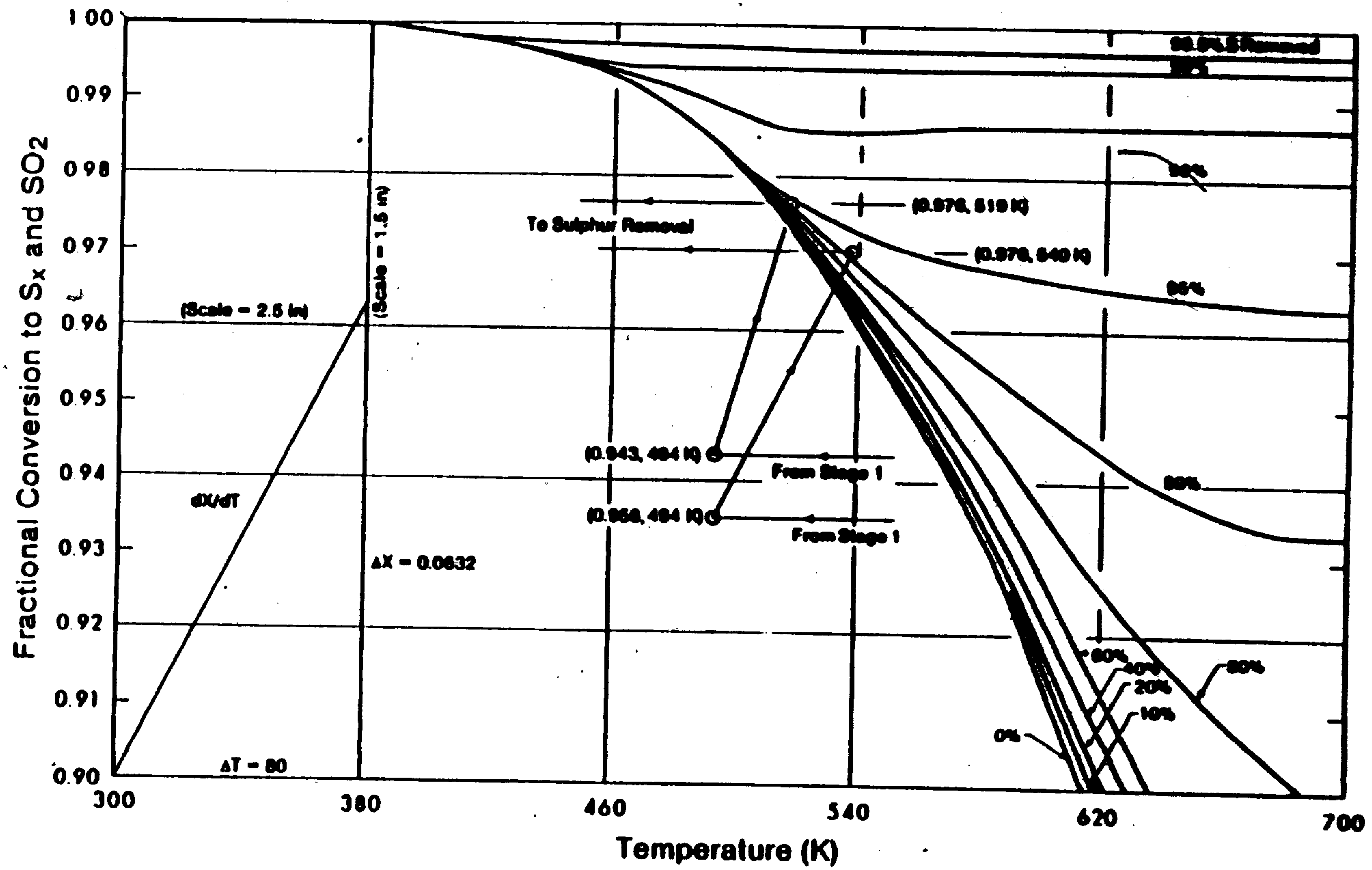


Fig. 43 Solution to Example 3 (2nd Stage Converter)

H_2S unreacted = 100 - 94.3 = 5.7

SO_2 unreacted = 5.7/2 = 2.9

Total unreacted S = 8.6

which locates equilibrium point on "91.4% sulfur removed" curve

(X,T)out = (0.976,519)

After condensing and removing sulfur from 2nd stage,

H_2S unreacted = 100 - 97.6 = 2.4

SO_2 unreacted = 2.4/2 = 1.2

3.6

Fractional conversion to S_y (81.37 feed gas basis)

x= (81.37 - 3.6)/81.37 = 0.956

(b)After locating (X,T)out for furnace at (0.86,1451), reaction paths may be traced on Fig. 42 or 43. Cool (horizontal line) until reach (0.86,505). Continue up adiabatic reaction path to intersect "79% S removed curve".

Since Figs. 42 and 43 do not contain adiabatic reaction paths, the slope of the appropriate reaction path may be obtained from Table 19. From Table 19, in the region, 500 to 600K, $dX/dT= 0.79 * 10^{-3}$

On Fig. 42, for 1st stage, ΔT = 100K, ΔX = 0.079 (conversion units)

On Fig. 43, for 2nd stage, ΔT = 80K, ΔX = 0.0632

(Lines with these slopes may be conveniently drawn on Figs. 42 and 43, respectively, and then transported where desired on the figure by parallel construction.)

From Fig. 42, obtain intersection of 1st stage adiabatic reaction path with "79% S removed" equilibrium conversion curve,

(X,T)out = (0.936,602)

Total unreacted S = 6.4 + 3.2 = 9.6

Next equilibrium stage must intersect on the 100 - 9.6 = "90.4% S removed" curve.

Cool along horizontal line from (0.936,602) to (0.936,494)

From Fig. 43, obtain intersection of 2nd stage adiabatic reaction path with "90.4% S removed" curve,

(X,T)out = (0.970,540)

Total unreacted S_y = 3.0 + 1.5 =4.5

Fractional conversion to S_x (81.37 acid gas basis)

$x = (81.37 - 4.55)/81.37 = 0.944$

(c) Composition of stream leaving waste-heat boiler (S_x):

Feed to process: $H_2S = 3.00$

$CO_2 = 0.68$

$CH_4 = 0.012$

Reactions in process:

(1) $H_2S + 1.5O_2 \longrightarrow SO_2 + H_2O$

(2) $2H_2S + SO_2 \longrightarrow 1.5S_2 + 2H_2O$

(3) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

x = fractional conversion of H_2S at burner outlet

= 0.86 (from part (b))

Stream composition:

	After H_2S Combustion	After Claus Reaction X = 0.86	After CH_4 Combustion ($S = S_2$)	After CH_4 Combustion ($S = S_8$)
H_2S	2	[illegible]	0.42	0.42
SO_2	1	0.21	0.21	0.21
O_2	0	0	0	0
N_2	5.64	5.64	5.73	5.73
H_2O	1	2.58	2.60	2.60
S_2(or S_8)	0	1.19	1.19	(0.29)
CO_2	0.68	0.68	0.69	0.69
CH_4	0.012	0.012	0	0
		TOTAL	10.84	9.94

(d) From (a) Conversion of H_2S to sulfur = 0.956

Sulfur production=

$(7.5 * 10^6/359)(14.65/14.7)(492/520)(0.8137)(0.956)(32.07/2000) = 245.7$ ton/day

TABLE 10

SLOPE OF ADIABATIC REACTION PATHS $(dX/dT) \cdot 10^{-3}$

FOR USE WITH FIGURES 42 AND 43

Acidgas Composition

H_2S	100	80	80	60
CO_2	0	10	20	40
H_2O	0	10	0	0
400	0.708	0.763	0.773	0. 87
450	0.710	0.773	0.783	0.887
500	0.714	0.782	0.783	0.899
550	0.722	0.783	0.786	0.911
600	0.730	0.791	0.801	0.922
650	0.736	0.800	0.808	0.932
700	0.743	0.807	0.817	0.942
750	0.749	0.815	0.824	0.951
800	0.755	0.822	0.831	0.959

6.4 Effect of inert

6.4.1 Introduction

In the report to CNGPA 1974, Cho et al (32) regarded acid gas of less than 100% H_2S content as a partially reacted acid gas from which sulfur product has been removed. According to Le Chatelier's principle the removal of sulfur will drive the reaction to the right to produce more products.

At burner temperature the effect of inert also increases the conversion of H_2S/SO_2 system because S_2 is formed (volume of system increases). Unfortunately the increases in conversion are not the same for these two driving forces on the basis of the amount of H_2S in acid gas. The difference between an acid gas of 80% H_2S content and an acid gas of 100% H_2S content after removal of 20% sulfur is the subtitution of H_2O, N_2 and some SO_2 for CO_2. Water decreases the equilibrium conversion while CO_2 increases conversion. Because of its greater heat capacity, the CO_2 acts as a heat sink to decrease the temperature of the gases leaving the furnace. (Ignoring this error is not significant in many real reactors because the temperature rise is compensated by the heat of formation of H_2,COS,CS_2, and CO.) The effect of inerts upon burner performance will be investigated in section 6.5.2.

At converter temperature, the effect of inert decreases the conversion of H_2S/SO_2 to sulfur. However since CO_2 acts as a heat sink to decrease the temperature of the gases and increase the possible equilibrium conversion to sulfur, the resulting effects of these two compromises will also be investigated in section 6.5.3.

6.4.2 Effect of inert on burner performance

Assume CO_2 acts as inert. Three cases are considered. In case 1, both dilution effect on equilibrium conversion and heat sink effect on adiabatic reaction path are calculated. In case 2, the effect of heat sink CO_2 alone is considered by using the true adiabatic reaction path and the equivalent to sulfur removal for equilibrium curve. In case 3, approximate graphical approach set up earlier (sulfur removal equivalent) when both dilution and heat sink effects are ignored is applied.

6.4.2.1 Carbon dioxide as inert

Table 20 was generated from Fig. 44. The limit of the graphical analysis of Claus plants can be determined through Table 20. At 40% CO_2 in acid gas, the difference in furnace conversion (case 1) and the calculated furnace conversion using assumption of sulfur removal (case 3) is 0.055, higher than the accuracy of graphs (0.05). Thus for acid gas less than 40% CO_2 content, the sulfur removal assumption is valid.

Fig. 45 shows the burner temperature as a function of CO_2 in acid gas. The decrease is almost linear up to 40% CO_2 in acid gas then the rate of temperature drop is doubled. Therefore Figs. 45 and 46 can be used to calculate the burner exit temperature and conversion for acid gas up to 40% CO_2 by subtracting the exit temperature at the rate of 2 K per % CO_2 in acid gas. Above 40% CO_2 in acid gas the result from Fig. 46 has to be modified with the aid of Fig. 47 for new burner temperature and conversion assuming the mean heat capacity of the gas mixture does not change significantly over the range of 278-1500 K.

From Table 20 the effect of CO_2 inert is to decrease the burner temperature and the conversion. However the decrease is within the accuracy of the graph (0.05) for acid gas with less than 40% CO_2 content.

6.4.2.2 Nitrogen as inert

Table 21 was generated from Fig. 48. Table 21 indicates the effect of nitrogen impurity on burner performance. For 10% N_2 in acid gas where total inert content is still less than 40%, the effect is neligible compared to the accuracy of equilibrium curve due to assumption of unreactive CO_2. It is noted that the exchange of 10% CO_2 for 10% N_2 results in a decrease in inert effect as expected, since the nitrogen heat capacity is smaller than the CO_2 heat capacity. Very seldom does acid gas contain above 10%N_2, (then pretreatment of acid gas was needed for economic operation), thus higher N_2 content acid gas was not investigated.

The effect of N_2 inert is to decrease the burner temperature and conversion, however the effect will be less severe than the effect of CO_2. Below 10% N_2 and 30%CO_2 acid gas, the inert effect is neligible.

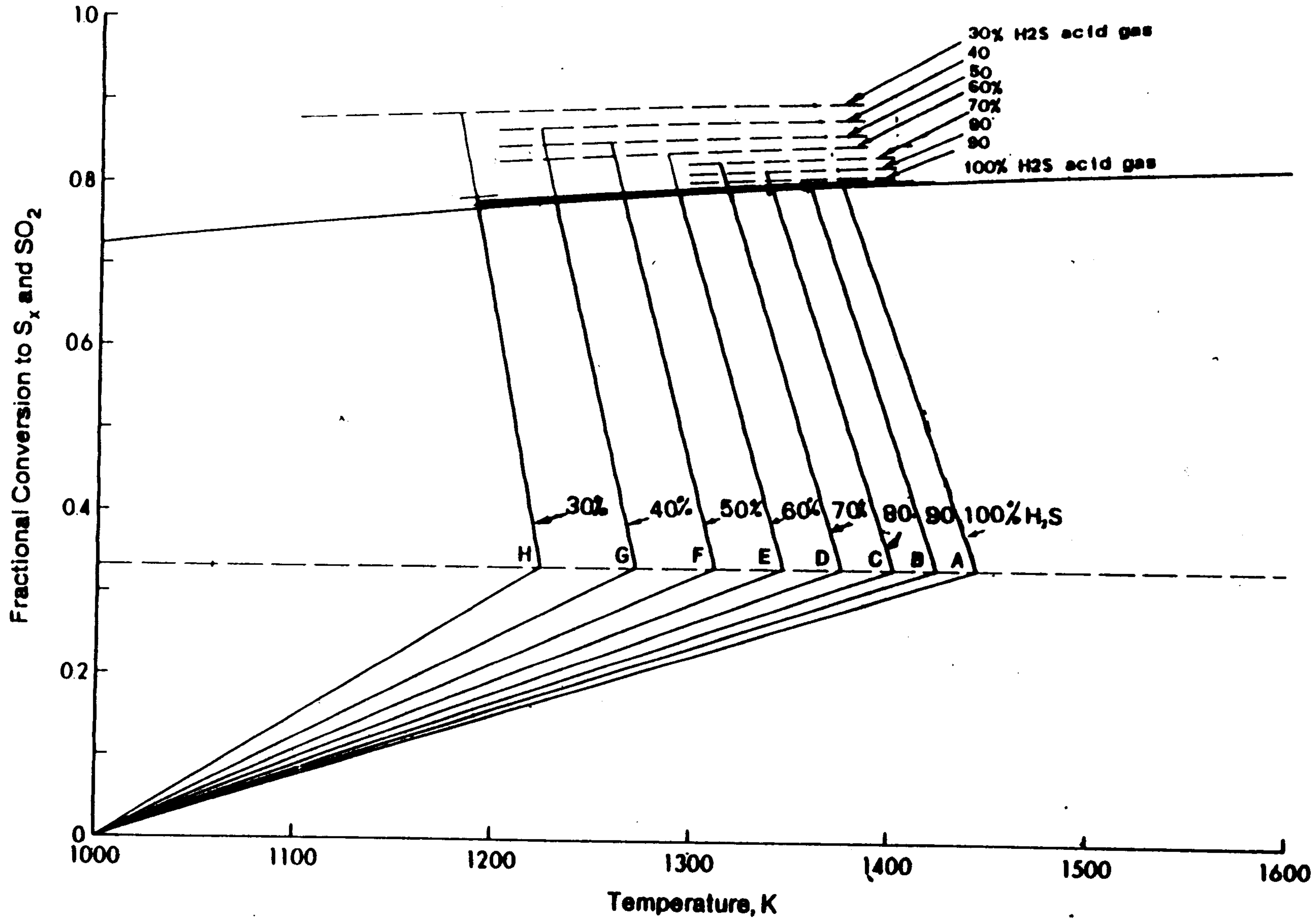


Fig. 44 Effect of CO_2 Inert on Burner Performance.

TABLE 20

EFFECT OF CO2 ON BURNER PERFORMANCE

(DILUTION & HEAT SINK EFFECT ONLY)

Acidgas		Burner Conversion			Burner Temperature (K)		
%H2S	%CO2	Case 1	Case 2	Case 3	Case 1	Case 2	Case 3
100	0	0.798	0.798	0.798	1374	1374	1374
90	10	0.796	0.807	0.808	1358	1357	1373
80	20	0.795	0.815	0.820	1329	1337	1371
70	30	0.794	0.825	0.832	1317	1313	1369
60	40	0.790	0.836	0.845	1291	1286	1367
50	50	0.788	0.850	0.860	1263	1256	1365
40	60	0.784	0.865	0.877	1229	1222	1363
30	70	0.781	0.883	0.897	1189	1182	1359

Notes:

1. Case 1: Both dilution and heat capacity effect considered.
2. Case 2: Heat capacity effect considered
3. Case 3: Both effects ignored (as per Cho)

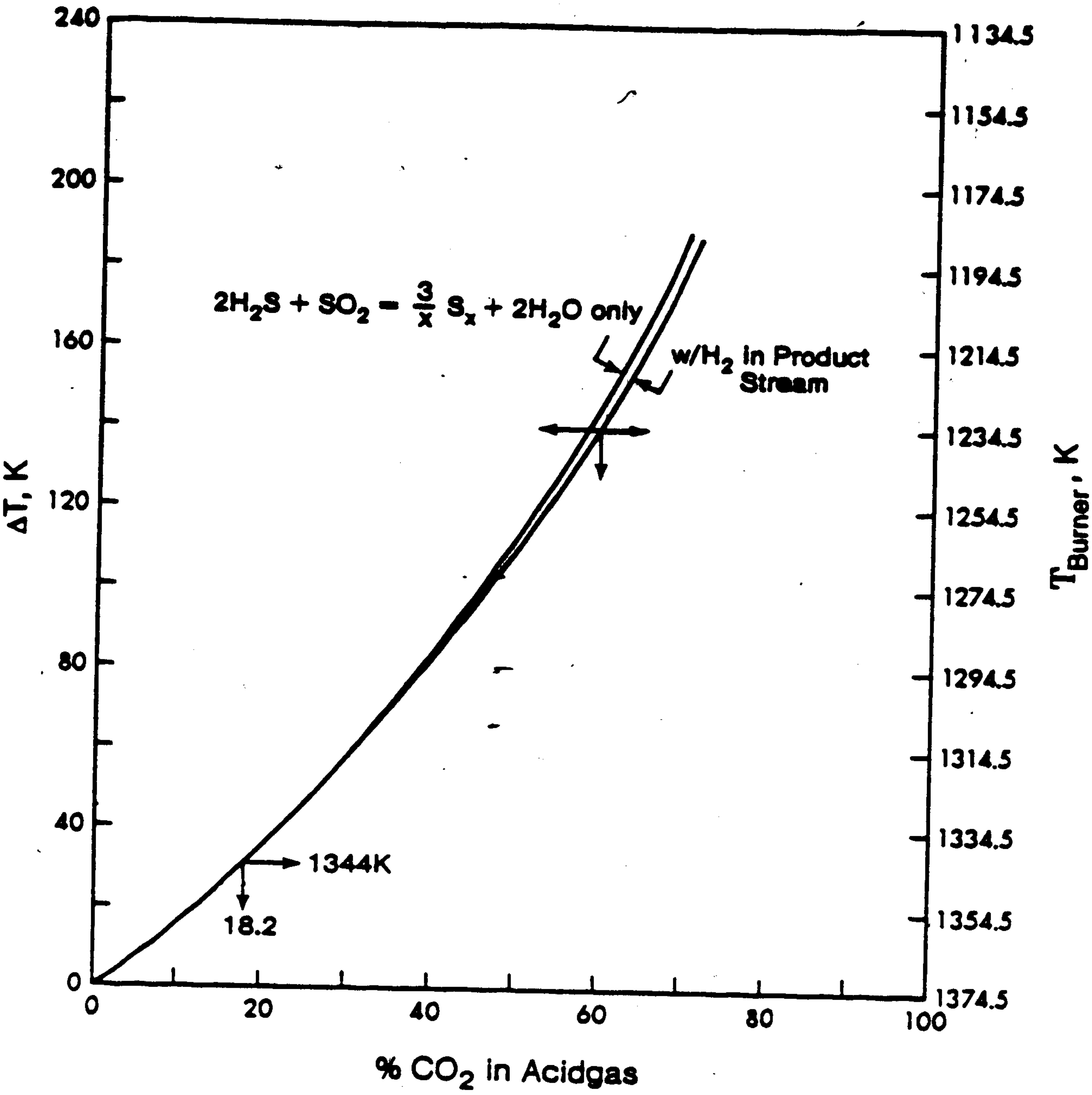


Fig. 45 Effect of CO_2 Inert on Burner Temperature.

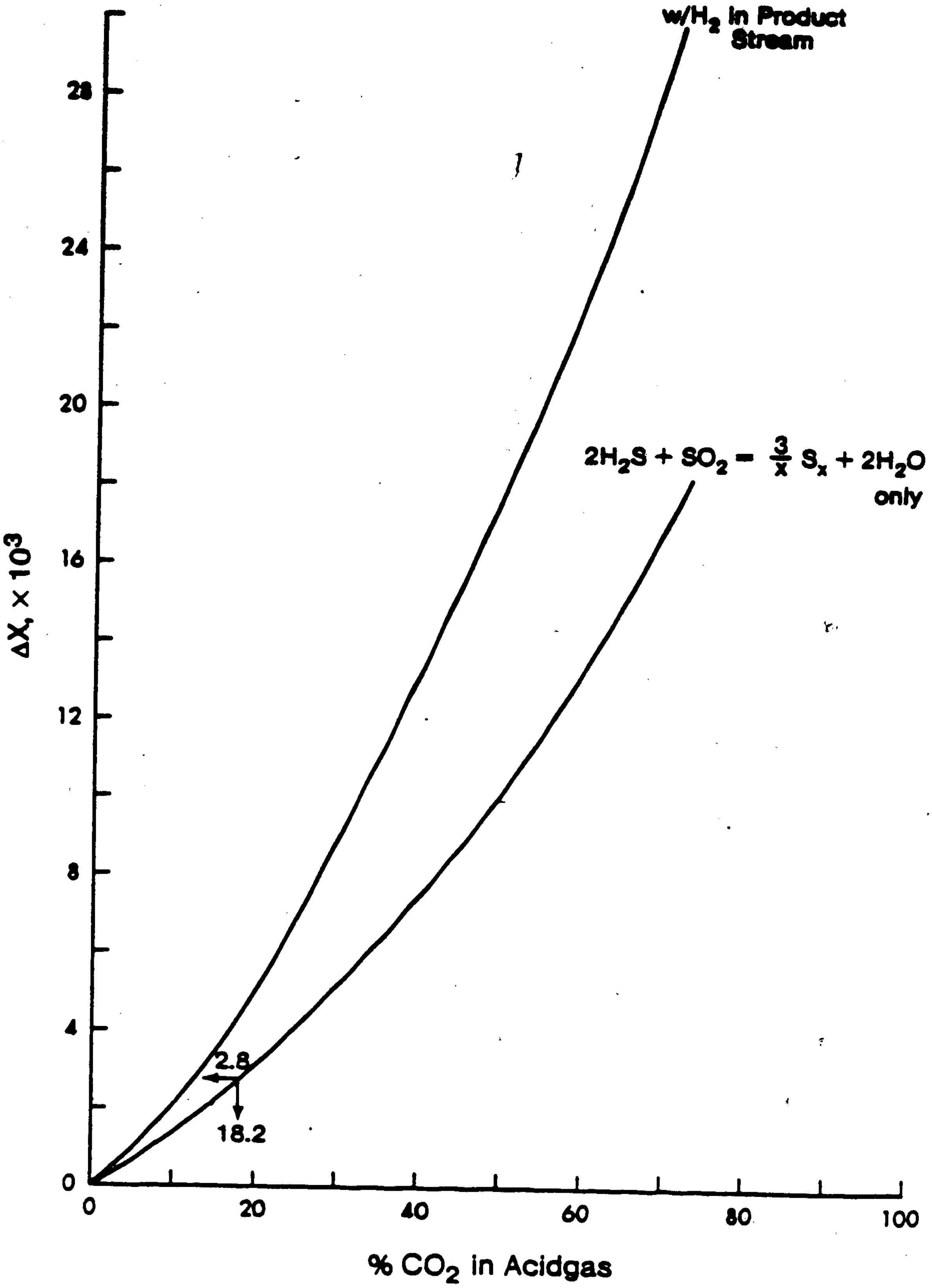


Fig. 46 Effect of CO_2 Inert on Burner Conversion.

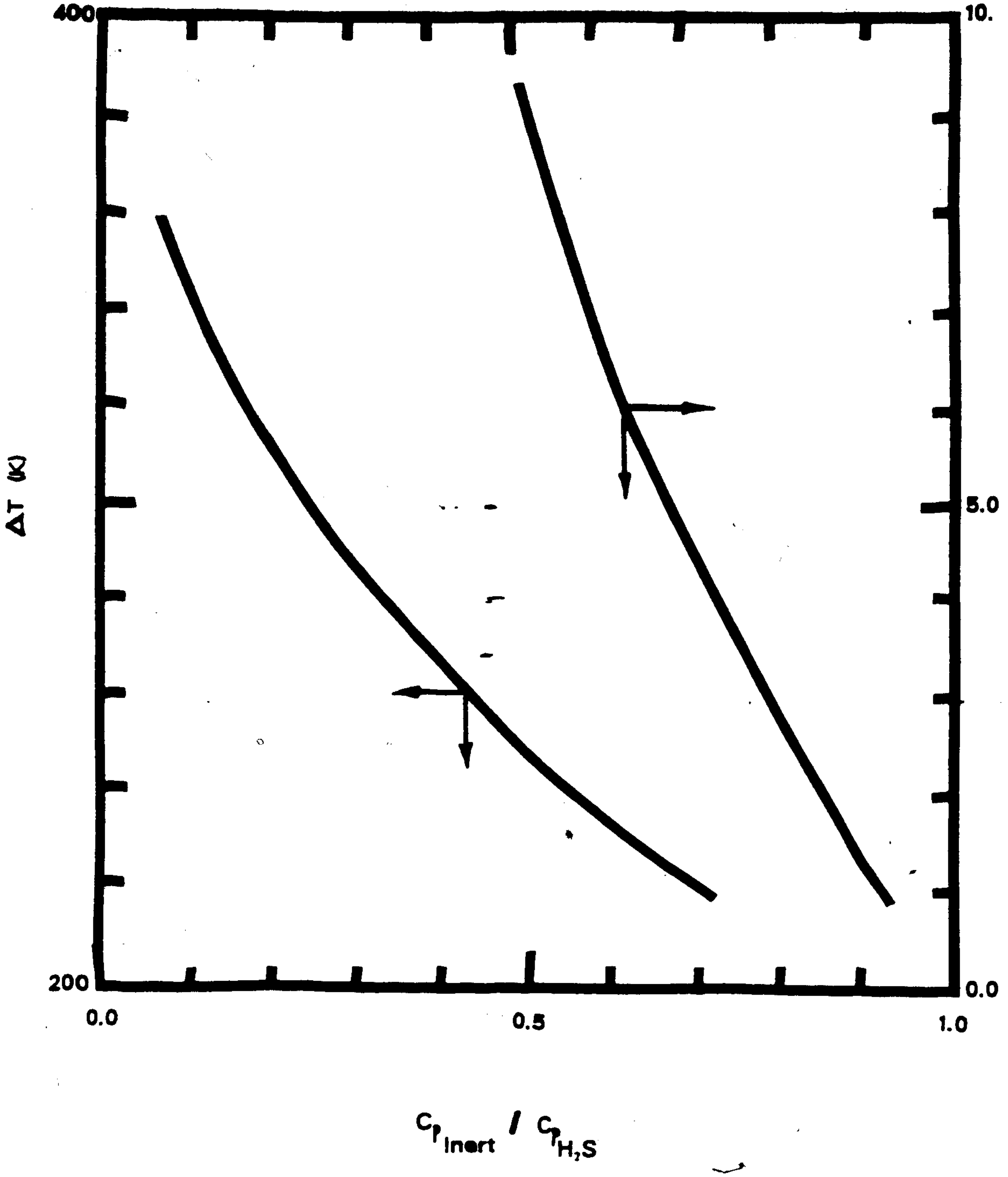


Fig. 47 Effect of Heat Capacity of Inert Components on Burner Performance

TABLE 21

EFFECT OF N2 ON BURNER PERFORMANCE

Acidgas			Burner Conversion			Burner Temperature (K)		
%H2S	%N2	%CO2	Case 1	Case 3	Case 1-Case 3	Case 1	Case 3	Case 1-Case 3
100	0	0	0.823	0.823		1370	1370	
90	10	0	0.823	0.808	0.013	1360	1373	13
80	10	10	0.819	0.820	0.001	1342	1371	29
60	10	30	0.811	0.034	0.034	0.845	1367	71

NOTE: EQUILIBRIUM CURVES INCLUDING THE DISSOCIATION OF H2S TO H2 AND SULFUR.

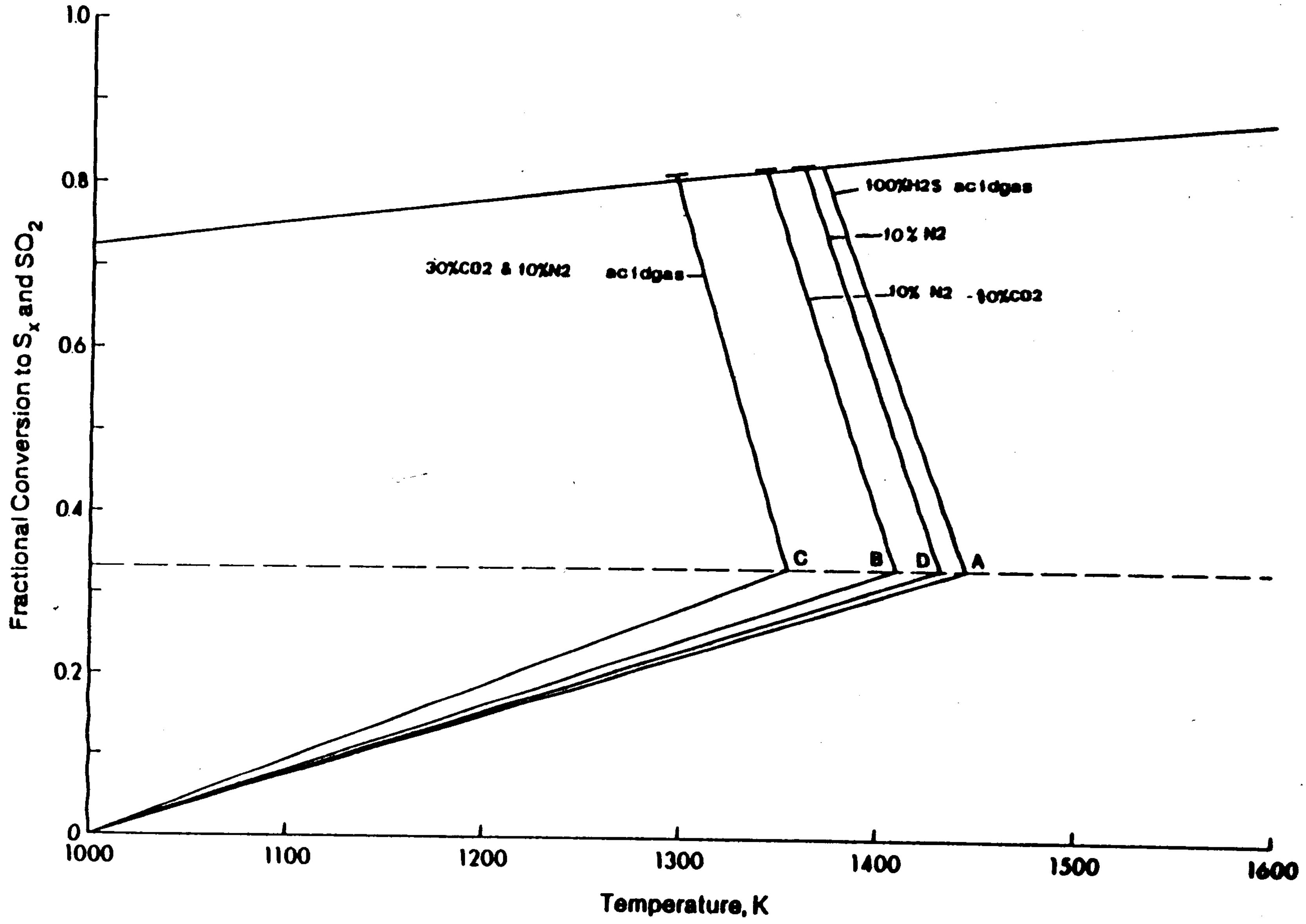


Fig. 48 Effect of N_2 on Burner Performance

6.4.2.3 Water vapor as impurity

Table 22 was generated from Fig. 49. Table 22 shows the effect of water impurity on burner performance. Water has a retarding effect upon the equilibrium conversion, but only the dilution and heat sink effects when generating the adiabatic reaction paths. From Table 23, the effect of 10% water acid gas on burner conversion is neligible. Similar to N_2 impurity, very seldom does acid gas contain above 10% H_2O, thus higher water content acid gas was not investigated.

6.4.2.4 Conclusion

Comparing the effect of CO_2, N_2 and water vapor, below 40% inert content, the effect upon burner conversion can be ignored. Water vapor with a higher heat capacity than for either CO_2 and N_2 will have the highest temperature effect. However water has lowered the equilibrium curve which causes the adiabatic path intercepting the equilibrium curves at a higher temperature than expected.

6.4.3 Effect of inert on converter performance

Example 3 will be used to study the effect of inert on converter performance assuming the condensers operate at the same condition of temperature due to the lack of of plant energy for reheating for the feed condition needed. Following is the result.

6.4.3.1 Carbon dioxide as inert

As defined the in previous section, case 1 is the true inert effect. Case 2 is for heat sink effect only and case 3 using equivalent to sulfur removal method. In case 4 converter exit temperature is assumed to be unaffected by the presence of inert. Only 2 acid gas compositions will be considered: 20% CO_2 and 40% CO_2 acid gas.

Assuming adiabatic operation, the equilibrium conversion at the first and second converters were obtained for 40% CO_2 acid gas using the graphical approach as illustrated in Fig. 50 and 51. Similarly the conversion for 20% CO_2 acid gas is obtained. The result is given in Table 23.

From Table 23, the effect of CO_2 inert as a heat sink and diluent is to shift the extent of sulfur conversion from the later converter to the previous converter i.e. first converter carries the most conversion while the importance of the second and third

TABLE 22

EFFECT OF H2O ON BURNER PERFORMANCE

Acidgas			Burner Conversion	Burner Temperature (K)
%H2S	%N2	%CO2		
100	0	0	0.823	1370
90	10	0	0.811	1360
80	10	10	0.806	1342
60	10	30	0.796	1305

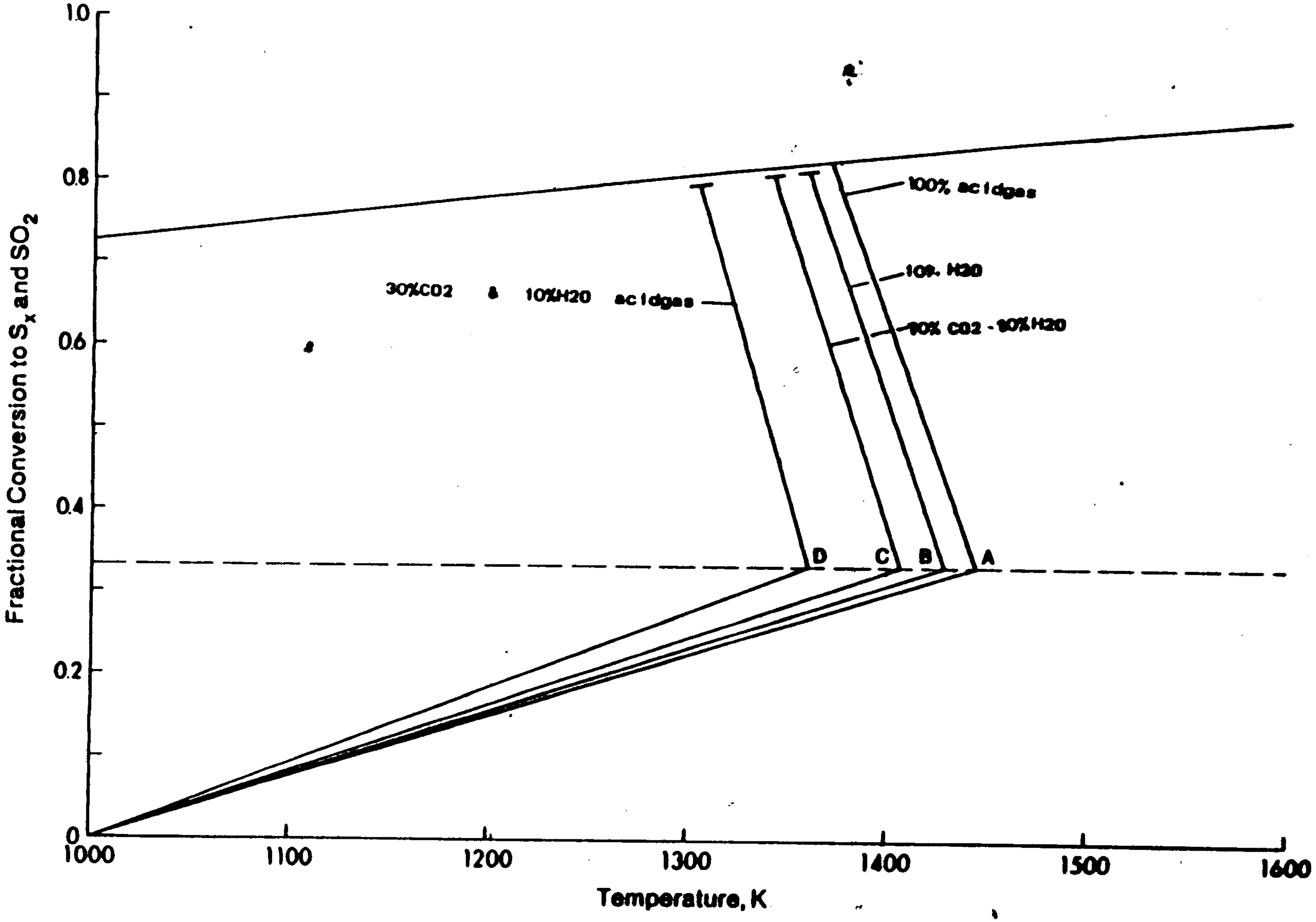


Fig. 49 Effect of H_2O on Burner Performance.

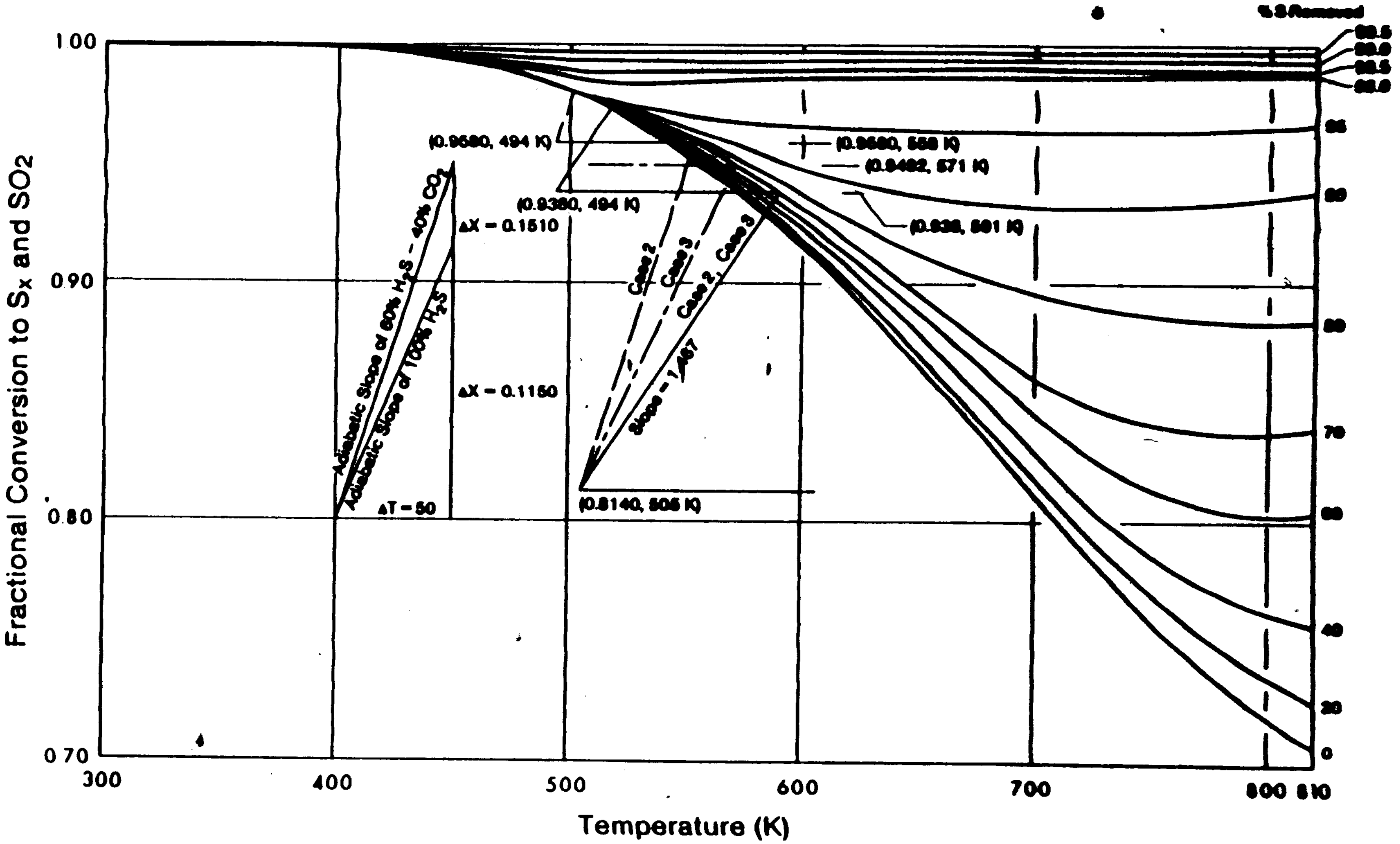


Fig. 50 Effect of 40% CO_2 Acidgas on 1st Converter Performance Assuming No Effect on Equilibrium Conversion.

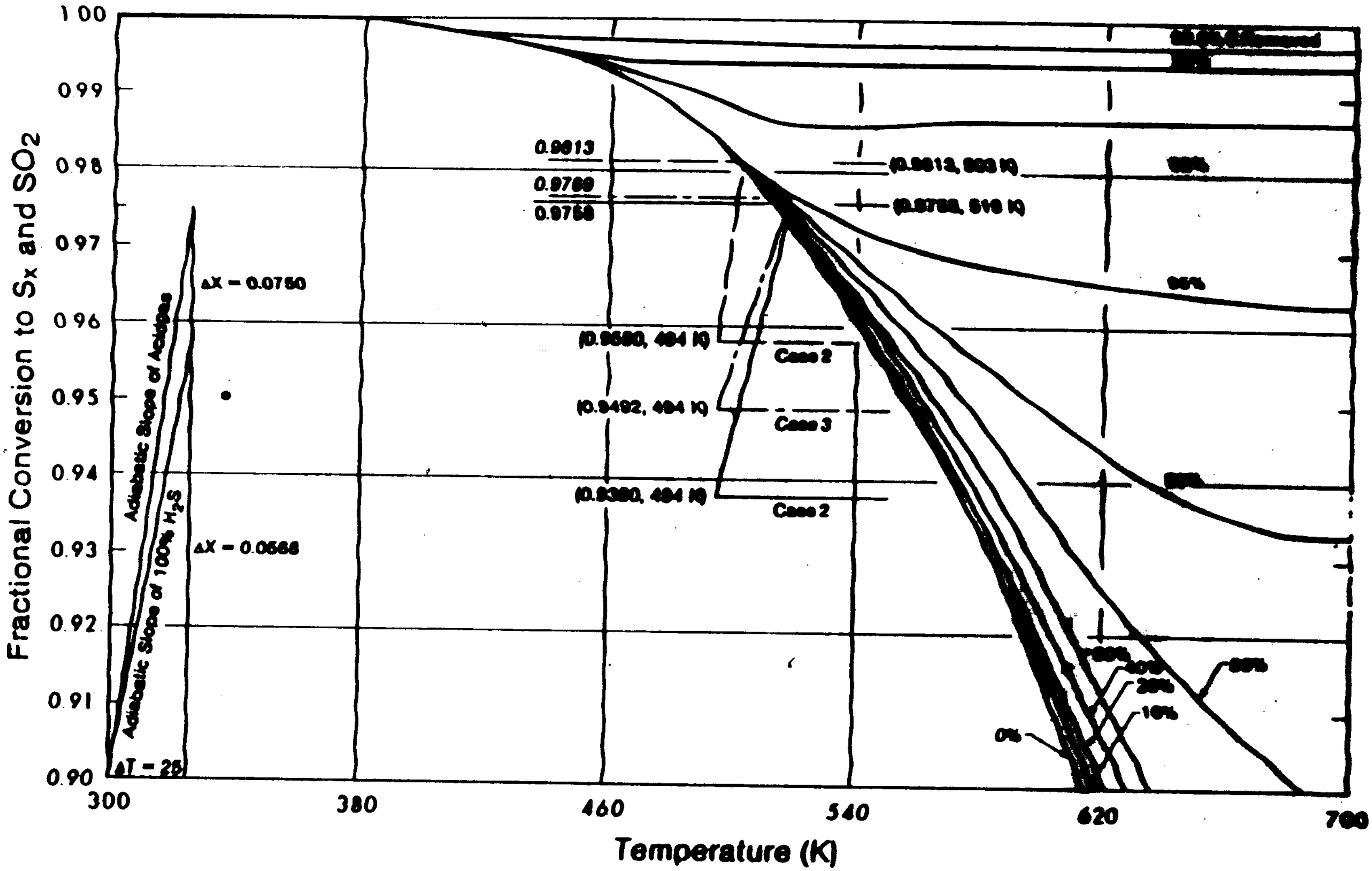


Fig. 51 Effect of 40% CO_2 in Acidgas on 2nd Converter Performance Ignoring Effect on Equilibrium Curves.

TABLE 23

EFFECT OF FEED GAS CO2 IMPURITY ON SULFUR RECOVERY

Acidgas (%CO2)	Furnace	Converter 1		Converter 2	
		Total	Device	Total	Device
0	0.806	0.9375	0.1315	0.979	0.0415
20	0.811	0.9378	0.1268	0.978	0.0402
40	0.814	0.9482	0.1352	0.9769	0.0389
Adiabatic Operation					
0	0.806	0.9535	0.1475	0.9825	0.029
20	0.811	0.955	0.144	0.9835	0.0285
40	0.814	0.958	0.144	0.9813	0.0213

converters decrease. However the total effect of sulfur recovery only slightly decrease for up to 40% CO_2 in acid gas (0.0021)

From Table 24, for acid gas of 40% CO_2, the assumption of sulfur removal equivalent predicts the conversion within the accuracy of the graph to the third significant digit (dx=0.01) though the effect on converter temperature is more pronounced at second converter.

6.4.3.2 Nitrogen as inert

Equilibrium conversion at the converters when acid gas contains nitrogen is given in Table 25 using the graphical method. For acid gas with 30% CO_2 and 10% N_2, the result from Fig. 52 and 53 is 0.958 and 0.98155 respectively. From Table 25, when 10% N_2 is used instead of 10%CO_2, the conversion duty shift to the second converter and the total conversion increases. Carbon dioxide and nitrogen have the same dilution effect, CO_2 has a higher heat capacity than N_2. Therefore the higher the heat capacity of the inert the higher the conversion will be in the first stage conversion.

From Table 26, for acid gas of 30% CO_2 and 10% N_2 inert content, the sulfur removal equivalent method gives the conversion within the accuracy of the graph though this method decreases the importance of conversion duty of each converter. These errors are approximately the same as 40% CO_2 acid gas (0.007 and 14 K).

6.4.3.3 Water vapor as impurity

Table 27 gives the equilibrium conversion at the converters when acid gas contains up to 10% H_2O with 30% CO_2. This table was generated using the graphical method as illustrated in Fig. 54 and 55 for acid gas with 10% H_2O and 30% CO_2. When the retarding effect of H_2O on conversion is considered together with the dilution and heat sink effect, water decreases the overall conversion and most significant in the furnace as shown in Table 27

From Table 28, for acid gas with 30% CO_2 and 10% H_2O content, the sulfur removal equivalent method gives the conversion within 1% of the rigorous graphical method (case 1) and the error in predicted exit converter temperature is the same as nitrogen.

TABLE 24

THE VALIDITY OF GRAPHICAL METHOD WHEN ACID GAS HAS CO2

Acidgas (%CO2)	Converter 1			Converter 2		
	Case 1	Case 2	Case 3	Case 1	Case 2	Case 3
0	0.9375	0.9375	0.9375	0.979	0.979	0.979
20	0.9378	0.938	0.9388	0.978	0.979	0.979
40	0.938	0.938	0.938	0.9775	0.9758	0.9758
Adiabatic Operation						
0	0.9535	0.9535	0.9335	0.9825	0.9825	0.9825
20	0.9568	0.9568	0.9578	0.984	0.984	0.983
40	0.959	0.958	0.9492	0.9845	0.9813	0.9769
Adiabatic Temperature (K)						
0	563	563	563	507	507	507
20	558	558	560	506	506	505
40	552	558	571.6	502	503	519

TABLE 28

EFFECT OF FEED GAS N_2 IMPURITY ON SULFUR RECOVERY

Acidgas			Furnace	Converter 1		Converter 2	
%H_2S	%CO_2	%N_2		Total	Device	Total	Device
100	0	0	0.806	0.9375	0.1315	0.979	0.0415
60	40	0	0.814	0.938	0.124	0.9775	0.0395
60	30	10	0.813	0.936	0.123	0.979	0.0430
Adiabatic Operation							
100	0	0	0.806	0.9535	0.1475	0.9825	0.029
60	40	0	0.814	0.959	0.145	0.9845	0.0255
60	30	10	0.813	0.958	0.145	0.9845	0.0265

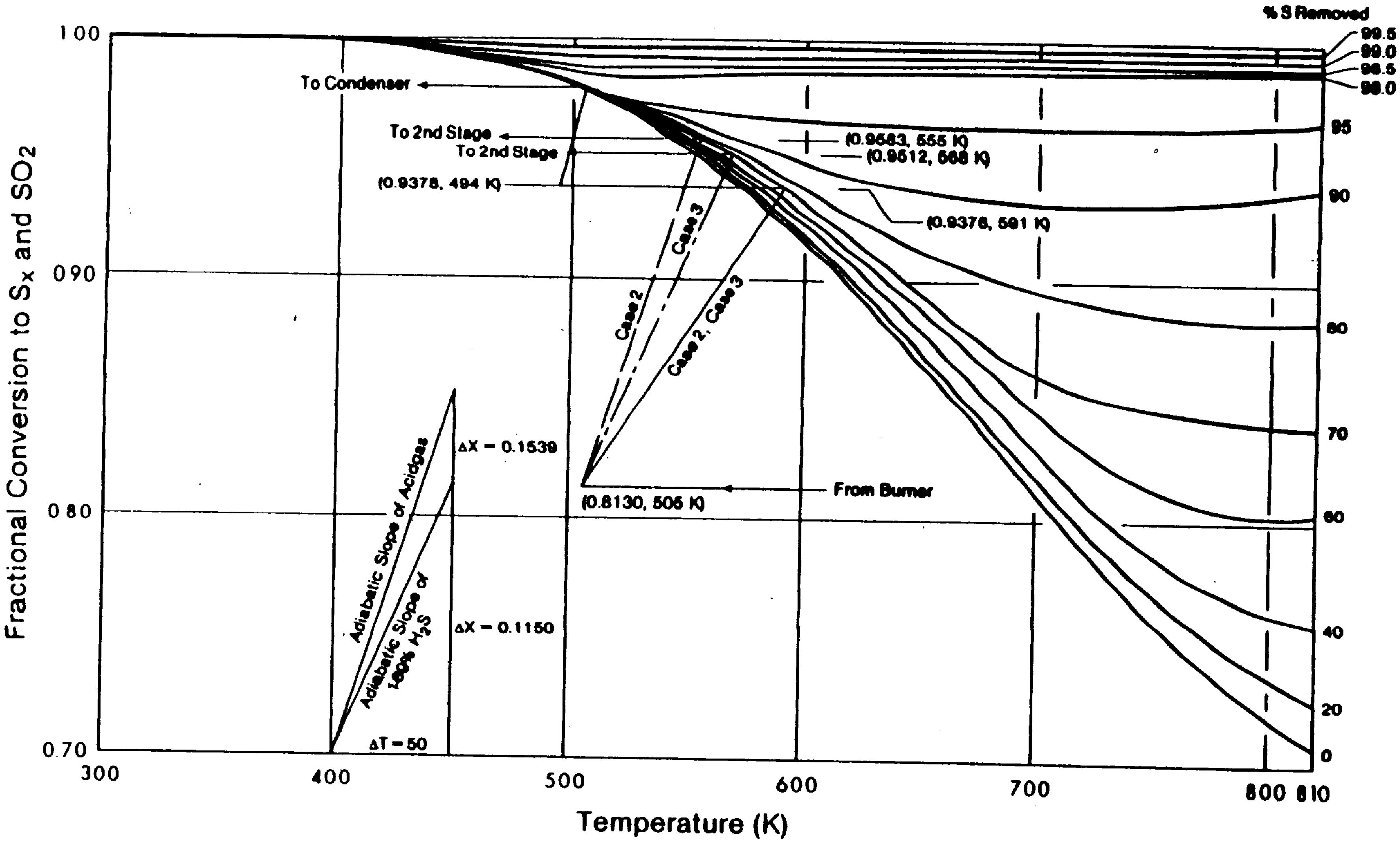


Fig. 52 Effect of N_2 on 1st Converter Performance.

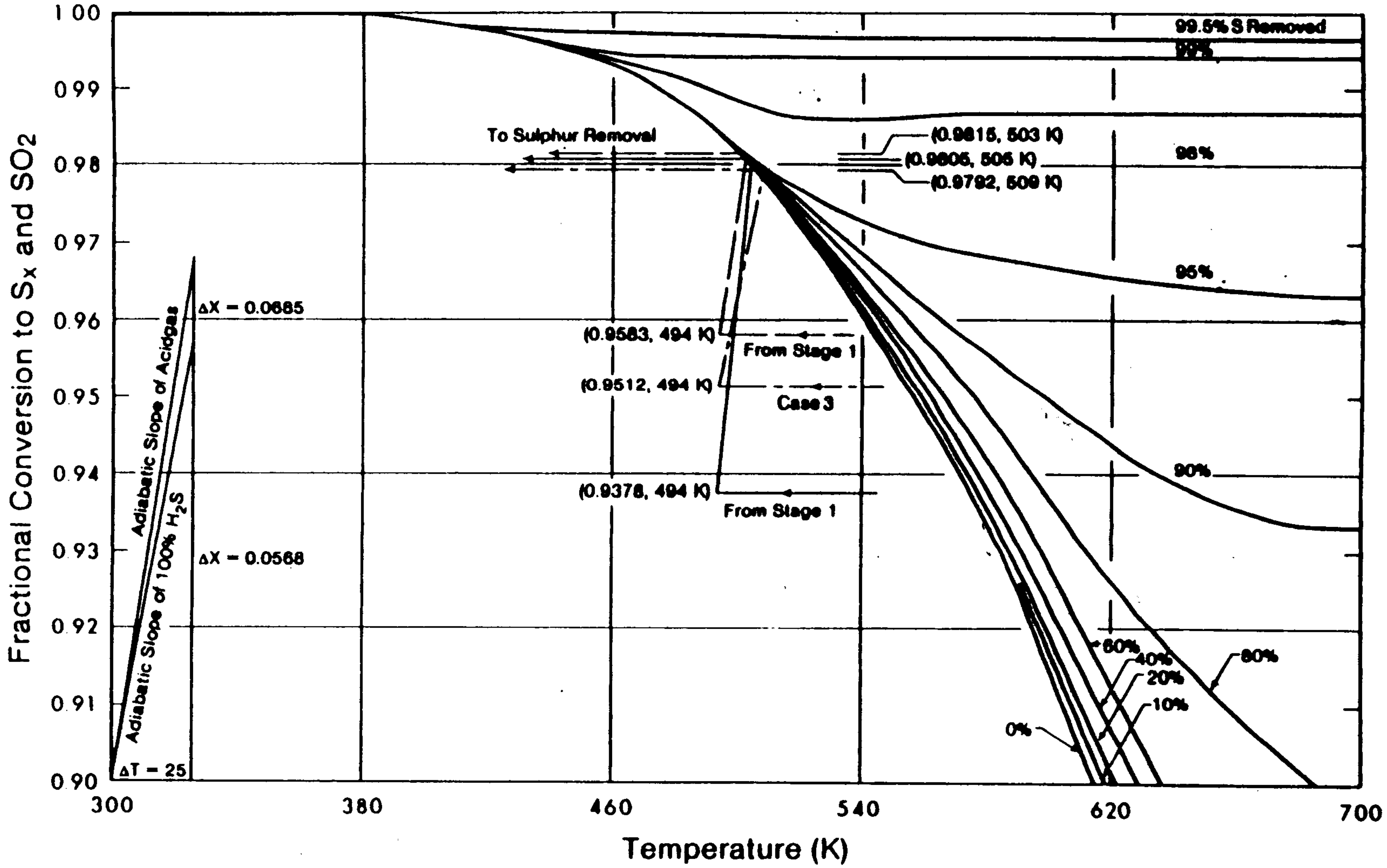


Fig. 53 Effect of N_2 on 2nd Converter Performance.

TABLE 26

THE VALIDITY OF GRAPHICAL METHOD WHEN ACID GAS HAS N2 AND CO2

Acidgas			Converter 1 Conversion			Converter 2 Conversion		
%H2S	%CO2	%N2	Case 1	Case 2	Case 3	Case 1	Case 2	Case 3
100	0	0	0.9375	0.9375	0.9375	0.979	0.979	0.979
60	40	0	0.958	0.938	0.938	0.9775	0.9758	0.9758
60	30	10	0.936	0.9378	0.9378	0.979	0.9805	0.9805
				Adiabatic Operation				
100	0	0	0.9535	0.9535	0.9535	0.9825	0.9825	0.9825
60	40	0	0.959	0.958	0.9492	0.9845	0.9813	0.9769
60	30	10	0.958	0.9583	0.9512	0.9845	0.9815	0.9792
				Adiabatic Temperature (K)				
100	0	0	563	563	563	507	507	507
60	40	0	552	558	571	502	503	519
60	30	10	554	555	568	502	503	509

TABLE 27

EFFECT OF FEED GAS WATER IMPURITY ON SULFUR RECOVERY

Acidgas			Furnace	Converter 1		Converter 2	
%H2S	%CO2	%H2O		Total	Device	Total	Device
100	0	0	0.806	0.937	0.131	0.979	0.041
60	40	0	0.814	0.938	0.124	0.977	0.039
60	30	10	0.795	0.926	0.131	0.975	0.049
Adiabatic Operation							
100	0	0	0.806	0.953	0.147	0.982	0.029
60	40	0	0.814	0.959	0.145	0.984	0.025
60	30	10	0.745	0.950	0.155	0.981	0.031

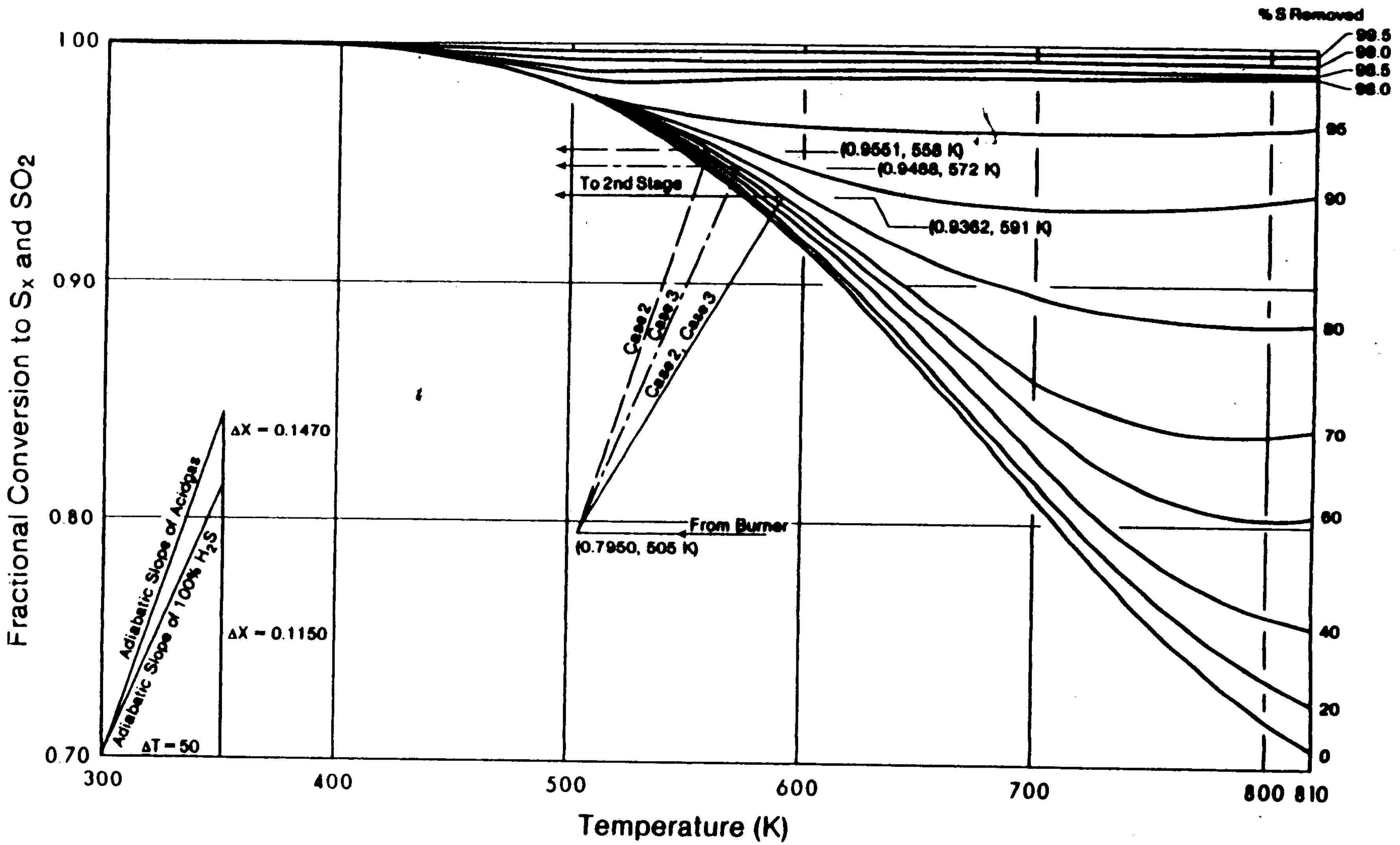


Fig. 54 Effect of H_2O on 1st Converter Performance Ignoring Effect on Equilibrium Curves.

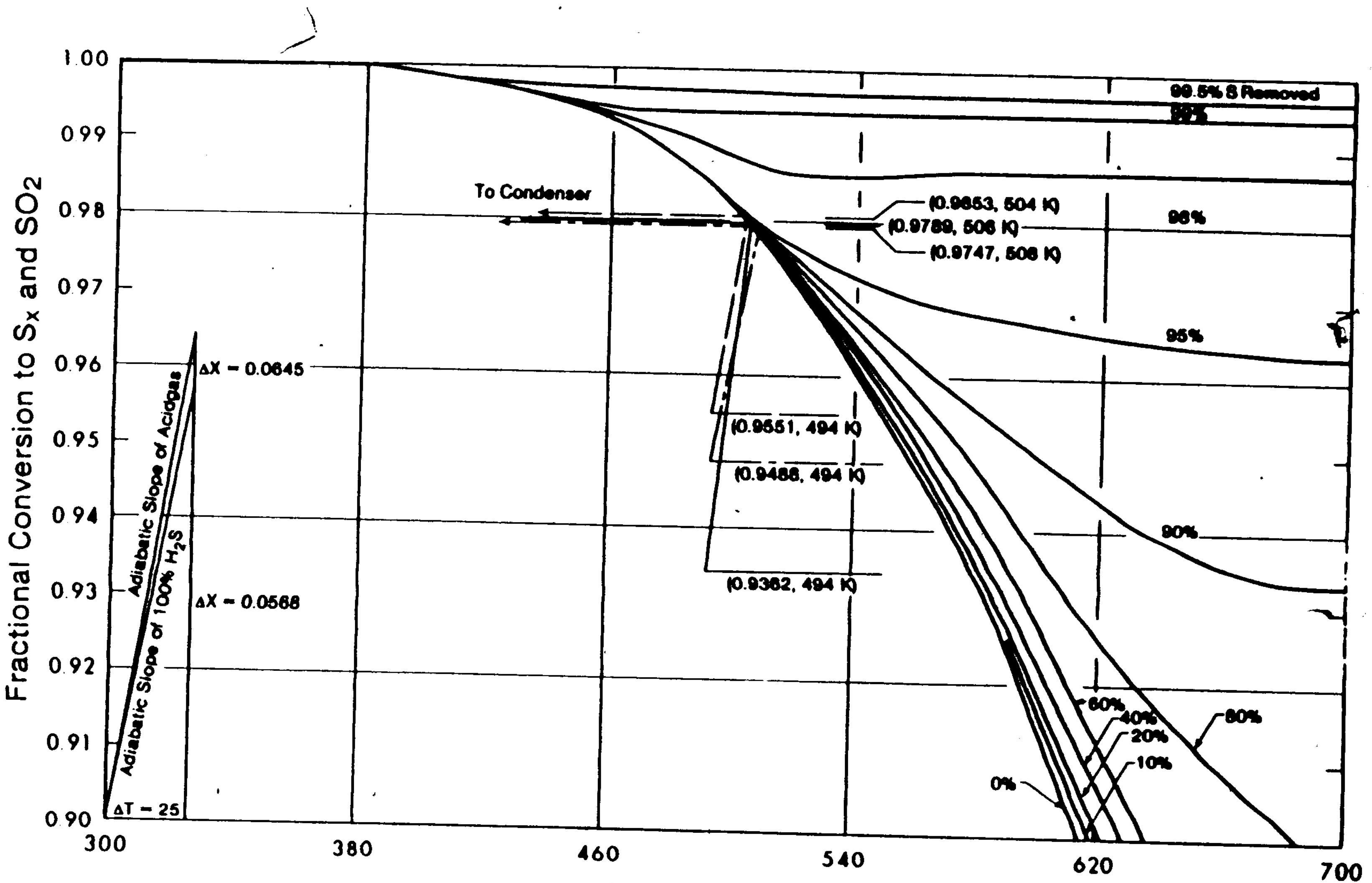


Fig. 55 Effect of H_2O on 2nd Converter Performance Ignoring Effect on Equilibrium Curves.

TABLE 28

THE VALIDITY OF GRAPHICAL METHOD WHEN ACID GAS HAS H2O AND CO2

Acidgas			1st Converter Conversion			2nd Converter Conversion		
%H2S	%CO2	%H2O	Case 1	Case 2	Case 3	Case 1	Case 2	Case 3
100	0	0	0.9375	0.9375	0.9375	0.979	0.979	0.979
60	40	0	0.938	0.938	0.938	0.9775	0.9758	0.9758
60	30	10	0.926	0.9362	0.9362	0.975	0.9789	0.9789
Adiabatic Operation								
100	0	0	0.9535	0.9535	0.9535	0.9825	0.9825	0.9825
60	40	0	0.959	0.958	0.9492	0.9845	0.9813	0.9769
60	30	10	0.950	0.9551	0.9488	0.981	0.9853	0.9747
Adiabatic Temperature (K)								
100	0	0	563	563	563	507	507	507
60	40	0	552	558	571	502	503	519
60	30	10	557	558	572	505	504	508

6.4.4 Accuracy of graphs

6.4.4.1 Effect of products of side reactions from CO_2 on burner performance

In studying the effect of products of side reactions from CO_2 on burner performance, the following assumptions are necessary:

1) Reactions of formation of H_2, COS, CS_2, and CO do not change the temperature of the product significantly.

2) The only effect of these side products is the heat sink effect after the oxidation by O_2.

Figs. 45 and 46 show the effect of ignoring the formation of H_2 at burner temperature. An increase of 0.006 in conversion of H_2S to S and H_2 can be realized for 40% CO_2 acid gas.

Table 29 was generated from Fig. 56. Table 29 shows the effect of ignoring the formation of COS, CS_2, CO and H_2 at burner temperature. At 40% CO_2 acid gas, the error caused by byproduct formation is 0.035 and 4 K. In case 4, COS, CS_2, CO, and H_2 acts as heat sink in the second part of adiabatic reaction path and the formation of COS, CS_2, CO and H_2 is allowed in generating the equilibrium conversion. However the conversion from H_2S is increased significantly due to the additional conversion to COS, and CS_2 though this increase is still within the accuracy of the error due to curve fitting of thermodynamic data.

6.4.4.2 Effect of products of side reactions from CO_2 in the furnace on tail gas clean up

The effect of products of side reactions from CO_2 in the burner on tail gas clean up is calculated for 50% CO_2 acid gas assuming the converter performance would not effect the products of CO_2 side reactions. At 1300K, the equilibrium composition contains H_2, COS, CS_2, CO as listed on Table 30.

If 98% sulfur in acid gas is converted, the amount of sulfur in COS and CS_2 amounts to 52% of the sulfur in the tail gas.

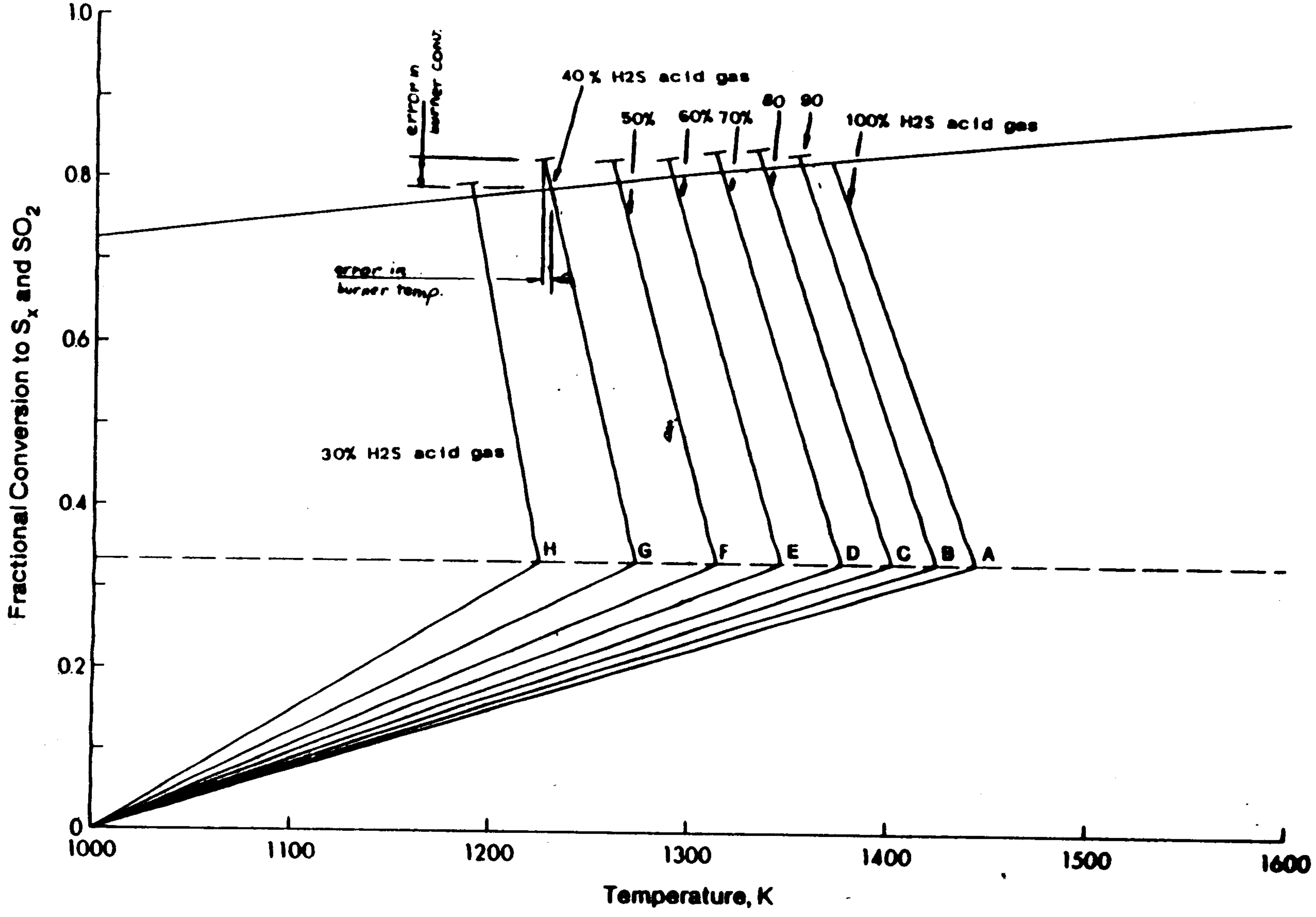


Fig. 56 Effect of CO_2 as Reactive Substance on Burner Performance.

TABLE 28

EFFECT OF COS, CS2, CO, H2 FORMATION ON BURNER TEMPERATURE AND CONVERSION

Acidgas (%CO2)	Burner Temperature (K)		Burner Conversion		Conversion due to COS, CS2 CO and H2 formation.
	Case 1	Case 4	Case 1	Case 4	
0	1374	1370	0.798	0.823	0.025
10	1358	1384	0.796	0.832	0.036
20	1339	1333	0.795	0.838	0.043
30	1317	1312	0.794	0.833	0.039
40	1291	1287	0.790	0.825	0.035
50	1263	1260	0.788	0.824	0.036
60	1229	1225	0.784	0.823	0.039
70	1189	1190	0.781	0.824	0.043

TABLE 30

EQUILIBRIUM COMPOSITION OF BYPRODUCTS OF 50% CO2 ACID GAS AT 1300 K

Species	Mole Percent
H_2	1.06
COS	0.20
CS_2	0.006
CO	2.13
C(g)	--
CH_4	--

Amount of S in COS: 1.04% S in acid gas

Amount of S in SC_2: 0.0055% S in acid gas

Amont of S due to H_2 formation: 4.6309% S in acid gas

Increase in conversion due to side reactions: 0.031.

TABLE 31

EQUILIBRIUM COMPOSITION OF 100% H_2S ACID GAS AT 1300 K

Species	Mole Percent
H_2S	0.057682
SO_2	0.03591
S_2	0.101161
S_3	0.000916
S_4	0.000021
H_2O	0.227098
N_2	0.562607
H_2	0.014241
SO	0.000185
SH	0.000171
Species with mole fraction less than program error.	S, S_5, S_6, S_7, S_8, O_2, CO_2 COS, CS_2, CO, C, CH_4, S_2O, SN
Temp. (K)	1300
Pressure (atm.)	1
Conversion of H_2S	0.807
Sulfur Recovery	0.687

6.4.4.3 Effect of other insignificant byproducts on equilibrium conversion

For 100% H_2S acid gas the equilibrium composition at 1300K is listed on Table 31.

At 1300 K, the insignificant species are S, S_2, S_4, S_5, S_6, S_7, S_8, H_2, CO_2, CS_2, CO, C, CH_4, SO, SH, S_2O, SN resulting in the increase of conversion from H_2S from 0.687 to 0.807.

Fig. 57 can be used with Table 31 to estimate the effect of insignificant byproducts on conversion at other operating temperature.

6.4.4.4 Estimation of the effect of the accuracy of graph on plant conversion

The graph should not be used for acid gas above 40% CO_2 content without adjustment from Fig. 45 and Fig. 46. The accuracy of burner conversion predicted is ± 0.035. The error in the equilibrium curve at the converter temperature range is neligible. The adiabatic slope does not change significantly, thus the guidelines given are sufficient. Fig. 58 show the effect of 0.035 uncertainty in burner conversion on the sulfur conversion calculated for converters. Table 32 summarizes the estimated error in 2 stage plant conversion using graphsical approach from these graph. The error is less than that due to the assumption of no formation of COS, CS_2, CO and H_2. The error is most significant at the first stage converter and for adiabatic operation (0.0085). Therefore caution should be used when calculating conversion for the third and fourth converters.

6.5 Application of graphical method to various process situations

In this section, procedures for applying the method to various processing situation for heat recovery or heat transfer (including direct and indirect methods) will be examined.

6.5.1 Preheating by indirect heating

Because the graphical method is not an exact method, other short cut calculation methods may also be incorporated when necessary. When two streams are to interchange their sensible heat contents but without combining of the streams, the simple heat balance equation is of the form:

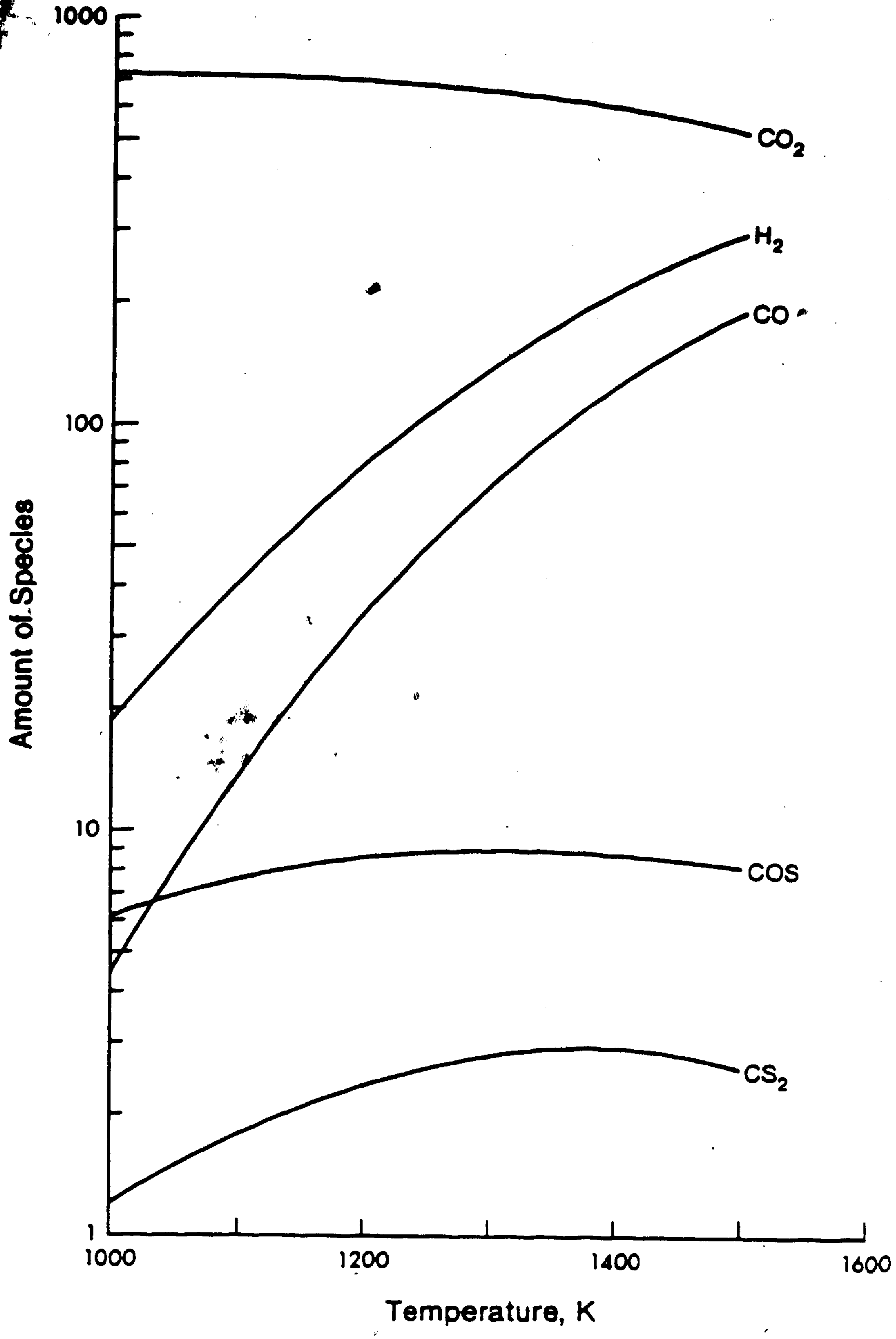


Fig. 57 Products of Side Reactions vs. Temperature.

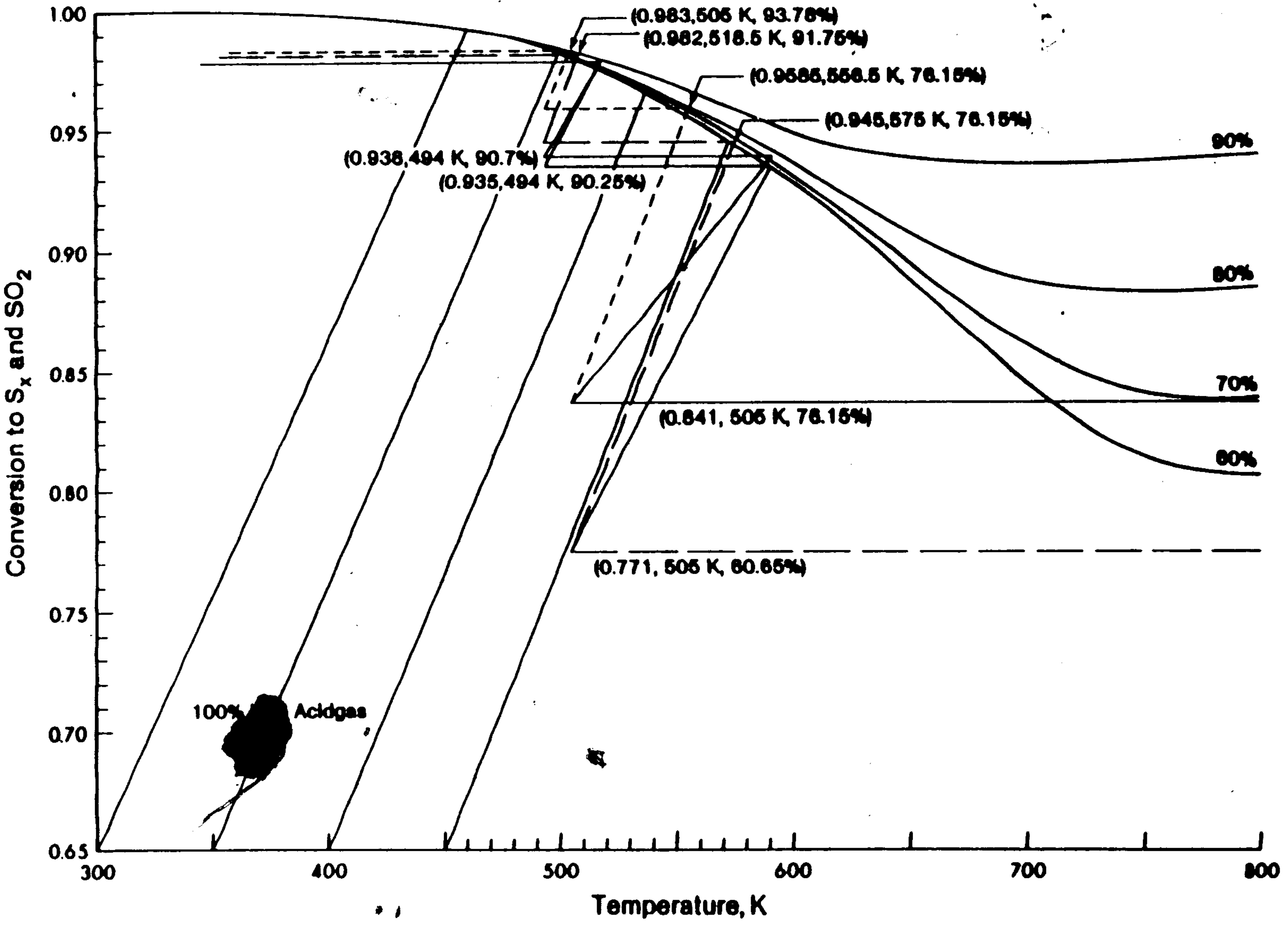


Fig. 58 Effect of the Accuracy of Burner Conversion on Sulfur Recovery.

TABLE 32

EFFECT OF BURNER CONVERSION ACCURACY ON 2 STAGE PLANT CONVERSION FOR 100% H2S ACID GAS

Device/ Conversion	Furnace	1st Converter	2nd Converter
Upper limit of burner Conv.	0.841	0.938	0.979
Conversion	0.806	0.9375	0.979
Lower limit of burner Conv.	0.771	0.935	0.979
Difference	0.035	0.0025	0.000
Adiabatic Operation			
Upper limit of burner Conv.	0.841	0.9585	0.983
Conversion	0.806	0.9535	0.9825
Lower limit of burner Conv.	0.771	0.945	0.982
Difference	0.035	0.0085	0.005

$$(M_1)\ (C_p)\ (T_1 - T_f) = (M_2)\ (C_p)\ (T_f - T_2)$$

In Claus process calculations, the mean specific heat per unit mass is nearly constant for all streams thus enabling the above equation to be solved for T_f very simply. Now, the preheated stream is to be located on the x-T plot for determining additional reaction paths, e.g. at the inlet to a catalytic converter. If T_f is known, only the second coordinate X_f needs to be evaluated, for the method to proceed. If the stream being heated is of known H_2S composition, then the composition need only be converted to "fractional conversion of H_2S to S plus H_2O", expressed in terms of original 100% H_2S acid gas. This procedure is generally very simple.

6.5.2 Preheating by direct heating

For economic reasons, converter feed streams may be preheated by combining the cooler stream leaving the preceding sulfur condenser directly with a hotter stream obtained by bypassing waste heat boiler exit stream or by using an inline burner. The composition of the bypass stream differs from that of the cool stream by containing more sulfur vapor. The composition of the much hotter inline burner stream generally approximates that of the stream in the front-end furnace prior to entering the waste heat boiler. In both cases, the streams are combined in such proportions that the desired preheat temperature is attained. The use of the simple heat balance to determine the ratio of masses of the two streams for the desired final temperature still applies. The two stream compositions are then combined on a relative mass basis to determine the composition of the combined stream. The H_2S content so determined is again converted to its comparable X coordinate and the point, (X_f, T_f), has again been established. (It is not clear whether the simple inverse lever law may generally be applied on the X-T coordinate scale; hence, this much simpler approach is not yet recommended.)

6.6 Final comments

The graphical method of evaluating reaction paths has been used to solve a number of processing problems posed at the University level. Its reliability in predicting real plant process conditions, assuming thermodynamic equilibrium is attained at each stage, has not been tested severely. In any event, the method is expected to give conservative answers because of the uncertainties deriving from the forms of molecular sulfur vapor present and their thermodynamic properties.

7. CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusion

7.1.1 Sensitivity study

Thermodynamic properties of each species have to be changed by a large amount to predict the experimental conversion. By changing each thermodynamic property by a cited uncertainty (±200 cal/mole for standard enthalpy, ±0.01 cal/mole-K for standard entropy and 4.2 for S_8 and 3.3 for S_6) with sulfur vapor as a combination of S_2, S_6, S_7, and S_8. The calculated conversion predicts the experimental conversion at 700 K for lean acid gas .

Comparing the effect of specie standard heat of formation on predicted conversion, water vapor has the highest effect then SO_2, S_2, H_2S, and S_8. For standard entropy effect, H_2S is the most sensitive then $H_2O(g)$, S_2, S_8, and SO_2. Except sulfur species, thermodynamic properties of other species have been determined to reasonable accuracy. Thus the thermodynamic properties of S_2 should be determined more accurately than those of S_8.

7.1.2 Equilibrium constant for H_2S/SO_2 mixture

Using experimental equilibrium data from France, equilibrium constant for H_2S/SO_2 mixture over the temperature range 225°C to 370°C is:

$$\ln K_p' = -17.885 + 1.5466 * 10^4/T$$

This equilibrium constant predicts the experimental conversion for lean acid gas to 10% accuracy.

7.1.3 Graphical approach to Claus plant prediction

By example application, the graphical approach is illustrated to predict sulfur recovery in the burner and each converter.

Below 40% inert content, Fig. 46 can be used to predict equilibrium conversion up to the third converter. Tables of slopes of adiabatic reaction paths can be used to predict the adiabatic temperature.

Above 40% impurity content, additional graphs as shown in Fig. 40 are needed to predict conversions in the converters.

7.2 Recommendations

7.2.1 Sensitivity study

Sulfur vapor model has to be modified to include S_7 to predict equilibrium conversion for the modified Claus process.

More reliable data on sulfur vapor distribution for intermediate range of temperature between West and Menzies' and Rau's for determination of sulfur vapor distribution over the whole temperature range are needed to determine a realistic model for sulfur vapor.

7.2.2 Software on Claus plant prediction

A major expansion of the graphical method would be the prediction of equilibrium plant performance for split flow and in-line burner without manual precalculation of feed composition for each reactor.

Equations of state or generalized compressibility should be used to describe real gas behaviour as well as non-ideal mixture behaviour. This may change the result somewhat due to the dipole effect of H_2S, and SO_2 molecules.

7.2,3 Graphical approach to Claus plant prediction

The effects of inerts may be betters examined using mean heat capacity parameters since inerts lowers the temperature as well as the partial pressure of the reactive species.

The effect of other impurities on the feed should be studied: hydrocarbon, ammonia... as well as the effect of side reactions.

The graphical approach can be expanded to help in design equipments besides the determination of the optimum reaction path by assigning the heat capacity parameter for each adiabatic reaction path thus the heat load of the devices can be determined.

NOMENCLATURE

$C_p(S_2)$	Heat capacity for the formation of S_2, cal/mole-K
$C_p(S_2=S_8)$	Heat capacity for the reaction $4S_2=S_8$, cal/mole-K
F	Free energy, cal/mole
$\Delta H^\circ_{f,298}$	Standard heat of formation, Kcal/mole
$H^T{}_{298}$	Sensible enthalpy from 298 K to T, Kcal/mole
K'_p	Pseudo-equilibrium constant for H_2S/SO_2 system
K	True equilibrium constant for H_2S/SO_2 system
K_1	Equilibrium constant for the formation of S_1 from S_2
K_4	Equilibrium constant for reaction $2S_2=S_4$
K_6	Equilibrium constant for reaction $3S_2=S_6$
K_8	Equilibrium constant for reaction $4S_2=S_8$
N	Number of moles
Ns_2	Number of moles of S_2
Ns_4	Number of moles of S_4
Ns_6	Number of moles of S_6
Ns_8	Number of moles of S_8
M_1	Mole number of stream 1 to heat exchanger, mole
M_2	Mole number of stream 2 to heat exchanger, mole
P	Pressure, atm.
Pc	Critical pressure, atm.
Pr	Reduced pressure, dimensionless
Ps	Partial pressure of sulfur, atm.
P_2	Partial pressure of S_2, atm.
P_4	Partial pressure of S_4, atm.
P_6	Partial pressure of S_6, atm.
P_8	Partial pressure of S_8, atm.
R	Gas constant
S	Entropy, cal/mole-K

S	Sulfur vapor with average atomic number
S_i	Sulfur vapor with average atomic number i
T	Temperature, K
t	Temperature, °C
Tc	Critical temperature, K
Tr	Reduced temperature, dimensionless
T_1	Temperature of stream 1 to heat exchanger, K
T_2	Temperature of stream 2 to heat exchanger, K
T_f	Final temperature of both steams from heat exchanger, K
X	Conversion of H_2S/SO_2 system
Zc	Critical compressibility
ν	Average atomic number of sulfur
π	Total pressure of sulfur system,atm.
Φ	Function

Superscripts

°	Standard condition, 60°F, 1atm.

Subscripts

cal	Calculated value
exp	Experimental value
f	Final condition
i	Of component i
Ref	Referenced condition
T	At temperature T and 1atm.
t	Total value

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APPENDICES

APPENDIX A Modification of Free Energy Minimization Programm

1) Theoretical considerations

Basically FREM uses the steepest descent method to find the convergence of the new chemical composition which is the solution of a set of linear equations developed by applying Lagrange multipliers to minimization problems with constraint. The volume of the condensed phase is also neglected.

SUMMARY OF MATHEMATICAL RELATIONSHIPS

In the free energy minimization method only free energy of the species is needed. The equilibrium composition search is a process of finding a set of non–negative mole numbers which both satisfy the mass balan[illegible] [illegible]nimize the system free energy.

Using Lagrange multipliers, this set of equations is transformed to a set of non–linear equations which can be solved by appropriate numerical iteration techniques.

1) *Numerical procedure*

In FREM Gaussian elimination is used to solve a set of linear equations set up using Lagrange multipliers and Taylor series approximation of system free energy polynomials. The new set of species mole number will be calculated until the different between subsequent calculation is less than the critical amount (10^{-1} moles). McGregor's thesis (102) described in detail the numerical and mathematical techniques in chapter 3.

When partial pressure of sulfur is greater than the vapor pressure, the steepest descent method is used to determine the composition of sulfur vapor as sulfur condenses until partial pressure equal vapor pressure.

Since the final mole number is inserted into the original equation:

$$x_i = -y_i(c_i + \ln(y_i/\bar{y})) + y_i(\bar{x}/\bar{y}) + \sum_{j=1}^{m} \pi_j a_{ij} y_i \qquad \text{(A-1)}$$

the error due to truncation in the Gaussian elimination c[illegible] will [illegible] effect the equilibrium composition.

2) *Model limitations*

Though the program is general, the modifications are only applied for the sulfur-sulfur compound system or selenium-selenium compound system where the species present in the gas phase as A1, A2,...A8 (A is the element) and is the only species in the liquid phase.

The program can only calculate equilibrium compositions using vapor pressures of sulfur; no other constituents are allowed to be present in the liquid phase. For the same reason, the frozen dew point and equilibrium dew point temperatures can only be calculated for sulfur.

3) *Thermodynamic data file*

Standard heats of formation and standard entropies for H_2S, SO_2, H_2O, N_2, S_2 and other minor species (SH, HO, S_2H_2, CH_4...) when used to determine the effect of insignificant species on equilibrium conversions are from JANAF, 2nd edition (74). The reader should refer to sec. 4.3.2 and 4.4.3 for justification of this source. Sensible enthalpy ($H_T - H^\circ_{298}$), and the different of entropy and standard entropy ($S_T - S^\circ_{298}$) are calculated using standard values at 298 K and the fitted heat capacity coefficients. Depending on the data source for the various species either of the following forms is used.

$$C_p = a + bT + cT^2 + dT^3 \qquad (A.2)$$

or

$$C_p = a + bT + c/T^2 + dT^3 \qquad (A.3)$$

The coefficients a, b, c and d were obtained from linear least square fitting of the values given by JANAF, 2nd ed. (74). The program of linear least square fitting is listed in Appendix B.

For sulfur, heat capacity coefficients for S_2 to S_8 and the standard heat of formation and standard entropies for S_3 to S_8 were taken from Rau(127). File DFREM lists the data used in thermodynamic data file.

The calculation of sensible enthalpy and entropy from standard values is incorporated in the main program, only the linear least square heat capacity coefficients are needed from the thermodynamic data file.

2) Program description

1) *Original version*

The original program written by McGregor (102) and modified by Liu (94) and Cho (32) consists of a main program and five subroutines written in FORTRAN IV.

The main program reads in variables characterized the chemical system specially its initial composition and the thermodynamic data (free energy coefficients) for all species suspecting to presence in either the original or final composition. The free energy is calculated from McBride equation:

$$F/RT = a_1(1-\ln T) - a_2T/2 - a_3T^2/6 - a_4T^3/16 - a_5T^4/20 + a_6/T - a_7 \quad \text{(A.4)}$$

The main program also calculates the molar free energy for each species and calculates the equilibrium composition by solving a set of linear equations (102). Test for convergence is included in the main program before the final equilibrium is printed.

Subroutine GAUSS solves the set of equations A*X=B using Gaussian elimination and back subtitution rotating about the elements of maximum modulus.

Subroutine GSET sets up the matrix equation for the set of equations (102).

Subroutine CONV calculates the percent conversion of the first component and of H_2S to sulfur if the input order is H_2S, SO_2, S_1, S_2,...S_8, H_2O, N_2...

Subroutine NEZE tests for negative or zero amounts of molecular species and takes the corrective action as indicated in White's paper (150) and McGregor's review (102).

Subroutine DISTR generates a positive set of mole number for all species in the system.

Subroutine FREN calculates the free energy contribution of each species to the system free energy.

2) *Modified version*

Besides a minor change in subroutine DISTR to improve the accuracy of mass conservation, all the subroutines are preserved as the original version. Two subroutines are added SCOND and TDEW.

Subroutine SCOND tests and calculates the amount of sulfur condensed so that the sulfur partial pressure is equal to or less than the sulfur vapor pressure. The sulfur vapor distribution is calculated in each imbedded iteration again using the steepest descent method but only for the isolated sulfur species.

Subroutine TDEW calculates the frozen dew point and equilibrium dew point temperatures of sulfur from the equilibrium composition.

The main program has been modified to read thermodynamic data as standard heat of formation, standard entropy and heat capacity coefficients. The program calculates sensible enthalpy and entropy from heat capacity coefficients:

$$H_T - H_{298} = a(T-298) + b(T^2-298^2)/2 + c(T^3-298^3)/3 + d(T^4-298^4)/4 + e(1/T-1/298) \tag{A.5}$$

$$S_T - S_{298} = a\ln(T/298) + b(T-298) + c(T^2-298^2)/2 + d(T^3-298^3)/3 + e(1/T^2-1/298^2) \tag{A.6}$$

and the molar free energy is :

$$F/RT = H/RT + S/R \tag{A.7}$$

Program has the flexibility of reading in also discrete values of sensible enthalpy and entropy when heat capacity coefficients are not available or of different functional forms.

Comment cards in the mainline program define each variable read in as data, and the format for the data is easily found by noting the appropriate READ and FORMAT statements in the program listing.

3) Listing of the program

```
C*********************************************************
C*                                                       *
C*                         FREM                          *
C*                                                       *
C* THIS PROGRAM CALCULATES EQUILIBRIUM                   *
C* COMPOSITIONS FOR COMPLEX REACTION SYSTEMS             *
C* USING THE FREE ENERGY MINIMIZATION METHOD             *
C* DEVELOPED BY WHITE AND COWORKERS. IT WILL             *
C* HANDLE UP TO THIRTY DIFFERENT MOLECULAR               *
C* SPECIES CONTAINING FIVE DIFFERENT                     *
C* ELEMENTS. FOR SYSTEMS WITH LARGER NUMBER              *
C* OF SPECIES AND ELEMENTS, CHANGE APROPRIATE*
C* DIMENSION STATEMENTS. ANY NUMBER OF CASES             *
C* CAN BE ATTEMPTED WITH AS MANY TEMPERATURE             *
C* AND PRESSURE DESIRED.                                 *
C*                                                       *
C* INPUT DATA:                                           *
C*    NCASE - NUMBER OF CASES                            *
C*    SNAM  - NAME OF THE SPECIES                        *
C*    X     - INITIAL AMOUNT OF THIS SPECIE              *
C*            (EITHER NUMBER OF MOLES OR MOLE*
C*             FRACTION)                                 *
C*    A     - SPECIE ROW IN MASS BALANCE                 *
C*            CONSTRAINT MATRIX                          *
C*    M     - NUMBER OF DIFFERENT ELEMENTS               *
C*    N     - NUMBER OF DIFFERENT SPECIES                *
C*    T     - TEMPERATURE OF THE SYSTEM IN               *
C*            KELVIN                                     *
C*    PRESS - PRESSURE OF THE SYSTEM IN ATM.             *
C*    SHTFN - STANDARD HEAT OF FORMATION OF              *
C*            THE SPECIE                                 *
C*    S298  - STANDARD ENTROPY OF THE SPECIE             *
C*                                                       *
C*********************************************************
C THIS SET OF SYSTEM ONLY I.E.S2-S8 WITH S SPECIES IN THIS
C ORDER FOLLOW H2S AND SO2 IN THE INPUT AND ONLY
C S MAY BE CONDENSED
      IMPLICIT REAL*8 (A-H,O-Z),INTEGER(I-N)
      INTEGER P
      LOGICAL L,L1,L2
      COMMON /MTDEW/TVP(601,2)
      COMMON /TDEWZ/X(30),PRESS
      COMMON /MCDEW/SHTFN(30),S298(30),ACP(30),BCP(30),
     &CCP(30),DCP(30),ECP(30),AACP(30),BBCP(30),
     &CCCP(30),DDCP(30),EECP(30)
      COMMON /NTOT/N
      COMMON /TDEWS/TDEW1,TDEW2
      DIMENSION SNAM(30,5),GA(30,30),GB(30) ,CONV(50,30),
     1TSTOR(50),F(30),A(30,5) ,Y(30),B(30),FRC(30),
     2NG1(30),XX(30) ,X0(30)
     U,GX(30),C(30) ,XREF(30),SFRC(30),CON(15)
     &,SACP(30),SBCP(30),SCCP(30),SDCP(30),SECP(30)
      DIMENSION ENTHY(30),ENTRY(30),DEW1S(50,30),DEW2S(50,30)
      DATAR/1.98718D0/
```

```
C SET UP TABLE FOR INTERPOLATION OF VAPOR PRESSURE
      DO 100 I=1,601
      T=300.D0+0.5D0*DFLOAT(I-1)
      TLOG=6.46543D0-7.63591D0*(0.9983D0**(T-253.16D0))
     &-6.936946D0*(0.9908234D0**(T-253.16))
      VP=10.D0**TLOG/760.D0
      TVP(I,1)=T
  100 TVP(I,2)=VP
      TR=298.16D0
      EPS=0.5D-8
      READ(5,1)M,N,P,NPT,IFLAG,DT
    1 FORMAT(5I5,F15.7,2I5,4F15.7)
      N2=N+P
      IF(IFLAG)509,510,509
  510 DO 502 I=1,N2
      READ(5,3)(SNAM(I,K),K=1,5),X(I)
      READ(5,4)(A(I,J),J=1,M)
      READ(5,5)ACP(I),BCP(I),CCP(I),DCP(I),
     1 ECP(I),SHTFN(I),S298(I)
  502 READ(5,5)AACP(I),BBCP(I),CCCP(I),DDCP(I),EECP(I)
      DO 514 I=1,N2
  514 X0(I)=X(I)
  509 DO 10 ND=1,NPT
      DO 524 I=1,N2
      ENTHY(I)=0.D0
  524 ENTRY(I)=S298(I)
      IF(ND.EQ.1)GOTO 511
  512 IF(IFLAG.EQ.0)GOTO 513
  511 READ(5,11)PRESS,T
   11 FORMAT(15D15.7)
      IF(IFLAG.EQ.1) GOTO 517
      T0=T
  513 T=T0+DFLOAT(ND-1)*DT
  517 DO 516 I=1,N2
  516 X(I)=X0(I)
C INITIALIZE FOR SLIQ AND FLAG OF THERMODYNAMIC
C READING USED IN SCOND SUBROUTINE
      L1=.TRUE.
      SLIQ=0.D0
C INPUT GASEOUS THERMODYNAMIC READING
      WRITE(6,604)
  604 FORMAT(1H1,40X,'THERMODYNAMIC PROPERTIES ')
      WRITE(6,612)
  612 FORMAT(42X,'JANAF 1971,S PROPERTIES FROM RAU 1973')
      IF(IFLAG)501,500,501
  500 CONTINUE
      TTR=TR
      ITP=0
      TT=T
      IF(TT.LE.1000.D0)GOTO 506
  507 T=1000.D0
  506 DO 505 I=1,N2
      ENTHY(I)=ACP(I)*(T-TR)+BCP(I)/2.D0*(T*T-TR*TR)
     &+CCP(I)/3.D0*
```

```
     &(T**3-TR**3)+DCP(I)/4.D0*(T**4-TR**4)
     &-ECP(I)*(1.D0/T-1.D0/TR) +ENTHY(I)
      ENTRY(I)=ACP(I)*DLOG(T/TR)+BCP(I)*(T-TR)+CCP(I)/2.D0*
     &(T*T-TR*TR)+DCP(I)/3.D0*(T**3-TR**3)-ECP(I)/2.D0*
     &(1.D0/T/T-1.D0/TR/TR)+ENTRY(I)
  505 CONTINUE
      ITP=ITP+1
      IF(TT.LE.1000.D0)GOTO 520
      IF(ITP.EQ.2)GOTO 520
      T=TT
      TR=1000.D0
      DO 519 I=1,N2
      SACP(I)=ACP(I)
      SBCP(I)=BCP(I)
      SCCP(I)=CCP(I)
      SDCP(I)=DCP(I)
  519 SECP(I)=ECP(I)
      DO 508 I=1,N2
      ACP(I)=AACP(I)
      BCP(I)=BBCP(I)
      CCP(I)=CCCP(I)
      DCP(I)=DDCP(I)
  508 ECP(I)=EECP(I)
      GOTO 506
  520 DO 521 I=1,N2
  521 WRITE(6,6)SHTFN(I),ENTHY(I),ENTRY(I)
      IF(TT.LE.1.D3)GOTO 523
  522 DO 518 I=1,N2
      ACP(I)=SACP(I)
      BCP(I)=SBCP(I)
      CCP(I)=SCCP(I)
      DCP(I)=SDCP(I)
  518 ECP(I)=SECP(I)
      TR=TTR
  523 CONTINUE
      GOTO 515
  501 DO 2 I=1,N2
      READ(5,3) (SNAM(I,K),K=1,5),X(I)
      WRITE(6,3)(SNAM(I,K),K=1,5),X(I)
    3 FORMAT(1X,A3,4A4, F15.7)
      READ(5,4) (A(I,J),J=1,M)
      WRITE(6,4)(A(I,J),J=1,M)
    4 FORMAT( 7(3X,F7.2))
      IF(I-2)616,616,620
  616 CONTINUE
  621 READ(5,5) SHTFN(I),ENTHY(I),ENTRY(I)
      GO TO 619
  620 IF(I-10)617,621,621
  617 READ(5,5)ACP(I),BCP(I),CCP(I),SHTFN(I),S298(I)
      ENTHY(I) = ACP(I)*(T-TR) +BCP(I)/2.D0*(T*T -TR**2)
     & -CCP(I)*(1.D0/T -1.D0/TR)
      ENTRY(I) = ACP(I)*DLOG(T/TR) + BCP(I)*(T - TR)
     & - CCP(I)/2.D0*(1.D0/T/T -1.D0/TR/TR)
      ENTRY(I)=ENTRY(I)+S298(I)
```

```
  5 FORMAT( 7(D15.7))
619 CONTINUE
    WRITE(6,6)SHTFN(I),ENTHY(I),ENTRY(I)
  6 FORMAT(19X,' STANDARD HEAT OF FORMATION = ',D15.7/,20X,
   1'SENSIBLE E
   1NTHALPY AT T = ',D15.7/,20X,'ABSOLUTE ENTROPY AT T = ',
   2D15.7)
  2 CONTINUE
515 IF(N2.GT.30) STOP
    IF(N2.EQ.30) GOTO 102
103 IIS=N2+1
    DO 705 II=IIS,30
705 X(II)=0.000
102 DO 101 II=1,30
101 XX(II)=X(II)
    DO 20 NS=1,28
C DEF OF %SULFUR REMOVAL: % OF ATOMS OF S FROM
C THE ACID GAS STREAM
    L2=.FALSE.
    IF(NS.EQ.1)GOTO 200
    CALL SREM(NS,X,N2,N,P,XX,SLIQ,Y,L2)
    IF(.NOT.L2)GOTO200
    GOTO 199
200 IF(NS.GT.1) GOTO 201
C RECORD INITIAL MIXTURE COMPOSITION
    WRITE(6,611)
    WRITE(6,7)
  7 FORMAT(1H1,40X,'FREE ENERGY MINIMIZATION'/30X,'MOLE'
   1,'CULAR SPECIES',10X,'INITIAL MOLE NUMBERS',10X,
   2'INITIAL MOLE FRACTION')
    CALL DISTR1(XX,Y,B,N2,M,A)
    CALL MOFR(Y,FRC,N,P)
    DO 8 I=1,N2
  8 WRITE(6,9) (SNAM(I,K),K=1,5),Y(I),FRC(I)
  9 FORMAT(30X,A3,4A4,10X,D15.7,10X,D15.7)
C FREE ENERGY MINIMIZATION METHOD BEGINS
201 SCALE=1.
    ISTORE=0
    DO 12 I=1,N2
    NG1(I)=0
    FRT = (SHTFN(I) + ENTHY(I) )/ (R*T) - ENTRY(I)/R
    C(I)=FRT+DLOG(PRESS)
    IF(I-N)12,12,13
 13 C(I)=FRT
 12 CONTINUE
985 ISCOND=0
    JBI=2
 999 CONTINUE
    ISCOND=ISCOND+1
    IF(ISCOND.GT.3)STOP
    DO 35 JB=1,JBI
    DO 14 ITER=1,200
    ISTORE=ISTORE+1
    CALL DISTR1(X,Y,B,N2,M,A)
```

```
      CALL FREN (Y,C,F,YBAR,N,P,NG1)
      MG=M+P+1
      CALL GSET (A,Y,GA,GB,B,F,P,M,MG,N,C)
      CALL GAUSS(GA,GB,MG,GX)
      IF(P)15,15,16
   16 DO 17 I=1,P
      II=I+1
      IC=N+I
   17 X(IC)=GX(II)
   15 CONTINUE
      DO 18 I=1,N
      IF(NG1(I)) 19,19,18
   19 X(I)=-Y(I)*((C(I)+DLOG(Y(I)/YBAR))-GX(1))
      DO 21 J=1,M
      IG=P+J+1
   21 X(I)=X(I)+GX(IG)*A(I,J)*Y(I)
   18 CONTINUE
      CALL NEZE (X,Y,N2,NG1)
      CALL SCOND(X,T,PRESS,L,L1,N,P,SNAM,SLIQ)
      QUIT=1. D0
      DO 22 I=1,N2
      IF(NG1(I)) 23,23,22
   23 TEST=(X(I)-Y(I))/X(I)
      IF(DABS(TEST)-EPS) 22,22,24
   24 QUIT=-1. D0
   22 CONTINUE
      IF(QUIT) 25,25,26
   25 DO 27 I=1,N2
   27 Y(I)=X(I)
   14 CONTINUE
   26 DO 32 I=1,N2
      NG1(I)=0
      IF(X(I)) 33,33,34
   34 Y(I)=X(I)
      GO TO 32
   33 Y(I)=0.000001D0
   32 CONTINUE
   35 CONTINUE
      IF(SLIQ.LT.1.D-6)GOTO 199
      IF(.NOT.L) GOTO 999
      P=1
      N2=N+P
      X(N2)=SLIQ
      Y(N2)=X(N2)
  199 CONTINUE
      WRITE(6,28)T,PRESS
   28 FORMAT(28X,'TEMPERATURE(DEG K) = ',F7.1,5X,'PRESSU'
     1'RE (ATM)=',D15.7)
      IF(NS.LE.10)XNS=10.*DFLOAT(NS-1)
      IF(NS.GT.10)XNS=100.D0*(0.905D0+0.005D0*(NS-10))
      WRITE(6,99)XNS
   99 FORMAT(1H ,30X,'SULFUR REMOVED = ',F6.1,3X,'PER CENT')
      WRITE(6,29) ISTORE
   29 FORMAT (1H0,30X,'NUMBER OF ITERATION =',I5/30X,
```

```
     U'MOLECULAR SPECIES'
     U,8X,'EQUILIBRIUM MOLE NUMBERS',8X,'MOLE FRACTION')
      DO 715 II=1,N2
 715  X(II)=Y(II)
      CALL MOFR (X,FRC,N,P)
      DO 30 I=1;N2
  30  WRITE(6,31)  (SNAM(I,K),K=1,5),X(I),FRC(I)
  31  FORMAT (30X,A3,4A4,10X,D15.7,10X,D15.7)
      CALL COND(X,XX)
      P=0
      N2=N+P
      CALL TDEW(FRC,T,SLIQ,N2)
 609  CONTINUE
      CONV(ND,NS)=(XX(1)-X(1))/XX(1)
      TSTOR(ND)=T
      DEW1S(ND,NS)=TDEW1
      DEW2S(ND,NS)=TDEW2
  20  CONTINUE
 706  CONTINUE
 611  FORMAT(1H1,' ')
      WRITE(2,300)TSTOR(ND),(CONV(ND,INS),INS=1,NS),
     &(DEW1S(ND,INS),INS=1,NS),(DEW2S(ND,INS),INS=1,NS)
  10  CONTINUE
 300  FORMAT(1X,F8.2/1X,10F8.4/1X,10F8.2/1X,10F8.2)
      STOP
      END
      SUBROUTINE DISTR1(X,Y,B,N2,M,A)
      IMPLICIT REAL*8 (A-H,O-Z),INTEGER(I-N)
      DIMENSION X(30),Y(30),B(30),A(30,5)
      DO 1 I=1,N2
      IF(X(I)) 2,2,1
   2  X(I)=0.0000001 D0
   1   Y(I)=X(I)
      DO 3 J=1,M
      B(J)=0.0
      DO 3 I=1,N2
   3  B(J)=B(J)+A(I,J)*Y(I)
      RETURN
      END
      SUBROUTINE COND(X,XX)
      IMPLICIT REAL*8 (A-H,O-Z),INTEGER(I-N)
      DIMENSION X(30),XX(30)
      CONV=(XX(1)-X(1))/XX(1)
      WRITE(6,1) CONV
   1  FORMAT(28X,'EQUILIBRIUM CONVERSION OF H2S TO SX AND SO2
     & (PCT)=', F6.3)
      CONV=(XX(1)-X(1)-X(2))/XX(1)
      WRITE(6,2)CONV
   2  FORMAT(28X,'EQUILIBRIUM CONVERSION OF
     1 H2S TO SX (PCT)=',F6.3)
      RETURN
      END
      SUBROUTINE GSET (A,Y,GA,GB,B,F,P,M,MG,N,C)
      IMPLICIT REAL*8(A-H,O-Z),INTEGER(I-N)
```

```
      INTEGER P
      DIMENSION R(5,5),A(30,30),Y(30),GA(30,30),GB(30),B(30),
     &F(30) ,C(30)
      DO 1 K=1,M
      DO 1 J=1,K
      R(J,K)=0.0D0
      DO 2 I=1,N
    2 R(J,K)=R(J,K)+A(I,J)*A(I,K)*Y(I)
    1 R(K,J)=R(J,K)
      DO 3 I=1,MG
      DO 3 J=1,MG
    3 GA(I,J)=0.0D0
      DO 4 IG=1,M
      DO 5 I=1,N
    5 GA(IG,1)=GA(IG,1)+A(I,IG)*Y(I)
      IF(P)6,6,7
    7 DO 8 I=1,P
      JG=I+1
      JGG=IG+P+1
      IGG=I+M+1
      II=N+I
      GA(IG,JG)=A(II,IG)
    8 GA(IGG,JGG)=GA(IG,JG)
    6 DO 9 J=1,M
      JG=J+P+1
    9 GA(IG,JG)=R(IG,J)
      JG=P+IG+1
      IGG=M+1
    4 GA(IGG,JG)=GA(IG,1)
      DO 10 J=1,M
      GB(J)=B(J)
      DO 10 I=1,N
   10 GB(J)=GB(J)+A(I,J)*F(I)
      JGB=M+1
      GB(JGB)=0.0D0
      DO 11 I=1,N
   11 GB(JGB)=GB(JGB)+F(I)
      IF(P)12,12,13
   13 DO 14 I=1,P
      JGB=M+I+1
      II=N+1
   14 GB(JGB)=C(II)
   12 CONTINUE
      RETURN
      END
      SUBROUTINE GAUSS (A,R,N,X)
      IMPLICIT REAL*8(A-H,O-Z),INTEGER(I-N)
      DIMENSION A(30,30),R(30),X(30)
      M=N-1
      DO 11 J=1,M
      S=0.0D0
      DO 12 I=J,N
      U= DABS(A(I,J))
      IF(U-S) 12,12,112
```

```
 112 S=U
     L=I
  12 CONTINUE
     IF(L-J) 119,19,119
 119 DO 14 I=J,N
     S=A(L,I)
     A(L,I)=A(J,I)
  14 A(J,I)=S
     S=R(L)
     R(L)=R(J)
     R(J)=S
  19 IF( DABS(A(J,J))-1.D-30) 115,115,15
 115 WRITE(6,3)
   3 FORMAT (1H ,'MATRIX SINGULAR')
     RETURN
  15 MM=J+1
     DO 11 I=MM,N
     IF( DABS(A(I,J))-1.D-30) 11,111,111
 111 S=A(J,J)/A(I,J)
     A(I,J)=0.0D0
     DO 16 K=MM,N
  16 A(I,K)=A(J,K)-S*A(I,K)
     R(I)=R(J)-S*R(I)
  11 CONTINUE
     DO 17 K=1,N
     I=N+1-K
     S=0.0D0
     IF(I-N) 117,17,117
 117 MM=I+1
     DO 18 J=MM,N
  18 S=S+A(I,J)*X(J)
  17 X(I)=(R(I)-S)/A(I,I)
     RETURN
     END
     SUBROUTINE NEZE (X,Y,N ,NG1)
     IMPLICIT REAL*8(A-H,O-Z),INTEGER(I-N)
     DIMENSION X(30),Y(30),NG1(30)
     TEST=1.0 D0
     DO 1 I=1,N
     IF(NG1(I)) 2,2,1
   2 IF(X(I)) 3,3,1
   3 SLAM=-0.99D0*Y(I)/(X(I)-Y(I))
     IF(SLAM-TEST)4,4,1
   4 TEST=SLAM
   1 CONTINUE
     DO 5 I=1,N
     IF(NG1(I))7,7,5
   7 X(I)=Y(I)+TEST*(X(I)-Y(I))
     IF(X(I)-0.10D-10) 6,6,5
   6 X(I)=0.0D0
     NG1(I)=1
   5 CONTINUE
     RETURN
     END
```

```
      SUBROUTINE FREN (Y,C,F,YBAR,N,P,NG1)
      IMPLICIT REAL*8(A-H,O-Z),INTEGER(I-N)
      INTEGER P
      DIMENSION Y(30),C(30),NG1(30) ,F(30)
      YBAR=0.0D0
      DO 1 I=1,N
    1 YBAR=YBAR+Y(I)
      DO 2 I=1,N
      IF(NG1(I)) 3,3,4
    3 F(I)=Y(I)*(C(I)+DLOG(Y(I)/YBAR))
      GO TO 2
    4 F(I)=0.0D0
    2 CONTINUE
      IF(P)10,10,6
    6 DO 7 I=1,P
      II=N+I
      IF(NG1(II))8,8,9
    8 F(II)=Y(II)*C(II)
      GOTO 7
    9 F(II)=0.0D0
    7 CONTINUE
   10 CONTINUE
      RETURN
      END
      SUBROUTINE MOFR (Y,FRC,N,P)
      IMPLICIT REAL*8(A-H,O-Z),INTEGER(I-N)
      INTEGER P
      DIMENSION Y(30),FRC(30)
      DEN=0.0D0
      DO 1 I=1,N
    1 DEN=DEN+Y(I)
      DO 2 I=1,N
    2 FRC(I)=Y(I)/DEN
      IF(P) 7,7,8
    8 DEN=0.0D0
      DO 3 I=1,P
      II=N+I
    3 DEN=DEN+Y(II)
      DO 4 I=1,P
      II=N+I
    4 FRC(II)=Y(II)/DEN
    7 CONTINUE
      RETURN
      END
      SUBROUTINE TDEW(FRT,T,SLIQ,N2)
      IMPLICIT REAL*8 (A-H,O-Z),INTEGER(I-N)
      INTEGER P
      COMMON /MTDEW/TVP(601,2)
      COMMON /TDEWZ/X(30),PRESS
      COMMON /FF/PPS
      COMMON /FZZ/ADEW(30,5),XDEW(30),YDEW(30),VP
      EXTERNAL FFCT
      EXTERNAL FCT
      DIMENSION FRT(30),ROOT(2)
```

```
C ISS-ISE: INDEX OF S SPECIES
      ISS=3
      ISE=10
      PPS=0.D0
      DO 10 I=ISS,ISE
 10   PPS=PPS+PRT(I)
      IF(SLIQ.LE.1.D-6)GOTO 24
      TDEW1=T
      WRITE(6,9)TDEW1,PPS
    9 FORMAT(20X,'FROZEN DEW POINT
     & & EQUILIBRATED DEW POINT (K)=',
     &F6.2,10X,'PARTIAL PRESSURE (ATM)=',E15.7)
      GOTO 22
   24 CONTINUE
C CALCULATE TDEW1 (FROZEN)
      EPS=0.5D0
      IEND=100
C CALCULATE INITIAL GUESS FROM VAPOR PRESSURE
   20 QUIT=0
      DO 31 IVP=1,601
      ALPHA=TVP(IVP,2)
      IF(PPS-ALPHA)32,33,34
   34 BETA=ALRHA
      QUIT=1
      IF(QUIT.EQ.2)GOTO 33
      QUIT=1
      GOTO 31
   32 IF(QUIT.EQ.1)GOTO 33
      IF(QUIT.EQ.2)GOTO 35
      QUIT=2
   31 CONTINUE
   33 XST=TVP(IVP,1)
      GOTO 37
   35 WRITE(6,36)
   36 FORMAT(1X,'PS IS SMALLER THAN AVAILABLE FROM TABLE')
      STOP
   37 CONTINUE
    2 FORMAT(F15.7)
      CALL DRTNI(TDEW1,F,DERF,FCT,XST,EPS,IEND,IER)
      IF(IER.EQ.0) GOTO 23
      IF(IER.EQ.1)IEND=IEND*2
      GOTO 20
   23 CONTINUE
   25 WRITE(6,4)TDEW1,PPS,F,IER
    4 FORMAT(20X,'FROZEN DEW POINT(K)=',F6.2,10X,
     &'PARTIAL PRESSURE (ATM)
     &=',E15.7/20X,'ACCURACY OF TDEW1=',E15.7,
     &'ERROR CODE=',I5)
C CALCULATE TDEW2 (SX EQUILIBRATED)
      XI=X(1)+X(2)
      DO 30 I=1,N2
   30 XI=XI+X(I)
      DO 170 I=1,30
      XDEW(I)=0.D0
```

```
170 YDEW(I)=0.D0
    DO 110 I=1,8
110 XDEW(I)=X(I+2)
    XDEW(9)=XI
    DO 130 I=1,9
    DO 130 J=1,2
130 ADEW(I,J)=0.D0
    DO 140 I=1,7
140 ADEW(I,1)=DFLOAT(I+1)
    ADEW(8,1)=1.D0
    ADEW(9,2)=2.D0
    READ(2,1)EPS,EPS2,ETA
  1 FORMAT(3E15.7)
    NSIG=5
    NROOT=1
    ITMAX=100
    ROOT(1)=TDEW1
    CALL ZREAL1(FFCT,EPS,EPS2,ETA,NSIG,NROOT,
   1 ROOT,ITMAX,IER)
    TDEW2=ROOT(1)
    WRITE(6,5)TDEW2,PPS,VP,IER
  5 FORMAT(28X,'DEW POINT (SX EQUILIBRATED)(K)=',F6.2,
   &4X,'PARTIAL PRESSURE(ATM)=',2E15.7,5X,'IER',I3)
 22 CONTINUE
    RETURN
     END

    SUBROUTINE FFCT(T)
    IMPLICIT REAL*8(A-H,O-Z),INTEGER(I-N)
    INTEGER P
    COMMON /FZZ/ADEW(30,5),XDEW(30),YDEW(30),VP
    COMMON /TDEWZ/X(30),PRESS
    COMMON /FF/PPS
    DIMENSION CDEW(30),T(2)
    N=9
    M=2
    P=0
    TT=T(1)
    CALL CDEW2(TT,CDEW)
    CALL FREM(TT,XDEW,YDEW,N,M,P,CDEW,ADEW)
    VP=6.46543D0-7.63591D0*(0.9983D0**(TT-253.16D0))
   & -6.936946D0*(0.9908234D0**(TT-253.16D0))
    VP=(10.D0**VP)/760.D0
    XT=0.D0
    DO 150 I=1,8
150 XT=XT+XDEW(I)
    XI=XDEW(9)
    PPS=PRESS*XT/(XT+XI)

    WRITE(8,21)PPS,VP,TT,ITER,(XDEW(IITR),IITR=1,9)
 21 FORMAT(1X,'PS,VP,TDEW2,IER=',3E15.7,I5/1X,
   1'XDEW=',9E15.7)
    FZ=PPS-VP
    RETURN
```

```
      END

      SUBROUTINE FCT(X,F,DERF)
      IMPLICIT REAL*8 (A-H,O-Z),INTEGER(I-N)
      COMMON /FF/PPS
      F=6.46543D0-7.63591D0*(0.9983D0**(X-253.16D0))
     & -6.936946D0*(0.9908234D0**(X-253.16D0))
      F=(10.D0**F)/760.D0-PPS
      DERF=DLOG(10.D0)*(F+PPS)*(-7.63591D0*(0.9983D0**
     &(X-253.16D0))*DLOG(0.9983D0)-6.936946D0*(0.9908234D0**
     &(X-253.16D0))*DLOG(0.9908234D0))
      RETURN
      END

      SUBROUTINE CDEW2(T,CDEW)
      IMPLICIT REAL*8(A-H,O-Z),INTEGER(I-N)
      COMMON /MCDEW/SHTFN(30),S298(30),ACP(30),
     &BCP(30),CCP(30),DCP(30)
     &,ECP(30),AACP(30),BBCP(30),CCCP(30),DDCP(30),EECP(30)
      COMMON /TDEWZ/X(30),PRESS
      COMMON /NTOT/N
C CP=A+BT+CT**2+DT**3+ET**-2
C HT=A(T-T0)+B/2(T**2-T0**2)+C/3(T**3-T0**3)
C +D/4(T**4-T0**4)-E(1/T-1/T0)
C ST=ALN(T/T0)+B(T-T0)+C/2(T**2-T0**2)+D/3(T**3-T0**3)
C -E/2(1/T/T-1/T0/T0)
C C=(SHTFN+HT)/RT-(ST+S298)/T
      DIMENSION ENTHY(30),ENTRY(30),C(30),CDEW(30)
C CALULATION OF C
      R=1.98718D0
      TR=298.16D0
      IF(T.LE.1.D3)GOTO 10
 20   DO 30 I=1,N
       ACP(I)=AACP(I)
       BCP(I)=BBCP(I)
       CCP(I)=CCCP(I)
       DCP(I)=DDCP(I)
 30    ECP(I)=EECP(I)
 10   DO 40 I=1,N
      ENTHY(I)=ACP(I)*(T-TR)
     &+BCP(I)/2.D0*(T*T-TR*TR)
     &+CCP(I)/3.D0*(T**3-TR**3)
     &+DCP(I)/4.D0*(T**4-TR**4)
     &-ECP(I)*(1.D0/T-1.D0/TR)
      ENTRY(I)=S298(I)+ACP(I)*DLOG(T/TR)
     &+BCP(I)*(T-TR)+CCP(I)/2.D0*
     &(T*T-TR*TR)+DCP(I)/3.D0*(T**3-TR**3)-ECP(I)/2.D0*
     &(1.D0/T/T-1.D0/TR/TR)
C      WRITE(6,1)SHTFN(I),ENTHY(I),ENT[illegible]
  1   FORMAT(1X,'SHTFN,ENTHY,ENTRY,TDEW2=',4E15.7)
 40   CONTINUE
      DO 50 I=1,N
      FRT=(SHTFN(I)+ENTHY(I))/(R*T)-ENTRY(I)/T
 50   C(I)=FRT+DLOG(PRESS)
```

```
C CALCULATE CDEW
      DO 60 I=1,8
   60 CDEW(I)=C(I+2)
      XI=X(1)+X(2)
      CDEW(9)=X(1)*C(1)+X(2)*C(2)
      DO 70 I=11,N
      XI=XI+X(I)
   70 CDEW(9)=CDEW(9)+X(I)*C(I)
      CDEW(9)=CDEW(9)/XI
C     WRITE(6,2)(CDEW(II),II=1,9)
    2 FORMAT(1X,'CDEW=',9F13.5)
      RETURN
      END
      SUBROUTINE FREM(T,XDEW,YDEW,N,M,P,C,ADEW)
C THIS SUBROUTINE IS USED TO CALCULATE THE MIN OF G
C FOR THE SULFUR DEWPOINT IN H2S/SO2 ONLY
      IMPLICIT REAL*8 (A-H,O-Z),INTEGER(I-N)
      INTEGER P
      LOGICAL L,L1,L2
      DIMENSION XDEW(30),GA(30,30),GB(30),ADEW(30,5),
     1F(30),SNAM(30,5)
     1,YDEW(30),B(30),FRC(30),NG1(30) ,GX(30),C(30)
      N2=N+P
      L1=.TRUE.
      L2=.FALSE.
      SLIQ=0.D0
      ISTORE=0
      IS=N2+1
      DO 1 I=IS,30
    1 XDEW(I)=0.D0
      DO 12 I=1,N2
      NG1(I)=0
   12 CONTINUE
      JBI=2
      DO 35 JB=1,JBI
      DO 14 ITER=1,200
      ISTORE=ISTORE+1
      CALL DISTR1(XDEW,YDEW,B,N2,M,ADEW)
      CALL FREN (YDEW,C,F,YBAR,N,P,NG1)
      MG=M+P+1
      CALL GSET (ADEW,YDEW,GA,GB,B,F,P,M,MG,N,C)
      CALL GAUSS(GA,GB,MG,GX)
      IF(P)15,15,16
   16 DO 17 I=1,P
      II=I+1
      IC=N+I
   17 XDEW(IC)=GX(II)
   15 CONTINUE
      DO 18 I=1,N
      IF(NG1(I)) 19,19,18
   19 XDEW(I)=-YDEW(I)*((C(I)+DLOG(YDEW(I)/YBAR))-GX(1))
      DO 21 J=1,M
      IG=P+J+1
   21 XDEW(I)=XDEW(I)+GX(IG)*ADEW(I,J)*YDEW(I)
```

```
   18 CONTINUE
      CALL NEZE (XDEW,YDEW,N2,NG1)
      QUIT=1. D0
      DO 22 I=1,N2
      IF(NG1(I)) 23,23,22
   23 TEST=(XDEW(I)-YDEW(I))/XDEW(I)
      IF(DABS(TEST)-EPS) 22,22,24
   24 QUIT=-1. D0
   22 CONTINUE
      IF(QUIT) 25,25,26
   25 DO 27 I=1,N2
   27 YDEW(I)=XDEW(I)
   14 CONTINUE
   26 DO 32 I=1,N2
      NG1(I)=0
      IF(XDEW(I)) 33,33,34
   34 YDEW(I)=XDEW(I)
      GO TO 32
   33 YDEW(I)=0.000001D0
   32 CONTINUE
   35 CONTINUE
      DO 715 II=1,N2
  715 XDEW(II)=YDEW(II)
      RETURN
      END
      SUBROUTINE SCOND(X,T,PRESS,L,L1,N,P,SNAM,SLIQ)
      IMPLICIT REAL*8(A-H,O-Z),INTEGER(I-N)
      INTEGER P
      LOGICAL L,L1
      DIMENSION W(30),RATIO(8),SNAM(30,5),FRC(30)
C DATA FOR LIQUID PHASE
      IF(.NOT.L1) GOTO 90
      L1=.FALSE.
      KKK=N+P+1
      READ(1,1)(SNAM(KKK,I),I=1,5)
    1 FORMAT(1X,A3,4A4)
C TEST FOR POSSIBLE CONDENSATION
   90 XLOGVP=6.46543D0-7.63591D0*((0.9983D0**(T-253.16D0)))
     &-6.936946D0*(0.9908**(T-253.16D0))
      VP=10.D0**XLOGVP
      VP=VP/760.D0
      YS=0.D0
      DO 10 I=1,N
   10 FRC(I)=0.D0
      CALL MOFR(X,FRC,N,P)
      STEST=X(1)+X(2)+2.*X(3)+3.*X(4)+4.*X(5)
     &+5.*X(6)+6.*X(7)+7.*X(8)
     &+8.*X(9)+X(10)+SLIQ
      DO 20 I=3,9
   20 YS=YS+FRC(I)
      PPS=YS*PRESS
      IF(DABS(PPS-VP)-1.D-4)30,30,100
  100 IF(PPS-VP)80,30,40
   30 L=.TRUE.
```

```
      RETURN
   80 IF(SLIQ.GT.1.D-6) GOTO 40
      RETURN
C DISTRIBUTIONOF SULFUR IN THE GAS PHASE
   40 L=.FALSE.
      SIGRA=0.D0
      SUM=0.D0
      DSLIQ=0.D0
      DO 50 I=2,8
      II=I+1
      RATIO(I)=X(II)/X(9)
   50 SIGRA=SIGRA+RATIO(I)
C NEW COMPOSITION OF SULFUR SPECIES
      DO 60 I=10,N
   60 SUM=SUM+X(I)
      SUM=SUM+X(1)+X(2)
      S8NEW=VP/PRESS*SUM/SIGRA/(1.-VP/PRESS)
      DO 70 I=3,9
      II=I-1
      DSLIQ=DSLIQ+(I-1)*(X(I)-S8NEW*RATIO(II))
   70 X(I)=S8NEW*RATIO(II)
      SLIQ=SLIQ+DSLIQ
      STEST=X(1)+X(2)+2.*X(3)+3.*X(4)+4.*X(5)+5.*X(6)
     &+6.*X(7)+7.*X(8)
     &+8.*X(9)+X(10)+SLIQ
      IF(SLIQ.GE.0.D0)GOTO 110
      S=-SLIQ/8.D0
      IF(S.GT.X(9))WRITE(6,99)
      IF(S.GT.X(9))STOP
   99 FORMAT(1X,'MODIFY SCOND FOR SLIQ')
      IF(S.LE.X(9))X(9)=X(9)-S
      SLIQ=0.D0
  110 RETURN
      END
      SUBROUTINE SREM(NS,X,N2,N,P,XX,SLIQ,Y,L2)
C THIS SUBROUTINE IS USED TO CALCULATE CONVERSION
C FROM TOTAL CONVERSION BACK
      IMPLICIT REAL*8(A-H,O-Z),INTEGER(I-N)
      LOGICAL L2
      INTEGER P
      DIMENSION X(30),XX(30),Y(30)
      IF(NS.LE.10)SREMD=XX(1)*DFLOAT(NS-1)/10.D0
      IF(NS.LE.10)GOTO 110
      SREMD=XX(1)*(0.005D0*(NS-10)+0.905D0)
      IF(SREMD.LE.SLIQ)GOTO 200
  110 X(1)=0.D0
      X(2)=0.D0
      DO 100 I=3,10
  100 X(I)=0.D0
      X(9)=XX(1)/8.D0-SREMD/8.D0
      X(11)=XX(1)+XX(11)
C ADD THE INERT SPECIES IF REQUIRED
      X(14)=XX(14)
      X(12)=XX(12)
```

```
      X(12)=0.80
      SLIQ=0.90
      NE=N
      P=0
      DO 101 I=1,NE
  101 Y(I)=X(I)
      GOTO 210
  200 L2=.TRUE.
      WRITE(6,1)
  210 CONTINUE
    1 FORMAT(1X,'AMOUNT OF SULFUR REMOVED IS LESS
     & THAN AMT OF LIQ ','SULFUR')
      RETURN
      END
```

Example of input data

```
     5,14,0,[illegible],0,25.
   HYDROGEN SULFIDE          2000.
   1.          2.          0.          0.          0.
  7.2,0.25D-2,0.198D-5,-0.944D-9,0.,-4820.,49.151,
  7.2,0.25D-2,0.198D-5,-0.944D-9,0.,-4820.,49.151,
   SULFUR DIOXIDE            0.0
   1.                2.          0.          0.
  6.45,0.01280,-0.803D-5,0.174D-8,0.,-70947.,59.3,
  6.45,0.01280,-0.803D-5,0.174D-8,0.,-70947.,59.3,
   DIATOMIC SULFUR        0.0
   2.          0.          0.          0.          0.
  8.54,0.00028,0.,0.,-79000.,31200.,54.4,
  8.54,0.00028,0.,0.,-79000.,31200.,54.4,
   TRIATOMIC SULFUR     0.0
   3.          0.                      0.          0.
  12.854,0.00104,0.,0.,-155400.,33810.,64.39,
  12.854,0.00104,0.,0.,-155400.,33810.,64.39,
   TETRATOMIC SULFUR  0.0
   4.          0.          0.          0.          0.
  19.092,0.000783,0.,0.,-282000.,34810.,74.22,
  19.092,0.000783,0.,0.,-282000.,34810.,74.22,
   PENTATOMIC SULFUR   0.0
   5.          0.          0.          0.          0.
  25.558,0.000253,0.,0.,-377100.,26140.,73.74,
  25.558,0.000253,0.,0.,-377100.,26140.,73.74,
   HEXATOMIC SULFUR    0.0
   6.          0.          0.          0.          0.
  31.58,0.00012,0.,0.,-440000.,24360.,84.6,
  31.58,0.00012,0.,0.,-440000.,24360.,84.6,
   HEPTATOMIC SULFUR      0.0
   7.          0.          0.          0.          0.
  37.038,0.000613,0.,0.,-472300.,27170.,97.41,
  37.038,0.000613,0.,0.,-472300.,27170.,97.41,
   OCTATOMIC SULFUR  0.0
   8.          0.          0.          0.          0.
  42.67,0.00086,0.,0.,-511000.,24320.,102.76,
  42.67,0.00086,0.,0.,-511000.,24320.,102.76,
   MONATOMIC SULFUR          0.0
   1.          0.          0.          0.          0.
  5.523448,-0.3125724D-3,0.0,0.0,0.3892077D4,66680.,40.1,
  5.523448,-0.3125724D-3,0.0,0.0,0.3892077D4,66680.,40.1,
   WATER VAPOR               0.0
               2.          1.          0.          0.
  8.12,-0.20D-2,0.66D-5,-0.3D-8,0.,-57797.9,45.106
  7.14,0.21D-2,0.98D-6,-0.4D-9,0.,-57797.9,45.106,
   NITROGEN                  5565.738
                                       2.          0.
  6.899,-0.3597D-3,0.19D-5,-0.669D-9,0.,0.,45.77,
  6.899,-0.3597D-3,0.19D-5,-0.669D-9,0.,0.,45.77,
   OXYGEN                    1479.5
                           2.          0.          0.
  6.424,0.2287D-2,-0.3124D-6,-0.109D-9,0.,0.,49.,
  6.424,0.2287D-2,-0.3124D-6,-0.109D-9,0.,0.,49.,
   CARBON DIOXIDE        739.75
```

APPENDIX B Computer Programs for Determination of Equilibrium Constant

This appendix contains the programs used in chapter 5.

LLS

This program uses linear least square to fit the straight line for ln K_p' vs 1/T. Output from this program is used as data for Fig. 37.

Notation:

Input :

ND : number of data points
BP : temperature (K), the independent value
RT : equilibrium constant value, the dependent value

Output :

RT : ln K_p', the dependent value
BP : 1/T, the independent value
D : the difference in calculated and input value for ln K_p'
D2 : the square of the difference in calculated and the input value
A0 : the intercept
A1 : the slope of the fitted straight line

```
      DIMENSION BP(21),RT(21),D(21),D2(21)
    1 FORMAT(3I2)
    3 FORMAT(2I4)
    5 FORMAT(10F8.2)
    2 FORMAT(///,' ',4X,'RT',10X,'BP',9X,'D',9X,'D2')
    4 FORMAT(' ',4F10.2)
    6 FORMAT(///,' ',' A0=',4X,E15.7,/,'  A1=',4X,E15.7)
      READ(5,1)ND
      READ(5,5)(BP(I),I=1,ND)
      DO 10 I=1,ND
      BP(I)=1./BP(I)
   10 CONTINUE
      READ(5,5)(RT(I),I=1,ND)
      DO 20 I=1,ND
      RT(I)=ALOG(RT(I))
   20 CONTINUE
      BP2=0.
      BP1=0.
      BPRT=0.
      RTY1=0.
      DO 11 I=1,ND
      BP1=BP1+BP(I)
      BP2=BP2+BP(I)*BP(I)
      BPRT=BPRT+BP(I)*RT(I)
      RTY1=RTY1+RT(I)
   11 CONTINUE
      CC=ND*BP2-BP1*BP1
      A0=(RTY1*BP2-BP1*BPRT)/CC
      A1=(ND*BPRT-BP1*RTY1)/CC
      DO 21 I=1,ND
      D(I)=RT(I)-A0-A1*BP(I)
      D2(I)=D(I)*D(I)
   21 CONTINUE
      WRITE(6,2)
      DO 36 I=1,ND
      WRITE(6,4)RT(I),BP(I),D(I),D2(I)
   36 CONTINUE
      WRITE(6,6)A0,A1
      STOP
      END
```

CONV

This program computes the equilibrium conversion for each data from the equilibrium constant and sulfur average atomic number. Output from this program is used as data for Fig. 38.

Notation:

Input :

T =temperature (°C)

N = number of data point

XK = equilibrium constant

XST = observed equilibrium conversion

OH2S = initial concentration of H2S

OSO2 = initial concentration of SO2

OH2O = initial concentration of H2O

PI = total pressure in mbar

XNU = sulfur average atomic number

Output

X = calculated equilibrium conversion

F = the difference between calculated and observed equilibrium conversion

PS = calculated sulfur partial pressure

```
      EXTERNAL FCT
      COMMON XK,SX,TOTM,PS,OH2S,OSO2,OH2O,PI,XNU
    1 FORMAT(8F10.5)
    2 FORMAT(I5,F15.7)
    3 FORMAT(1X,7E14.6,I3,2E14.6)
    4 FORMAT(1X,'OH2O',10X,'OSO2',10X,'OH2O',
     &10X,'PI',12X,'X',13X,
     &'F',13X,'XST',11X,'IER',2X,'XNU',11X,'PS')
    5 FORMAT(45X,'T=',I3,'C')
      READ(5,2)IT
      WRITE(6,5)IT
      WRITE(6,4)
      READ(5,2)N,XK
      DO 10 II=1,N
      READ(5,1)XST,OH2O,OSO2,OH2O,PI,XNU
      PI=PI/1000.*0.986923
      EPS=1.E-6
      IEND=50
      CALL RTNI(X,F,DERF,FCT,XST,EPS,IEND,IER)
      WRITE(6,3)OH2O,OSO2,OH2O,PI,X,F,XST,IER,XNU,PS
   10 CONTINUE
      STOP
      END

      SUBROUTINE FCT(X,F,DERF)
      COMMON XK,SX,TOTM,PS,OH2S,OSO2,OH2O,PI,XNU
      H2S=OH2S*(1.-X)
      SO2=OSO2-OH2S*X/2.
      S=OH2S*X*1.5/XNU
      H2O=OH2O+OH2S*X
      TOTM=100.+S-OH2S*X/2.
      EXP=1.-3./XNU
      PS=S/TOTM*PI*760.
      F=(S**(3./XNU)*H2O*H2O/H2S/H2S/SO2
     &*((TOTM/PI)**EXP))-XK
      DU1DX=4.5*OH2S/XNU/XNU*(S**(3./XNU-1.))*H2O*H2O
     &+S**(3./XNU)*2.*H2O*OH2S
      DV1DX=-2.*OH2S*OH2S*(1.-X)*(OSO2+OH2S*(0.25-0.75*X))
      U1=(S**(3./XNU))*H2O*H2O
      V1=H2S*H2S*SO2
      DUDX=DU1DX/V1-U1/V1/V1*DV1DX
      U=(S**(3./XNU))*H2O*H2O/H2S/H2S/SO2
      V=(TOTM/PI)**(1.-3./XNU)
      DVDX=(1.-3./XNU)*(TOTM/PI)**(-3./XNU)
     &*((-OH2S/2.+1.5*OH2S/XNU)/PI)
      DERF=DUDX*V+U*DVDX
      RETURN
      END
```

KEQ

This program computes the equilibirum constant for each data point from the input equilibrium conversion and sulfur average atomic number. Output from this program is used in Fig. 39 to 42.

Notation:

Input:

XO = initial value of sulfur average atomic number

DELTA = step of sulfur average atomic number

OH2S = initial mole number of H2S

OSO2 = initial mole number of SO2

OH2O = initial mole number of H2O

Output :

PI = total pressure in mbar

XK = equilibrium constant

```
      DIMENSION XO(10),DELTA(10),OH2S(10),
     +OSO2(10),OH2O(10),PI(10),
     +XN2(10),H2S(10),SO2(10),S(10),H2O(10),
     +SIGM(10),XK(10)
      XNU=5.
      DO 2 II=1,10
      READ(5,101) XO(II),DELTA(II)
      READ(5,101)OH2S(II),OSO2(II),OH2O(II),PI(II)
  101 FORMAT(4F15.7)
      XN2(II)=100.-OH2S(II)-OSO2(II)-OH2O(II)
      PI(II)=PI(II)*0.986923/1000.
      WRITE(6,103)
  103 FORMAT(4X,'X',14X,'K')
      DO 1 I=1,10
      X=XO(II)+DELTA(II)*I
      IF(OH2S(II).LT.2.*OSO2(II)) GOTO 10
      H2S(II)=OH2S(II)*(1.-X)
      SO2(II)=OSO2(II)-OH2S(II)*X/2.
      S(II)=OH2S(II)*X*1.5/XNU
      H2O(II)=OH2O(II)+OH2S(II)*X
      GO TO 11
   10 S(II)=OSO2(II)*X*3./XNU
      H2O(II)=OH2O(II)+OSO2(II)*X*2.
      SO2(II)=OSO2(II)*(1.-X)
      H2S(II)=OH2S(II)-OSO2(II)*X*2.
   11 SIGM(II)=H2S(II)+SO2(II)+S(II)+H2O(II)+XN2(II)
      EXP=1.-3./XNU
      XK(II)=H2O(II)*H2O(II)*(S(II)*(3./XNU))/SO2(II)
     1/H2S(II)/H2S(II)*(SIGM(II)*EXP)/(PI(II)**EXP)
    1 WRITE(6,100)X,XK(II)
  100 FORMAT(2X,F6.2,5X,F12.4)
    2 CONTINUE
      STOP
      END
```

APPENDIX C Sulfur Vapor Pressure Fitting

West and Menzies' vapor pressure data was fitted to the Biot equation using Rosenbrock hill climbing technique of non-linear least square fitting of vapor pressure data. The resulting vapor pressure equation is

$$\log vp(\mathrm{mm\ Hg.}) = 6.46543 - 7.63591(0.9983)^{-273.16}$$

$$-6.936946(0.9908)^{-273.16}$$

To provide confidence on this resulting equation as it is much different from the coefficients given by West & Menzies' paper, a small program was written to regenerate vapor curve and compared to West & Menzies' data. Table C.1 is the result of program. The fitness of this vapor pressure equation is shown in Fig. C.1.

Table C.1

Result of Sulfur Vapor Fitting

TEMPERATURE (K)	VAPOR PRESSURE (MM HG.)	VAPOR PRESSURE (ATM.)
400.00	0.0532	0.0000700
410.00	0.0964	0.0001268
420.00	0.1685	0.0002217
430.00	0.2850	0.0003750
440.00	0.4676	0.0006152
450.00	0.7460	0.0009815
460.00	1.1598	0.0015261
470.00	1.7609	0.0023170
480.00	2.6156	0.0034416
500.00	5.4393	0.0071570
510.00	7.6375	0.0100493
520.00	10.5536	0.0138863
540.00	19.2945	0.0253875
550.00	25.5808	0.0336590

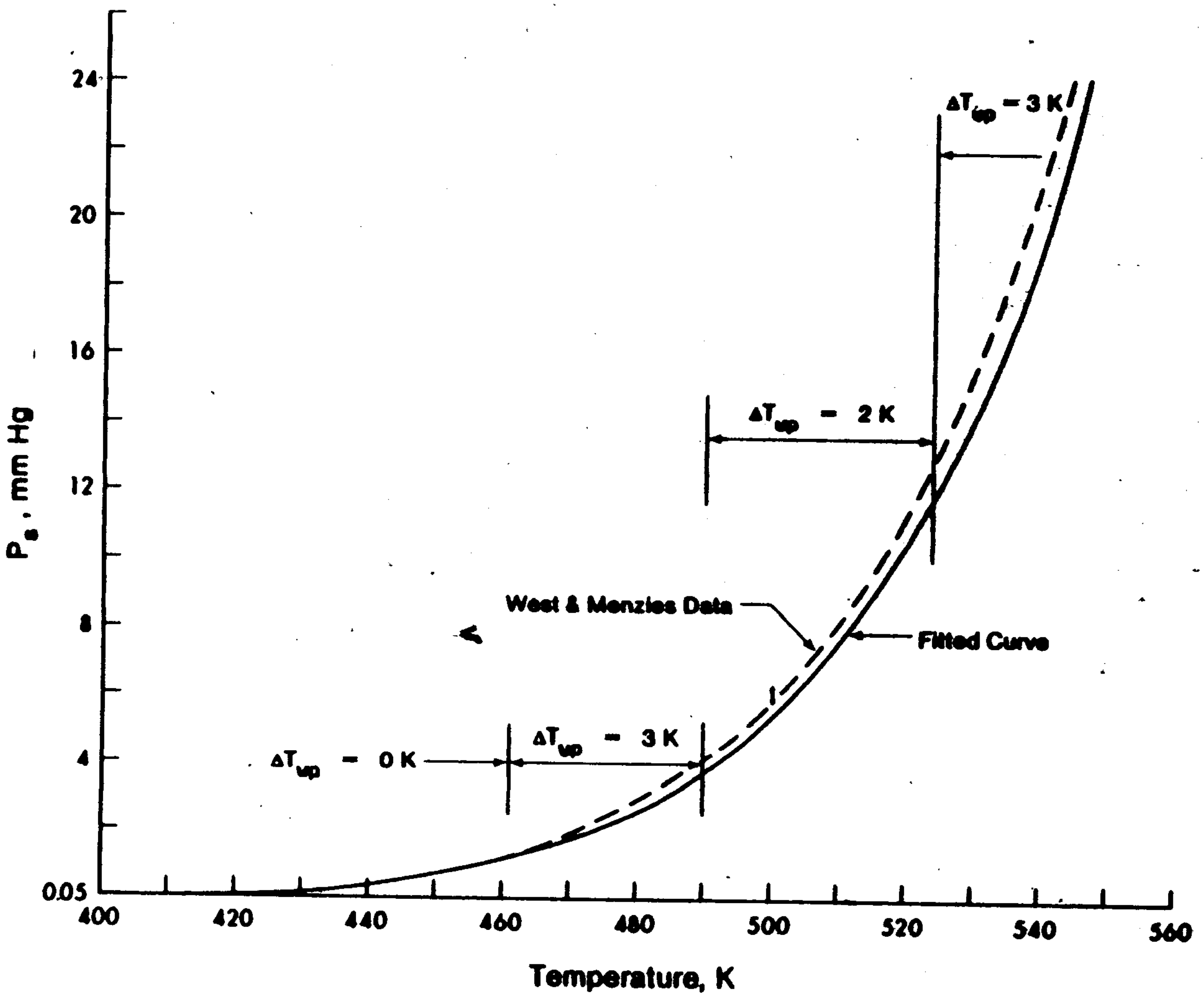

Fig.C.1 Accuracy of Fitted Equation for Sulfur Vapor.
Log_{10} VP (mm Hg) = 6.46543 − 7.63591 $(0.9983)^{T-263.16}$
− 6.936946 $(0.9908234)^{T-263.16}$