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UNIVERSITY OF ALBERTA

PHASE BEHAVIOUR IN THE SYSTEM WATER-HYDROGEN SULPHIDE

by

JOHN J. CARROLL ©

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMICAL ENGINEERING

EDMONTON, ALBERTA
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled PHASE BEHAVIOUR IN THE SYSTEM WATER-HYDROGEN SULPHIDE submitted by JOHN J. CARROLL in partial fulfilment of the requirements for the degree of DOCTOR OF PHILOSOPHY.

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This thesis is dedicated to
my parents, James E. and Mary A. Carroll,
with deepest love and respect.

Abstract

This thesis is a exhaustive study of the phase equilibria in the system water-hydrogen sulphide. Initially a thorough review of the literature was conducted. As a result of this search and subsequent analysis of the data, some inconsistencies in the established phase behavior were found. New experimental data were obtained to supplement the existing data. Thermodynamic models were used to correlate virtually all of the data. Smoothed values were not used. Other data were found to be of poor quality and were rejected. What resulted, this thesis is the definitive study of the phase equilibria for the system water-hydrogen sulphide.

High pressure fluid phase equilibria (vapour-liquid, liquid-liquid and vapour-liquid-liquid) were modelled using a modified Peng-Robinson equation of state. The solubility of hydrogen sulphide was modelled using the Henry's law approach. The pressure and temperature along the three-phase loci were correlated empirically. The composition of the hydrate was calculated using a modified van der Waals-Platteeuw method.

Many investigators have attempted to correlate the phase equilibria for this system. Unfortunately, those studies were severely impaired by their unquestioning reliance on the smoothed data of Selleck et al. This study does not make that mistake. In fact errors in the smoothing of Selleck et al. are clearly demonstrated.

Acknowledgement

The assistance of Dr. A.E. Mather, my mentor, is gratefully acknowledged. His considerable knowledge of thermodynamics and of the literature were invaluable. I know that this project, and my career as a graduate student in general, did not work out as he had hoped. For that I am very sorry. I will never know why he never quit on me, even when I started to give up on myself. My sincerest hope is that he also learned something from the many hours we spent in discussion.

The love and support of my family was very important. These past years have been hard on them. However, it was only with their encouragement and understanding that this project was completed. I will never be able to repay the debt I owe them. A special thanks to my best friend Brad Gardiner, who was almost like family. He helped me survive the bad times, it is only fitting that he share in the good.

I am indebted to all the members of the academic staff of the Department of Chemical Engineering. They were a source of much needed assistance and intellectual stimulation. I learned a great deal from them, both inside and outside of the classroom.

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I would like to express my appreciation for the comradeship of my fellow graduate students, especially: R.A. Tomcej, F.B. Russell, B.A. Smillie, E.E. Roberts, W.R. Cluett, J.R. Spence, W.R.C. Graham and D. Shook. They helped to keep my life and work in perspective. Special thanks to R.A. Tomcej and F.B. Russell for reviewing my papers and providing constructive criticism.

The generous financial support of the Natural Sciences and Engineering Research Council and the University of Alberta is gratefully acknowledged.

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Nomenclature

Abbreviations

AAD	absolute average deviation
BIAS	bias
CP	critical point
H	hydrate
I	ice
K	three-phase critical end point
L_A	aqueous liquid
L_S	H_2S-rich liquid
L_2	non-aqueous liquid
LLE	liquid-liquid equilibrium
LLVE	liquid-liquid-vapour equilibrium
PR	Peng-Robinson
PRSV	Peng-Robinson-Stryjek-Vera
PT	Patel-Teja
Q	quadruple point
RE	relative error
RMS	root mean squared
RK	Redlich-Kwong
S	solid H_2S
SRK	Soave-Redlich-Kwong
V	vapour
VLE	vapour-liquid equilibrium
VLLE	vapour-liquid-liquid equilibrium

Symbols

Roman:

A	Margules constant, kJ/mol
a	parameter in several equations of state, $MPa \cdot m^6/kmol^2$
B	second virial coefficient
b	parameter in several equations equations of state, co-volume, $m^3/kmol$
C	coefficient in polytropic expansion model
C	parameter in Huron-Vidal mixing rule
c	parameter in several equations equations of state, $m^3/kmol$
$c_{j(i)}$	interaction parameter in Luedecke mixing rule
d	parameter in Mathias equation
F	parameter in PT equation
f	fugacity of pure component, kPa
$\hat{f}$	fugacity of component in solution, kPa
G	Gibbs function, J/mol
G_i	parameter in Kabadi-Danner mixing rule
g_∞^E	excess Gibbs function at infinite pressure
H_{21}	Henry's constant, MPa/mol frac
K_{eq}	equilibrium constant
k	parameter in Heyen equation
k	exponent in polytropic expansion model
k_{ij}	interaction parameter in several mixing rules
M	molar mass, kg/kmol
m	parameter in SRK and Heyen equations

n	parameter in Heyen equation
NP	number of points
P	pressure, kPa
P°	vapour pressure, kPa
p	parameter in Mathias equation
R	gas constant, $R = 8.314$ kPa·m^3/(kmol·K)
T	absolute temperature, K
t	Celsius temperature, °C
v	molar volume, m^3/kmol
$\bar{v}_2^{\infty}$	partial molar volume at infinite dilution, m^3/kmol
X	parameter in Gibbons-Laughton equation
x	mole fraction in liquid
Y	parameter in Gibbons-Laughton equation
y	mole fraction in vapour
z	compressibility factor, ($z = Pv/RT$)

Greek:

α	parameter in PR and PRSV equations
β	general parameter in equation of state (a, b or c)
γ	activity coefficient
δ	parameter in generic equation of state
δ_{ij}	interaction parameter in original mixing rule
ϵ	parameter in generic equation of state
ζ_C	parameter in PT equation
θ	parameter in generic equation of state
θ	parameter in Heyen equaiton
κ	parameter in PR and PRSV equations
κ_0	parameter in PRSV equation

κ_1	parameter in PRSV equation
ρ	density
τ	interaction parameter in PR and Heyen mixing rules
ϕ	fugacity coefficient of pure component
$\hat{\phi}$	fugacity coefficient of component in solution
Ω_a	parameter in PT and Heyen equations
Ω_b	parameter in PT and Heyen equations
Ω_c	parameter in PT and Heyen equations
ω	acentric factor

Subscripts:

A	aqueous
c	critical
f	liquid
h	hydrocarbon
i	component i
j	component j
n	non-polar
p	polar
R	reduced
S	H_2S-rich
v	vapour
w	water
1	component 1, solvent
2	component 2, solute

Superscripts:

E	excess
L	liquid

V	vapour
∞	infinite dilution
$\circ$	reference state

I. Introduction

The system water-hydrogen sulphide is an important system worthy of a thorough investigation. Although this system has been studied quite often, there exists much controversy. An examination of previous work revealed some misinterpretation of the experimental observations. This work presents some new experimental measurements of the L_A-L_S-V, L_A-H-V and L_S-H-V loci and a thorough review of the literature. As a result, a new description is presented for the phase equilibria for this system.

The remainder of this chapter is an overview of hydrogen sulphide-water phase equilibria in general and some of the areas where its application is important. Chapter II reviews the copious literature. New experimental work is presented in Chapter III. A detailed review of the work of Selleck et al. (1951,1952), one of the most important studies of this system, is given in Chapter IV. Fluid phase equilibrium calculations are presented in Chapters V of and VI. Chapter V details the use an equation of state and Chapter VI discusses the use of Henry's law. Finally, the hydrate formation is covered in Chapter VII. Throughout this thesis the phases will be designated as follows: S - solid H_2S, I - ice, H - hydrate, L_A - aqueous liquid, L_S - H_2S-rich liquid and V - vapour.

A. Phase Equilibria

In a landmark work in the area of fluid phase equilibria, Scott and van Konynenburg (1970) [also see van Konynenburg and Scott (1980)] used the van der Waals (1873) equation of state to predict qualitatively most of the known types of fluid phase equilibria. As a result of their work an often used system of classification was developed. Their system is summarized in Table 1.1 and Fig. 1.1. The system hydrogen sulphide-water is Type III in this system of classification. The system hydrogen sulphide-water has an interrupted critical locus (that is, its critical locus does not extend between the two pure-component critical points). Also, it exhibits liquid-liquid immiscibility. A small critical locus extends from the critical point of hydrogen sulphide to the three-phase (L_A-L_S-V) critical end point. A second critical locus extends from the critical point of water to lower temperatures and higher pressures.

Another of the interesting features of the phase behavior in the system H_2O-H_2S is the formation of a gas hydrate. Hydrates belong to a class of compounds called inclusion compounds or clathrates. A guest molecule, in this case H_2S, fits into a chamber formed by the host molecules, water. At the right conditions, and often well above the freezing point of pure water, the hydrate becomes stable and precipitates. Gases can form two hydrate structures, types I and II. Hydrogen sulphide forms a type I hydrate. In a type I hydrate, 46 water molecules are hydrogen bonded to form

Table 1.1 The Classsification of Fluid Phase Equilibria
Based on Scott and van Konynenburg

Type I: One critical locus from CP_1 to CP_2

Type II: Two critical loci
- from CP_1 to CP_2
- starts at K and extends to high pressure

Type III: Two critical loci
- from CP_1 to K
- starts at CP_2 and extends to high pressure

Type IV: Three critical loci
- starts at K_1 and extends to high pressure
- from K_2 to CP_2
- from CP_1 to K_3

Type V: Two critical loci
- from K_1 to CP_2
- from CP_1 to K_2

Type VI: Two critical loci*
- from CP_1 to CP_2
- from K_1 to K_2

CP_i - critical point of pure i
K - three-phase critical end point

* - not predicted by Scott and van Konynenburg (1970), see Rowlinson and Swinton (1982).

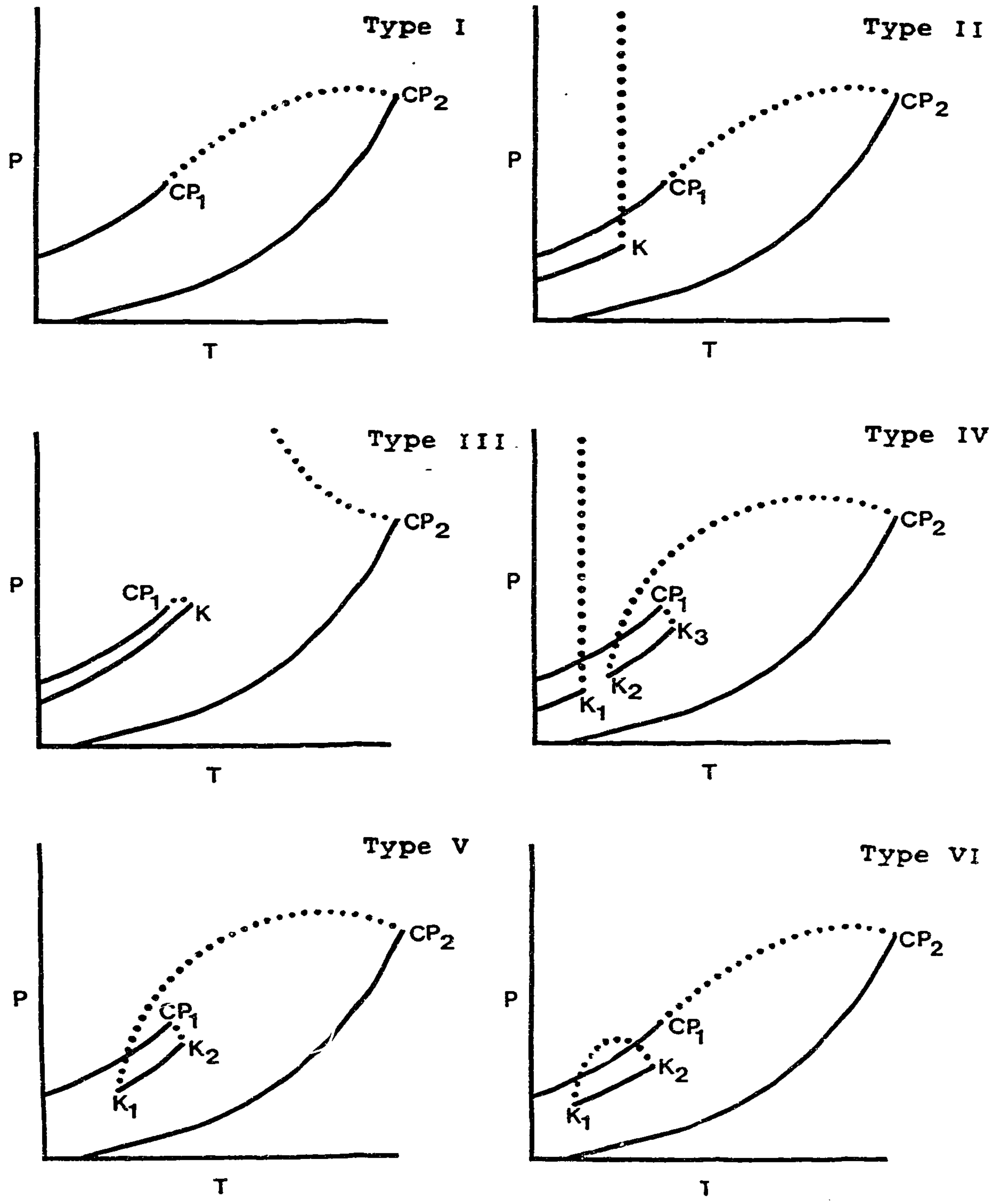

Fig. 1.1 The Classification of Fluid Phase Behavior Based on Scott and van Konynenburg (1970)

eight polyhedra: two dodecahedra (12 sides, all regular pentagons) and six tetrakaidecahedra (14 sides, two regular hexagons and twelve regular pentagons). This structure for the type I hydrate results in two different sized cages. Hydrogen sulphide is sufficiently small that it can occupy both cages. Larger molecules can only occupy the large cages. Even larger molecules form type II hydrates which have larger cages. Molecules which are larger still do not form hydrates. This results in a theoretical formula of 8 $H_2S \cdot 46$ H_2O or $H_2S \cdot 5.75$ H_2O; but hydrates are non-stoichiometric. Stable crystals form without a guest molecule in all of the cages. The degree of saturation is a function of temperature and pressure. A more detailed discussion of gas hydrates is given by van der Waals and Platteeuw (1959).

Combining fluid phase equilibria with those involving solids reveals the complex equilibria for this system. Fig. 1.2 depicts schematically the pressure-temperature diagram for the system water-hydrogen sulphide. This figure shows the two-phase loci for the pure components and the three-phase loci for the binary. The Gibbs phase rule says that for a two-component system the possibility exists for a quadruple point (four phases in equilibrium). Such a point would represent a single point on the temperature-pressure projection and the compositions of all of the phases are fixed - there are zero degrees of freedom. A quadruple point is at the intersection of four three-phase loci. The system

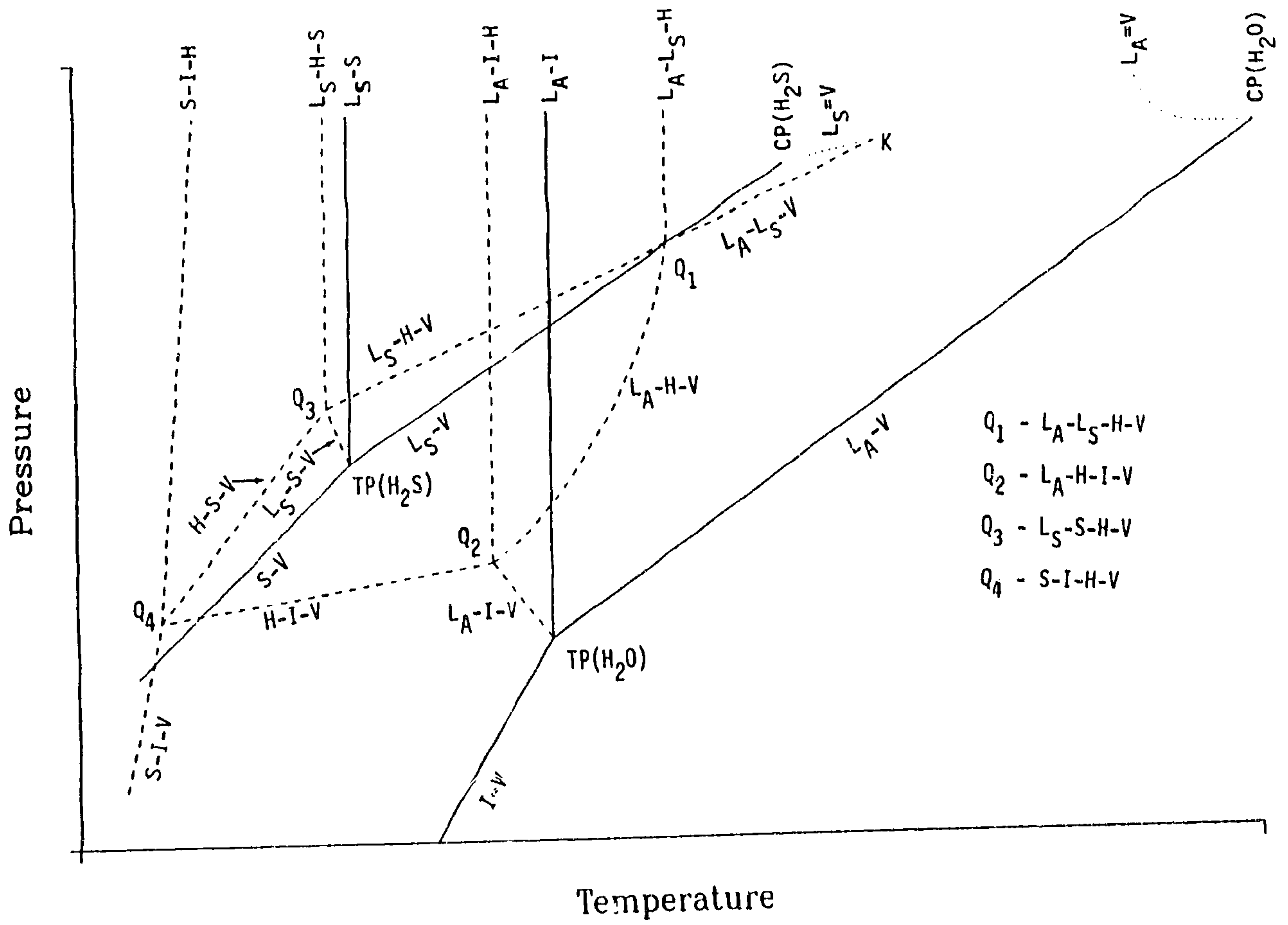

Fig. 1.2 Schematic Pressure-Temperature Diagram for the System Hydrogen Sulphide-Water (Not to Scale)

hydrogen sulphide-water has four such points: (1) L_A-L_S-H-V (2) L_A-V-I-H, (3) L_S-S-H-V and (4) S-I-H-V. The first two have been studied, but the other two have not been found experimentally. The Gibbs phase rule also says that a quadruple point is impossible for a one-component system. Table 1.2 lists the pressure and temperature at some of the fixed points. Table 1.3 lists equations for some of the three-phase loci in P-T space. These were obtained in this work and the details of their derivations are presented later. A few sections (pressure-composition and temperature-composition) were then taken from this diagram. These are shown on Figs. 1.3 through 1.13. These plots are not drawn to scale, but the appropriate pressures or temperatures are indicated. Note the diversity of phase equilibria encountered.

The system hydrogen sulphide-water behaves similarly to the system carbon dioxide-water. However, there is some controversy about the exact behavior of the fluid phase equilibrium for the system CO_2-H_2O. Experimental studies have been reported by Tödheide and Franck (1964) and Takenouchi and Kennedy (1964) for the high pressure fluid phase equilibrium. Although quantitatively these studies disagree, qualitatively they give a similar description. Song and Kobayashi (1984) report equilibria involving solid phases. This description is analogous to the one presented here for H_2S-H_2O.

Table 1.2 Fixed Points on the Pressure-Temperature Plane for the System Hydrogen Sulphide-Water

	Temp (°C)	Press (MPa)	Ref
Triple Point of H_2S	-85.5	0.02320	3
Triple Point of H_2O	0.01	6.113×10^{-4}	2
Critical point of H_2S	100.3	8.963	3
Critical Point of H_2O	374.2	22.09	2
H-I-L_A-V Quadruple Point	-0.4	0.0931	4
L_A-L_S-H-V Quadruple Point	29.4	2.23	1
L_A-L_S-V Critical End Point	106.2	9.39	1

1 - This Work
2 - Keenan et al. (1978)
3 - Goodwin (1983)
4 - Korvezee and Scheffer (1931)

Table 1.3 Three-Phase Loci on the Pressure-Temperature Plane for the System Hydrogen Sulphide-Water

L_S-L_A-V

$$\ln P = 14.836 - 2156.9/T$$
$$302.6 < T < 380.1 \text{ K}$$

L_S-H-V

$$\ln P = 14.5229 - 2061.05/T$$
$$278.0 < T < 302.6 \text{ K}$$

L_A-H-V

$$\ln P = -26.8952 + 0.15139\, T + 2788.88/T - 3.5786 \ln T$$
$$272.7 < T < 302.6 \text{ K}$$

L_S-L_A-H

$$P = 11083\, T - 3352515$$
$$302.6 < T < 305.4$$

H-I-V

$$\ln P = 15.8059 - 3070.13/T$$
$$243.2 < T < 272.7 \text{ K}$$

L_A-I-V*

$$\ln P = 3347.944 - 12.2581\, T$$
$$272.75 < T < 273.16 \text{ K}$$

where P is in kPa and T in K

* - estimated

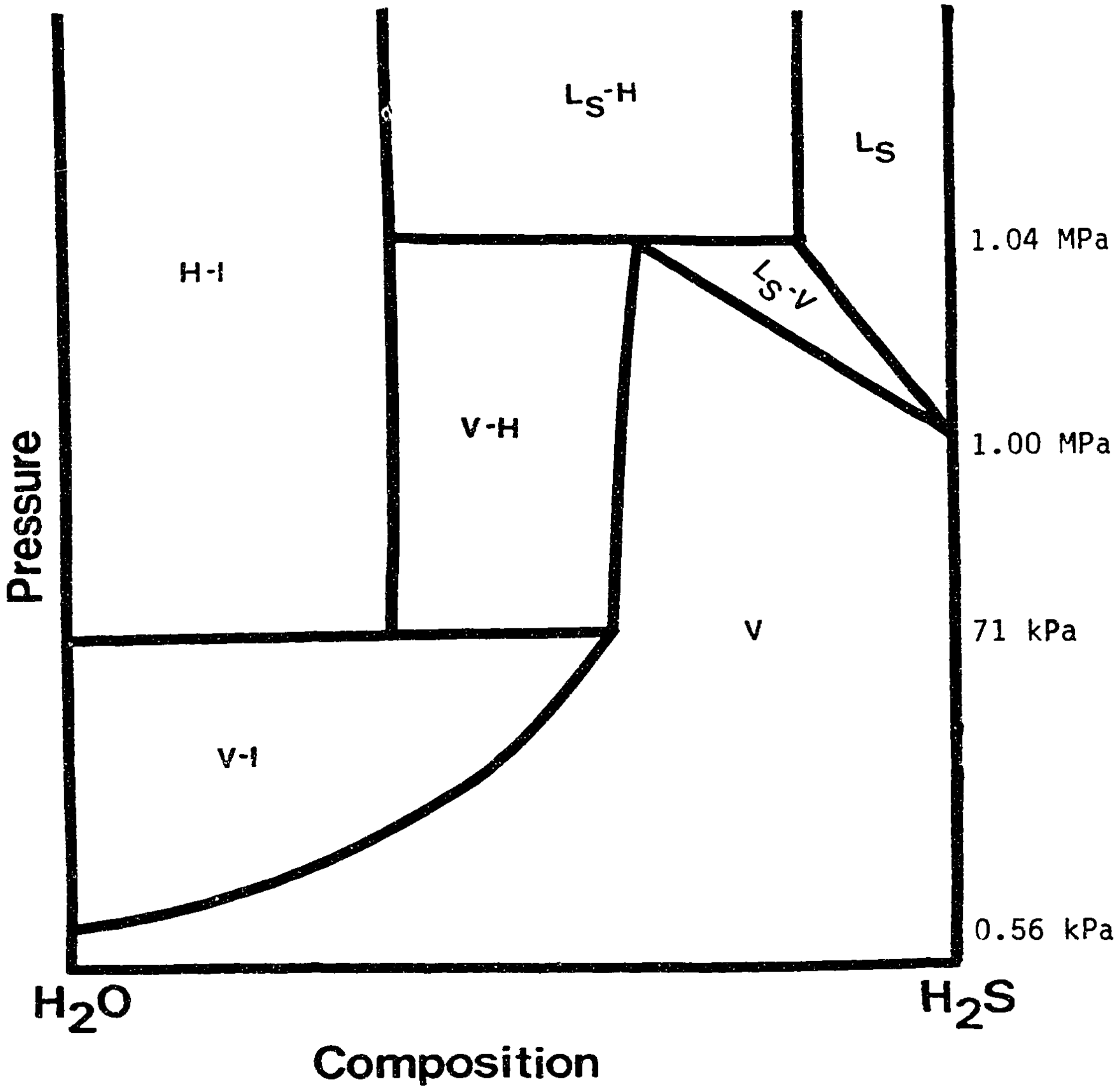

Fig. 1.3 Schematic Pressure-Composition Diagram for the System Hydrogen Sulphide-Water at -1°C

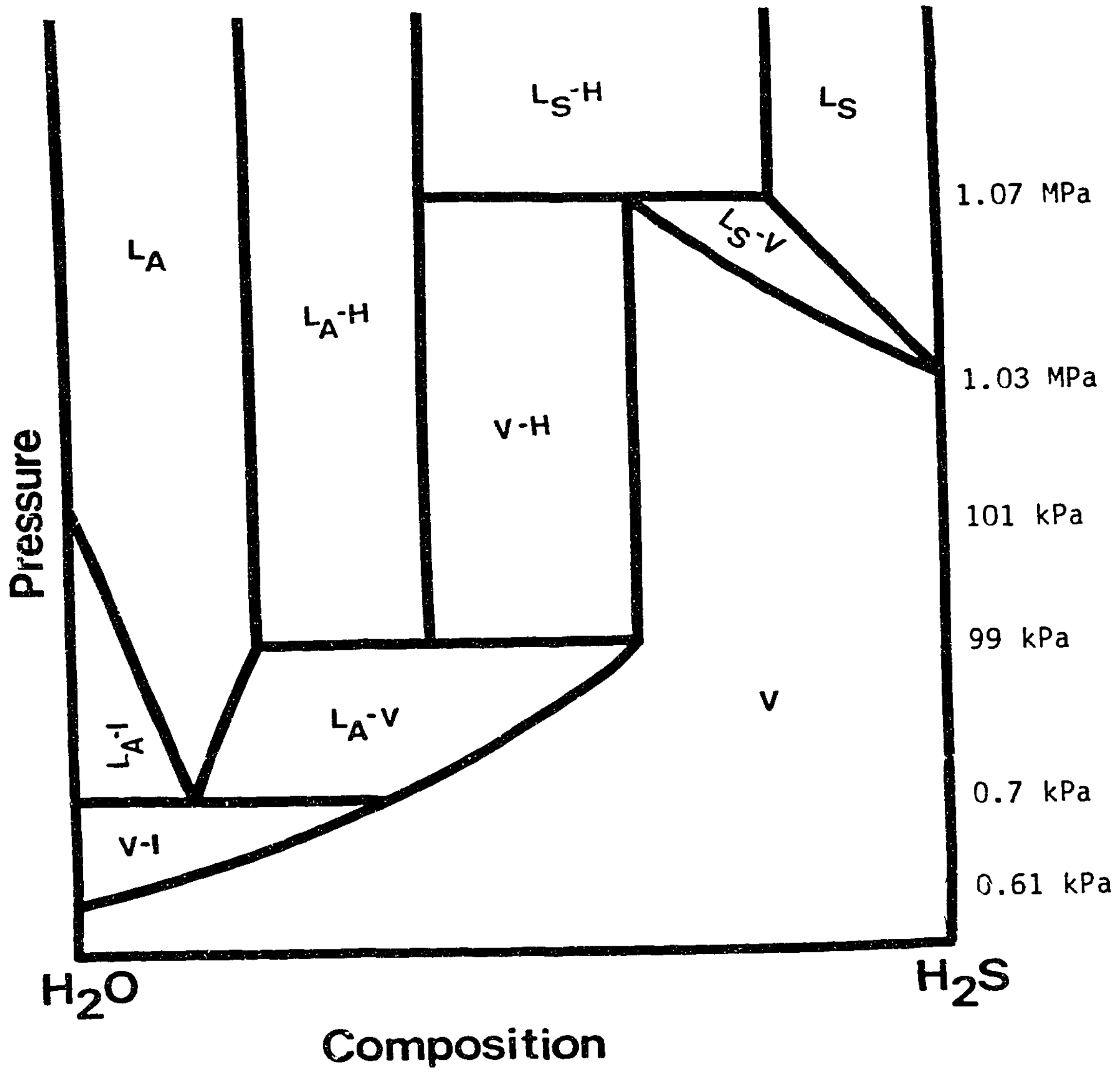

Fig. 1.4 Schematic Pressure-Composition Diagram for the System Hydrogen Sulphide-Water at 0°C

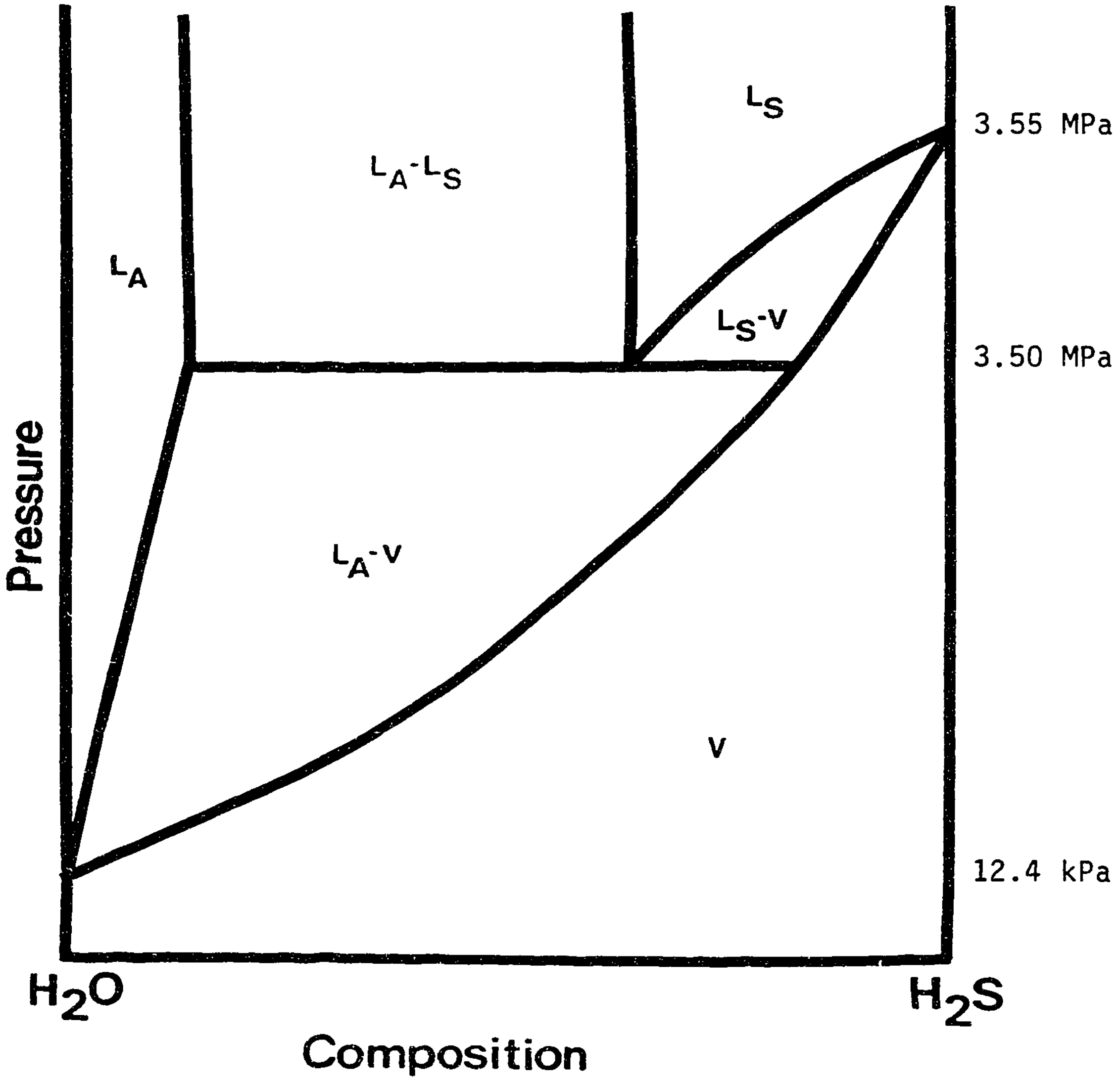

Fig. 1.5 Schematic Pressure-Composition Diagram for the System Hydrogen Sulphide-Water at 50°C

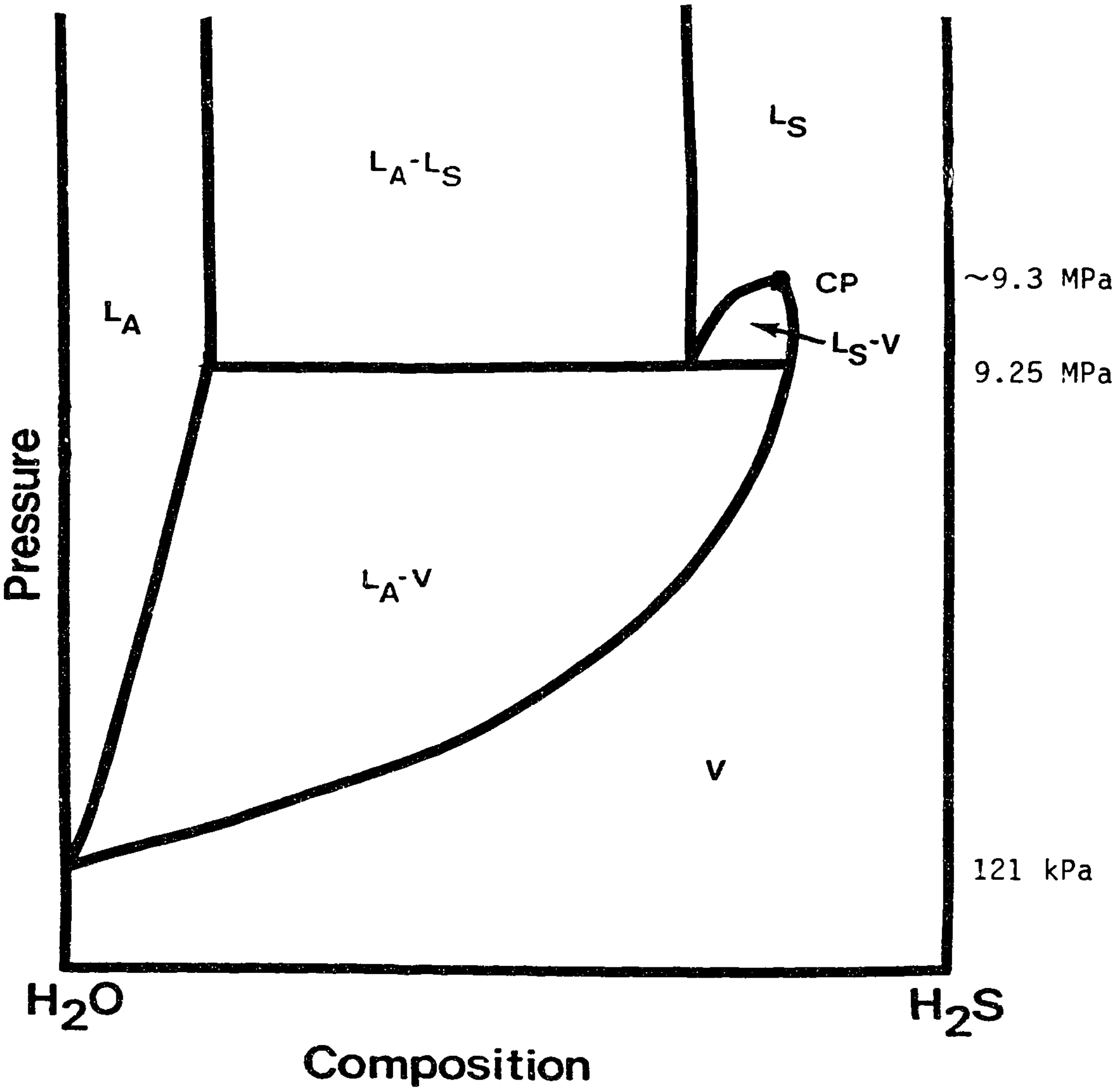

Fig. 1.6 Schematic Pressure-Composition Diagram for the System Hydrogen Sulphide-Water at 105°C

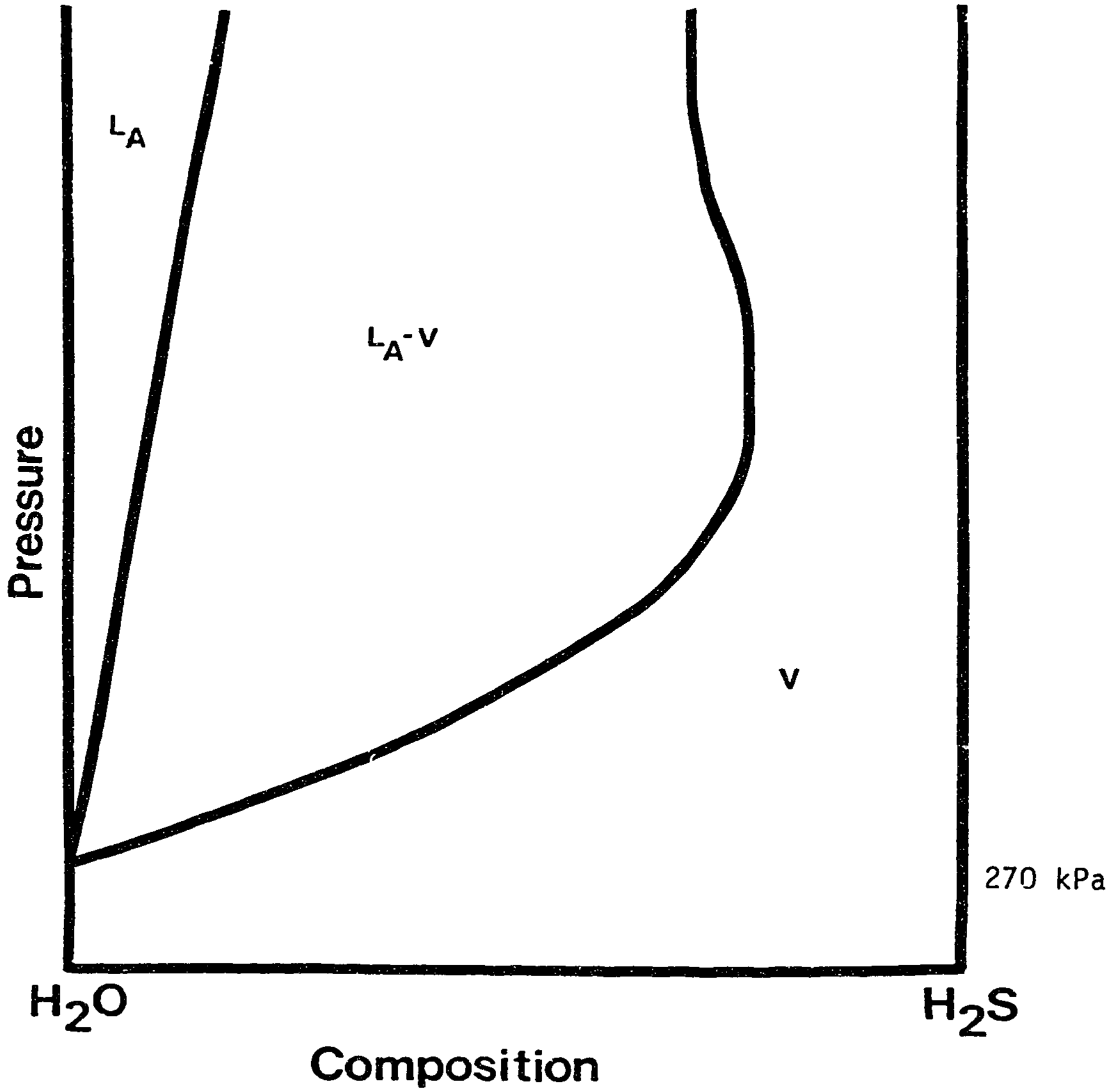

Fig. 1.7 Schematic Pressure-Composition Diagram for the System Hydrogen Sulphide-Water at 130°C

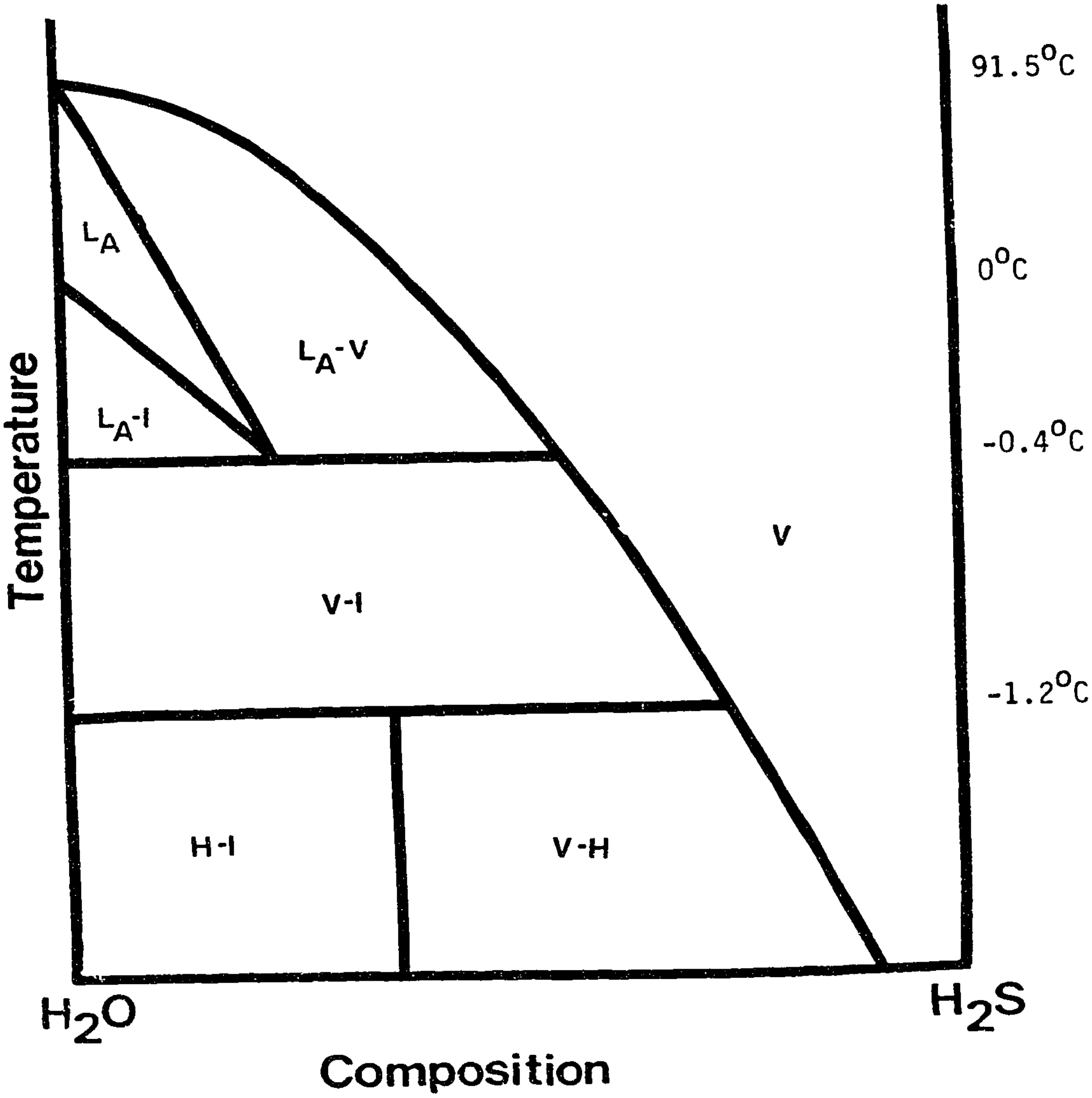

Fig. 1.8 Schematic Temperature-Composition Diagram for the System Hydrogen Sulphide-Water at 75 kPa

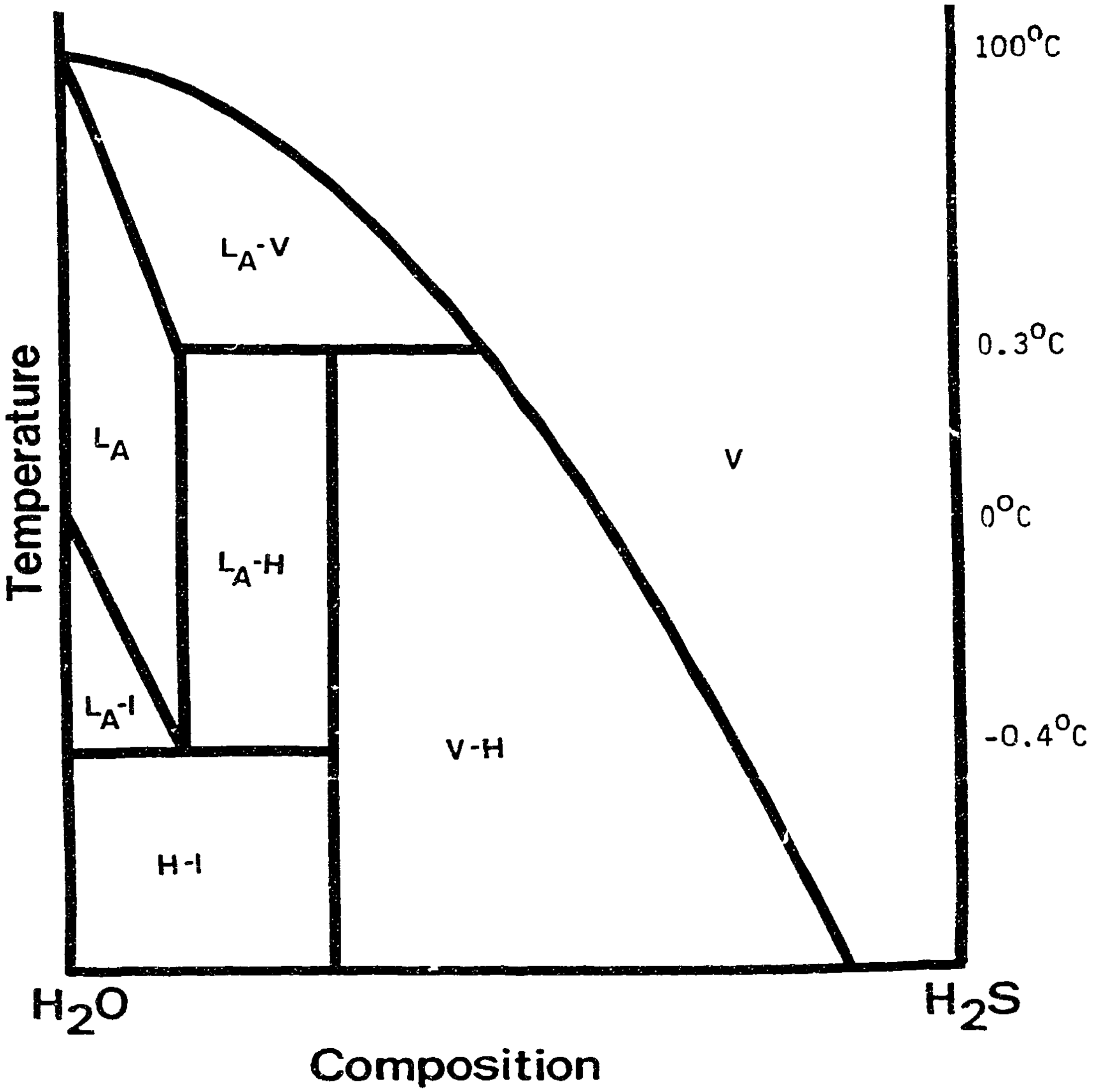

Fig. 1.9 Schematic Temperature-Composition Diagram for the System Hydrogen Sulphide-Water at 101.325 kPa

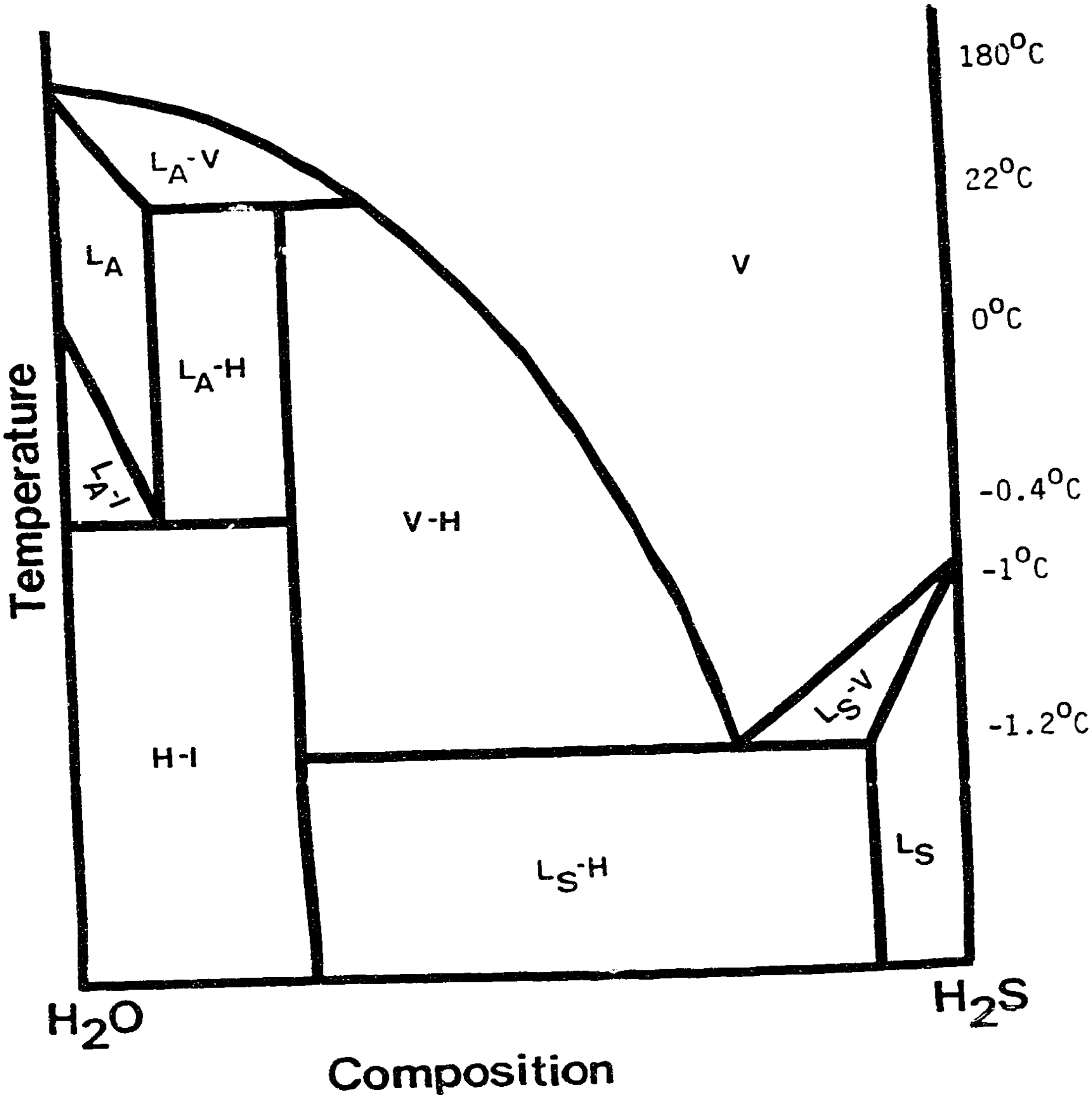

Fig. 1.10 Schematic Temperature-Composition Diagram for the System Hydrogen Sulphide-Water at 1 MPa

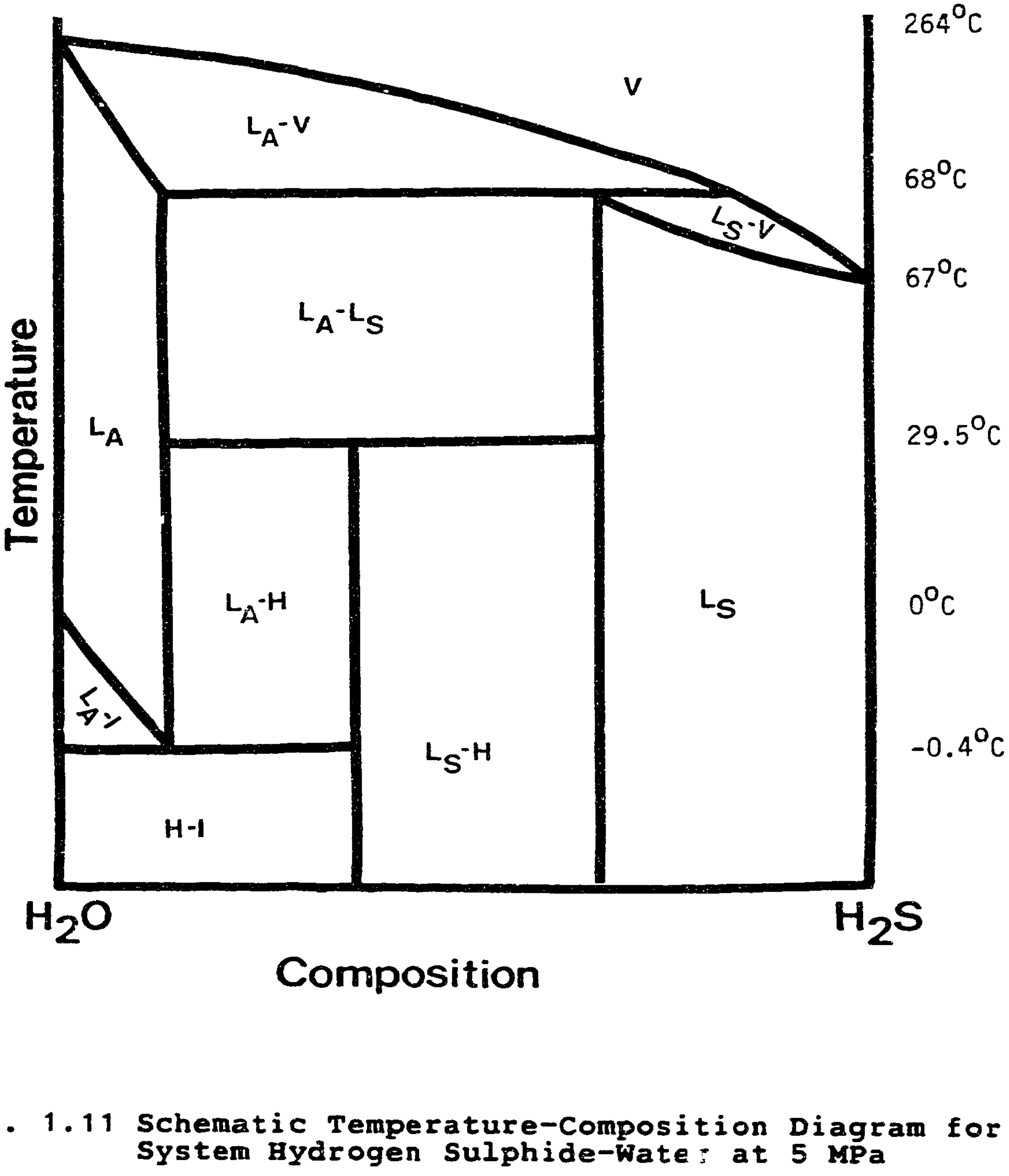

Fig. 1.11 Schematic Temperature-Composition Diagram for the System Hydrogen Sulphide-Water at 5 MPa

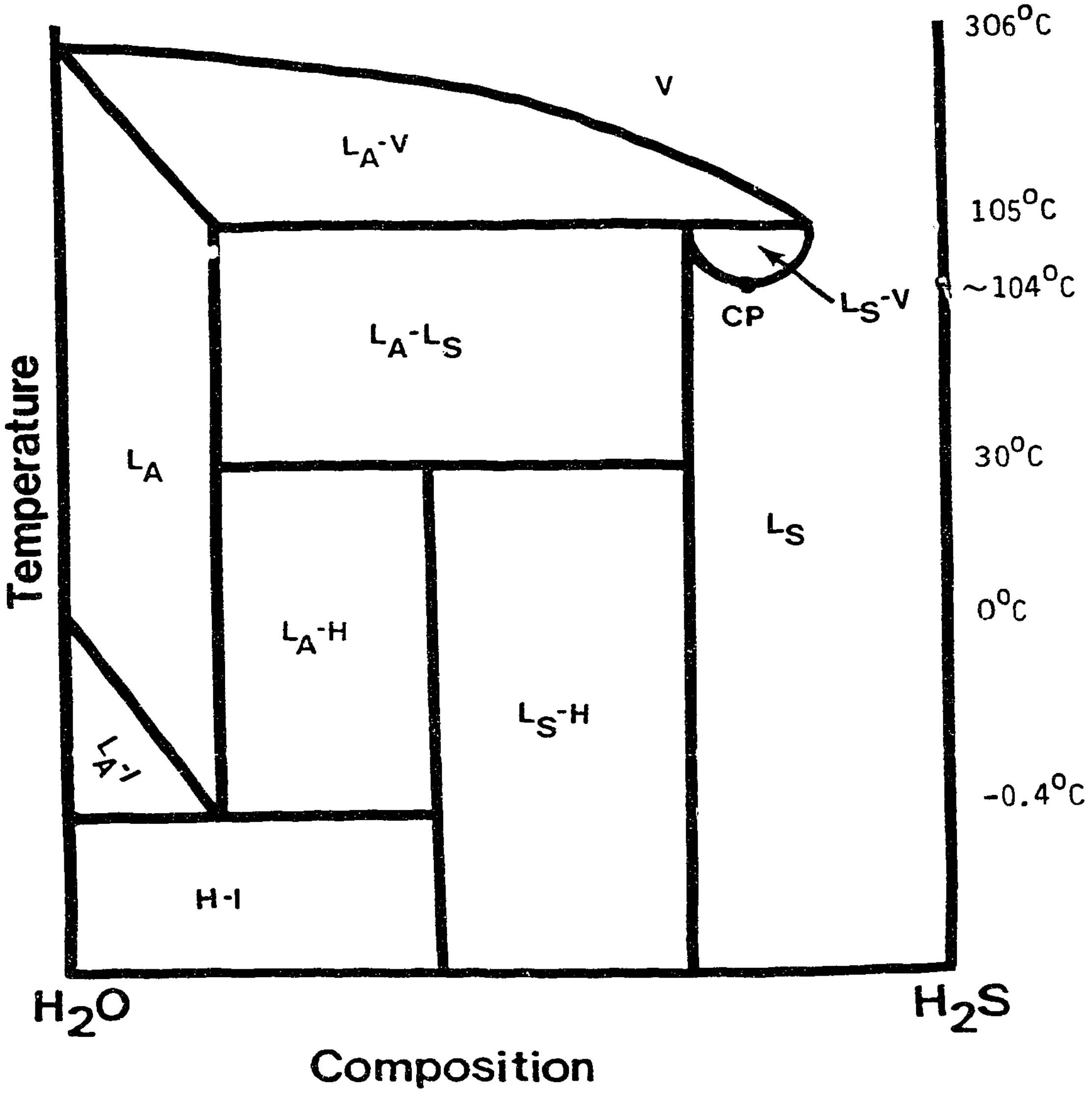

Fig. 1.12 Schematic Temperature-Composition Diagram for the System Hydrogen Sulphide-Water at 9.25 MPa

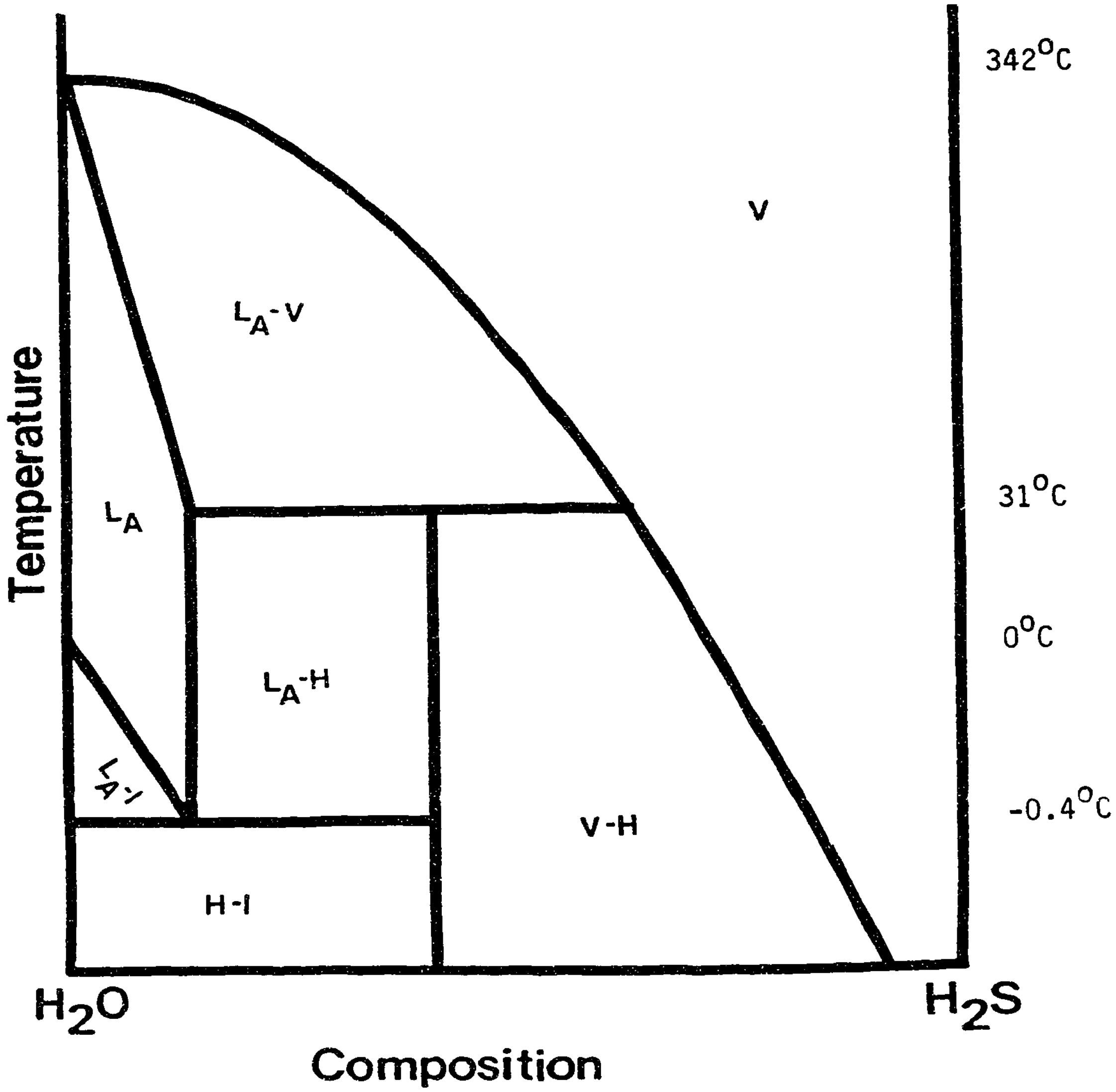

Fig. 1.13 Schematic Temperature-Composition Diagram for the System Hydrogen Sulphide-Water at 15 MPa

B. Applications

The system water-hydrogen sulphide is an important one in industrial practice. Several situations where both water and hydrogen sulphide occur will be discussed. A thorough understanding of the phase behavior in this system is important for the understanding of these processes.

Petroleum Reservoir Engineering

Petroleum reservoir fluids are complex mixtures composed of many components (both hydrocarbons and non-hydrocarbons) occurring in one or more phases. Two important components are water and hydrogen sulphide.

Petroleum reservoirs are marine in origin and thus usually have some water (usually brine) associated with them. Since water and petroleum are essentially immiscible, they form separate phases, with the water usually underlying the petroleum. Production of water is an indication of the behavior of the reservoir.

Perhaps the most common method of secondary recovery is waterflooding. Water is injected into the formation to increase the fluid pressure and thus increase oil production. An important thermal recovery method involves the injection of steam into the reservoir. This is accomplished by injecting the steam into the formation and producing the fluids via the same well (called "huff and puff"). Alternatively, separate wells for injection and production may be used ("steam flood"). The steam heats the viscous reservoir fluid, thus decreasing its viscosity and making it flow more easily. The steam also increases the reservoir pressure.

In general, phase behavior is very important in petroleum engineering. Thus the understanding of the phase equilibrium in the system H_2S-H_2O provides another volume in the library of systems of importance to the oil and gas industry.

Natural Gas Processing

Hydrogen sulphide and carbon dioxide are common components in natural gas, especially in Alberta. When they are in contact with water, they form weak acids and thus they are called "acid gases". When natural gas contains hydrogen sulphide it is called "sour gas". The acid gases must be separated from the hydrocarbons for several reasons. Hydrogen sulphide must be removed because of its toxicity, corrosivity, offensive odour and because it is a valuable source of sulphur. The common methods for separating the acid gases from the hydrocarbons use aqueous-based solvents.

Two general types of gas sweetening solvents are (1) chemical and (2) physical. Physical solvents simply dissolve the acid gases. Chemical solvents react with the acid gases, thus greatly increasing the solubility, especially at low acid gas pressures. The chemical solvents form basic solutions and, since the sour gases form acidic solutions, the reactions involve proton tranfers. Typical chemical solvents are monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA). Selexol (dimethyl ether of polyethylene glycol), Purisol (n-methyl-2-pyrrolidone) and Rectisol (methanol) are examples of physical solvents.

Regardless of whether a chemical or a physical solvent is used, the process involves the same two basic steps. The first step is the absorption of the acid gas by the solvent. The sour gas is contacted with lean solvent producing "sweet" gas and spent solvent. The spent solvent is sent to the second step. Here, in the regeneration, the hydrogen sulphide and/or carbon dioxide are stripped from the solvent. The purified solvent is returned to the absorption stage and the liberated acid gas is sent for further processing (for example to a Claus plant where hydrogen sulphide is oxidized to elemental sulphur). Fig. 1.14 depicts a simplified flowsheet for this process. Details of these processes can be found in Kohl and Riesenfeld (1985).

Heavy Water Production

Hydrogen sulphide and water are important components in the production of heavy water. The dual-temperature process (also known as the Girdler-Sulphide (GS) process) involves the exchange of deuterium between the hydrogen sulphide and the water. Fig. 1.15 shows schematically a single stage in the GS process. At low temperatures the deuterium moves to the hydrogen sulphide and at high temperatures to the water.

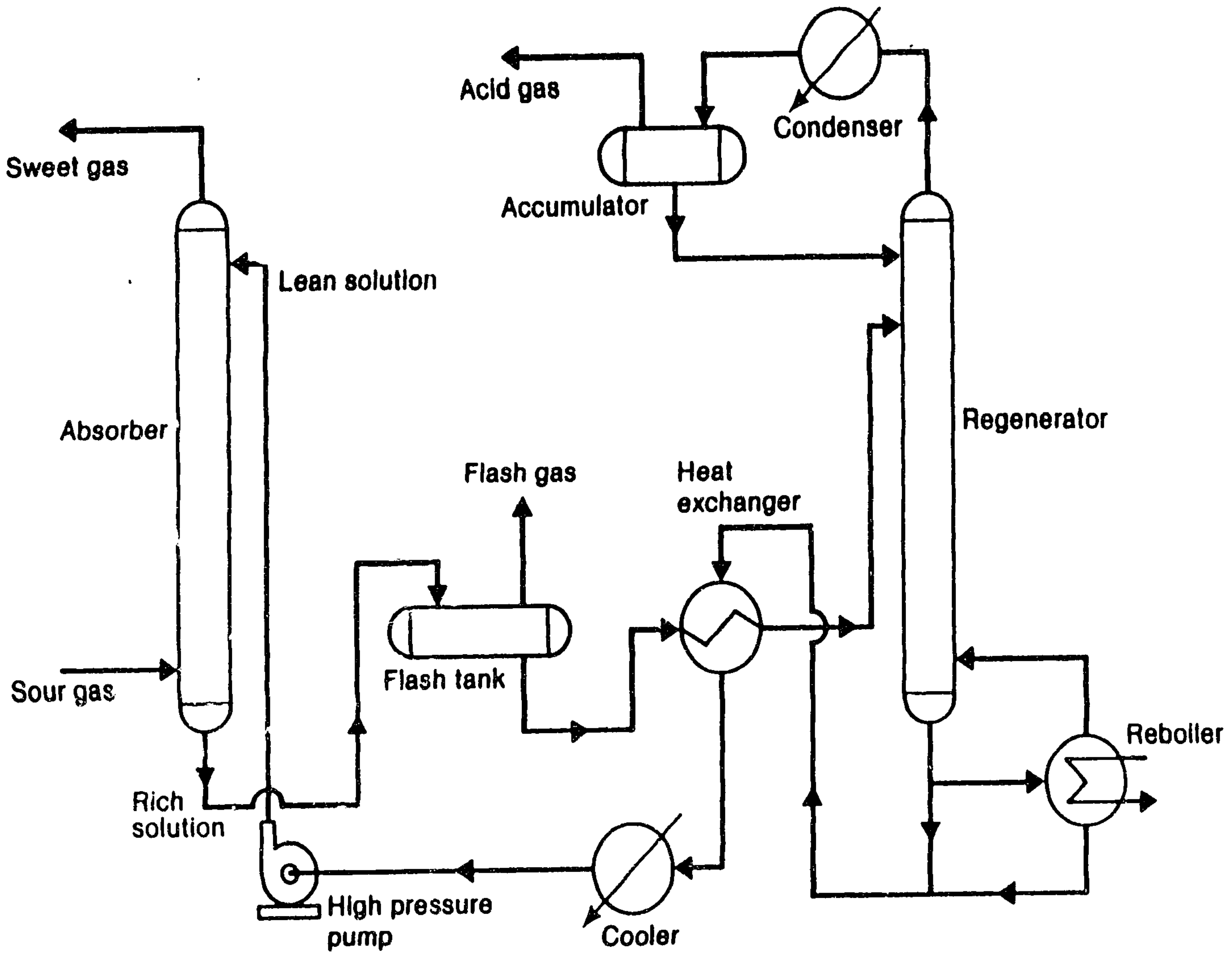

Fig. 1.14 Simplified Flowsheet for an Acid Gas Removal Process

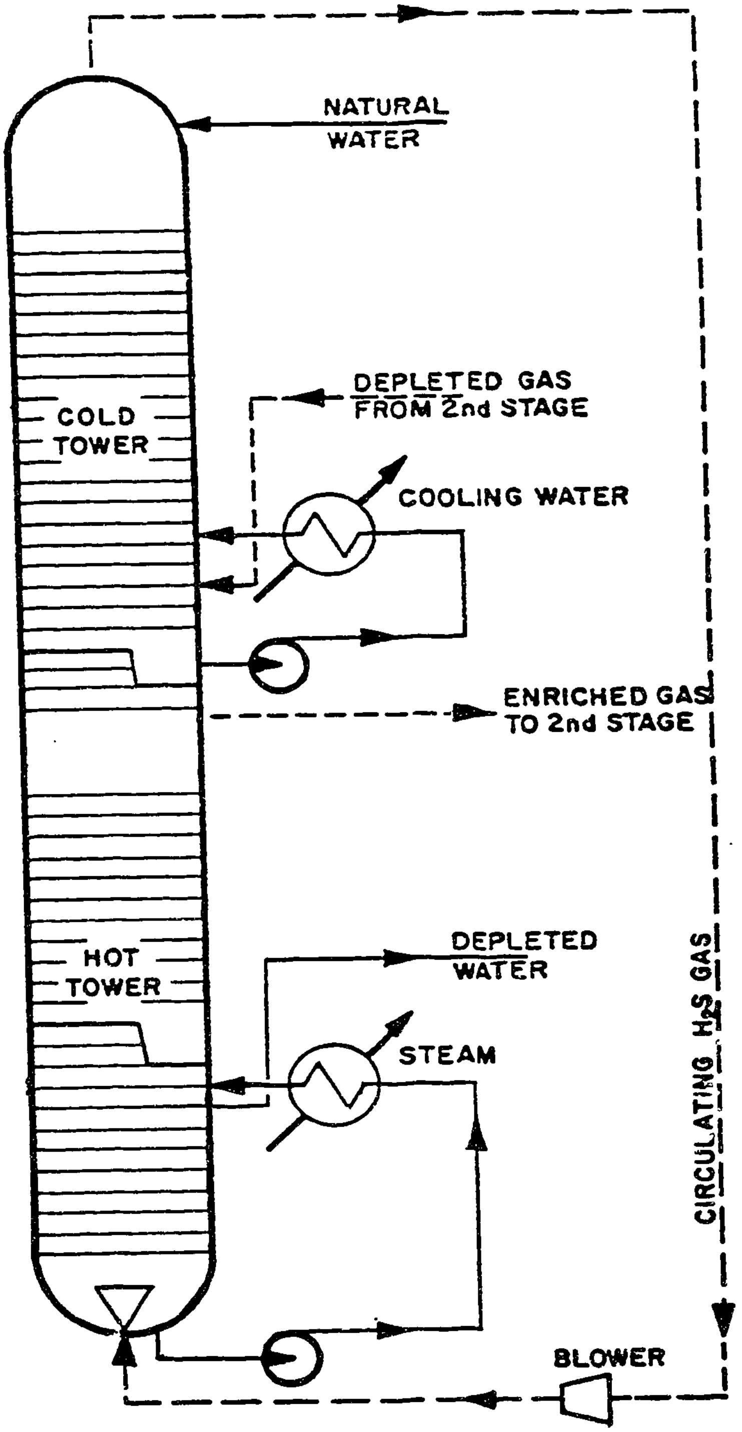

Fig. 1.15 Schematic Diagram of a Single Stage of the Dual-Temperature Process

Temperatures in the cold section are typically 30° to 40°C and 120° to 140°C in the hot. Since the reactions occur in the aqueous phase, it is desirable to operate at as high pressure as possible. Pressures in the cold section are limited by the formation of a third phase (either a hydrate or H_2S-rich liquid). Natural, fresh water, which contains minute amounts of deuterium, (typically 130 to 150 ppm deuterium as HDO) is fed to the process. The deuterium is concentrated in the product stream and a waste stream containing "light" water results. To produce pure heavy water several of these stages are placed in series. Since the transfer rates are quite low, this process is carried out in many tall tray towers. Therefore accurate phase and chemical equilibrium data are needed for optimal design and operation of these plants.

More information about the GS process can be found in Bebbington and Thayer (1959), Haywood and Lumb (1975) and Icely and Grange (1975).

Sour Water Stripping

Two important processes during the upgrading of crude oil are desulphurization and denitrogenation. Undesirable by-products from these processes are hydrogen sulphide and ammonia, which usually find their way into aqueous waste streams. Thus these wastes are called "sour water". Before the sour water can be reused or discarded, the hydrogen sulphide, ammonia and other components (such as phenols) must be stripped from the water. Because the concentration of hydrogen sulphide and ammonia in the water must be reduced to very low levels, accurate solubility and chemical equilibrium data are required for the design of these strippers.

Typically, sour water stripping takes place in two steps. The first is the removal of hydrogen sulphide which takes place at about 40°C and 700 kPa. The aqueous ammonia stream is then sent to an ammonia stripper. The ammonia is stripped at about 100°C and 350 kPa. The produced water contains less than 300 ppm ammonia and less than 100 ppm hydrogen sulphide. A detailed design procedure is given in Beychok (1967).

Paper Pulp Production

The kraft process is the most common process for producing wood pulp. Details of this process can be found in Kline (1982). It will be described briefly here. A $NaOH/Na_2S$ solution (called white liquor) is fed along with wood chips into a digestor. The hydroxide breaks down the lignin (a phenolic substance that "glues" the wood fibers together and typically makes up 20 to 40% of the wood) into simple components. The sulphide performs two functions: (1) it reacts with the simpler lignin molecules to make them more soluble and (2) it helps to maintain the desired pH level (which in turn reduces damage to the pulp due to low pH). The effluent from the digestor (called brownstock) is sent to washers. Here the sodium salts and sulphurized lignin compounds are washed out of the pulp, producing weak black liquor. The pulp is sent on for further processing. The weak black liquor is first concentrated in an evaporator, which produces strong black liquor, and then further concentrated in a furnace to produce slag. Sodium sulphate is added to the strong black liquor and in the furnace the sulphate is reduced to sulphide. The slag is mixed with lime to produce a solution containing NaOH and Na_2S (called green liquor). The green liquor is sent to a clarifier where the calcium compounds are recovered and fresh white liquor is produced. In turn, the white liquor is fed to the digestor.

Many undesirable sulphur compounds, including H_2S, are produced during this process. These sulphur compounds contribute to the odour associated with pulp mills. The chemistry of these compounds, including their solubility in water, is important for thorough understanding of the kraft pulping process.

Hydrometallurgy

Hydrometallurgy is the extraction and production of metals from ore or waste utilizing reactions in an aqueous media. Usually hydrometallurgy is employed with poorer grades of ore where pyrometallurgy (the traditional extraction with heat) is too expensive.

The first step in the process is to leach the desired minerals from the undesired gangue. A metal-rich (pregnant) solution is thus produced. This solution, rarely containing only one metal, must be separated and purified. Several processes are possible at this stage, but only precipitation will be discussed here. A reagent is added to the pregnant solution which will precipitate selectively metal compounds. The precipitate may contain either the desired product or the impurities. Hydrogen sulphide is an important reagent for this purpose. With the proper pH adjustment, metal sulphides can be selectively precipitated quite efficiently. For example, H_2S is used commercially to separate copper from a solution containing copper and nickel. The solubilities of the copper sulphides are several orders of magnitude smaller than those of nickel. The solubility of hydrogen sulphide in water is an important parameter in such an extraction method.

Jackson (1986) explains in detail many hydrometallurgical processes and Simmons (1964) expounds the use of hydrogen sulphide as a hydrometallurgical reagent.

Geological Processes

The system water-hydrogen sulphide is also of geochemical interest for more than just petroleum geology. Many mineral deposits are formed by the precipitation of solids from hot aqueous (hydrothermal) solutions. If these solutions are in contact with hydrogen sulphide, the formation of sulphide minerals may result. Thus a thorough understanding of the phase behavior in the system water-hydrogen sulphide is important for the accurate analysis of these mineral forming processes. Anderson (1983) explains the importance of hydrogen sulphide in these hydrothermal processes.

Also, these hydrothermal reservoirs are important sources of energy. One of the problems with the further development of these resources is the presence of hydrogen sulphide in the produced steam (Parkinson, 1982). Processes must be developed to strip the hydrogen sulphide from the geothermal steam without drastically reducing its energy value.

C. Summary

From the discussion just presented, it is clear that the system hydrogen sulphide-water is important from both a scientific and technological point of view. Thus it is not surprising that this system has been studied often. The next chapter reviews the vast literature of investigations of this system.

II. Literature Review

The importance of the system water-hydrogen sulphide is reflected by the large number of investigations of this system and by the range of the fields of journals that publish this information. This chapter is an attempt to review all of the work on this system. It is separated into four sections depending upon the type of investigation undertaken and further subdivided chronologically.

A. High Pressure Studies

One of the first investigations of the phase behavior in the system water-hydrogen sulphide was by Scheffer (1911a,b,1913). He measured the three-phase loci in the region near the L_A-L_S-H-V quadruple point. He found this quadruple point to be at 29.5°C and 2.24 MPa.

The investigation of Selleck, Carmichael and Sage (1951,1952) is considered to be the benchmark study for the system water-hydrogen sulphide. Properties reported in the 1952 paper were smoothed and extrapolated from the raw data, which were presented in the 1951 supplementary publication. It also incorporated work from some previous investigations, especially the work of Scheffer. The experimental portion of the Selleck et al. study was performed in three parts. First a variable volume cell was used to determine bubble points. A mixture of known composition, lean in hydrogen sulphide, was injected into the cell and compressed isothermally. A discontinuity in the derivative of volume with respect to pressure at constant temperature indicated the phase transition. Second, a constant volume cell was used for direct measurement of the composition of a gas in equilibrium with an aqueous phase of unknown composition. In the vapour-liquid region, they examined five isotherms: 37.8°, 71.1°, 104.4°, 137.8° and 171.1°C (100°, 160°, 220°, 280° and 340°F) and pressures up to about 35 MPa (5000 psia) for the vapour phase. The bubble points were measured at pressures up to 13 MPa (2000 psia). A few hydrogen sulphide-rich phase compositions were measured at 37.8° and 71.1°C in the liquid-liquid region. Finally, phase boundaries on the P-T projection (points along the three-phase loci) were obtained using a cell which was nearly constant volume. Discontinuities in the derivative of temperature with respect to pressure at constant volume indicated a phase transition. A detailed and critical discussion of the work of Selleck et al. is presented in Chapter IV.

Kozintseva (1964,1965) studied the phase equilibrium of the binary system from 160° to 330°C, but the partial pressures of hydrogen sulphide were less than 210 kPa. On the P-T diagram, her data lie very close to the water vapour pressure curve. She also investigated the solubility of hydrogen sulphide in aqueous solutions of sodium chloride, calcium chloride and sodium sulphate at similar conditions. To perform a run, the cell was initially flushed with nitrogen in order to remove oxygen from the system. Water was then added to the cell, followed by H_2S. It is unclear how the nitrogen was purged from the equipment (and it is suspected that the nitrogen was not removed). Samples of both phases were taken. The compositions were determined by passing the sample through a series of traps. The H_2S content of the sample was determined using iodometric titrations and the mass balance. She reports the partial pressure of hydrogen sulphide (which she defines as $p_{H2S} = y_{H2S} \cdot P$) and the mole ratio of H_2S in both phases. From her values, the mole fractions and the total pressure can be calculated. The difference between the total pressure, thus calculated, and the vapour pressure of pure water is much larger than her reported partial pressures. Another way of expressing this is that most of her vapour compositions deviate from simple Raoult's law ($y_{H2S} = 1 - P°_{H2O}/P$), some by more than an order of magnitude. Such an error seems to be unusually large.

In a study of the solubility of sour gas mixtures in water and brine, Vogel (1971) made some measurements for hydrogen sulphide in water at 104.4°C (220°F). Initially he tried to measure the composition of the aqueous phase directly. A mixture of hydrogen sulphide and water was injected into a constant volume cell and allowed to equilibrate. A sample of the liquid was withdrawn and analysed. He rejected this method and the results thus obtained because the hydrogen sulphide concentrations were significantly less than the extrapolated values of Selleck et al. Unfortunately, Vogel did not report these solubility data. Subsequently he used a variable volume cell to measure bubble points. At low pressures the bubble points were in good agreement with Selleck et al. However, at higher pressure, Vogel's measured solubilities were much smaller than those reported by Selleck et al. (by as much as 24%). Also, for some compositions, the isothermal pressure-volume curves showed two discontinuities. Vogel coupled his observations with the smoothed values of Selleck et al. and erroneously interpreted this as a three-phase region - a violation of the Gibbs phase rule. A better interpretation of the observations of Vogel is given in Chapter V.

Lee and Mather (1977) measured the solubility of hydrogen sulphide in water for eleven isotherms (10°, 20°, 30°, 40°, 50°, 60°, 71°, 90°, 120°, 150° and 180°C). The pressure for these measurements was either up to about 7 MPa or until a third phase was encountered, depending upon the temperature. A flow-type sampled cell was used in this investigation. Liquid phase compositions were obtained by flashing a sample to room conditions. The hydrogen sulphide that evolved was collected in a burette. Residual hydrogen sulphide in the water was determined using gas chromatography. A few vapour compositions were also measured at 90°, 120° and 150°C and pressure between 1.9 and 3.4 MPa. These compositions were measured using gas chromatography. Unfortunately, they were not highly reproducible, especially at low water concentrations.

Drummond (1981), in an investigation of hydrothermal fluids, measured mass-temperature-pressure-volume data for the systems H_2S-water, H_2S-brine, CO_2-water and CO_2-brine. The temperatures ranged from 30° to 355°C and pressures to about 20 MPa. These data were neither along isotherms nor along isobars; each point was at a different temperature and pressure. The experimental procedure consisted of charging a known amount of water and hydrogen sulphide into a cell of known volume. The cell was rocked until equilibrium was attained. From the measured temperature, pressure, feed composition and total volume, along with several assumptions, the compositions of the coexisting phases were calculated. Some of the assumptions that he made are:

1. Raoult's Law: The partial pressure of water was estimated as the mole fraction of water in the aqueous phase times the vapour pressure of pure water.
2. Lewis Rule: The fugacity of hydrogen sulphide in the vapour phase was calculated by multiplying the fugacity of pure hydrogen sulphide and the mole fraction in the vapour. This was assumed in spite of vapours estimated to be as lean as 10% hydrogen sulphide. Fugacities were calculated using the generalized correlations of Lee and Kesler (1975).
3. Amagat's Law: The volume of the vapour was calculated as the sum of the volumes of the pure components at the given temperatures and pressures. Compressibilities were obtained from Lee and Kesler (1975).

These assumptions are not valid at the conditions of these experiments. Thus, the values reported are of questionable quality. Subsequently, Drummond (1985) analyzed the errors involved in this type of experiment. Unfortunately, his analysis incorporated only the errors involving the measured quantities (mass, temperature, pressure and volume) and not the assumptions made. The errors arising from his assumptions are more significant than those due to the measured quantities.

Gillespie, Owens and Wilson (1984) [also see Gillespie and Wilson (1980) and Gillespie and Wilson (1982)], in a study of sour water systems, examined the system water-hydrogen sulphide from 37.8° (100°) to 315.6°C (600°F) up to 20.7 MPa (3000 psia). They used a static-type sampled cell. This investigation included vapour-liquid and liquid-liquid equilibria. Samples from both phases were analyzed. For hydrogen sulphide-water, samples were passed through a cadmium sulphate solution and then a tube packed with Drierite. The amount of hydrogen sulphide in the sample was determined by titrating the sulphuric acid formed by the reaction of hydrogen sulphide with cadmium sulphate (cadmium sulphide precipitates). The mass of the sample was obtained by weighing the collection train before and after sampling. The water content was determined by difference.

B. Low Pressure and Solubility Studies

One of the classic experimental methods for measuring the solubility of a gas in a liquid was devised by Bunsen (1855a,b,c). A known volume of gas was brought in contact with a quantity of gas-free solvent. The system was left to equilibrate and then the volume of the gas was again measured. The difference in volumes represented the amount dissolved. Solubilities thus obtained were reported as the volume of gas dissolved (corrected to STP - 0°C and 1 atm) per unit volume of pure solvent - today this is called the Bunsen coefficient. Schoenfeld (1855) used this method for hydrogen sulphide in water from 2° to about 43°C. The precision of these data was not very high (as will be demonstrated in Chapter VI).

Prytz and Holst (1895) used a method similar to that devised by Bunsen, but they measured the amount of gas dissolved gravimetrically rather than volumetrically.

McLaughlan (1903) measured the solubility of hydrogen sulphide, iodine and bromine in aqueous solutions of electrolytes and non-electrolytes. As a part of this study, he measured the solubilities in pure water. These measurements were at 25°C.

Garelli and Falciola (1904) used a freezing point depression method to measure the solubility of several gases (including H_2S) in several liquids (including water). The solubility of H_2S in water was reported at 0°C and 1 atm.

Winkler (1906) reported the solubility of several gases (including hydrogen sulphide) in water at 1 atm for temperatures from 0° to 100°C. Winkler was among the first to use a chemical technique for measuring gas solubilities. The liquid was saturated by bubbling the gas through it. Then the solubility was measured using a chemical method (for example iodometric titration). The International Critical Tables (Washburn, 1928) list Henry's constants for H_2S in water. These values were based primarily on the work of Winkler. The values reported in the International Critical Tables have been repeated in other source books. For example, they are in the Chemical Engineer's Handbook (Perry and Chilton, 1973; and Perry and Green, 1984). However, there is an error in these compilations. They are in error by three orders of magnitude. Correct Henry's constants and the proper use of Henry's Law are presented in Chapter VI.

Pollitzer (1909) studied the reaction between H_2S and I_2. As a part of this research, the solubility of H_2S in water was measured at 25°C.

Kendall and Andrews (1921) measured the solubility of hydrogen sulphide in hydrochloric acid solutions (including pure water) at 25°C and 1 atm. Interestingly, they found that the solubility of hydrogen sulphide in hydrochloric acid solutions went through a minimum at approximately 0.4 M HCl. The solubilities were measured using iodometric titrations. Kapustinsky and Anvaer (1941) also measured the solubility of hydrogen sulphide in hydrochloric acid at 25°C and atmospheric pressure. Included in this study was a single measurement of the solubility in pure water. Syrkina, Krashennikova and Zaliopo (1969) measured the solubility of hydrogen sulphide in hydrochloric acid as well.

Wright and Maass (1932a) determined the solubility of hydrogen sulphide in water over the range of temperature 5° to 60°C and pressures up to 500 kPa. They assumed that the partial pressure of water in the vapour phase was equal to its vapour pressure. Liquid phase compositions were obtained from volumetric and gravimetric methods. They also measured a few pressure-temperature points along the $H\text{-}L_A\text{-}V$ three-phase locus. In a subsequent paper, Wright and Maass (1932b) report additional data on the solubility of hydrogen sulphide. However, the main focus of the second paper was the electric conductivity of these solutions and the state of the aqueous H_2S.

Kiss, Lajtai and Thury (1937) reported values for the solubility of hydrogen sulphide in water and solutions of ethanol, glycerine and urea at 0.05°, 12.5° and 25°C. Several measurements were made near atmospheric pressure and the reported values were corrected to 1 atm. Concentrations of the hydrogen sulphide in the aqueous phase were determined using iodometric titrations.

Harkness and Kelman (1967) made some measurements of the solubility of methyl mercaptan in water and various electrolyte solutions. They also made a single measurement of the solubility of hydrogen sulphide at 30°C. The solubilities were obtained using a volumetric technique.

Gamsjäger, Rainer and Schindler (1967) measured the solubility of H_2S in solutions of $HClO_4$ and $NaClO_4$ at 25°C and 1 atm. Included in their study was a single measurement for H_2S in pure water.

Clarke and Glew (1971) measured vapour-liquid equilibrium data for hydrogen sulphide and deuterium sulphide in water and heavy water. Temperatures ranged from 0° to 50°C, and pressures were below 100 kPa. Both liquid and vapour phase compositions were obtained from experimental data and a rigorous theoretical model of the phase equilibrium. their values are the most accurate of all the solubility data.

Gerrard (1972) measured the solubilities of several gases in various solvents including hydrogen sulphide in water. The measurements for H_2S in water were at atmospheric pressure and at 0°, 10° and 20°C. A volumetric method was used to obtain the concentration in the liquid phase.

Douabul and Riley (1979) measured the solubility of hydrogen sulphide in water and seawater from about 2° to 30°C. Pressure for these experiments was 1 atm. The raw experimental data were evaluated and a table of smoothed values was also presented. The hydrogen sulphide content of the aqueous phase was measured using iodometric titration.

Byeseda, Deetz and Manning (1985a,b) in a study of the solubility of H_2S, CO_2 and propane in several solvents measured a single point for H_2S in water at 23.9°C (75°F) and 101.6 kPa (14.73 psia).

Barrett, Anderson and Lugowski (1988) measured solubilities at about 25°, 60°, 80° and 95°C and 1 atm in pure water and NaCl solutions of concentrations up to 5 molal. Several results were reported for each temperature. The solubilities were obtained using iodometric titrations and a gravimetric technique. There was good agreement between the two methods. In an earlier work, Barrett and Anderson (1982) mention some solubility values at about 80°C, but little detail about these values is given.

In an investigation of the solubilities of gases in liquids, Markham and Kobe (1941) reviewed the experimental and theoretical methods employed up to that time. They rate the reliability of the available data and all were considered to be of the highest quality with the exception of those of Bunsen and McLaughlan. This rating was based solely on the method used. Wilhelm, Battino and Wilcock (1977) made a thorough and critical review of the solubility of gases in water. For hydrogen sulphide, they concluded that the data of Wright and Maass and Clarke and Glew were the most reliable. A thorough discussion of the solubility is presented in Chapter VI.

C. Hydrates

The first report of the hydrogen sulphide hydrate was by Wöhler (1840). Loir (1852) reported a double hydrate in the system hydrogen sulphide-chloroform-water. However, the first detailed investigation of the H_2S hydrate was that by de Forcrand and co-workers (de Forcrand, 1882a; de Forcrand, 1882b; de Forcrand, 1883; de Forcrand and Villard, 1888a; de Forcrand and Villard, 1888b; de Forcrand and Villard, 1888c; de Forcrand, 1902a and de Forcrand, 1902b). These studies included measurements of the L_A-H-V locus for hydrogen sulphide, the study of several double hydrates with hydrogen sulphide as one of the components, and the compositions of the hydrates. Although in their earlier work de Forcrand and co-workers estimated that the formula for the hydrate was $H_2S.12\ H_2O$ or $H_2S \cdot 16\ H_2O$, in 1902 he calculated that it was $H_2S \cdot 5.96\ H_2O$ which is close to the accepted value. But, assuming that the ratio should be an integer he rounded it off to 6. At about the same time Cailletet and Bordet (1882) also reported values for the pressure and temperature along the L_A-H-V locus.

As noted earlier, Scheffer investigated the hydrate forming conditions. Scheffer (1911b) measured the composition of the aqueous liquid along the L_A-H-V locus and the H_2S-rich liquid along the L_S-H-V locus. Scheffer and Meyer (1919a,b) also investigated the hydrate. Korvezee and Scheffer (1931) reported measurements and results along the

H-I-V and L_A-H-V loci. They concluded that the composition of the hydrate at the L_A-H-I-V quadruple point was 6.06±0.13 molecules of water per molecule of hydrogen sulphide. However, they too believed that the value should be an integer and thus rounded it to 6.

Bond and Russell (1949) investigated the L_A-H-V locus and the effect of several "antifreeze agents" (NaCl, $CaCl_2$, methanol, ethanol, ethylene glycol, diethylene glycol, dextrose and sucrose). All of these chemicals were found to reduce the temperature at which the hydrate would form at a given pressure. Ng and Robinson (1985) performed a similar experiment to study the effect of methanol on the hydrate formation of several gases including hydrogen sulphide. No measurements were made for the binary mixture water-hydrogen sulphide, however.

The first thorough study of the nature and properties of all hydrates was by Stackelberg and co-workers (Stackelberg, 1949; Stackelberg and Müller, 1954; Stackelberg and Meinhold, 1954; Stackelberg, 1954; Stackelberg and Frühbuss, 1954; and Stackelberg and Jahns, 1954). Among other things, they established a semi-empirical relation for determining which substances will form hydrates. They also investigated the crystal structure of the two types of hydrates.

Cady (1981) made precise measurements of hydrate compositions for several substances. For hydrogen sulphide in water at 0°C, he found that n=5.99 at 164 kPa and 5.86 at

349 kPa and was a decreasing function of pressure.

D. Other Studies

Pohl (1961) and Burgess and Germann (1969) correlated data for the water-hydrogen sulphide system in the region of interest for the dual temperature process. Both of these works present equations suitable for computer calculations as well as tables of interpolated values. Unfortunately, both works are highly dependent on the smoothed values of Selleck et al. (1952) for their mixture values.

Another important investigation of the system water-hydrogen sulphide was performed by Murphy and Gaines (1974). They measured the densities of saturated hydrogen sulphide solutions from 21° to 41°C for pressures between 0.101 and 1.824 MPa. They also measured the viscosities of the solutions at the same conditions.

A thorough investigation of the properties of H_2S-H_2O mixtures is the report by Neuberg, Atherly and Walker (1977). Although they use several sources of data, this report is highly reliant on the smoothed values of Selleck et al.

Shvedenov, Kalinin and Nazarov (1986) modelled the vapour-liquid equilibrium in the system H_2O-H_2S. Their purpose was to construct a model that could be used to extrapolate the experimental data to higher pressure. They used an activity coefficient model for the liquid phase non-idealities and the Peng-Robinson equation of state for the vapour. Again, their model was highly dependent on the smoothed data of Selleck et al.

A valuable compilation of data for the solubility of hydrogen sulphide is in the IUPAC Solubility Series (Fogg and Young, 1988). Solvents include water and aqueous mixtures. However, this listing is not as complete as that presented in this thesis.

E. Summary

This chapter was an attempt to review the copious literature for the system hydrogen sulphide-water. These data will be incorporated into the models developed in subsequent chapters. One region where the literature is inconclusive is the liquid-liquid-vapour equilibrium. This will be investigated in the next chapter. Also, there is some controversy about the solubility of hydrogen sulphide in water. This problem is addressed in Chapter VI. Finally, there is a lack of accurate high pressure equilibrium data.

III. Experimental Work

The literature for hydrogen sulphide-water, as reviewed in the previous chapter, has a few of inconsistencies. Perhaps the most important of these is the liquid-liquid-vapour locus and in particular the location of the three-phase critical end-point. It is the purpose of this chapter to detail an experiment for measuring the L_A-L_S-V locus. As a part of this work, the hydrate forming conditions were also examined.

A. Liquid-Liquid-Vapour Equilibrium

Apparatus

For this work, experiments were conducted in a flow-type, sampled cell (see Appendix A for a discussion of the types of equilibrium cells). The cell is a high pressure liquid level gauge, (Jerguson #17-T-30) designed for clear viewing of its contents. The volume of the cell is about 75 cm^3. To ensure sufficient mass within the system, a vapour reservoir of about 250 cm^3 is attached to the top of the cell. To encourage equilibrium, vapour is drawn off the reservoir and circulated through the condensed phases. The recirculation pump is a magnetic piston pump, similar to the one devised by Ruska et al. (1970). The void volume of the

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A portion of this [illegible]ter has been published. Carroll, J.J. and Mather, A.E., [illegible]hase Equilibrium in the System Water-Hydrogen Sulphide: Experimental Determination of the LLV Locus", Can. J. Chem. Eng., 67, 468-470, (1989).

pump is about 100 cm^3. All parts in contact with the wet H_2S are constructed from 316 stainless steel with the exception of the piston in the recirculation pump. Since it had to be ferromagnetic, the piston was made from Carpenter 450. The cell, reservoir and pump are housed in a constant temperature air bath. Pressure was measured using two 16-inch Heise bourdon tube gauges. One of the gauges was 6.9 MPa (1000 psi) and the other 20.7 MPa (3000 psi). The gauges were accurate to 0.1% of full scale and were calibrated against a dead weight gauge. Temperature was measured with an iron/constantan (Type J) thermocouple. The thermocouple was calibrated against a platinum resistance thermometer. Output from the thermocouple was measured using a Hewlett-Packard Model #3450A digital voltmeter. The temperature of the air bath was controlled using a Hallikainen Thermotrol controller. Since the pressure gauges were at ambient temperature, the lines leading to the gauges were wrapped with heating tape to prevent hydrate formation. The apparatus is illustrated in Fig. 3.1.

Procedure

To perform a run, approximately 20 cm^3 of water was placed in the cell. Hydrogen sulphide was bubbled through it for about half an hour to ensure that all of the air was flushed out of the system. Using only the pressure in the H_2S bottle, pressures of about 1.7 MPa could be attained in the system. A spindle press was then used to increase the

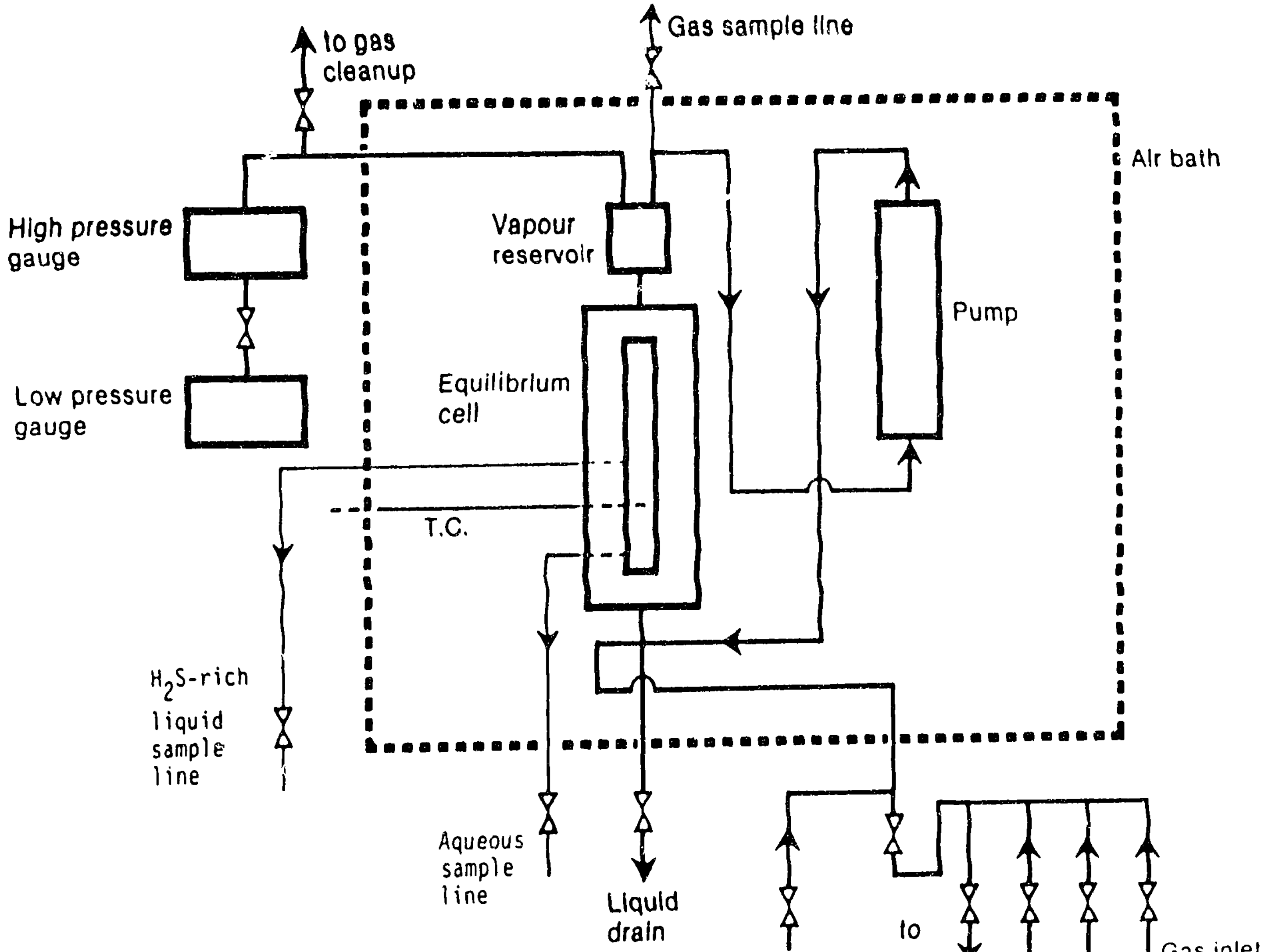

Fig. 3.1 Schematic Diagram of Apparatus

amount of H_2S in the system. The outside of the barrel of the spindle press was packed with ice, and H_2S was condensed inside the pump. This liquid was pumped into the cell. Injection continued until there was sufficient amount of H_2S-rich liquid. To construct the pressure-temperature locus, the controller was set and the system was allowed about 24 h to attain equilibrium. As the critical point at the end of the three-phase locus was approached, longer times were allowed. As the temperature changed the pressure tracked the L_A-L_S-V locus in much the same way a pure component would track its vapour pressure. Once equilibrium was reached, the pressure and temperature were recorded. The controller settings were then changed to obtain another point.

Sampling

The three phases were sampled in a similar fashion. Samples were withdrawn from the cell through 1.59 mm (1/16 in) tubing and were absorbed into an approximately 1 M NaOH solution. The H_2S-rich phases were collected in a steel bomb with a volume of about 150 cm^3 and the aqueous phase in a 50 mL Erlenmeyer flask. The mass of the sample was determined by weighing the collection vessel before and after sampling. These measurements were made to the nearest 0.1 mg using a Mettler single-pan analytical balance; however, they are probably accurate to only ±1 mg. Samples of the H_2S-rich phases were 1 to 2 g and were absorbed in

125 to 150 mL of caustic. Aqueous samples were 3 to 5 g and were absorbed in about 30 mL of caustic. The exact amount of caustic was obtained by weighing the collection vessel empty and after the addition of the caustic. To keep the pressure drop to a minimum, the samples were withdrawn quite slowly. Thus during sampling, the pressure never decreased by more than 0.7 MPa.

The H_2S content of the sample-caustic solution was determined by iodometric titration (Kolthoff et al., 1969 and Bethge, 1953). An exact volume of 0.1 N iodine (typically 20-25 mL) was pipetted into a flask. An equal volume of glacial acetic acid was added to the iodine. A small aliquot of sample, weighed to the nearest 0.1 mg, was added to the iodine/acid solution. The amount of iodine was always such that it would be in excess. The excess iodine was titrated with 0.1 M sodium thiosulphate. The thiosulphate was added to the sample/iodine solution from a burette. It was slowly added until the solution became a pale yellow colour. A modified starch was added. The reaction between the starch and iodine turned the solution blue. The titration continued until the blue colour disappeared. From the amount of iodine consumed by the H_2S in the solution, the amount of H_2S in the sample could be calculated. The mass of water in the sample was calculated by subtracting the mass of H_2S from the weight of the sample.

The errors in these values are estimated to be ±1 mol% for the H_2S-rich phases and ±0.1 mol% for the aqueous phase. Temperatures in this table are accurate to the nearest degree Celsius. At the lowest two temperatures, the determination of the water content of the vapour was not sufficiently accurate. Hence, the results are given as 99+% H_2S.

Originally, it was proposed that the compositions of the H_2S-rich phases would be measured using gas chromatography. A Hewlett-Packard model 5710A GC with a thermal conductivity detector and a Hewlett-Packard model 3390A integrator were used. This proved to be unreliable as reproducible results were not obtainable despite using several different columns (packings, lengths and tubing material), oven conditions and carrier gas (helium) flow rates.

Materials

The hydrogen sulphide was Matheson C.P grade (purity 99.6%, the balance being mostly propylene [0.27%] and propane [0.08%]). The H_2S was used without further purification. The water was first softened in an ion exchanger. It was further purified in a laboratory still. The purity of the water was checked by measuring its electrical conductivity using an Industrial Instruments Inc. conductivity bridge (model 16B1) and a Beckmann dip cell. The resistivity of the water was 4 MΩ·cm.

Certified standard solutions of iodine and sodium thiosulphate obtained from Fisher Scientific Co., were used for the iodometric titrations. The I_2 was 0.1000±0.0005 N and the thiosulphate was 0.1000±0.0002 N.

Observations

The measured L_A-L_S-V locus for the system H_2O-H_2S is presented in Table 3.1. The temperatures listed are accurate to about ±0.2°C and the pressures to ±0.02 MPa. The vapour pressure of H_2S is also listed because of its proximity to the L_A-L_S-V locus for this system. The vapour pressure was obtained from the correlation of Goodwin (1983). This information is plotted on Fig. 3.2. Table 3.2 lists the compositions of the co-existing phases along the LLV locus. Temperatures in this table are accurate to the nearest degree Celsius. At the lowest two temperatures, the determination of the water content of the vapour was not sufficiently accurate. Hence, the results are given as 99+% H_2S.

A critical locus extends from point K, the three-phase critical end point, to the critical point of H_2S. The point labelled Q is the L_A-L_S-H-V quadruple point. Below this temperature, the L_A-L_S-V equilibrium does not exist (except for unstable supercooling). The data obtained in this laboratory were correlated with a Clausius-Clapeyron-type equation to obtain the following:

Table 3.1 Experimental Data for the Three-Phase Locus for the System Water-Hydrogen Sulphide

Temp (°C)	Three-Phase Press (MPa)	Vapour Press of H_2S^* (MPa)
29.4 (Q)	2.23	2.25
30.7	2.29	2.31
39.6	2.80	2.83
43.4	3.05	3.08
49.7	3.50	3.52
59.8	4.25	4.33
62.2	4.45	4.53
74.4	5.58	5.71
78.2	5.97	6.12
80.2	6.20	6.34
86.5	6.86	7.09
90.8	7.46	7.64
97.1	8.17	8.50
99.9	8.59	8.91
101.2	8.74	(-)
103.8	9.06	(-)
104.1	9.09	(-)
104.8	9.25	(-)
105.1	9.24	(-)
105.5	9.30	(-)
106.2 (K)	9.39	(-)

Q - quadruple point
K - three-phase critical end point
* - Goodwin (1983) (above 100.3°C H_2S is supercritical)

Table 3.2 Compositions of Co-existing Phases Along the LLV Locus for the System Hydrogen Sulphide-Water

Temp. (°C)	Mole Fraction H_2S		
	Aqueous Liquid	H_2S-Rich Liquid	Vapour
40	0.0335	0.987	0.99+
60	0.0341	0.973	0.99+
80	0.0385	0.965	0.987
100	0.0440	0.951	0.975
105	0.0451	0.955	0.973

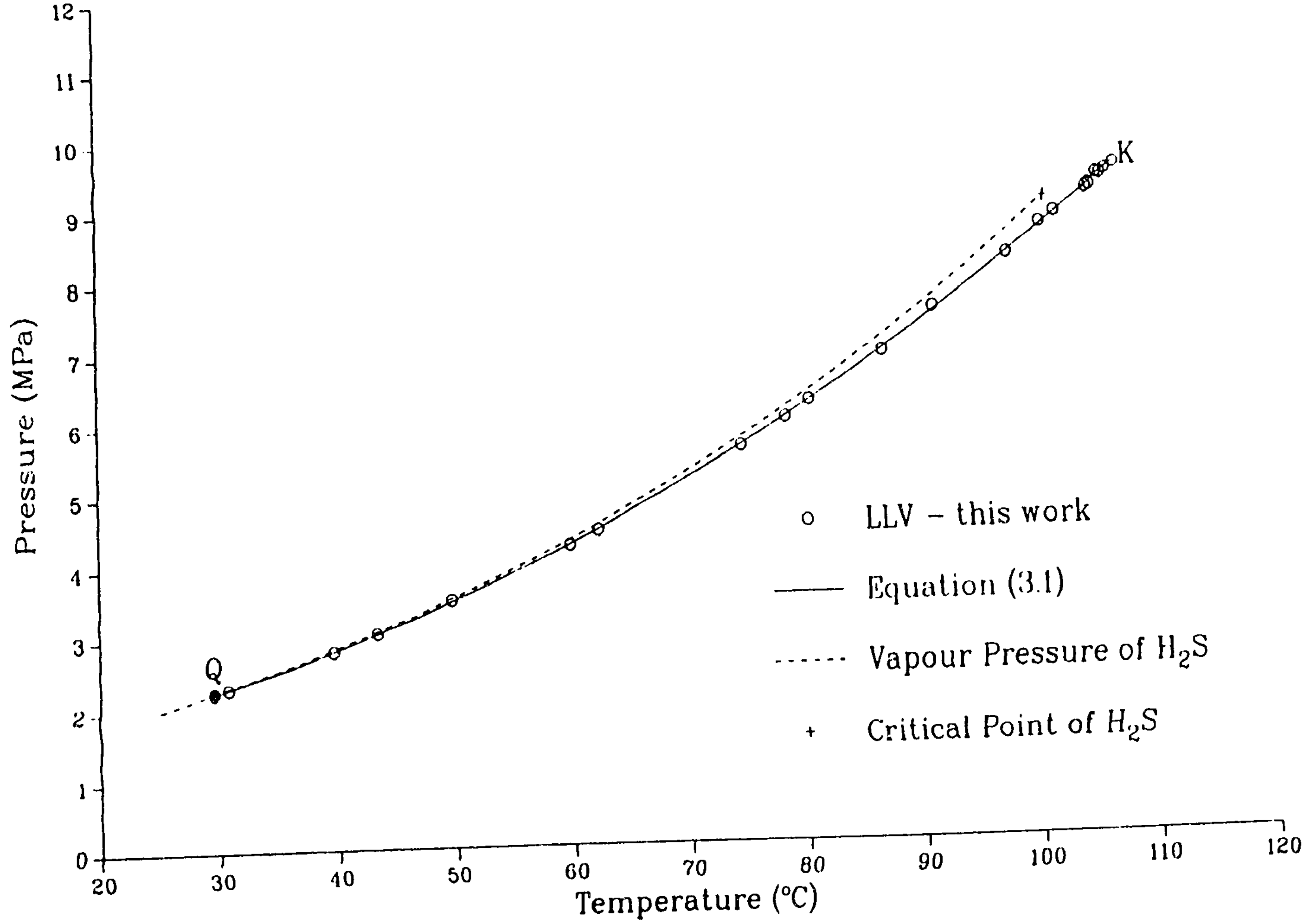

Fig. 3.2 The Liquid-Liquid-Vapour Locus for the System Water-Hydrogen Sulphide (Q - H-L_A-L_S-V Quadruple Point and K - Three-Phase Critical End Point)

$$\ln P = 7.928 - 2156.9/T \qquad (3.1)$$

where P is in MPa and T is in K. This equation fits the data with an average absolute error of 0.02 MPa and a maximum error of 0.06 MPa. The maximum error occurs at 90.8°C. Only the data obtained in this study were used to formulate Equation (3.1).

Equation (3.1) predicts the values obtained by Scheffer with a maximum error of 0.01 MPa. Between the quadruple point and about 45°C, there is essentially no difference between the smoothed values of Selleck et al. and Equation (3.1). For temperatures from 45° to about 93°C, the agreement is still quite good - an average error of 0.04 MPa and a maximum of 0.06 MPa. However, the smoothed values of Selleck et al. are at lower pressures than predicted by Equation (3.1). Above 93°C, the deviations are as large as 0.42 MPa.

At the lower temperatures, the aqueous phase was colourless to a pale yellow colour and the H_2S-rich phases were colourless. At approximately 106.2°C both the H_2S-rich liquid and the vapour became red-brown. This is the critical opalescence and indicative of the end point of the three-phase locus. At higher temperatures the H_2S-rich phase again becomes colourless. (Note, above the critical temperature there is only one H_2S-rich phase.) If one passes through the critical point rapidly (such as cooling the system by opening the door to the air bath) the H_2S-rich phases become opaque. This fixes the endpoint of the three-phase locus at 106.2 ± 0.2°C and 9.39 ± 0.02 MPa. This is approximately 6°C higher than reported by Selleck et al.; 100.2°C and 9.00 MPa. It appears that Selleck et al. believed that the L_A-L_S-V locus ends at the critical point of H_2S. Reamer et al. (1950), from the same laboratory as Selleck et al., reported the critical point of H_2S as 100.1°C and 9.005 MPa.

B. Hydrate Formation

A few points were obtained along the H-L_S-V and the H-L_A-V loci. These values are tabulated in Tables 3.3 and 3.4. Because of its proximity, the vapour pressure of H_2S is included with the tabulation of the H-L_S-V locus. This apparatus was not suited for examining solid phases. Mixing was difficult as the solids plugged the recirculation pump. Also, temperature control at near ambient conditions is very difficult and almost impossible at temperatures below about 25°C. These data are probably only accurate to about ±0.4°C and 0.05 MPa. In spite of the difficulties, the few values obtained were in good agreement with those reported by Scheffer. These points were measured to verify the location of the quadruple point. The estimated quadruple point is 29.4 ± 0.2°C and 2.23 ± 0.02 MPa which is in excellent agreement with the value reported by Scheffer (29.5°C and 2.24 MPa). Also, no compositions were measured in the hydrate regions. Finally, it was observed that the hydrates

Table 3.3 Measured L_S-H-V Locus
for the System Hydrogen Sulphide-Water

Temp (°C)	Three-Phase Press (MPa)	Vapour Press of H_2S* (MPa)
24.8	2.03	2.01
25.8	2.05	2.06
25.9	2.06	2.06
26.2	2.08	2.08
26.4	2.08	2.09
26.5	2.09	2.09
26.6	2.09	2.10
26.9	2.09	2.11
27.3	2.12	2.13
27.6	2.11	2.15
27.8	2.13	2.16
27.9	2.15	2.16
28.0	2.17	2.17
28.1	2.15	2.17
28.2	2.17	2.18
28.3	2.18	2.18
28.4	2.20	2.19
28.5	2.22	2.22
29.4	2.23	2.24

* - from Goodwin (1983)

Table 3.4 Measured L_A-H-V Locus for the System Hydrogen Sulphide-Water

Temp (°C)	Three-Phase Press (MPa)
25.5	1.61
25.6	1.62
25.8	1.71
25.9	1.68
26.1	1.70
26.3	1.70
26.6	1.75
26.7	1.77
26.9	1.81
27.1	1.85
27.2	1.87
27.6	1.97
27.7	2.07

were more dense than the aqueous phase as they settled to the bottom of the cell. No measurements of the density of the hydrates were made however.

A detailed discussion of the three-phase hydrate loci and the quality of the data presented in this work will be given in Chapter VII.

C. High Pressure Cell

A series of high pressure-high temperature experiments was also proposed. Equipment for such experiments was procured and assembled. Continuing problems hampered this aspect of the investigation. A detailed discussion of this apparatus and the problems with it are given in Appendix A.

D. Summary

New data were obtained for the L_A-L_S-V, L_A-H-V and L_S-H-V loci for the system hydrogen sulphide-water. The L_A-L_S-V locus is at slightly lower pressure than the vapour pressure of pure H_2S. It extends from the L_A-L_S-H-V quadruple point (29.4°C and 2.23 MPa) and to the three-phase critical end-point (106.2°C and 9.39 MPa). The L_A-L_S-V locus obtained here disagreed with those given by Selleck et al. (1952). Thus a re-evaluation of the work of Selleck et al. was conducted. This is the subject of the next chapter.

IV. Review of the Work of Selleck et al.

The L_A-L_S-V locus observed in this work was significantly different from that reported by Selleck et al. (1952). This prompted a thorough review of their data.

The raw data of Selleck et al. (1951) were collected by three methods: (1) essentially isochoric pressure-temperature measurements at constant composition, (2) isothermal pressure-volume measurements at constant composition (bubble point measurements) and (3) H_2S-rich phase compositions (both vapour and H_2S-rich liquid) at five temperatures and various pressures. Selleck et al. (1952) state that the errors associated with their measurements are as follows: (1) temperature: ±0.06°C (±0.1°F), (2) pressure: ±0.1% or 7 kPa (1 psi) whichever was greater, (3) volume: ±0.2% for the isochoric measurements and ±3% for the isothermal measurements and (4) composition: ±0.2 mol%.

A. Constant Volume Measurements

An essentially constant volume cell was used to find points along the various three-phase loci. The vessel was nearly spherical with a volume of about 950 cm^3 (0.0337 ft^3). The vessel was "blind"; that is, it had no windows to observe the contents. Thus visual confirmation of the number and nature of the phases was not possible. The pressure and temperature were measured and a discontinuity in the derivative of pressure with respect to temperature indicates a phase transition. Unfortunately, the criterion of a discontinuous derivative is difficult to apply to discrete experimental data.

In the manner that Selleck et al. present their data, it is difficult to make precise determinations. Consider the 0.0687 m^3/kg (1.10 ft^3/lb), 71.65 mol% H_2S isochore which is plotted on Fig. 4.1. From this plot, there is a dew point at about 125°C, but the precise location of this phase transition is difficult to establish. However, Selleck et al. seem to have been unconcerned with this dew point. There does not appear to be a phase transition at lower temperatures. However, this ischore intersects the L_A-H-V locus at about 20.6°C and 0.85 MPa. A possible explanation for this observation is supercooling. Thus the reported P-T values would be for a metastable equilibrium. Supercooling of about 5°C was observed in this study and reported in Chapter III. Almost 10°C of supercooling was reported by Scheffer (1913). Often some disturbance is required to initiate the formation of the solid phase. Again, it is important to note that Selleck et al. used a blind cell and were unable to observe the number of phases present. The 0.189 m^3/kg (3.03 ft^3/lb), 26. mol% H_2S; 0.132 m^3/kg (2.11 ft^3/lb), 69.91 mol% H_2S; and 0.0393 m^3/kg (0.63 ft^3/lb), 90.65 mol% H_2S also pass through the L_A-H-V locus without showing discontinuous derivatives. Only two of the six isochores that pass through the L_A-H-V locus show a discontinuity.

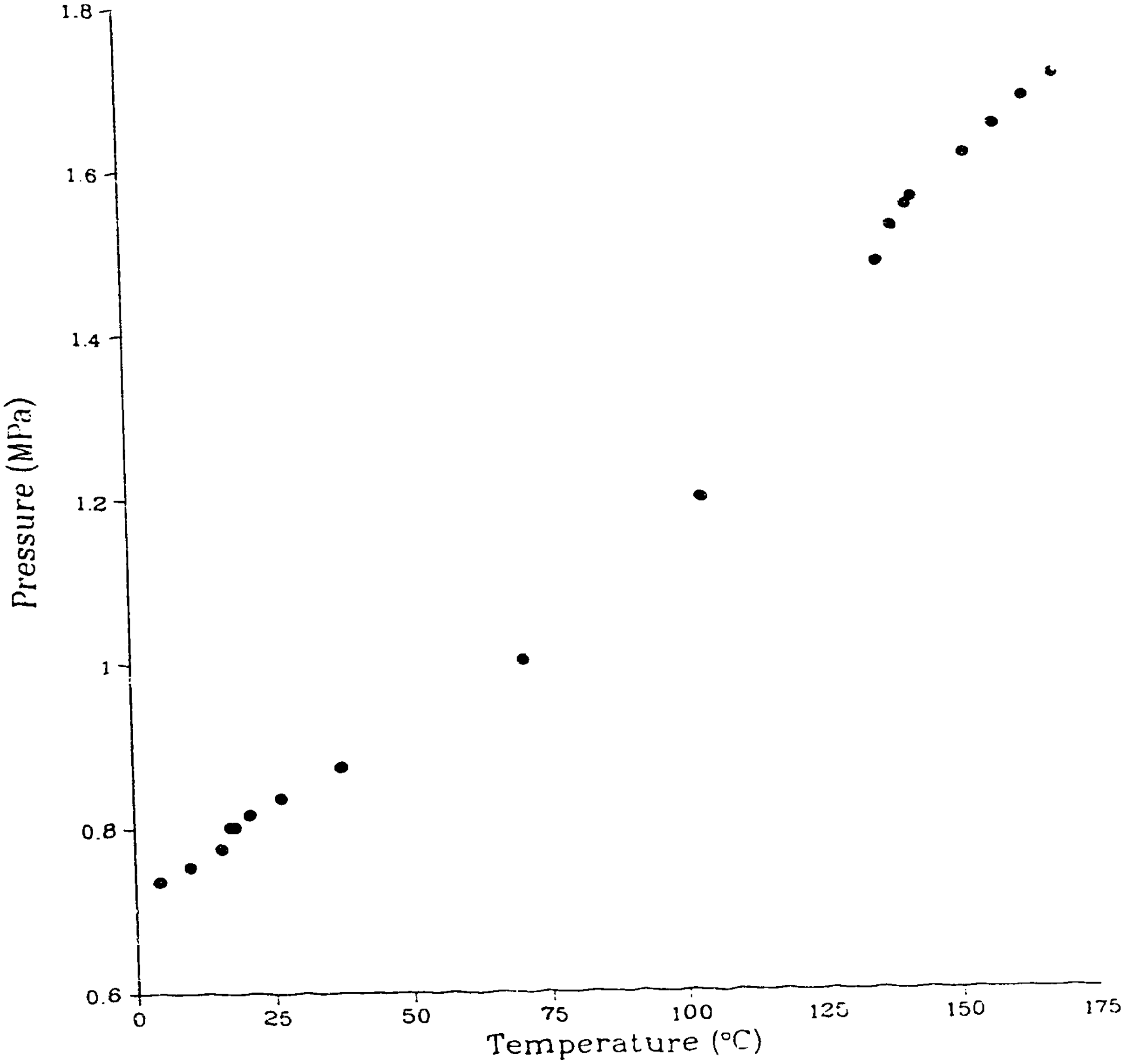

Fig. 4.1 Pressure-Temperature Diagram for a 71.65 mol % Hydrogen Sulphide Mixture at a Volume of 0.0687 m^3/kg

As demonstrated above, the direct interpretation of the isochoric data is difficult. But, with the aid of some of the figures provided by Selleck et al. (1952) it is possible to obtain pressure and temperature measurements along the L_S-L_A-V, L_A-H-V, L_S-H-V and L_A-L_S-H loci. Raw values are presented in Tables 4.1 through 4.4. Also included on these tables are values from the smoothed data from Selleck et al. and for the L_A-L_S-V locus, from Equation (3.1). Where necessary interpolations of the smoothed values were done using a natural spline (Gerald, 1978). The differences between the raw and the smoothed values are quite large; up to 0.24 MPa (35 psi) for the L_A-L_S-V, 0.04 MPa (6 psi) for the L_A-H-V 0.35 kPa (5 psi) for the L_A-H-V and 4.95 MPa (718 psi) for the L_A-L_S-H. Note, all are significantly larger than the 0.007 MPa or 0.1% stated by Selleck et al. Although Selleck et al. present a table of smoothed values along the H-I-V locus, they made no measurements there. These values are based on the work of Scheffer and co-workers.

B. Isothermal P-v Measurements

The raw data of Selleck et al. includes P-v measurements for 37.8°, 54.4°, 71.1°, 87.8°, 104.4°, 121.1°, 137.8°, 154.4° and 171.1°C (100°, 130°, 160°, 190°, 220°, 250°, 280°, 310° and 340°F) at 2.267, 4.351 and 5.723 mol% H_2S. However, Selleck et al. (1952) report only five isotherms in the paper containing the smoothed data.

Table 4.1 Points Along the L_S-L_A-V Locus for the System Hydrogen Sulphide-Water From Selleck et al. (1951,1952)

Temp (°C)	Pressure (MPa) Raw	Smooth	Eq'n (3.1)
32.2	2.425	2.380	2.376
37.8	2.742	2.690	2.695
48.9	3.469	3.403	3.424
48.9	3.397	3.403	3.424
54.4	3.855	3.810	3.835
60.0	4.277	4.251	4.280
60.0	4.245	4.251	4.280
65.6	4.718	4.727	4.760
76.7	6.021	5.776	5.827
82.2	6.340	6.351	6.416
87.8	6.989	6.986	7.045
87.8	7.014	6.986	7.045
93.3	7.694	7.697	7.71[illegible]
98.9	8.671	8.672	8.42[illegible]

Table 4.2 Points Along the L_A-H-V Locus for the System Hydrogen Sulphide-Water From Selleck et al. (1951,1952)

Temp (°C)	Pressure (kPa) Raw	Smooth
11.7	361	332
12.8	384	372
13.3	399	394
23.9	1206	1167
24.4	1262	1238

Table 4.3 Points Along the L_S-H-V Locus for the System Hydrogen Sulphide-Water From Selleck et al. (1951,1952)

Temp (°C)	Pressure (kPa) Raw	Smooth
4.4	1222	1202
4.4	1193	1202
4.4	1208	1202
6.1	1265	1258
7.8	1322	1315
9.4	1374	1373
10.0	1419	1393
11.1	1437	1434
12.8	1506	1497
21.1	1874	1839
26.7	2132	2097

Table 4.4 Points Along the L_S-L_A-H Locus for the System Hydrogen Sulphide-Water From Selleck et al. (1951,1952)

Temp (°C)	Pressure (MPa) Raw	Smooth
30.92	18.545	18.561
31.47	25.380	25.402
32.22	30.117	35.067

Two types of phase transitions were observed with the isothermal apparatus. The first of these is a bubble point. In this case the mixture is compressed from the $V-L_A$ region until no gas remains. This process is similar to the compression of a gas. Initially, small changes in the pressure have a large effect on the volume of the mixture. Once all of the gas is dissolved, the process becomes the compression of a liquid. This portion of the P-v curve is very steep. The second type of phase transition observed is a three-phase point. In this case, the mixture is compressed from the $V-L_A$ region until the L_S-dew point (a three-phase point) is reached. The mixture is compressed through the three-phase point until no gas remains. The compression of a two-component, three-phase mixture is both isothermal and isobaric as dictated by the phase rule. Finally, the liquid-liquid region is entered (a three-phase bubble point). Again, this is an essentially incompressible mixture. This entire process is analogous to the isothermal compression of a pure component from the vapour, through the two-phase region and into the liquid phase. (Note, there is no pure component analogue for the bubble point process.) The first and last stages of the three-phase process are similar to the two steps in the bubble point compression. The three-phase process is distinguished by the isobaric region.

Bubble Points

At temperatures below 104.4°C, only the leanest compositions have a bubble point. The rich mixtures would have three-phase points and these will be discussed later. At 104.4°C both the 2.267 and 4.351 mol% H_2S have bubble points. The 104.4°C and 5.723 mol% H_2S is a special case and will also be discussed separately. It was this isotherm that prompted the re-evaluation of all of the raw data of Selleck et al. Three methods were used to re-interpret the P-v bubble point data.

First, a graphical technique was used. Large graph paper was employed such that plots could be constructed on a grid that could be read to the nearest 0.04 MPa (5 psi) and 1.5×10^{-5} m^3/kg (2.5×10^{-4} ft^3/lb). Smooth curves were drawn through the points (a somewhat subjective procedure) and the intersections were determined. Table 4.5 lists the bubble points thus obtained. Also listed in this table are the bubble points that Selleck et al. (1952) obtained from the same data (as listed in Table V of their 1952 paper).

The second method was to approximate the derivatives of volume with repect to pressure using a forward differencing scheme

$$(\partial v/\partial P)_T \simeq (v_{i+1} - v_i)/(P_{i+1} - P_i) \qquad (4.1)$$

The derivatives were thus computed and the discontinuity interpreted - again a somewhat subjective approach. The data

Table 4.5 Summary of Bubble Points for the System Hydrogen Sulphide-Water

Temp (°C)	Mol% H_2S	Bubble Point (MPa)			
		Graphical	Derivative	Polytropic	Selleck[1]
37.8	2.267	1.79±0.08	2.14±0.32	1.80±0.05	1.88
71.1	2.267	2.93±0.08	3.35±0.35	2.98±0.09	3.05
104.4	2.267	4.00±0.08	4.23±0.23	4.03±0.12	4.07
137.8	2.267	4.90±0.08	5.21±0.33	4.91±0.15	4.96
171.1	2.267	5.72±0.08	6.14±0.39	5.78±0.17	5.80
87.8	4.351	7.05±0.08	7.49±0.28	7.08±0.21	–
104.4	4.351	8.59±0.08	8.89±0.23	8.38±0.25	8.12
137.8	4.351	9.90±0.08	10.61±0.68	9.60±0.29	9.78
171.1	4.351	10.31±0.08	10.65±0.42	10.33±0.31	10.34
121.1	5.723	11.79±0.08	11.51±0.04	11.74±0.35	–
137.8	5.723	12.20±0.08	12.67±0.21	11.87±0.36	12.38
154.4	5.723	12.34±0.08	12.40±0.11	12.38±0.37	–
171.1	5.723	12.60±0.08	12.52±0.17	12.24±0.37	13.00

1 - From Table V in Selleck et al. (1952)

are neither at equal intervals of pressure nor volume making the application of a higher order approximation of the derivative difficult. Table 4.5 also lists the bubble points obtained via this method. The pressures reported are the average of P_{i+1} and P_i where the discontinuity occurs and the range is $(P_{i+1} - P_i)/2$.

Finally, the process was modelled as a two stage process. First, the compression through the V-L_A region was treated as a polytropic process. Thus:

$$Pv^k = C \tag{4.2}$$

The liquid was treated as an incompressible fluid (constant density). For each isotherm k and C were obtained by a non-linear, least-squares fit. The density of the liquid was calculated by taking the average. Any points that were not clearly in either one region or the other were omitted - usually only one or two points per isotherm. These points were included in the subsequent analysis though. Also, some rogue points were eliminated. This procedure reproduced the experimental volumes to within 3% (the accuracy stated by Selleck et al.). Of the three methods, this is probably the most objective. Table 4.6 lists the parameters obtained from this model and Table 4.5 lists the bubble points thus obtained. The errors stated for the estimated bubble points are 3%.

Table 4.6 Summary of Polytropic Expansion–Incompressible Fluid Model of Bubble Points

Temp (°C)	Mole % H_2S	k (-)	c [kPa $(m^3/kg)^k$]	v_L (m^3/kg)
37.8	2.267	0.766	9.082	0.001 005
71.1	2.267	1.087	1.681	0.001 029
104.4	2.267	1.278	0.638 5	0.001 061
137.8	2.267	1.422	0.303 7	0.001 099
171.1	2.267	1.626	0.096 9	0.001 160
87.8	4.351	1.523	0.204 2	0.001 046
104.4	4.351	1.870	0.023 10	0.001 064
137.8	4.351	1.936	0.018 20	0.001 108
171.1	4.351	1.965	0.017 79	0.001 165
137.8	5.723	1.888	0.031 29	0.001 109
154.4	5.723	2.450	0.000 765	0.001 142
171.1	5.723	1.631	0.200 7	0.001 164

In spite of the differences between bubble points estimated by Selleck et al. (Table V in the 1952 paper, not the smoothed values in Table III) and those obtained in this analysis, the estimates of Selleck et al. will be used in the subsequent chapters. No major differences were observed between the values of this analysis and those reported by Selleck et al. However, the magnitude of the errors revealed in this interpretation should be heeded. The errors in these bubble points are of the order of 0.1 MPa although the errors in the measured pressures are reportedly only 0.07 MPa or 0.1%.

The 104.4°C Isotherm

The 104.4°C and 5.723 mol% H_2S is a special case. At this temperature, Selleck et al. did not believe that there was a three-phase point. This work shows that there is.

According to this work, there should be an isobaric region at 9.17 MPa. Selleck et al. report a bubble point at 10.34 MPa. The raw data are plotted on Fig. 4.2. From this plot two things are clear: (1) there appears to be no isobaric region and (2) the phase transition point is about 9.25 MPa (and not 10.34 MPa). The fact that there is no plateau can be explained as follows. If we return to the one-component analogy, this temperature is close to the critical point (a pseudo-reduced temperature of about 0.995). Thus the isobaric region is becoming very narrow. On the scale of these experiments, the data probably step over

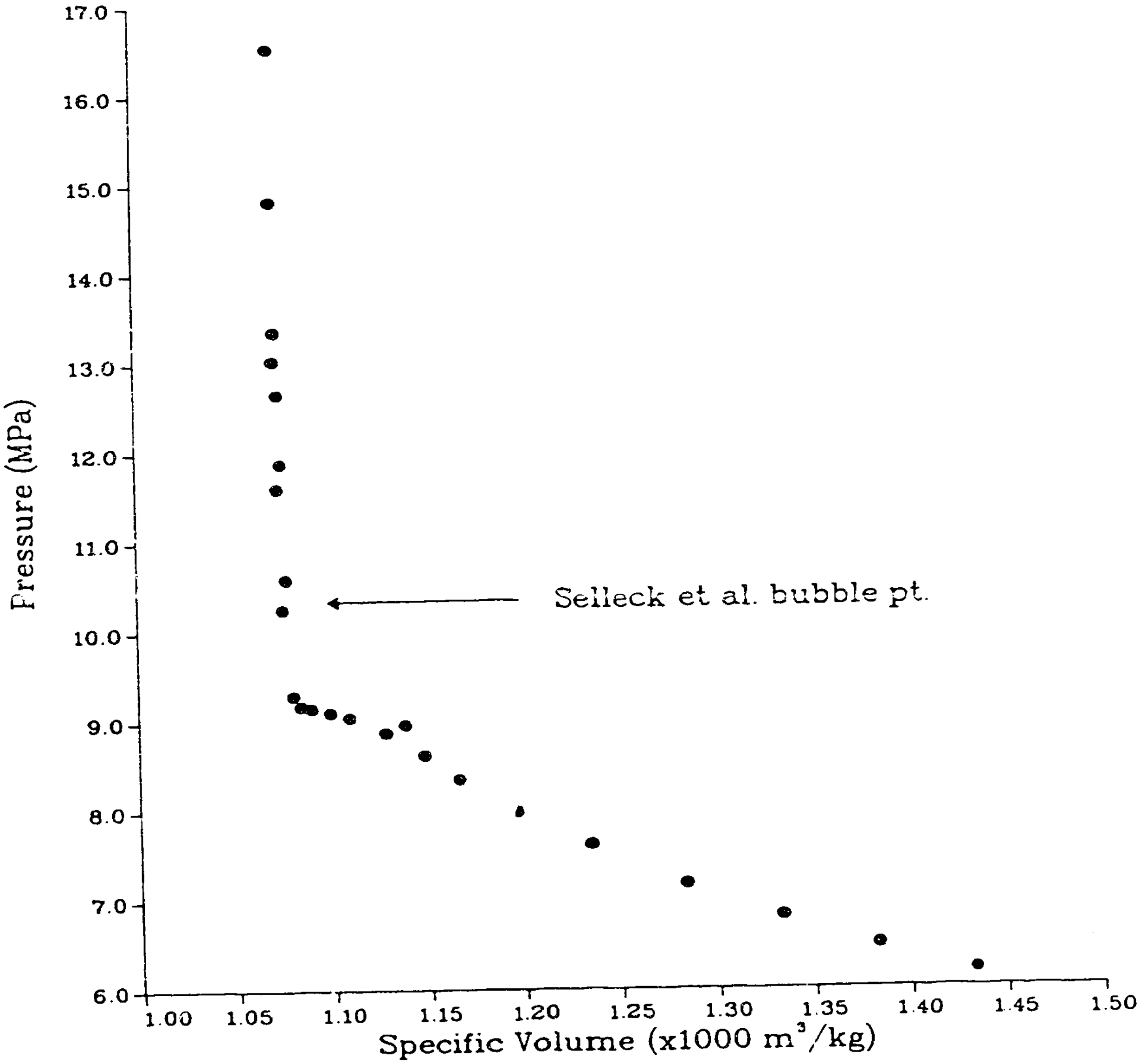

Fig. 4.2 Pressure-Volume Diagram at 104.4°C and 5.723 mol % Hydrogen Sulphide

the three-phase region, or perhaps a single point is in this region. If it is concluded that one point is in the L_A-L_S-V region, then the three-phase pressure is estimated to be 9.17±0.12 MPa. It is difficult to see how Selleck et al. obtained 10.34 MPa at this temperature. Using a similar experimental method Vogel (1971) found an L_A-L_S-V point at 104.4°C and 8.90±0.17 MPa. However, Vogel misinterpreted his result. From Equation (3.1), the three-phase pressure is 9.17 MPa - excellent agreement with the one-point hypothesis.

Three-Phase Points

Fig. 4.3 shows the P-v diagram for the 87.8°C, 5.723 mol% H_2S isotherm. The three regions are marked on this figure. The curves on this figure are the author's interpretation and not that of Selleck et al. This is a temperature where both Selleck et al. and this work indicate an L_S-L_A-V point. The raw data of Selleck et al. show that the pressure increases by about 0.12 MPa (16 psi) over the three-phase region. From their data it is estimated that the three-phase pressure is 6.95±0.06 MPa (1008±8 psia) and Equation (3.1) predicts 7.04 MPa. The value from the data of Selleck et al. was obtained by averaging the six points in the plateau region. Selleck et al. performed a replicate run at these conditions and this is shown on Fig. 4.4. Again the data indicate that the pressure increases over the L_A-L_S-V plateau (this time by 0.04 MPa [6 psi]). From the eleven

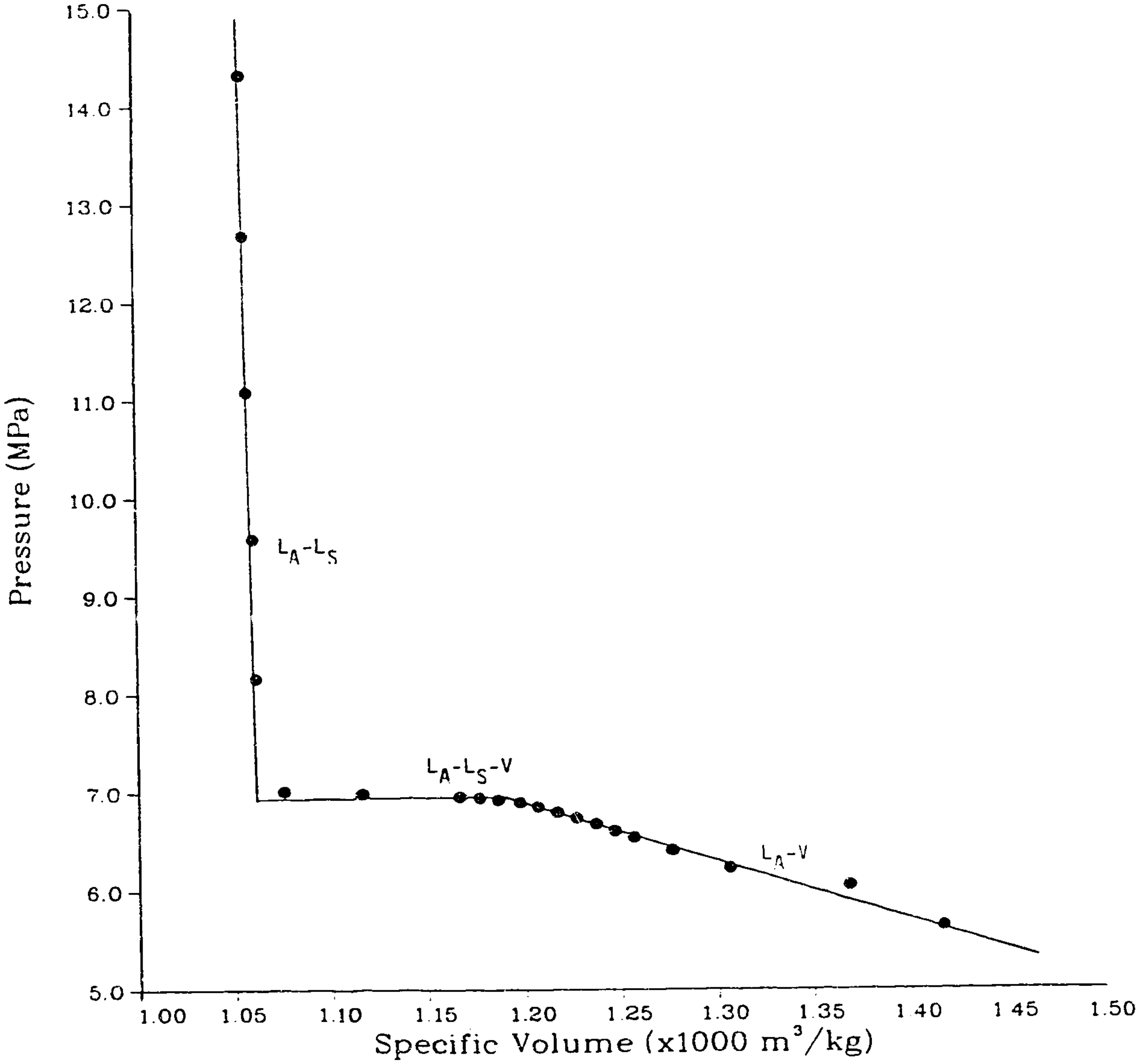

Fig. 4.3 Pressure-Volume Diagram at 87.8°C and 5.723 mol % Hydrogen Sulphide (Data Set #1)

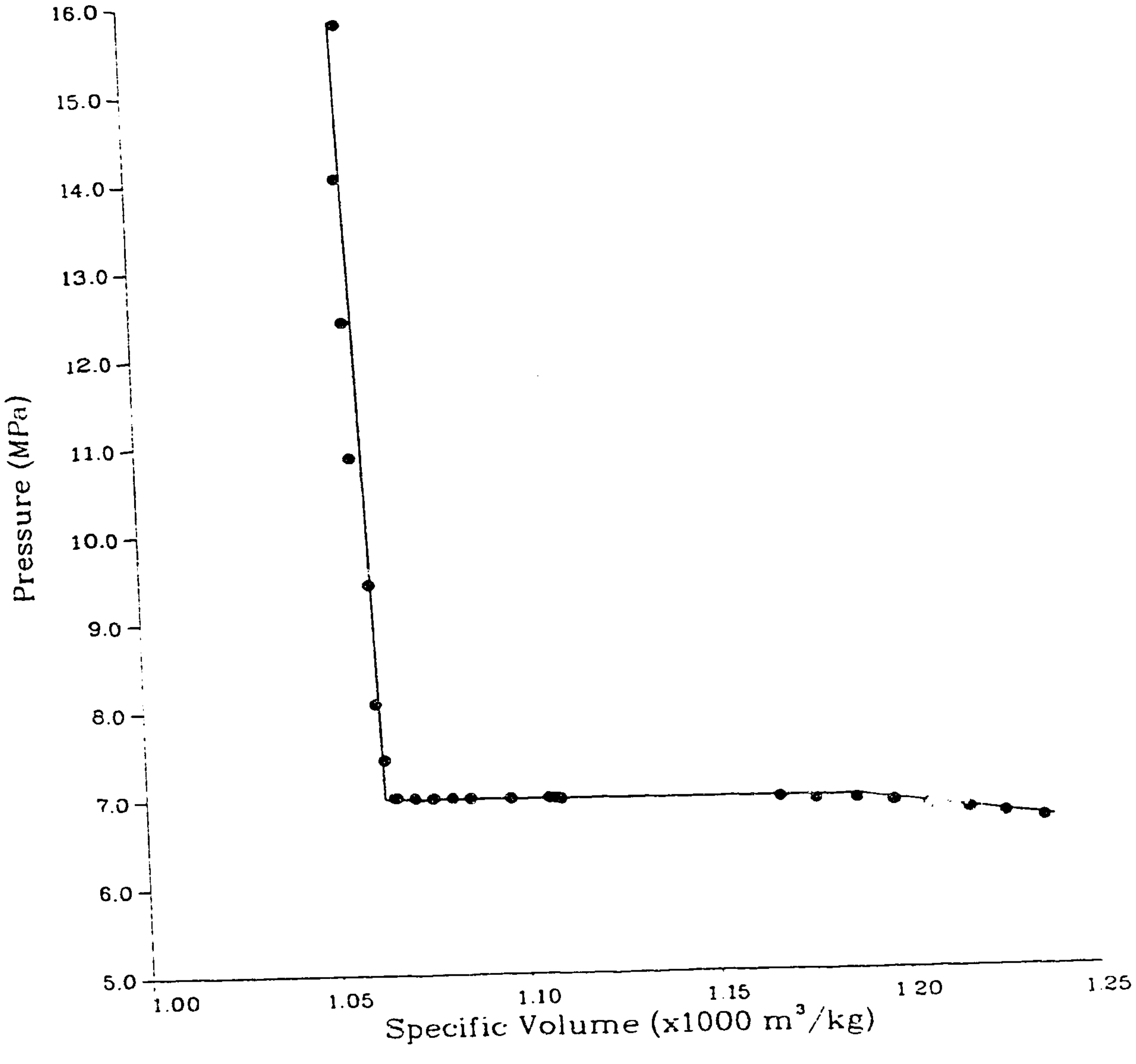

Fig. 4.4 Pressure-Volume Diagram at 87.8°C and 5.723 mol % Hydrogen Sulphide (Data Set #2)

points on the plateau, the three-phase pressure is estimated to be 6.99±0.02 MPa (1014±3 psia). Other isotherms in the three-phase region showed similar problems. The phase rule dictates that the pressure is constant for an isothermal compression of a two-component mixture existing in three phases. Two possible explanations for the observed increase in pressure are: (1) the points along the plateau are not at equilibrium or (2) there may be an impurity in the sample.

Table 4.7 lists three-phase points obtained in a similar fashion for the other conditions. The stated ranges were obtained in the manner described above. Also listed in this table are values from Equation (3.1) and from the smooth data of Selleck et al. (1952).

C. Hydrogen Sulphide-Rich Phase Compositions

The 1951 paper lists the actual compositions for the H_2S-rich phases (either vapour or H_2S-rich liquid) for five temperatures: 37.8°, 71.1°, 104.4°, 137.8° and 171.1°C and for several pressures. Table 4.8 lists the measured compositions along with interpolated values values from the smoothed data. Interpolations were performed using the natural spline and all the data at a given temperature. Since the smoothed data are indeed very smooth, the interpolation should not result in a significant error. The average error for all of the points was 0.40 mol% and the maximum error was 1.49 mol%.

Table 4.7 Liquid-Liquid-Vapour Points for the System Hydrogen Sulphide Water From the Isothermal Data of Selleck et al. (1951)

Temp	Mol%		Pressure (MPa)	
(°C)	H_2S	Estimate	Smooth	Eq'n (3.1)
37.8	4.351	2.72±0.07	2.69	2.70
54.4	4.351	3.86±0.06	3.81	3.84
71.1	4.351	5.28±0.05	5.24	5.27
37.8	5.723	2.70±0.02	2.69	2.70
87.8	5.723	6.95±0.06	6.99	7.04
87.8	5.723	6.99±0.02	6.99	7.04

Table 4.8 H_2S-Rich Phase Compositions for the System Hydrogen Sulphide-Water

Press	Mole Fraction Hydrogen Sulphide		
(MPa)	Raw	Smooth	$\lvert \Delta y \rvert$
t=37.8°C			
2.694	0.9958	0.9960	0.0002
4.171^{L}	0.9840	0.9841	0.0001
5.460^{L}	0.9824	0.9825	0.0001
t=71.1°C			
1.389	0.9692	0.9728	0.0036
1.632	0.9777	0.9761	0.0016
2.179	0.9837	0.9809	0.0036
2.422	0.9837	0.9823	0.0014
2.450	0.9798	0.9824	0.0026
2.677	0.9798	0.9834	0.0036
4.746	0.9889	0.9868	0.0021
5.234	0.9867	0.9869	0.0002
7.877^{L}	0.9685	0.9686	0.0001
8.819^{L}	0.9705	0.9705	0.0000
t=104.4°C			
2.388	0.9397	0.9388	0.0009
2.626	0.9412	0.9449	0.0037
4.044	0.9617	0.9594	0.0023
4.317	0.9632	0.9604	0.0028
5.671	0.9654	0.9651	0.0003
7.706	0.9694	0.9666	0.0028
8.648	0.9722	0.9665	0.0057
8.862	0.9733	0.9664	0.0069
19.640	0.9419	0.9475	0.0056
21.433	0.9367	0.9434	0.0067
31.894	0.9294	0.9181	0.0113

Table 4.8 continued

Press (MPa)	Mole Fraction Hydrogen Sulphide Raw	Smooth	|Δy|
t=137.8°C			
3.340	0.8816	0.8835	0.0037
3.574	0.8836	0.8892	0.0056
7.102	0.9315	0.9257	0.0058
7.146	0.9298	0.9259	0.0039
8.944	0.9191	0.9314	0.0123
10.283	0.9413	0.9330	0.0083
10.586	0.9412	0.9331	0.0081
14.176	0.9257	0.9295	0.0038
14.751	0.9236	0.9282	0.0046
15.050	0.9344	0.9275	0.0069
24.356	0.8913	0.8978	0.0065
25.215	0.8943	0.8949	0.0006
34.040	0.8794	0.8645	0.0149
t=171.1°C			
3.776	0.7573	0.7638	0.0065
7.898	0.8584	0.8581	0.0003
8.145	0.8563	0.8605	0.0042
9.015	0.8696	0.8675	0.0021
9.652	0.8647	0.8712	0.0065
19.276	0.8669	0.8668	0.0001
19.538	0.8667	0.8657	0.0010
29.278	0.8130	0.8156	0.0026
29.718	0.8140	0.8132	0.0008
34.733	0.7965	0.7851^{e}	0.0114
35.312	0.7865	0.7819^{e}	0.0041

L - L-L equilibrium
e - extrapolated

Fig. 4.5 shows the H_2S-rich phase compositions at 71.1°, 137.8° and 171.1°C. The 104.4°C isotherm was left off for clarity and because it will be discussed in more detail in Chapter V. The 37.8°C was also omitted because it consisted of only three points. The width of the points on this plot is about 0.25 mol%, the accuracy claimed by Selleck et al. Clearly their measurements of these compositions are not as accurate as they claim. Note, the strange behavior of the liquid-liquid curve at 71.1°C and approximately 14 MPa is the point where the smoothed data of Selleck et al. switch from four significant figures to three.

D. Smoothing/Extrapolations

The technique used by Selleck et al. to smooth/extrapolate the data is not stated. However, least squares regressions of x_{H2S} versus $y_{H2S} \cdot P$ yield straight lines. The correlation coefficients for the 37.8°, 71.1°, 104.4°, 137.8° and 171.1°C isotherms are 1.0000, 1.0000, 0.9839, 0.9933 and 0.9952 respectively. This assumes that the strict Henry's Law applies over this range of pressure. As will be shown in Chapter VI, the strict Henry's Law does <u>not</u> apply. Furthermore, from this approach, the intercept should equal the vapour pressure of pure water at the given temperature. Curiously, this is not the case.

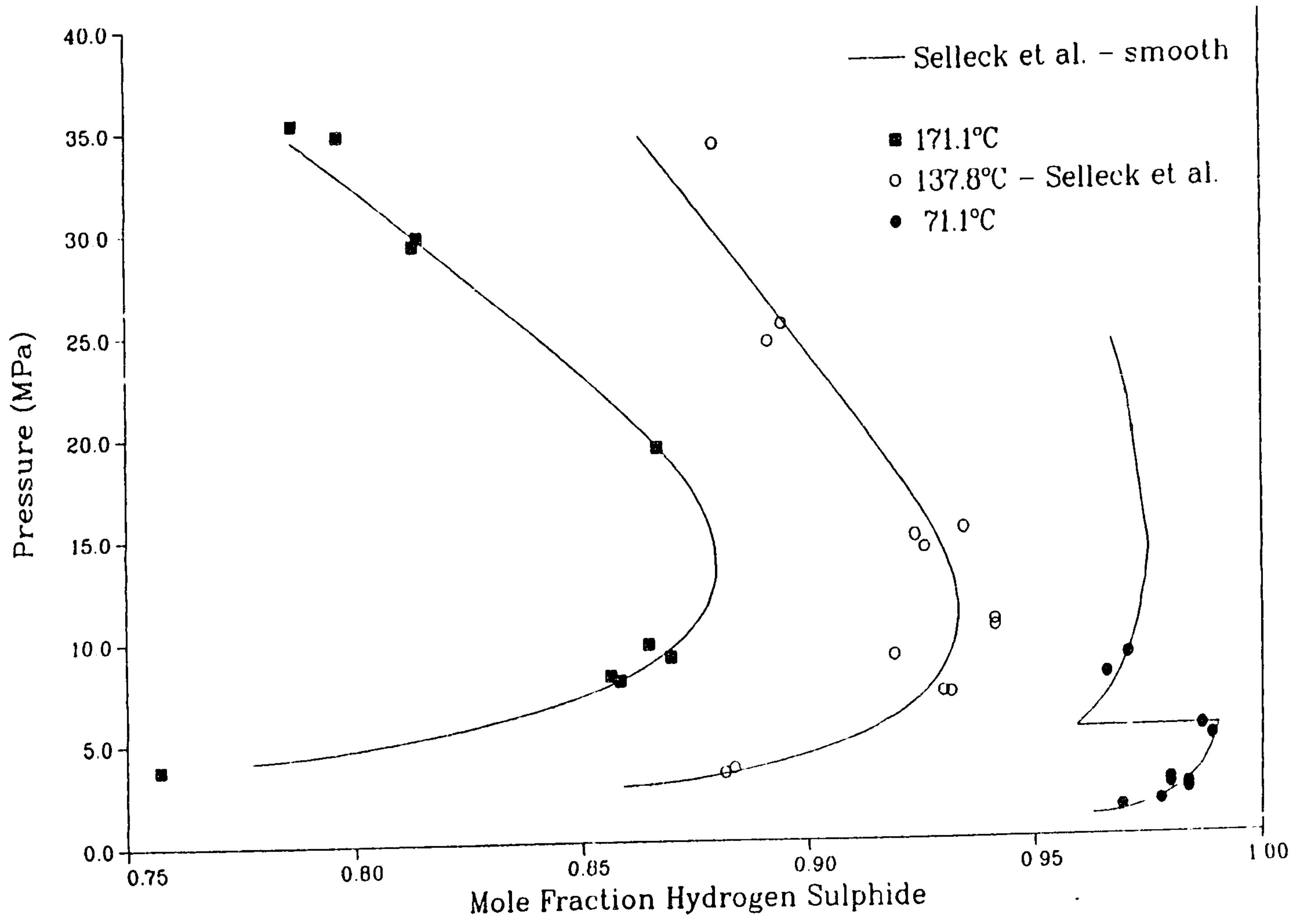

Fig. 4.5 H_2S-Rich Phase Composition from Selleck et al. (1951,1952) Showing Both the Raw and Smoothed Data

E. Summary

The purpose of this review was twofold. First, was it possible that the three-phase point at 104.4°C could be observed in the raw data of Selleck et al.? This analysis indicates that this indeed was the case. The second purpose was to see if there were any other problems with the data. The only other problem is that the data are not as accurate as Selleck et al. indicate.

The purpose of this review was not to discredit Selleck et al. Their raw data are valuable; but, their smoothed data are dubious. Any future reference to the work of Selleck et al. should use the raw and not the smoothed data (in particular, Table III in the 1952 paper should not be used). The data along the three-phase loci involving hydrates extracted from the raw data of Selleck et al. (Tables 4.2, 4.3 and 4.4) will be examined in more detail in Chapter VII. New correlations will be presented which replace Table I in the 1952 paper of Selleck et al.

V. Modelling With a Cubic Equation of State

Hydrogen sulphide-water is a system often associated with petroleum fluids. The usual method for modelling fluid phase equilibria in petroleum systems is using an equation of state. It is thus desirable to incorporated hydrogen sulphide-water into such a model. Cubic equations of state have gained wide acceptance in the process industry. The combination of robustness and accuracy makes them very attractive. Two equations have become very popular: (1) the Soave (1972) modification of the Redlich-Kwong (1949) equation (SRK) and (2) the Peng and Robinson (1976a) equation (PR). Since a large data base exists for these two equations it is highly desirable to use an equation and mixing rule compatible with either the SRK or the PR equation.

One of the major disadvantages of the SRK and PR equations is that they are not applicable to polar substances such as water. The exclusion of water was particularly important since water is often associated with petroleum fluids. A prerequisite for accurate multicomponent vapour-liquid equilibrium calculations is the accurate correlation of the pure component vapour pressure. As discussed in Appendix B, many modifications of these equations have been proposed to make them more widely

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A portion of this chapter has been published. Carroll, J.J. and Mather, A.E., "Phase Equilibrium in the System Water-Hydrogen Sulphide: Modelling the Phase Behavior With an Equation of State", Can. J. Chem. Eng., 67, 999-1003, (1989).

applicable.

A. Peng-Robinson-Stryjek-Vera Equation

Peng and Robinson (1976a) proposed the following equation

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) + b(v-b)} \tag{5.1}$$

The constants **a** and **b** are obtained from the inflection of the critical isotherm at the critical point. The temperature dependence of the a was obtained by fitting the pure component vapour pressure. The co-volume, **b**, was assumed to be a constant for a given substance.

$$a(T) = a(T_c)\cdot\alpha \tag{5.2}$$

$$a(T_c) = 0.45724\ R^2T_c^2/P_c \tag{5.3}$$

$$\alpha = [1 + \kappa(1 - T_R^{1/2})]^2 \tag{5.4}$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{5.5}$$

$$b = 0.07780\ RT_c/P_c \tag{5.6}$$

$$z_c = 0.3074 \tag{5.7}$$

The critical compressibility for this equation is larger than the experimental values for most substances. However, this equation worked very well for light hydrocarbons, a few associated non-hydrocarbons (hydrogen sulphide, carbon dioxide, carbon monoxide and nitrogen for example) and mixtures of these substances. It does not work as well for water and aqueous systems. This equation does not accurately predict the vapour pressure of water. This is true for the SRK equation as well.

Stryjek and Vera (1986a) proposed the following modification of the Peng-Robinson (PRSV) equation for use with both polar and non-polar substances.

$$\kappa = \kappa_0 + \kappa_1(1 + T_R^{1/2})(0.7 - T_R) \tag{5.8}$$

where

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.019655\omega^3 \tag{5.9}$$

and κ_1 is a empirical parameter and was obtained by fitting the pure component vapour pressure and was found to be uncorrelated with any pure component property, even for hydrocarbons. Even for nonpolar compounds $\kappa_1 \neq 0$. For example $\kappa_1 = -0.00159$ for methane. For most substances, excluding water and alcohols, better results were obtained for $T_R > 0.7$ using $\kappa_1 = 0$ and for all substances in the supercritical region they recommend using $\kappa_1 = 0$.

To apply an equation of state to a mixture, a set of mixing rules is required. For a, a geometric mean is used and frequently an empirical parameter is included.

$$a = \sum_i\sum_j x_i x_j \, (a_i a_j)^{1/2}(1 - \delta_{ij}) \tag{5.10}$$

The value of δ_{ij} is obtained from experimental data, usually vapour-liquid equilibrium and $\delta_{ij} = \delta_{ji}$. For **b**, the arithmetic mean is used.

$$b = \sum_i x_i b_i \tag{5.11}$$

Ternary and higher order interactions are usually neglected. Many new mixing rules have been proposed in order to make cubic equations more widely applicable. A thorough discussion of mixing rules is included in Appendix B.

Table 5.1 lists the parameters used in this work. Hydrogen sulphide was not included in the list of substances given by Stryjek and Vera, so κ_1 for H_2S was obtained by fitting the vapour pressure data given by Goodwin (1983). As with water, the κ_1 for H_2S was <u>not</u> set equal to zero in the region $0.7 < T_R < 1$, but it was set equal to zero for $T_R > 1$. Subsequently, Proust and Vera (1989) published an additional set of parameters which included hydrogen sulphide and was slightly different from that given here. However, the values given above in Table 5.1 above were used throughout this study. Methanethiol was not included in either Stryjek and Vera or Proust and Vera. Vapour pressure data for this mercaptan were taken from Berthoud and Brum (1924) and Russell et al. (1942).

The PRSV equation was used to correlate $V\text{-}L_A$, $L_S\text{-}L_A$ and $L_S\text{-}L_A\text{-}V$ equilibria for this system. There have been other

Table 5.1 Parameters for the PRSV Equation of State

Comp	T_c(K)	P_c(kPa)	ω(-)	κ_1(-)
H_2O	647.3	22090.	0.3440	-0.06635
H_2S	373.4	8960.	0.1000	0.15981
CH_3OH	512.6	8096.	0.5653	-0.16816
CH_3SH	470.0	7235.	0.1491	0.05060
N_2	126.2	3400.	0.0373	0.01996

attempts to correlate the phase behavior of the system H_2O-H_2S using an equation of state. Two noteworthy examples are Evelein et al. (1976) and Peng and Robinson (1980). These works were among the first to accurately correlate the fluid phase equilibria for aqueous systems with a cubic equation of state including LLV equilibria. Although both of these studies were important contributions to the study of the system H_2S-H_2O, they were were impaired by their reliance on the smoothed data of Selleck et al. (1952). The model presented in this chapter is not dependent on the interpretation of Selleck et al. and this model incorporates data from other sources as well.

B. Low Temperature Region

An initial series of calculations was performed in the low temperature region ($t <$ 200°C). Calculations in this region include $V-L_A$, L_A-L_S and L_A-L_S-V equilibria.

Interaction Parameter Evaluation

Initially, the original mixing rules were examined. Optimum interaction parameters were obtained by minimizing the error in the predicted bubble-point pressure from the data of Wright and Maass (1932a,b) Selleck et al. (1951), Clarke and Glew (1971), Lee and Mather (1977) and Gillespie et al. (1984). These interaction parameters are plotted on Fig. 5.1. A least squares regression was performed to obtain the following correlation:

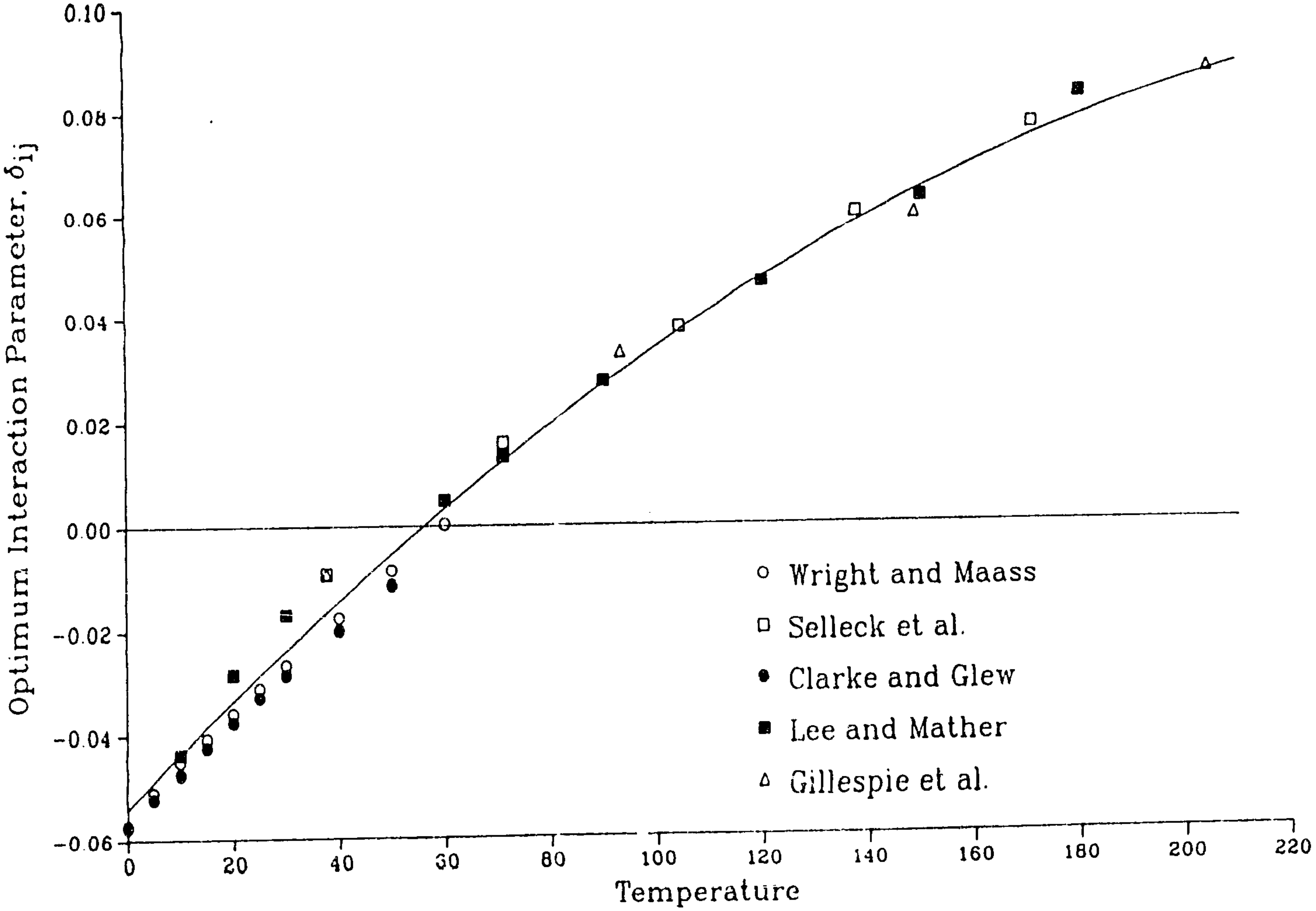


Fig. 5.1 Optimum Interaction Parameters for the System Hydrogen Sulphide-Water Using the Original Mixing Rule

$$\delta_{ij} = 0.2874 - 94.439/T \quad (5.12)$$

Unlike petroleum systems where the interaction parameter is nearly a constant for a given system, the interaction parameter for this system shows a strong temperature dependence. A more subtle effect is the composition dependence. Below 60°C there is a definite trend - the parameter from the Lee and Mather data is greater than that from Wright and Maass which in turn is greater than Clarke and Glew. This is the order of increasing H_2S concentration in the aqueous phase. Above 60°C, the scatter about the regression is more random and could probably be explained in terms of experimental error. Thus a more advanced mixing rule is required.

A mixing rule was proposed by Stryjek and Vera (1986b) which incorporates a composition effect, the van Laar-type rule, was used (see Appendix B). Optimum interaction parameters were obtained from the raw data of Selleck et al. (1951) and Gillespie et al. (1984). These parameters are presented in Table 5.2 where component 1 is water. In this case both $V-L_A$ and L_A-L_S equilibria data were considered. The optimization was conducted by minimizing the error for both the H_2S-rich and aqueous phases. A least squares regression yields

$$k_{12} = 0.819 - 0.00159\ T \quad (5.13)$$

Table 5.2 Optimum Interaction Parameters for the System Hydrogen Sulphide-Water

Temp. (°C)	Original Rule δ_{12}	van Laar-type k_{12}	van Laar-type k_{21}	REF
71.1	0.0159	0.301	0.017	1
71.1	-	0.300	0.017	2
93.3	0.0333	0.226	0.032	2
98.9	-	0.206	0.035	2
100.4	-	0.211	0.037	2
104.4	0.0379	0.188	0.035	1
137.8	0.0598	0.155	0.035	1
148.9	0.0596	0.153	0.059	2
171.1	0.0767	0.102	0.074	1
204.4	0.0872	0.082	0.099	2

1 - Selleck et al. (1951).
2 - Gillespie et al. (1984).

$$k_{21} = -0.190 + 0.000605\ T \tag{5.14}$$

Unfortunately the parameters are also a function of temperature. Also, the form of van Laar-type mixing rule requires that k_{12} and k_{21} have the same sign. Thus Equations (5.13) and (5.14) are limited to the range $315 < T < 513$ K ($42° < t < 240°$C).

Equilibrium Calculations

First consider the 104.4°C isotherm. Fig. 5.2 shows the pressure-composition diagram at this temperature. Included on this plot are the raw data of Selleck et al. (1951), the data of Vogel (1971), the smoothed values of Selleck et al. (1952) and the prediction based on the PRSV equation with the van Laar-type mixing rule using the optimum interaction parameters listed in Table 5.2. The insert on Fig. 5.2 shows schematically the equilibria in the region of the binary critical point. The insert is not drawn to scale. The smoothing of Selleck et al. indicates that they did not believe that this three-phase point existed. Vogel observed the formation of three phases at this temperature, but, as discussed in Chapter II, he misinterpreted his results. The experimental work given in Chapter III confirms the existence of the L_A-L_S-V point at this temperature. The fit of the raw data of Selleck et al. for this temperature using the PRSV equation is quite good with the exception of one point. As noted in Chapter IV, the interpretation of Selleck

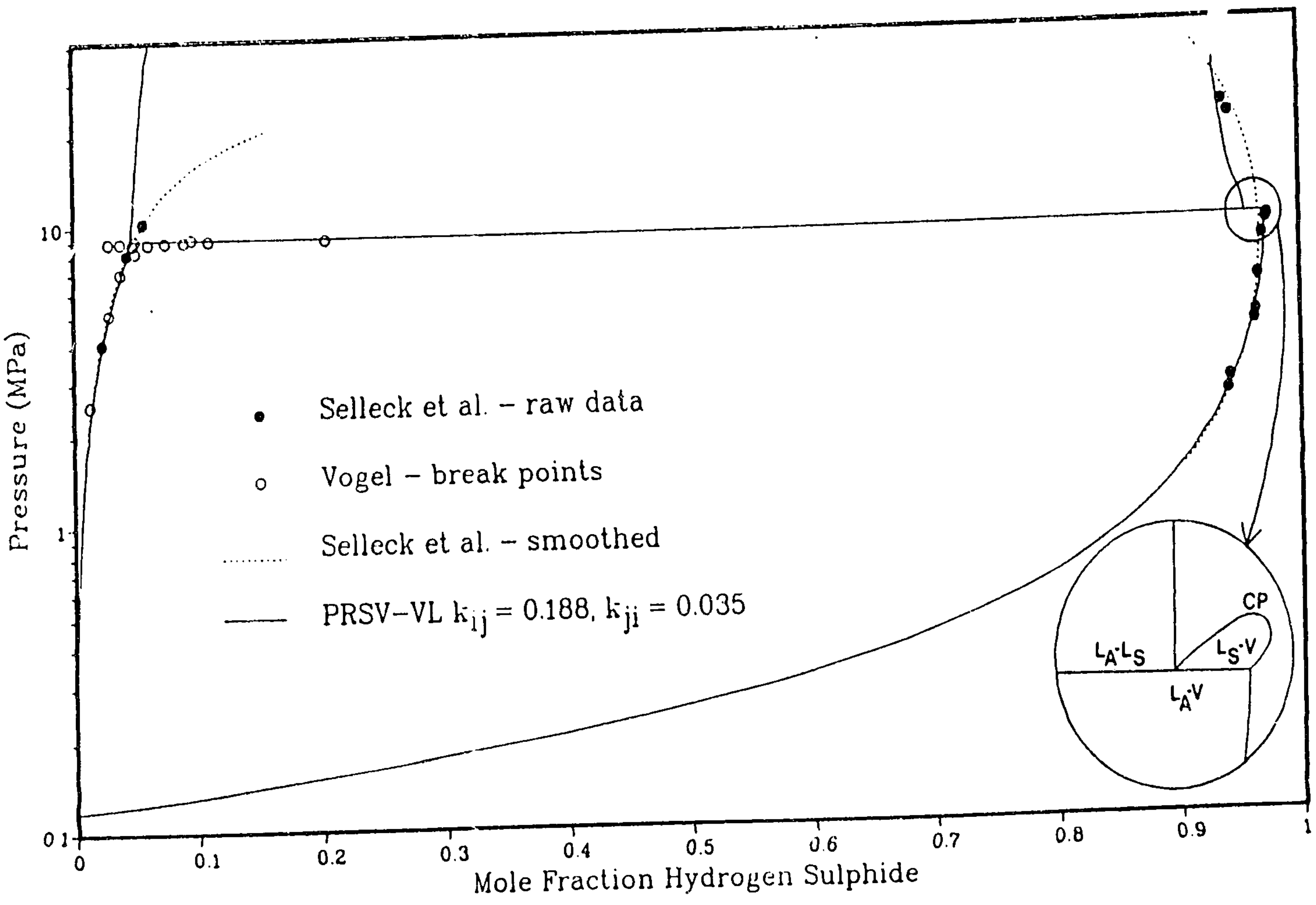


Fig. 5.2 Pressure-Composition Diagram at 104.4°C for the System Hydrogen Sulphide-Water

et al. for the 5.723 mol% H_2S bubble point is incorrect at this temperature. From this work, the three-phase pressure at 104.4°C is estimated to be 9.16 MPa. This is in reasonable agreement with the value estimated in Chapter IV from the Selleck et al. data. Thus, all of the raw data of Selleck et al. at 104.4°C fit the interpretation presented here. The major consequence of this model is that the extrapolated aqueous phase compositions of Selleck et al. are too rich in H_2S by perhaps a factor of three.

Figs. 5.3 and 5.4 show the 71.1°, 137.8° and 171.1°C isotherms. These are the pressure-composition diagrams for these temperatures, but they have been separated for clarity. Aqueous phase compositions are on Fig. 5.4 and H_2S-rich on Fig. 5.3. Although presented separately, these curves were generated simultaneously. Predictions using the PRSV equation were performed using the optimum interaction parameters listed in Table 5.2 and not the correlations. Included on these figures are the L_A-L_S equilibrium data of Gillespie et al. for the 71.1°C isotherm and the solubility data of Lee and Mather (1977) at 71°C. At 71.1°C Selleck et al. measured only a single bubble point. In general, the equation of state fits the raw data as well as the smoothing of Selleck et al., but the extrapolations of the aqueous phase compositions to higher pressures deviate significantly.

Figs. 5.5 and 5.6 show the PRSV predictions for the 93.3°, 148.9° and 204.4°C isotherms along with the data of

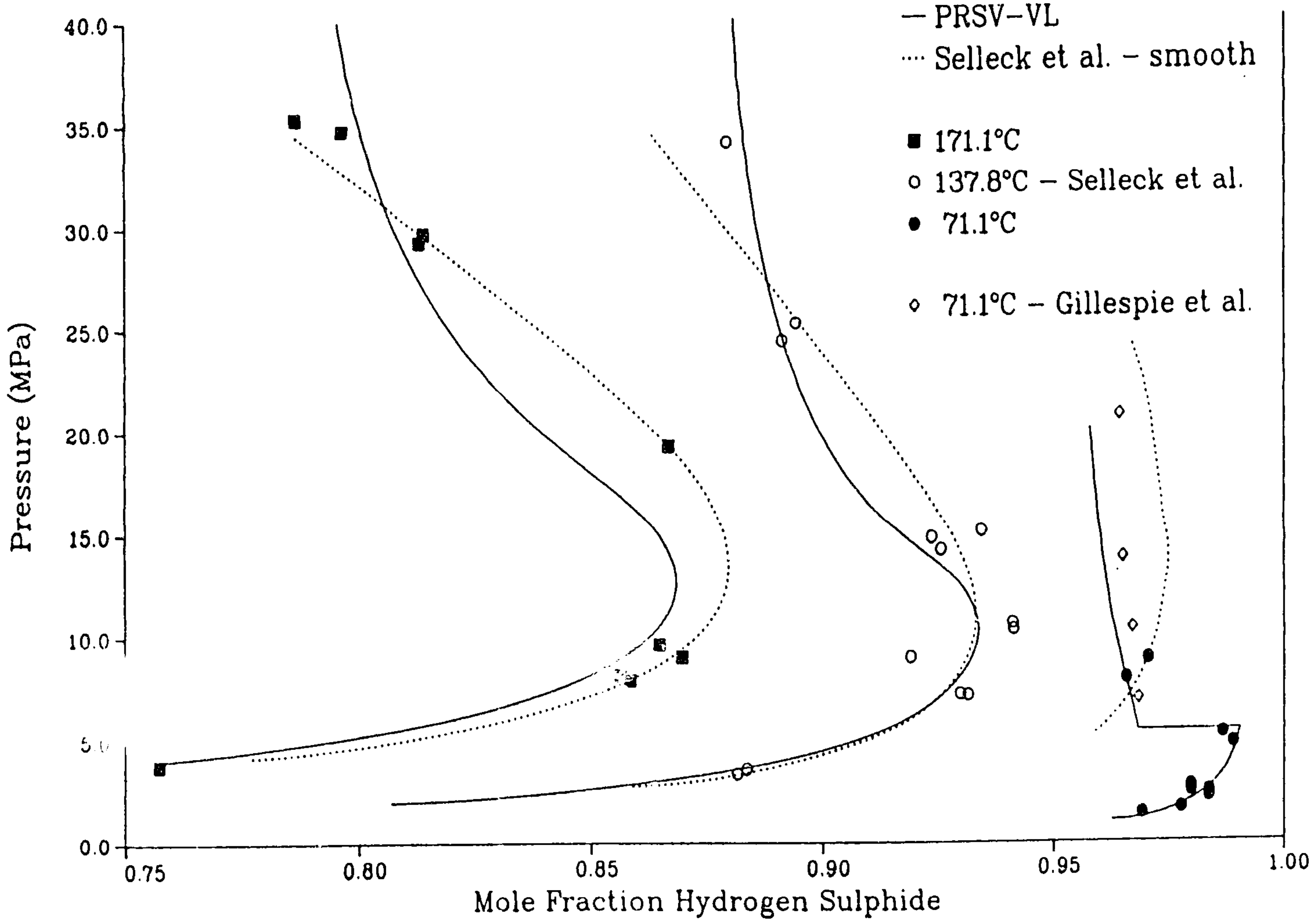


Fig.5.3 Vapour Phase Compositions at 71.1°, 137.8° and 171.1°C for the System Hydrogen Sulphide-Water

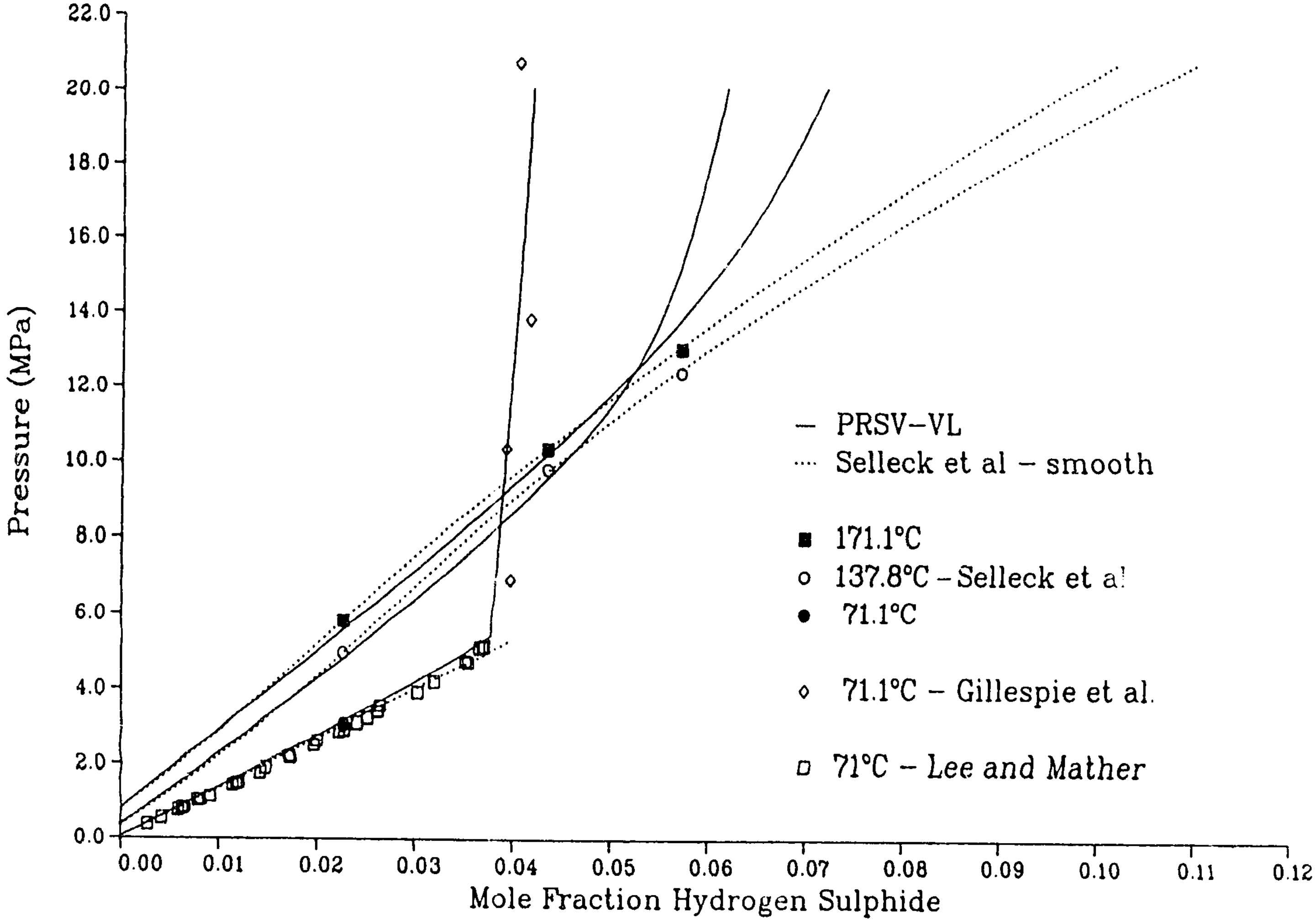


Fig.5.4 Liquid Phase Compositions at 71.1°, 137.8° and 171.1°C for the System Hydrogen Sulphide-Water

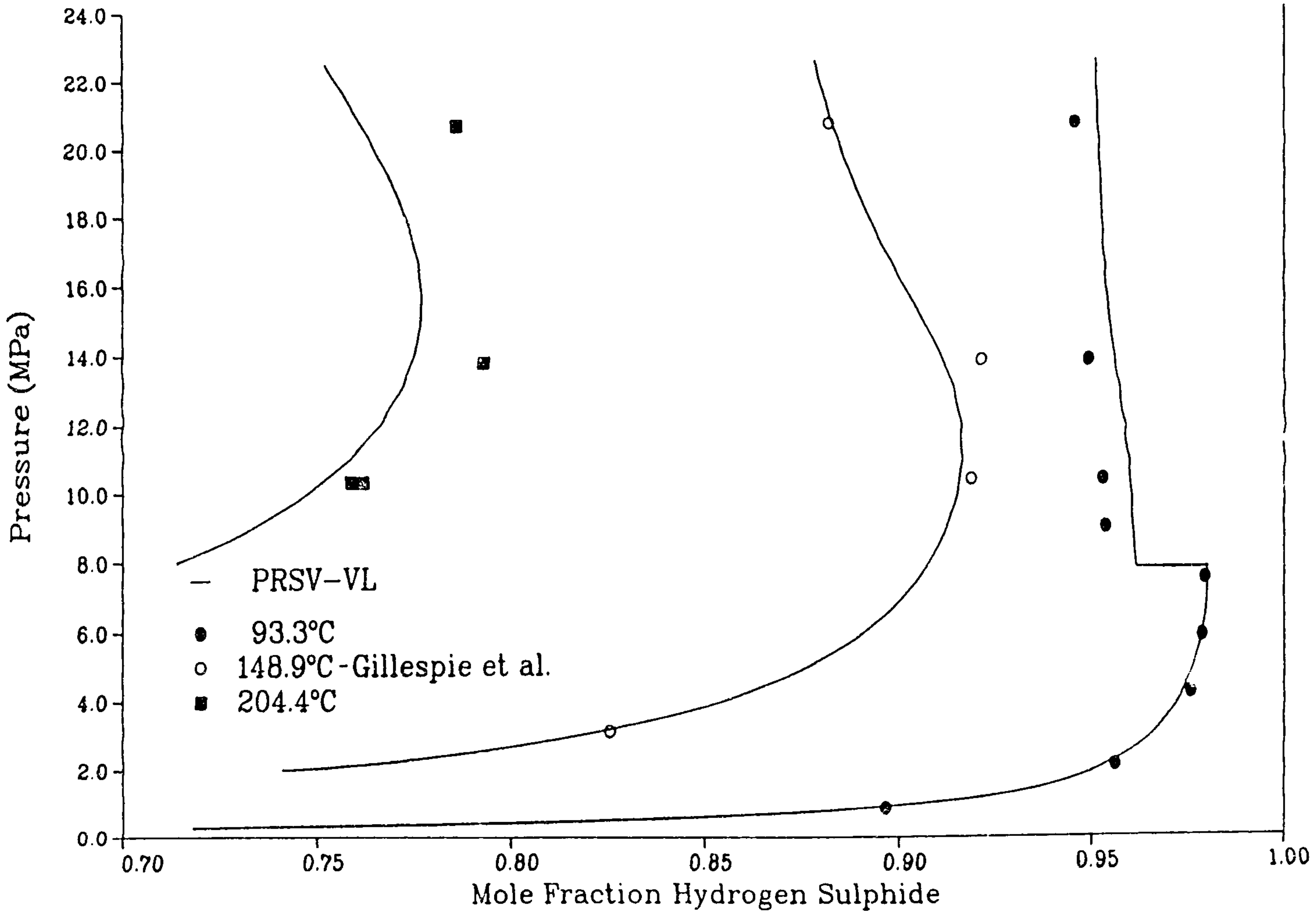


Fig.5.5 Vapour Phase Compositions at 93.3°, 148.9° and 204.4°C for the System Hydrogen Sulphide-Water

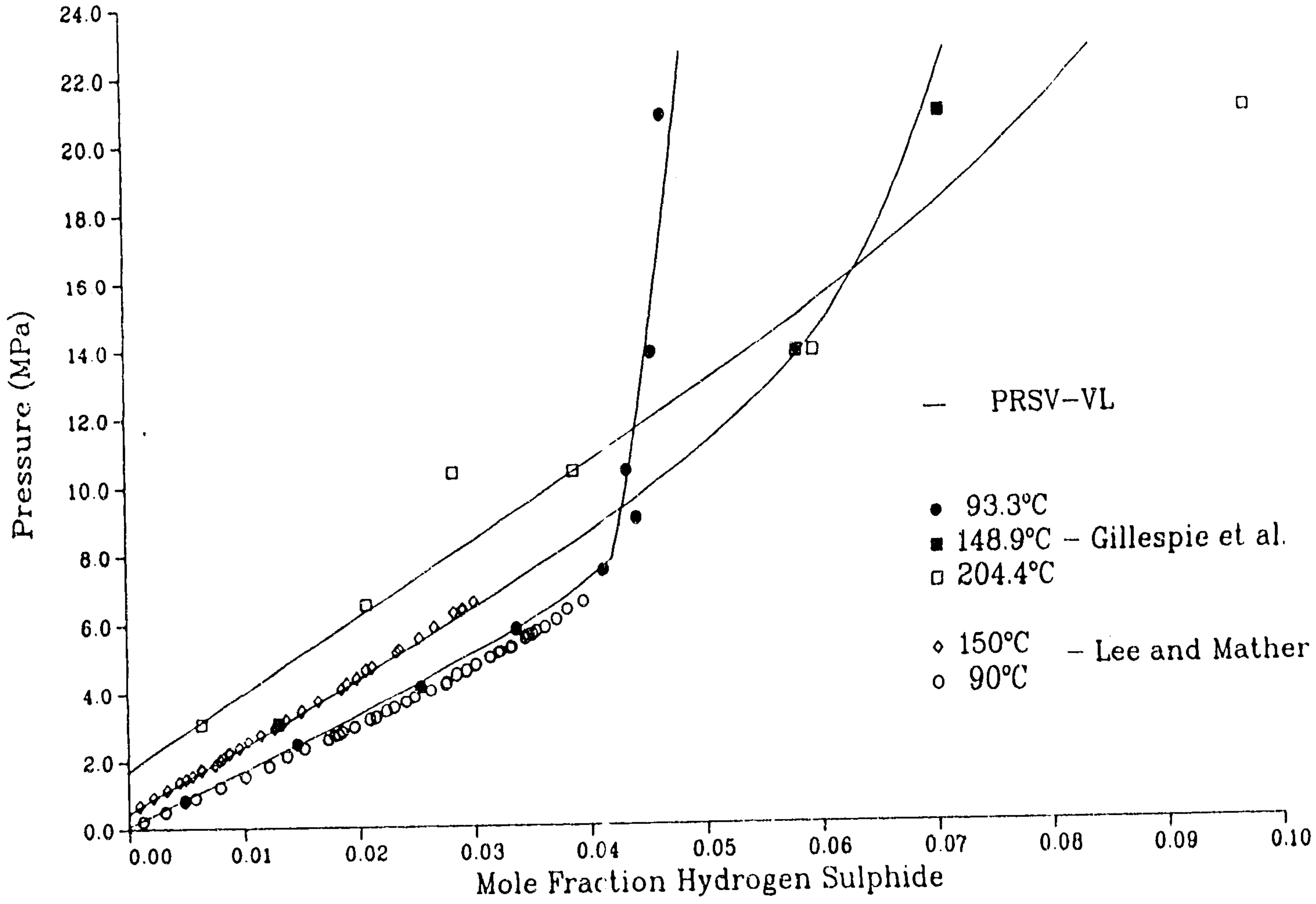


Fig.5.6 Liquid Phase Compositions at 93.3°, 148.9° and 204.4°C for the System Hydrogen Sulphide-Water

Gillespie et al. (1984). Once again, the aqueous and H_2S-rich phases are presented separately. Also shown on the aqueous phase plot are the 90° and 150°C isotherms of Lee and Mather. The fit of the lower two temperatures is excellent. Also, the agreement between the Lee and Mather data and the prediction is quite good considering that the interaction parameters at these temperatures were based solely on the Gillespie et al. data. The fit of the 204.4°C isotherm is not quite as good. This can be partially explained by the scatter in the experimental data. At 10.34 MPa Gillespie et al. report bubble points at both 3.87 and 2.83 mol% H_2S - a significant difference.

Predictions for the L_A-L_S equilibrium are quantitatively not as good as the V-L_A equilibrium, but they provide a good qualitative interpretation. The L_A-L_S equilibrium predictions show a weak pressure dependence, unlike the smoothing of Selleck et al. This is true for the temperatures which are not shown on the previously mentioned figures.

Finally, the effect of the mixing rule will be demonstrated. Fig. 5.7 shows a predicted pressure-composition diagram at 104.4°C for the original mixing rule with $\delta_{ij} = 0$ and $\delta_{ij} = 0.13$ and the van Laar-type rule with $k_{12} = 0.188$ and $k_{21} = 0.035$. First, consider the original mixing rule. As a first approximation, one would assume $\delta_{ij} = 0$. This procedure adequately fits the dew point locus, but it overestimates the H_2S solubility and the water content of

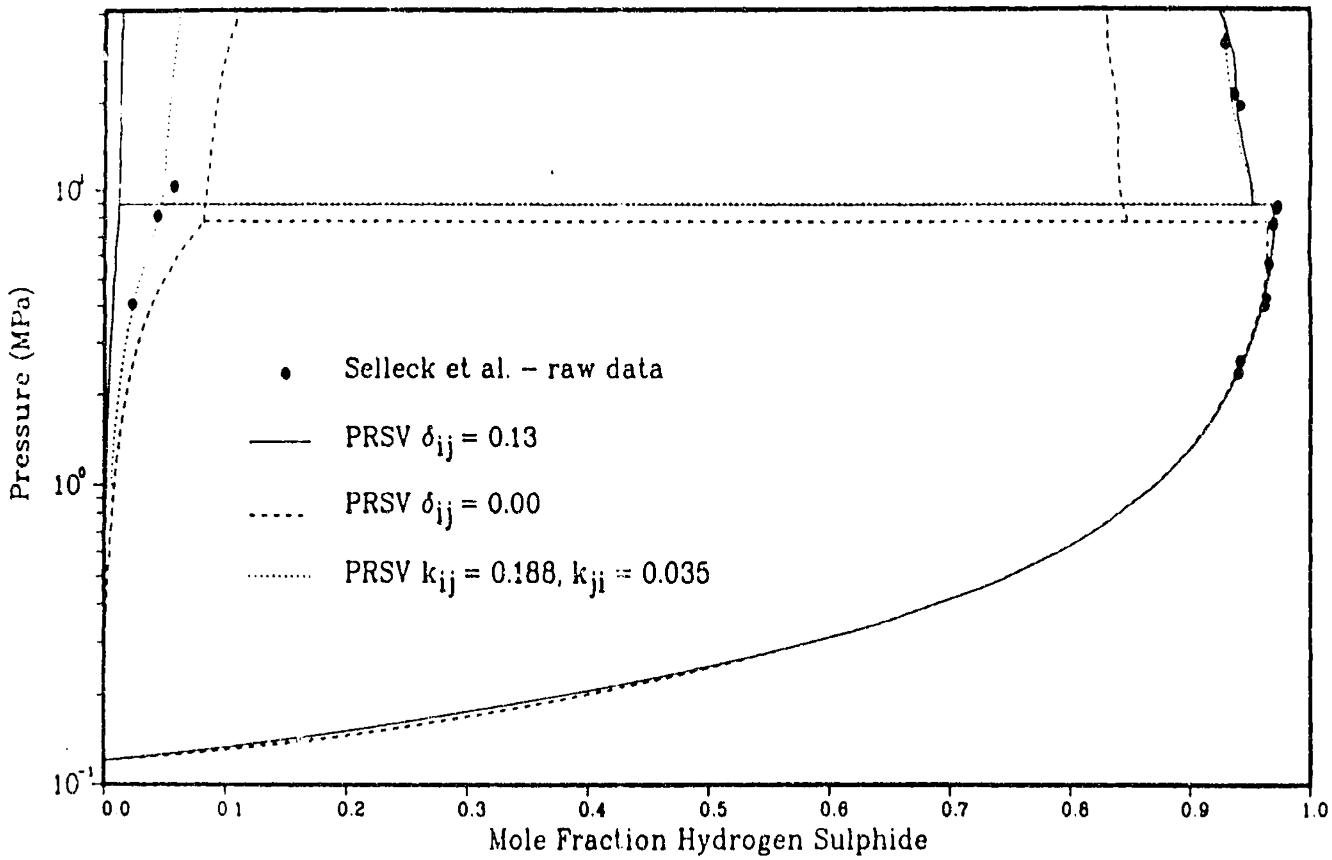


Fig. 5.7 Pressure-Composition Diagram at for the System Hydrogen Sulphide-Water 104.4°C Showing Several Mixing Rules

the H_2S-rich phase at high pressure. This is shown on Fig. 5.7. Optimizing the interaction parameter by fitting the H_2S-rich phase composition, it was found that $\delta_{ij} = 0.13$. This procedure fits the H_2S-rich phases very well, but it underestimates the H_2S solubility. This is also shown on Fig. 5.7. On the other hand, if the parameter is obtained by minimizing the error in the predicted bubble point, then $\delta_{ij} = 0.038$. This method overestimates the water content of the H_2S-rich liquid. This is <u>not</u> shown on Fig. 5.7. The van Laar-type rule was applied and the parameters were obtained by simultaneously fitting both the H_2S-rich and the aqueous phases. As shown in Fig. 5.7 this yields an excellent fit of the raw data of Selleck et al.

Liquid-Liquid-Vapour Equilibrium Predictions

Fig. 5.8 shows predictions of the L_A-L_S-V locus based on the PRSV equation along with the data obtained in Chapter III. Two mixing rules are shown and the optimum interaction parameters were taken from the correlations [Equations (5.12), (5.13) and (5.14)]. The three-phase predictions were performed using the bubble-point algorithm of Peng and Robinson (1976b). A small critical locus would extend from the critical point of pure H_2S to the end of the L_A-L_S-V locus. The point Q is the H-L_A-L_S-V quadruple point at 29.4°C and 2.24 MPa. Using the original mixing rule with Equation (5.12), the predicted three-phase locus is at a lower pressure and extends to a higher temperature than the

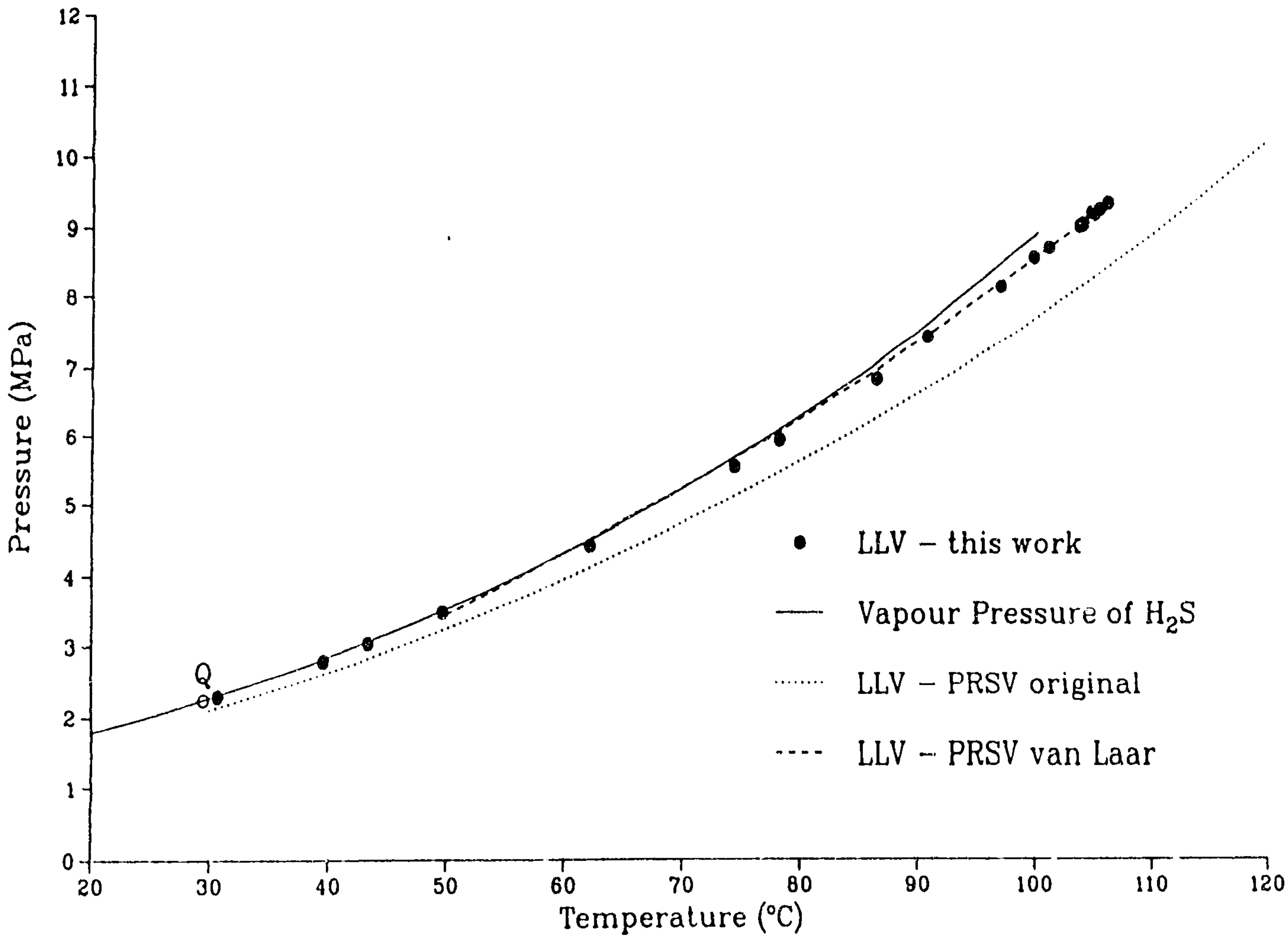


Fig. 5.8 The Liquid-Liquid-Vapour Locus for the System Hydrogen Sulphide-Water

observed values. The three-phase pressure could be fit using the original mixing rule. This is discussed in the next section. The agreement between the experiment and the van Laar-type rule is excellent, except that the prediction ends at about 104.5°C, slightly lower than the observed value of 106.2°C.

Effect of Impurites on the LLV Locus

The effect of three components (nitrogen, methanol and methanethiol) on the LLV locus are estimated using the PRSV equation. Nitrogen tends to concentrate in the vapour; methanol in the aqueous phase and methanethiol in the H_2S-rich liquid. Note, methanethiol and water also form immiscible liquids.

Table 5.3 summarizes the interaction parameters used for this portion of the study.

For this portion of the investigation, new interaction parmeters for the binary H_2S-H_2O were used. The new interaction parameters were obtained by minimizing the error in the predicted three-phase pressure. This results in an interaction parameter different from than those presented earlier. Although this results in an excellent fit of the pressure and temperature along the LLV locus and a good fit of the aqueous and vapour phases, the H_2S-rich liquid compositions are poor. The prediction, however, is satisfactory for this purpose.

Table 5.3 Interaction Parameters For LLV Study

System	Interaction Parameter	Source of Data
H_2O-H_2S	0.6318-168.752/T	1
H_2S-CH_3OH	0.065	2
H_2S-N_2	0.165	3
H_2S-CH_3SH	0.150	4
H_2O-CH_3OH	-0.0249-19.369/T	5,6,7
H_2O-N_2	0.4773-332.057/T	8,9
H_2O-CH_3SH	0.165	10

1. This Work
2. Leu et al. (1990)
3. Besserer and Robinson (1975)
4. Lee et al. (1978)
5. McGlashan and Williamson (1976)
6. Broul et al. (1969)
7. Griswold and Wong (1952)
8. Wilhelm et al. (1977)
9. Wiebe et al. (1933)
10. Gillespie and Wilson (1984)

For nitrogen-water, the solubility values given by Wilhelm et al. (1976) were fit. The interaction parameters thus obtained were then used to estimate the high pressure values of Wiebe et al. (1933). The agreement between the experimental aqueous compositions and those calculated with the equation of state was excellent. Unfortunately, this approach does not accurately predict the composition of the vapour. Again, these interaction parameters are satisfactory for the purposes of this study.

Experimental data for the system hydrogen sulphide-methanol were recently obtained by Leu et al. (1990). Their work includes a discussion of equilibrium calculations using the PRSV equaiton. Their interaction parameter will be used here.

The data of Besserer and Robinson (1975) were used to obtain the interaction parameter for the binary system nitrogen-hydrogen sulphide. The parameter was obtained by minimizing the error in the predicted bubble point pressure. A single, temperature-independent parameter was found to adequately fit both the vapour and the liquid phases.

Few data exist for the system hydrogen sulphide-methanethiol. Lee et al. (1978) report some VLE data at approximately 2400 kPa. These data exhibit a large amount of scatter, but are adequately fit using a single, temperature-independent interaction parameter.

The literature of experimental data for the system methanol-water is vast. A representative set of data was selected which covered the desired range of temperature. Although the interaction parameter was a function of temperature, it provides an excellent fit of both the vapour and liquid phases.

To obtain the interaction parameter for the system water-methanethiol, the LLV data of Gillespie and Wilson (1984) were used. A single, temperature-independent parameter results in a very good fit of the pressure and temperature along the LLV locus. The predicted aqueous and vapour phase compositions are quite good, but the CH_3SH-rich liquid compositions are poor.

Fig. 5.9 shows the calculated LLV loci for H_2S-H_2O and CH_3SH-H_2O along with experimental data. Also shown on this plot are the calculated L_2-dew point (where L_2 is a H_2S-rich or CH_3SH-rich liquid depending on the feed) loci for three mixtures of H_2O-H_2S-CH_3SH. The feed compositions for these calculations are given on the figure. From this plot it is clear that a small amount of methanethiol can have a significant effect on the L_2-dew point. From this calculation, an impurity of 1% CH_3SH in an equimolar mixture of H_2O-H_2S reduces the L_2-dew point by between 0.7 and 1 MPa depending on the temperature.

Fig. 5.10 shows the L_S-dew points for three mixtures of H_2O-H_2S-N_2. Again, the feed compositions are given on the figure. Note, from this calculation, the effect of nitrogen is to increase the pressure at which the third phase would form. At low temperatures, the effect is quite small.

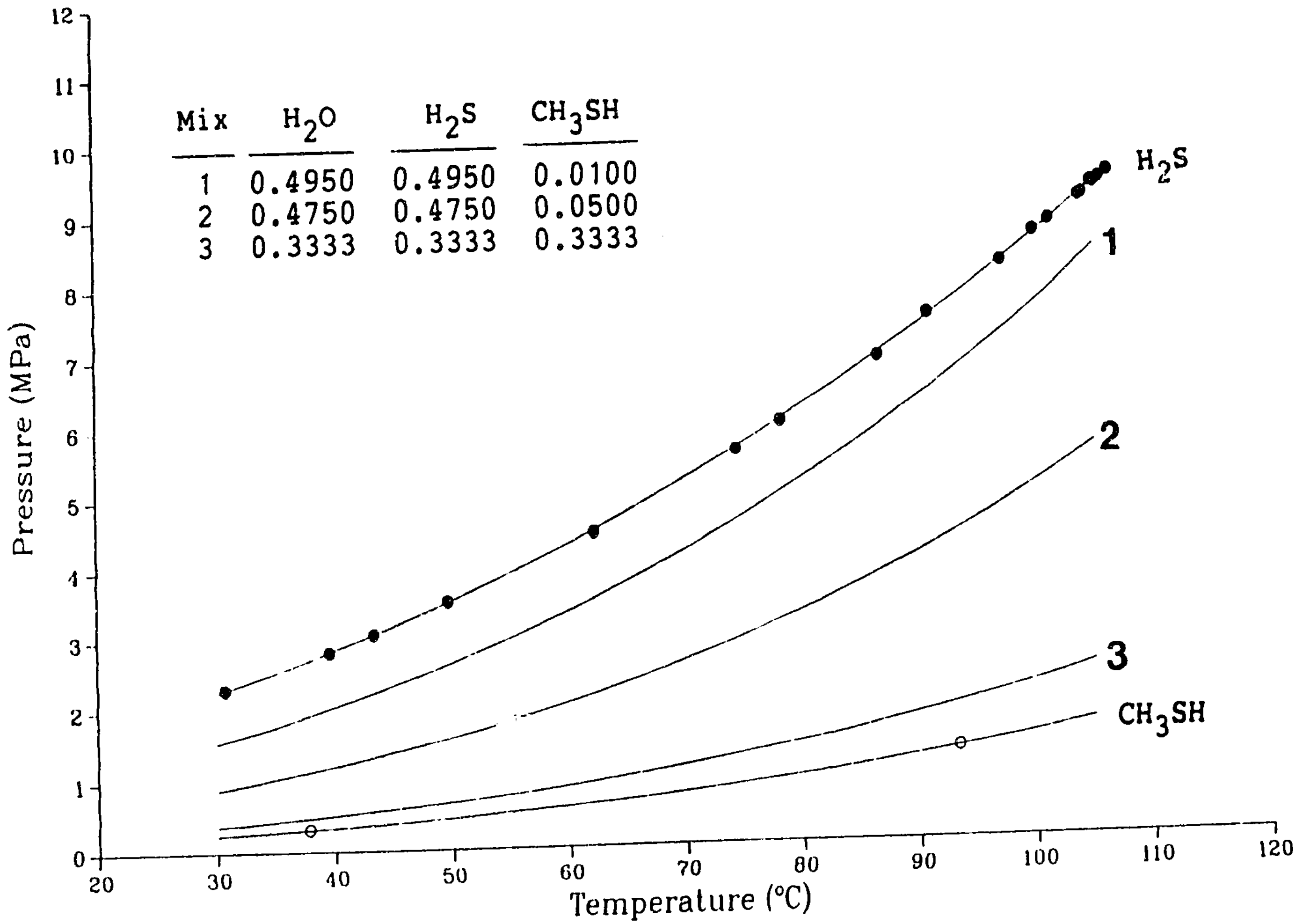


Fig. 5.9 The Three-Phase L_2-Dew Point Loci For Three Mixtures of Hydrogen Sulphide-Water-Methanethiol

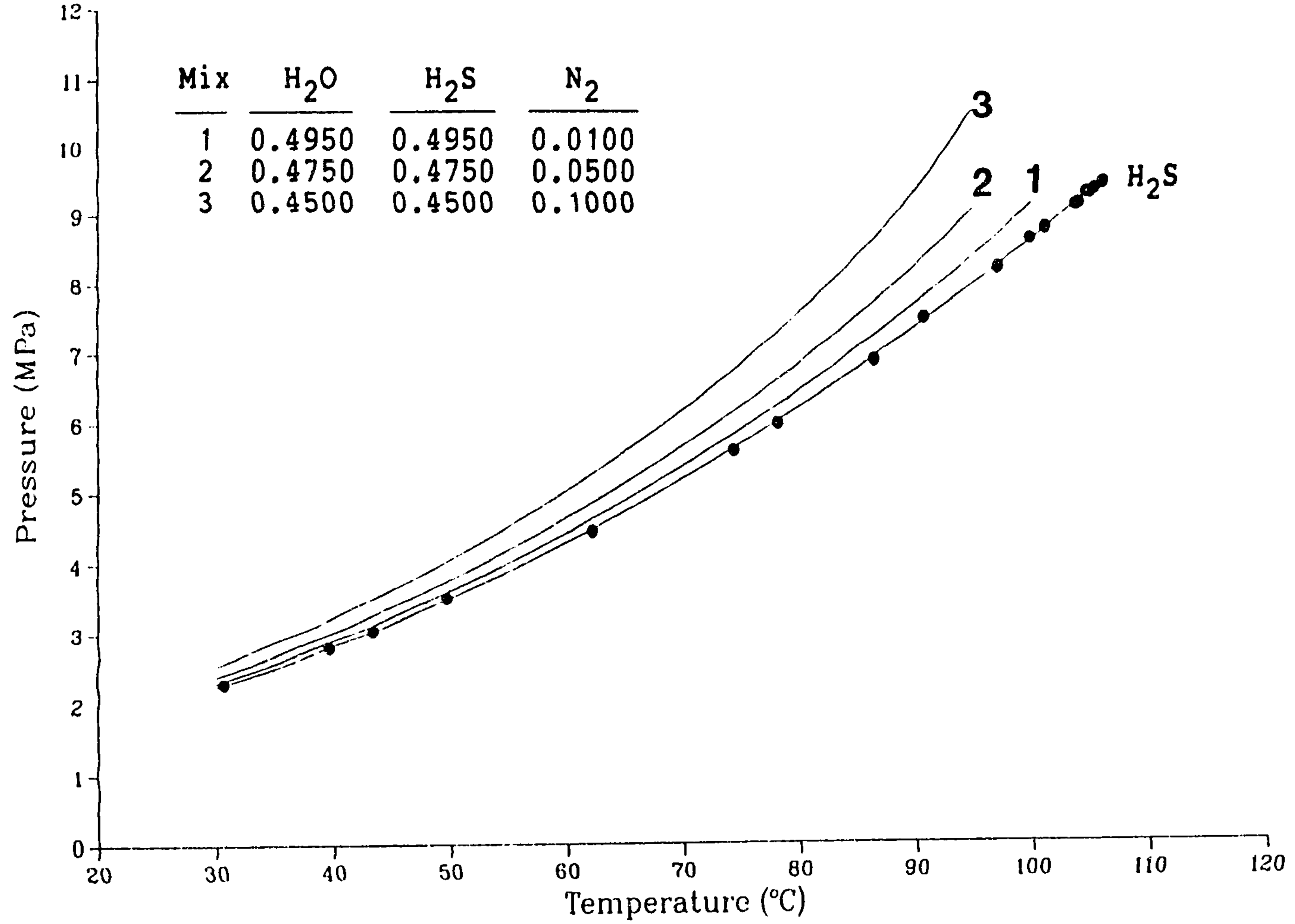


Fig. 5.10 The Three-Phase L_S-Dew Point Loci For Three Mixtures of Hydrogen Sulphide-Water-Nitrogen

However, at high temperatures, the effect increases. Also, the presence of nitrogen reduces the temperature of the three-phase critical end point. In the experimental work presented in Chapter III, it is believed that the major impurity is nitrogen. Nitrogen was used to pressure test the apparatus. Although the equipment was thoroughly flushed with H_2S, there is a possibility that some N_2 remained. However, from this analysis, a trace of nitrogen would have a negligible effect on the measured L_A-L_S-V locus.

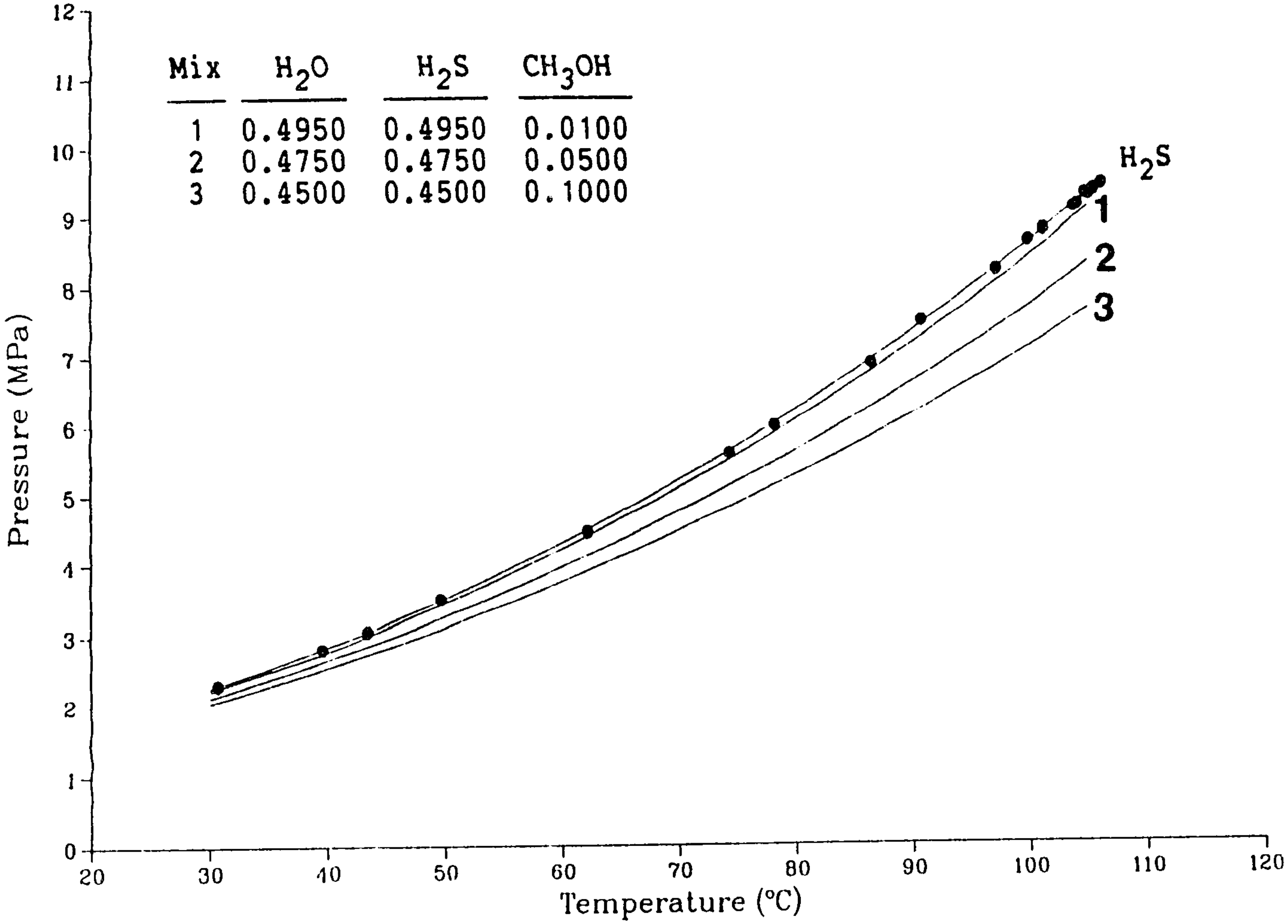
Fig. 5.11 shows the L_S-dew points for three mixtures of H_2O-H_2S-CH_3OH. The effect of methanol on the L_S-dew point is quite small and increases with increasing temperature.

C. High Temperature Region

In the region 200° < t < 365°C few experimental data exist.

To test the extrapolating power of the equation of state, the original mixing rule with the temperature-dependent interaction parameter [Equation (5.12)] was used to predict the equilibrium at 204.4°, 260.0° and 315.6°C. Fig. 5.12 shows the predicted phase envelopes along with the experimental data of Gillespie et al. (1984). The fit is quite good. Thus, the use of an advanced mixing rule is not justified. Problems with the data of Gillespie et al. were noted in the previous section of this chapter.

The only other data that are in this range of temperature are those of Kozintseva (1964,1965) and



Mix	H_2O	H_2S	CH_3OH
1	0.4950	0.4950	0.0100
2	0.4750	0.4750	0.0500
3	0.4500	0.4500	0.1000

Fig. 5.11 The Three-Phase L_S-Dew Point Loci For Three Mixtures of Hydrogen Sulphide-Water-Methanol

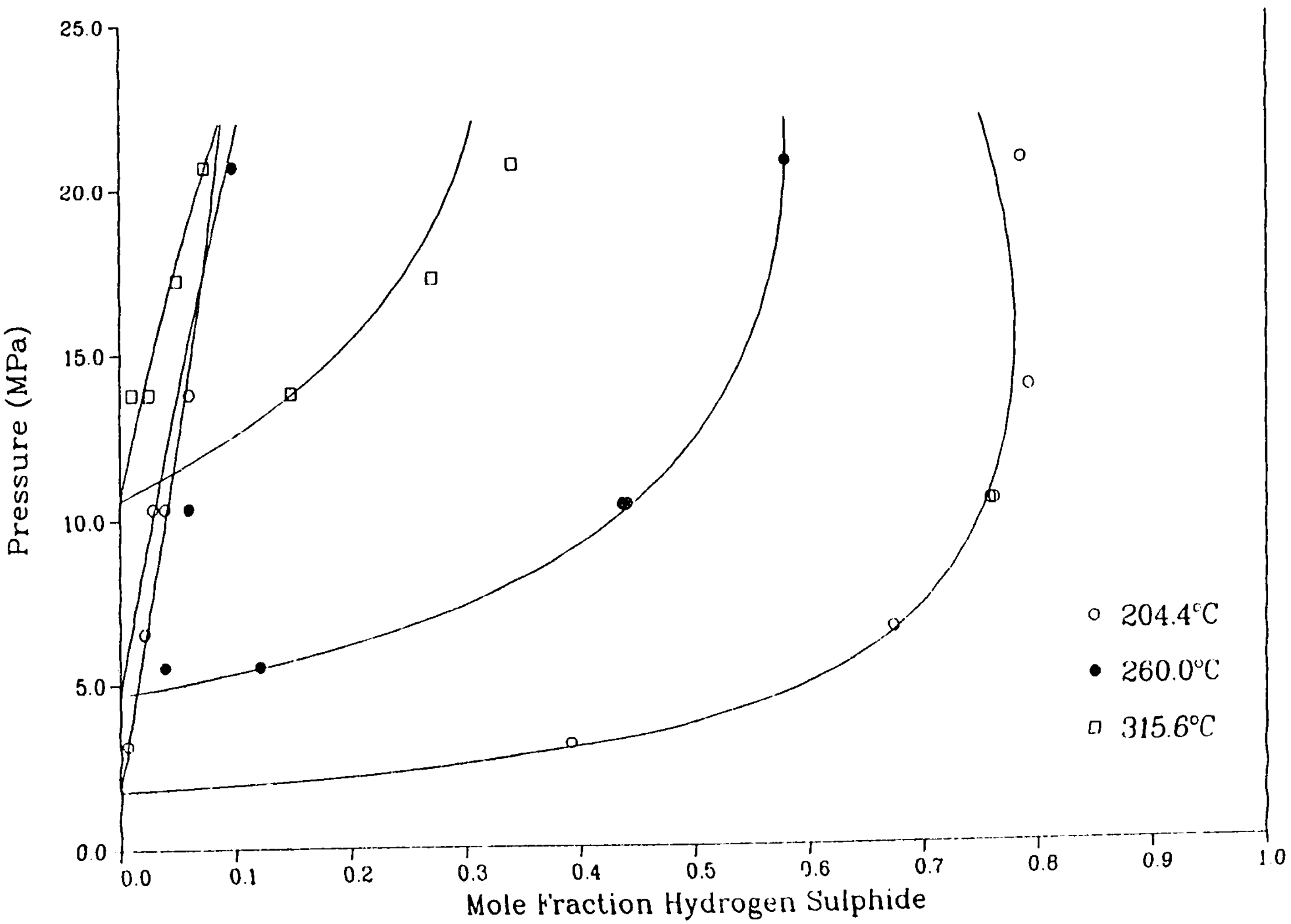


Fig. 5.12 Pressure-Composition Diagrams at 204.4°, 260.0° and 315.6°C for the System Hydrogen Sulphide-Water [Data from Gillespie et al. (1984)]

Drummond (1981). However, as discussed in Chapter II, there are some problems with these data sets.

Upper Critical Locus

The criteria for a critical point in a binary mixture were established by Gibbs more than a century ago. The second and third derivatives of Gibbs function with respect to mole fraction vanish at a binary critical point.

$$(\partial G^2/\partial x_1^2)_{T,P} = 0 \tag{5.15}$$

$$(\partial^3 G/\partial x_1^3)_{T,P} = 0 \tag{5.16}$$

These equations can be transformed into the following

$$(\partial \ln \hat{f}_1/\partial x_1)_{T,P} = 0 \tag{5.17}$$

$$(\partial^2 \ln \hat{f}_1/\partial x_1^2)_{T,P} = 0 \tag{5.18}$$

Using these equations, an equation of state and a set of mixing rules, one can calculate the critical point of a binary mixture. Perhaps the first to accurately calculate binary critical points using this method was Spear et al. (1969). They used the Redlich-Kwong equation to predict the critical points of several petroleum fluids. Peng and Robinson (1977) used the PR equation to calculate multicomponent critical points.

The PRSV equation with the original mixing rule [Equation (5.12)] was used to calculate the upper critical locus for hydrogen sulphide-water. The predicted locus is plotted on Fig.5.13 This is similar to the critical behavior in the system CO_2-H_2O (Takenouchi and Kennedy, 1964 and Tödheide and Franck, 1964).

D. Summary

A modified Peng-Robinson equation of state (PRSV) was used to correlate the fluid phase equilibria in the system hydrogen sulphide-water. It was demonstrated that the fit using an equation of state was as good as the smoothing of Selleck et al. Also, from the fit of all of the experimental data, it is shown that the aqueous phase extrapolation of Selleck et al. (1952) are in error.

Some of the limitations of the equation of state method when applied to aqueous systems are demonstrated. The simple linear and quadratic mixing rules which have been successfully applied to hydrocarbon systems are less useful for the system H_2S-H_2O. Interaction parameters for this system are shown to be a strong function of temperature and a function of composition as well.

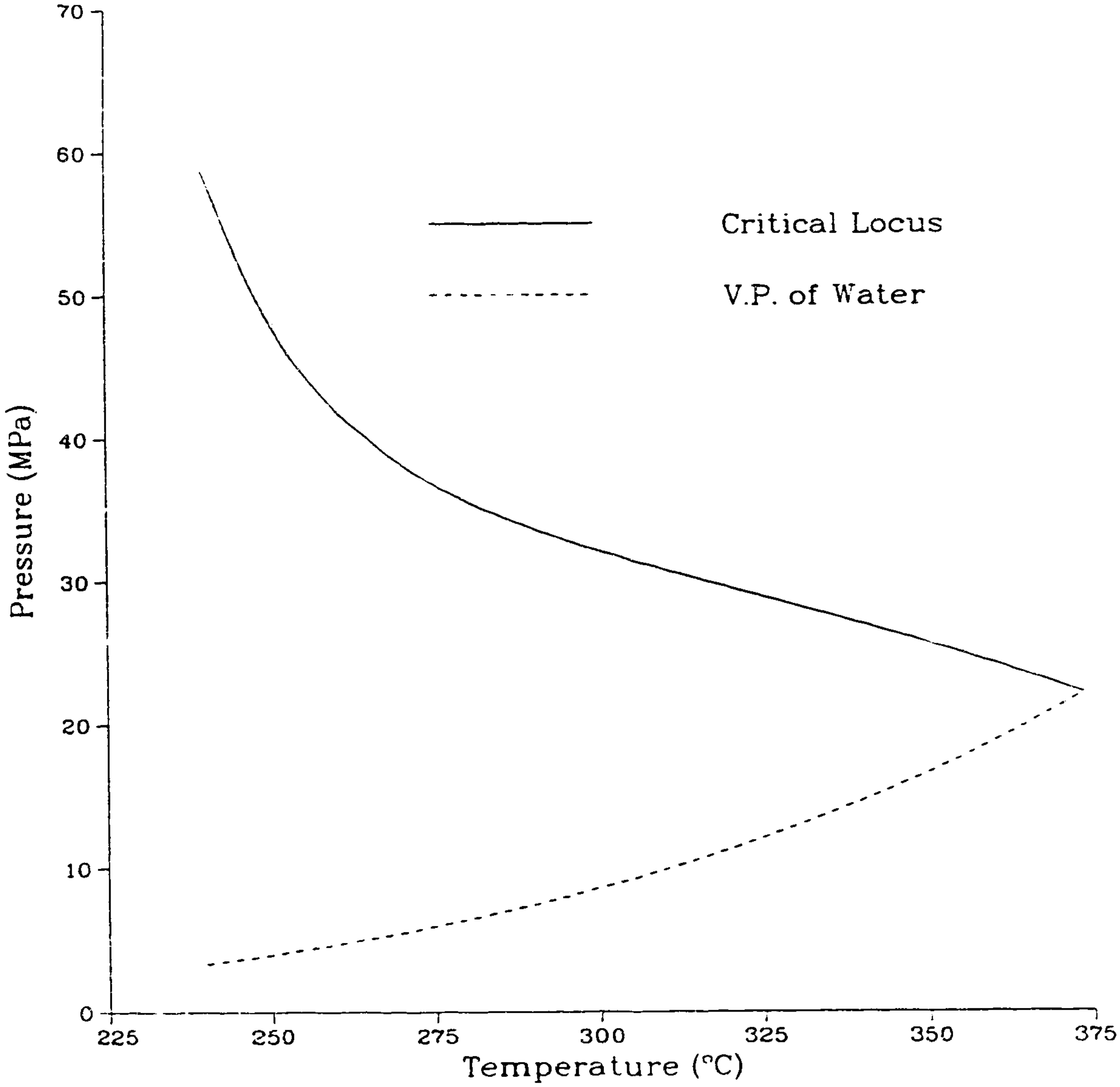


Fig. 5.13 The Estimated Upper Critical Locus for the System Hydrogen Sulphide-Water

VI. Henry's Law Approach

An alternative to the equation of state method is the Henry's law approach. Henry's law is often used when the liquid is dilute in one of the components. The major advantage of Henry's law over the equation of state method is the relative ease with which Henry's law can be extended to systems involving ionic equilibria.

Early in the nineteenth century, Henry (1803) reported the effect of pressure on the solubility of gases in water. Although his equipment was crude and his materials impure, he observed that the amount of gas that dissolved in water increased proportionally with the pressure. He made measurements for several different gases. Throughout the nineteenth century, many people attempted to prove or disprove Henry's law. But, by late in the century, it was generally accepted with a few exceptions. In fact many of the early solubility experiments involved measuring the solubility at near atmospheric pressure and reporting the values at 1 atm by assuming that Henry's law applied. [For example: Winkler (1906), Kendall and Andrews (1921) and Kiss et al. (1937) for H_2S in water.] Late in the nineteenth century, Raoult (1887) performed experiments on the vapour pressures of mixtures. He found that the vapour pressure of a solvent was nearly equal to the product of the mole fraction of the solvent and the vapour pressure of the pure

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A portion of this chapter has been published. Carroll, J.J. and Mather, A.E., "The Solubility of Hydrogen Sulphide in Water From 0 to 90°C and Pressures to 1 MPa", Geochim. Cosmochim. Acta, 53, 1163-1170, (1989).

solvent. As experiments improved, it became clear that Henry's law and Raoult's law were approximations valid for low concentrations and relatively low pressures. Classical thermodynamics provided a theoretical basis for extending Henry's and Raoult's law to higher pressures and concentrations.

A. Henry's Law

The condition for phase equilibrium in a closed system is that each component must have the same chemical potential in all phases. Equivalently, the fugacities of each component must also be the same in all phases. One approach to modelling phase equilibrium is the "two-fluid model". In this model different reference states are used for calculating the fugacities of the two phases.

For binary systems where the liquid phase is dilute in one component, it is convenient to use a combined Henry's law-Raoult's law approach to correlating the composition of co-existing phases. This method is a two-fluid model. The solvent is modelled as

$$\gamma_1 x_1 P_1^\circ \phi_1^\circ \exp[v_1(P - P_1^\circ)/RT] = y_1 P \hat{\phi}_1 \qquad (6.1)$$

For the solute:

$$\gamma_2 x_2 H_{21} \exp[\bar{v}_2^\infty(P - P_1^\circ)/RT] = y_2 P \hat{\phi}_2 \qquad (6.2)$$

For the solvent, the reference fugacity is the fugacity of the pure, saturated liquid at the temperature of the system. For the solute, the reference fugacity is the Henry's constant. In Equations (6.1) and (6.2) the exponential terms are the Poynting correction: the effect of pressure on the reference fugacity. In these equations it is assumed that v_1 and $\bar{v}_2^{\infty}$ are independent of pressure. This is the only assumption in the derivation of Equations (6.1) and (6.2). The activity coefficients are the effect of composition on the fugacity. This method uses the unsymmetric convention for activity coefficients

$$\lim_{x_1 \to 1} \gamma_1 = 1 \qquad (6.3)$$

$$\lim_{x_2 \to 0} \gamma_2 = 1 \qquad (6.4)$$

For a binary system containing water and a light gas this approach is often used.

In Equation (6.2) H_{21} is the Henry's constant. The original definition of Henry's law stated that the solubility of a gas in a liquid was proportional to its partial pressure. The proportionality constant implied by this definition was thus called the Henry's constant. The modern definition of a Henry's constant is

$$\lim_{x_2 \to 0} \hat{f}_2/x_2 = H_{21} \qquad (6.5)$$

However, this definition is difficult to apply directly to a set of experimental data.

Krichevsky Analysis

To obtain Henry's constants from solubility data, the method of Krichevsky is often used. The Krichevsky-Kasarnovsky (1935) equation is

$$\ln(\hat{f}_2/x_2) = \ln H_{21} + \bar{v}_2^{\infty}(P - P_1^{\circ})/RT \qquad (6.6)$$

This equation assumes that the concentration of the dilute component is sufficiently small, such that the activity coefficients are unity. It is further assumed that $\bar{v}_2^{\infty}$ is independent of pressure. Therefore a plot of $\ln(\hat{f}_2/x_2)$ versus $(P - P_1^{\circ})$ should yield a straight line with an intercept of $\ln H_{21}$ and a slope of $\bar{v}_2^{\infty}/RT$. The liquid phase composition as a function of pressure at constant temperature is obtained from experiments and the fugacity is calculated using an equation of state. For a detailed discussion of the Krichevsky-Kasarnovsky equation see Prausnitz et al. (1986).

If there is a significant deviation of the activity coefficients from unity, then they must be incorporated into the model. A simple model for activity coefficients is the two-suffix Margules equation. For the solvent

$$\ln \gamma_1 = \frac{A}{RT} x_2^2 \tag{6.7}$$

and for the solute

$$\ln \gamma_2 = \frac{A}{RT}(x_1^2 - 1) \tag{6.8}$$

where A is an empirical parameter. Thus Equation (6.6) becomes

$$\ln (\hat{f}_2/x_2) = \ln H_{21} + \frac{A}{RT}(x_1^2 - 1) + \bar{v}_2^{\infty}(P - P_1^{\circ})/RT \tag{6.9}$$

This equation is called the Krichevsky-Iliinskaya (1945a,b) equation. Equation (6.9) has three unknown quantities: H_{21}, A and $\bar{v}_2^{\infty}$. Even with experimental data of high accuracy it may not be possible to obtain A, H_{21} and $\bar{v}_2^{\infty}$ from this equation. Competing effects are difficult to separate. The usual approach to implementing this equation is to use a value of $\bar{v}_2^{\infty}$ obtained from volumetric measurements (Orentlicher and Prausnitz, 1964; and Gibbs and Van Ness, 1971). Then a plot of $[\ln (\hat{f}_2/x_2) - \bar{v}_2^{\infty}(P - P_1^{\circ})/RT]$ versus $(x_1^2 - 1)$ is constructed. If this relation applies, then the intercept is $\ln H_{21}$ and the slope is A/RT.

The Krichevsky approach should be used with caution. It can be shown that just because the Krichevsky-Kasarnovsky plot is linear does not mean that the activity coefficients are unity nor that the slope is the actual partial molar volume at infinite dilution (Mathias and O'Connell, 1981).

Also, it is difficult to calculate liquid phase fugacity coefficients. One approach is to calculate the vapour phase fugacities using an equation of state and then obtain the liquid phase fugacities from the criteria for equilibrium

$$\hat{f}_i^L = \hat{f}_i^V \tag{6.10}$$

However, this method requires the composition of the vapour phase which is in equilibrium with the liquid; often it is unknown. This may be a significant problem when attempting to use this approach. Often researchers assume a vapour composition. As well, for an equation of state to accurately correlate mixture properties, interaction parameters are required. These interaction parameters must be obtained from experimental data - usually the equilibrium data.

Finally, the two-suffix Margules equation is a very simple model for activity coefficients. It should not be expected to be applicable over a wide range of concentration.

B. Low Pressure Solubility Model

An analysis of the data for hydrogen sulphide in water shows that, for temperatures between 0 and 90°C and pressures to 1 MPa, the activity coefficients and Poynting factors are unity (or at least the product of the two is unity). Thus Equations (6.1) and (6.2) reduce to:

$$x_1 P_1^{\circ} = y_1 P \hat{\phi}_1 \qquad (6.11)$$

$$x_2 H_{21} = y_2 P \hat{\phi}_2 \qquad (6.12)$$

In this work, the following parameters were used. The vapour pressure of water is taken from Keenan et al. (1978) Fugacity coefficients of the vapour phase are calculated using the Redlich-Kwong (1949) equation of state. The mixing rules used are those proposed by Redlich and Kwong and do not include interaction parameters. A discussion of the Redlich-Kwong equation can be found in Appendix B. Critical constants, required for the equation of state, were taken from Keenan et al. for water and from Goodwin (1983) for hydrogen sulphide. New values for the Henry's constants were obtained by minimizing the deviations of the predicted solubilities from the experimental values. A single Henry's constant was calculated at each temperature by using the combined data of Wright and Maass (1932a,b), Clarke and Glew (1971), and Lee and Mather (1977). These Henry's constants, called the optimum values, are listed in

Table 6.1 and are shown graphically on Fig. 6.1. A least-squares regression yields the following correlation:

$$\ln H_{21} = -3.3747 + 0.072437\ T - 1.10765\times10^{-4}\ T^2 - 1549.159/T + 0.144237 \ln T \qquad (6.13)$$

where T is in K and H_{21} is in MPa/mol frac. The correlation fits the optimum values with an average error of 0.43% and a maximum error of 1.03%. For comparison purposes, Henry's constants calculated from the correlations of Clarke and Glew, and Lee and Mather are also tabulated in Table 6.1. In the results presented later in this paper, the calculations were performed using the optimum values and not the correlation except where noted. This prevents an error due to the correlation from entering the calculation. Equation (6.13) is provided for interpolation purposes.

The beauty of this model is its simplicity. Non-idealities in the liquid phase are neglected. For the vapour phase, the non-idealities are modelled using a simple equation of state. The justification for these approximations is the excellent fit of experimental data from three independent sources.

In this study, the ionization of H_2S in the aqueous phase has been neglected. Hydrogen sulphide is a weak diprotic acid. The ionization constant for the first dissociation of H_2S is 3.9×10^{-8} at 0°C and 3.0×10^{-7} at 100°C and is an increasing function of temperature over the

Table 6.1 Henry's Constants for Hydrogen Sulphide in Water (MPa/mol frac)

Temp (°C)	Optimum Values	Correlations		
		Equation (6.13)	Clarke and Glew	Lee and Mather
0	26.517	26.706	26.668	29.130
5	31.433	31.385	31.467	33.438
10	36.878	36.546	36.694	38.102
15	42.278	42.319	42.319	43.113
20	48.478	48.243	48.309	48.461
25	54.745	54.708	54.622	54.129
30	60.889	61.515	61.212	60.097
40	75.574	75.859	75.020	72.834
50	90.398	90.565	89.312	86.443
60	104.972	104.771	103.668	100.651
71	119.338	118.708	119.070*	116.616
90	134.911	135.327	143.514*	143.834

* - extrapolated

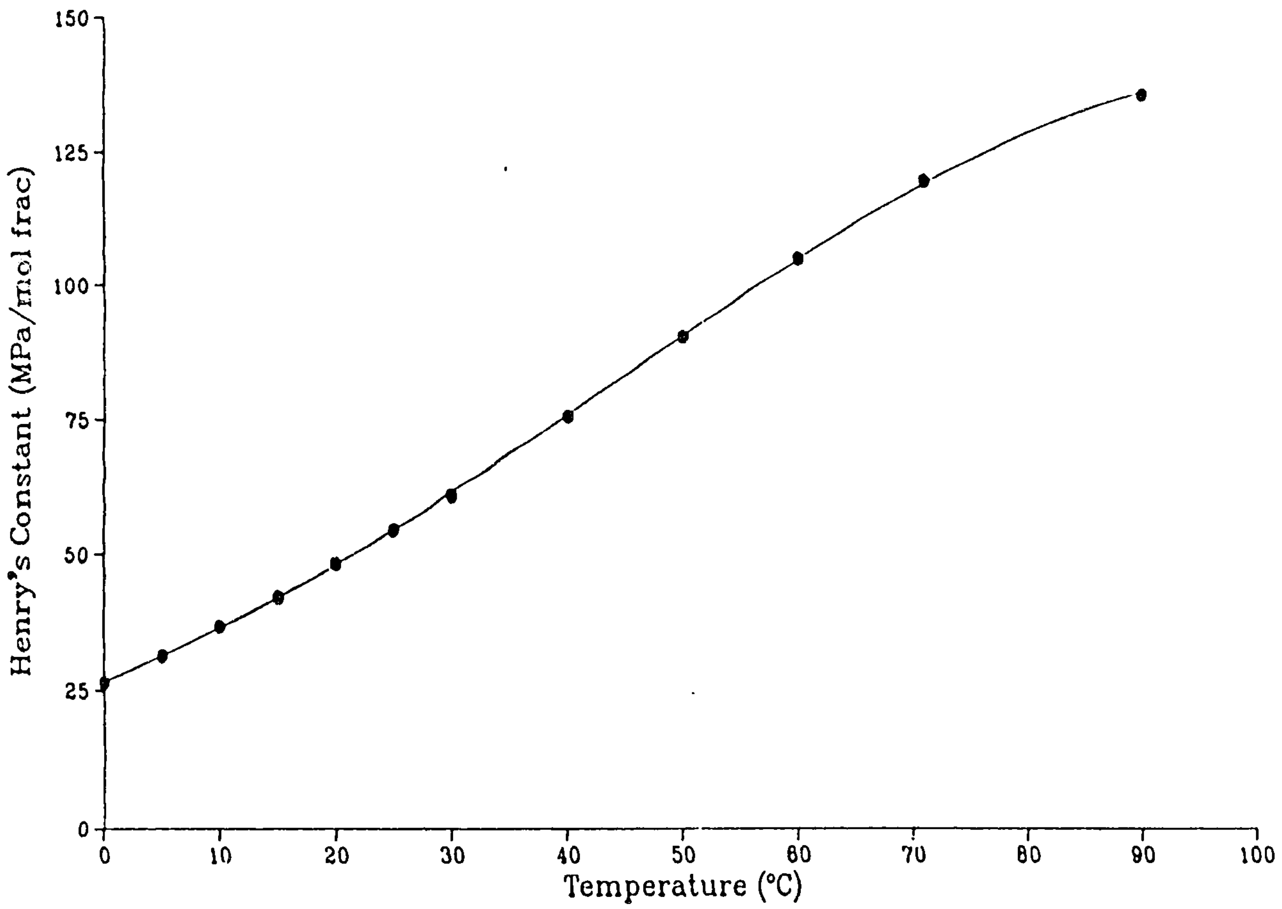

Fig. 6.1 Henry's Constants for Hydrogen Sulphide in Water at Temperatures Below 90°C

indicated range (Barbero et al., 1982). Myers (1986) reviewed the literature and concluded that 1 x 10^{-19} is the "best" value for the second ionization constant at 25°C. There is however, some controversy about its exact value; but, it is exceedingly small. Thus, the assumption that all of the H_2S in the aqueous phase is in the molecular form is a good one.

Low Pressure Solubility

The above model was used to calculate the vapour-liquid equilibrium for the system H_2O-H_2S from 0 to 90°C and pressures to 1 MPa.

The predicted solubilities at atmospheric pressure are plotted on Fig. 6.2 along with experimental data from Winkler (1906), Kendall and Andrews (1921), Kiss et al. (1937), Harkness and Kelman (1967), Gerrard (1972), and Douabul and Riley (1979). Most of the data lie within 3% of the prediction. An exception is the point of Harkness and Kelman which deviates by 5.7%. The value obtained by Harkness and Kelman is significantly different from the 30°C point of Winkler as well. Douabul and Riley compared their data with previously published values. They state that their solubilities agree to within 0.7%, but their values were consistently larger than the values of the other researchers. They did not do a detailed comparison with the data of Winkler stating that Winkler's data were "mainly of historical interest". Deviations between the data of Douabul

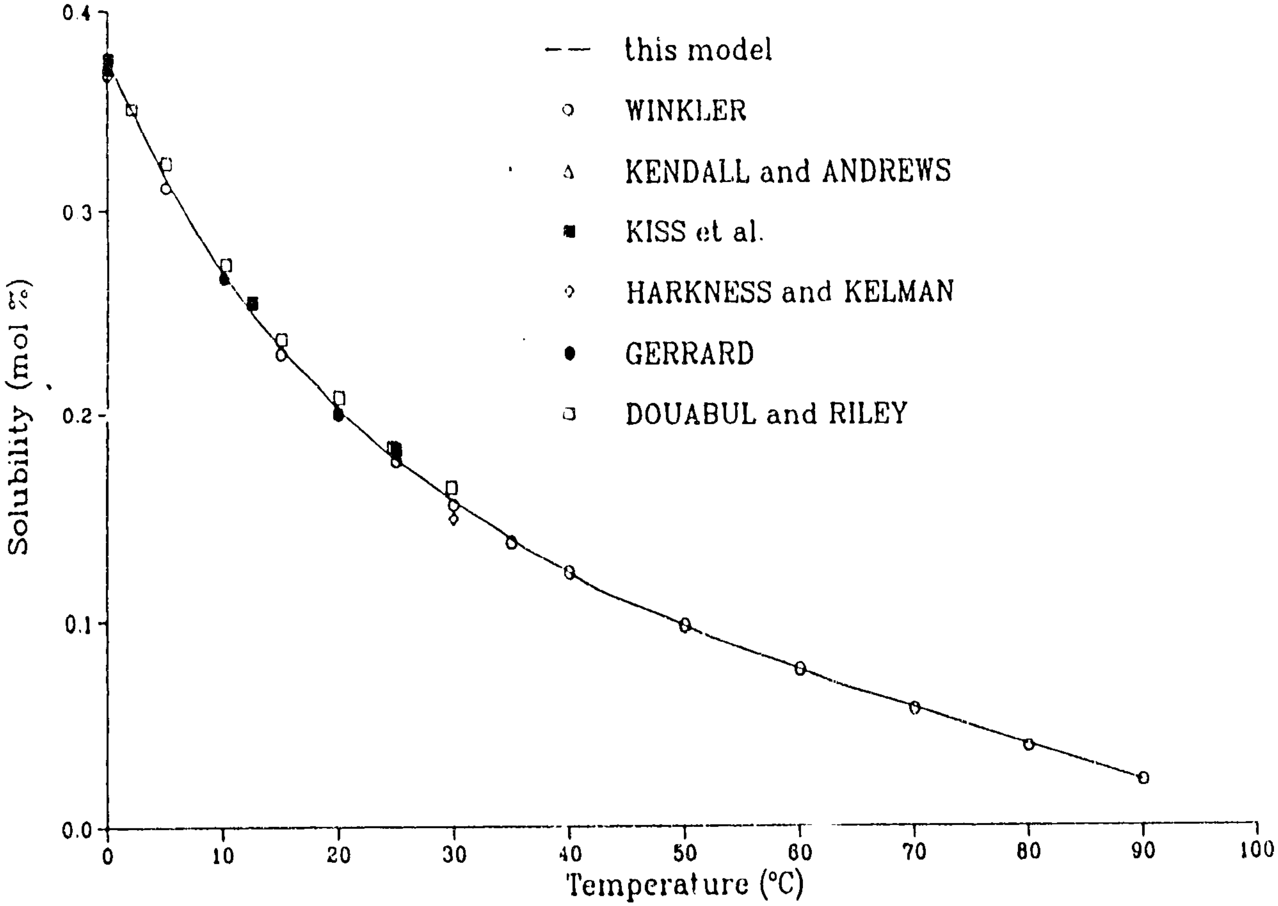

Fig. 6.2 The Solubility of Hydrogen Sulphide in Water at 101.325 kPa (1 atm) With Most of the Experimental Data

and Riley and this model are about 1 to 4%. Also, this model predicts solubilities lower than reported by Douabul and Riley. It is important to note that none of the experimental points shown on Fig. 6.2 was used to calculate the optimum Henry's constants. Table 6.2 lists the solubilities at atmospheric pressure from several sources. The experimental values are compared with those calculated in this work. Table 6.3 tabulates the solubility at 25°C and 1 atm from several other sources. The solubilities are given in both mole fraction and molarity since most of these values were reported in mol/L. Again, none of these data was used to obtain the parameters in the model.

In Fig. 6.3 a comparison is made with the data of Barrett et al. (1988) and this model. Also plotted is the correlation of Barrett et al. The agreement between this work and the experimental data of Barrett et al. is quite good. Barrett et al. extrapolate their correlation to 10°C and at this point there is a significant difference between their extrapolated values and that predicted by this model. This demonstrates a well-known problem with extrapolating empirical correlations.

Wilhelm et al. (1977) give the following general correlation for the solubility of gases in water

$$R \ln x_2 = A + B/T + C \ln T + D T \qquad (6.14)$$

where R is the gas constant, A, B, C and D are empirical

Table 6.2 The Solubility of Hydrogen Sulphide in Water at Atmospheric Pressure From Various Sources

	Solubility (mol %)						
	Calculation		Experimental Values				
Temp (°C)	(A)	(B)	(1)	(2)	(3)	(4)	(5)
0.0	0.376	0.374	0.368	–	–	0.371	–
0.05	–	0.373	–	0.376	–	–	–
2.10	–	0.348	–	–	–	–	0.351
5.0	0.317	0.317	0.312	–	–	–	–
5.05	–	0.317	–	–	–	–	0.324
10.0	0.269	0.272	0.267	–	–	0.267	–
10.19	–	0.270	–	–	–	–	0.274
12.5	–	0.252	–	0.255	–	–	–
15.0	0.233	0.234	0.230	–	–	–	–
15.04	–	0.234	–	–	–	–	0.237
20.0	0.203	0.204	0.201	–	–	0.200	–
20.10	–	0.203	–	–	–	–	0.208
24.72	–	0.179	–	–	–	–	0.184
25.0	0.178	0.178	0.177	0.183	–	–	–
29.82	–	0.157	–	–	–	–	0.164
30.0	0.158	0.157	0.156	–	0.149	–	–
35.0	–	0.139	0.138	–	–	–	–
40.0	0.123	0.123	0.123	–	–	–	–
50.0	0.098	0.098	0.098	–	–	–	–
60.0	0.077	0.077	0.077	–	–	–	–
70.0	–	0.059	0.058	–	–	–	–
71.0	0.057	0.058	–	–	–	–	–
80.0	–	0.042	0.040	–	–	–	–
90.0	0.023	0.023	0.023	–	–	–	–

(A) Optimum Henry's Constants
(B) Henry's Constants From Equation (6.13)

(1) Winkler (1906) (2) Kiss et al. (1937)
(3) Harkness and Kelman (1967) (4) Gerrard (1972)
(5) Douabul and Riley (1979)

Table 6.3 The Solubility of Hydrogen Sulphide in Water at 25°C and 101.325 kPa

	mol/L	mol%
This Model	0.0989	0.1779
Bunsen (1855a,b,c)[1]	0.1163	0.2093
Winkler (1906)	0.0988	0.1778
Pollitzer (1909)	0.1041	0.1873
Kendall and Andrews (1921)	0.1023	0.1840
Kiss et al. (1937)	0.1014	0.1824
Kapustinsky and Anvaer (1941)	0.1013	0.1822
Gamsjäger et al. (1967)	0.1021	0.1837
Douabul and Riley (1979)[1]	0.1020	0.1835
Barrett et al. (1989)[1]	0.0984	0.1770

1 - from smoothed data

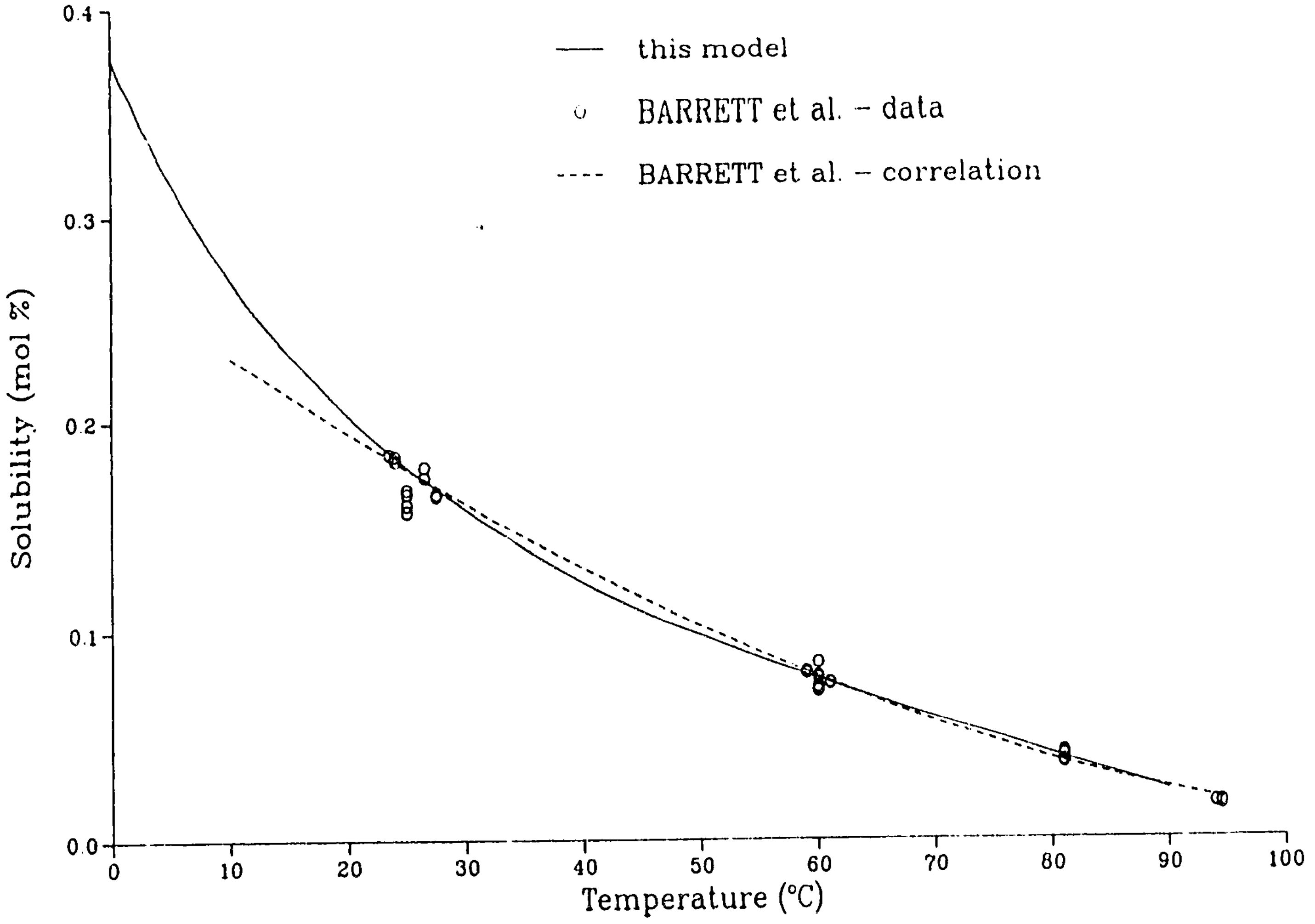

Fig. 6.3 The Solubility of Hydrogen Sulphide in Water at 101.325 kPa (1 atm) With the Data of Barrett et al. (1988)

parameters and x_2 is the mole fraction in the liquid at a partial pressure of the gas of 1 atm (as opposed to a total pressure of 1 atm as in the previous calculations). For H_2S they give A = -297.158 cal/mol K, B = 16347.7 cal/mol, C = 40.2024 cal/mol K, D = 0.00257153 cal/mol K^2 and R = 1.987 cal/mol K. These values were obtained from an analysis of the data of Wright and Maass; and Clarke and Glew. Table 6.4 compares the values obtained from this model with the values of Wilhelm et al. The values of Wilhelm et al. are slightly larger, an average of 0.0023 mol%, than those predicted with this model. Also in this table are the total pressure and the calculated mole fraction of hydrogen sulphide in the vapour. From these one can calculate the partial pressure of H_2S. Wilhelm et al. state that corrections for non-ideality were not made. This probably explains the difference between their correlation and the one presented here.

Fig. 6.4 shows a comparison between the data of Schoenfeld (1855) and this model. Also on this plot is the measurement of Prytz and Holst (1895) and the broken curve is the correlation of Bunsen (1855a,b,c). Since this model adequately fits virtually all of the other solubility data, then it must be concluded that the data of Schoenfeld (and hence Bunsen) are inaccurate. The value of Prytz and Holst is in good agreement with the model.

Finally, the effect of pressure on the solubility is demonstrated. Fig. 6.5 shows the calculated aqueous phase

Table 6.4 Comparison Between This Model and the Correlation of Wilhelm et al. (1977)

Temp (°C)	Total Press (kPa)	y_{H2S}	Mole Per Cent H_2S This Model	Mole Per Cent H_2S Wilhelm
0	101.943	0.99393	0.3786	0.3807
5	102.207	0.99137	0.3196	0.3218
10	102.567	0.98789	0.2724	0.2755
15	103.049	0.98327	0.2377	0.2387
20	103.689	0.97720	0.2074	0.2091
25	104.528	0.96936	0.1837	0.1851
30	105.613	0.95940	0.1652	0.1654
40	108.782	0.93145	0.1332	0.1358
50	113.791	0.89045	0.1114	0.1153
60	121.446	0.83432	0.0959	0.1008

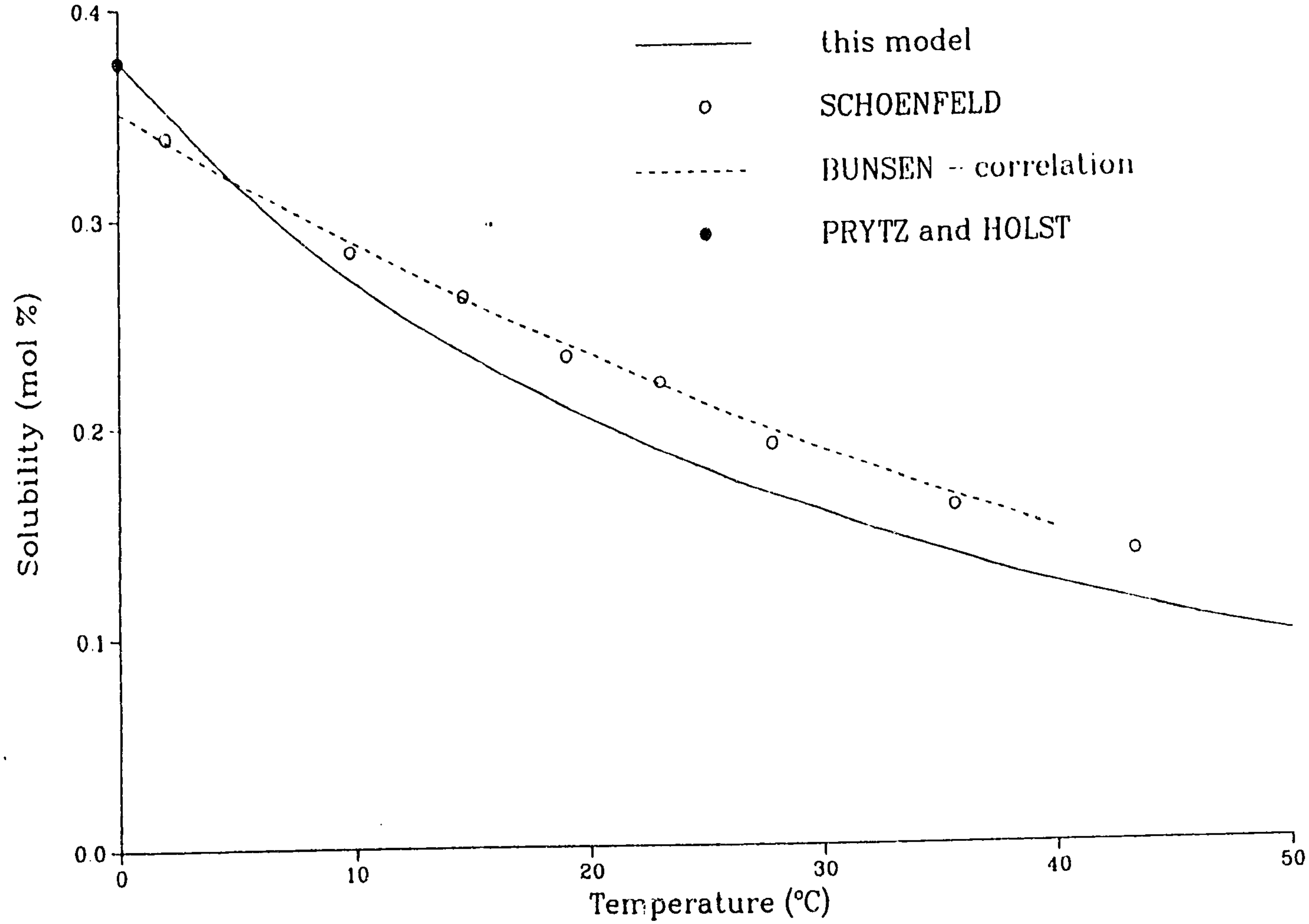

Fig. 6.4 The Solubility of Hydrogen Sulphide in Water at 101.325 kPa (1 atm) With the Older Data

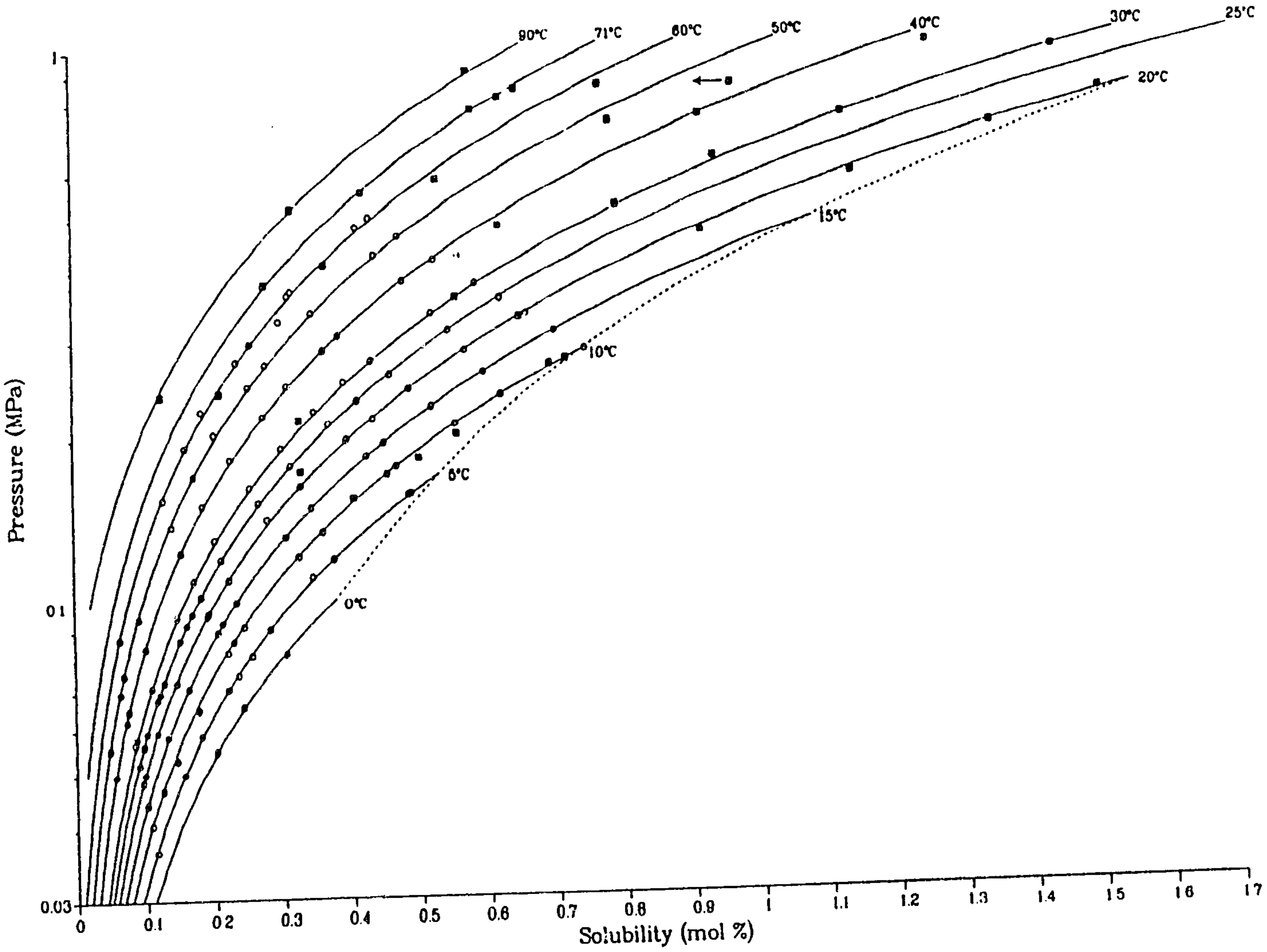

Fig. 6.5 The Solubility of Hydrogen Sulphide at Pressure Below 1 MPa [Data: o Wright and Maass (1932a,b), • Clarke and Glew (1971) and ■ Lee and Mather (1977)]

compositions from 0 to 90°C for twelve isotherms. Included on this plot are the experimental data of Wright and Maass, Clarke and Glew, and Lee and Mather. The agreement among the three sets of data is very good. Also, the model presented is a good fit of the data. Note, these were the data used to obtain the Henry's constants. The broken line on this figure is the hydrate-aqueous liquid-vapour locus and is estimated from Chapter VII.

Low Pressure Vapour Compositions

The literature contains few data for the vapour compositions for this system at low pressure. Clarke and Glew report compositions up to 100 kPa. Selleck et al. (1951) and Gillespie et al. (1984) also report a few compositions, but most of these are at pressures above 1 MPa. Wright and Maass give vapour phase compositions, but these were obtained by assuming that the partial pressure of water equals its vapour pressure.

Fig. 6.6 shows the water content of the vapour at pressures below 100 kPa. The points on this plot are the data of Clarke and Glew. Note, at these low pressures, the partial pressure of water is very nearly equal to its vapour pressure since the fugacity coefficients are near unity at these pressures and the liquid is essentially pure water. Fig. 6.7 shows the vapour compositions at higher pressures as predicted by the model presented earlier. The points on this graph are from Gillespie et al. at 37.8°C.

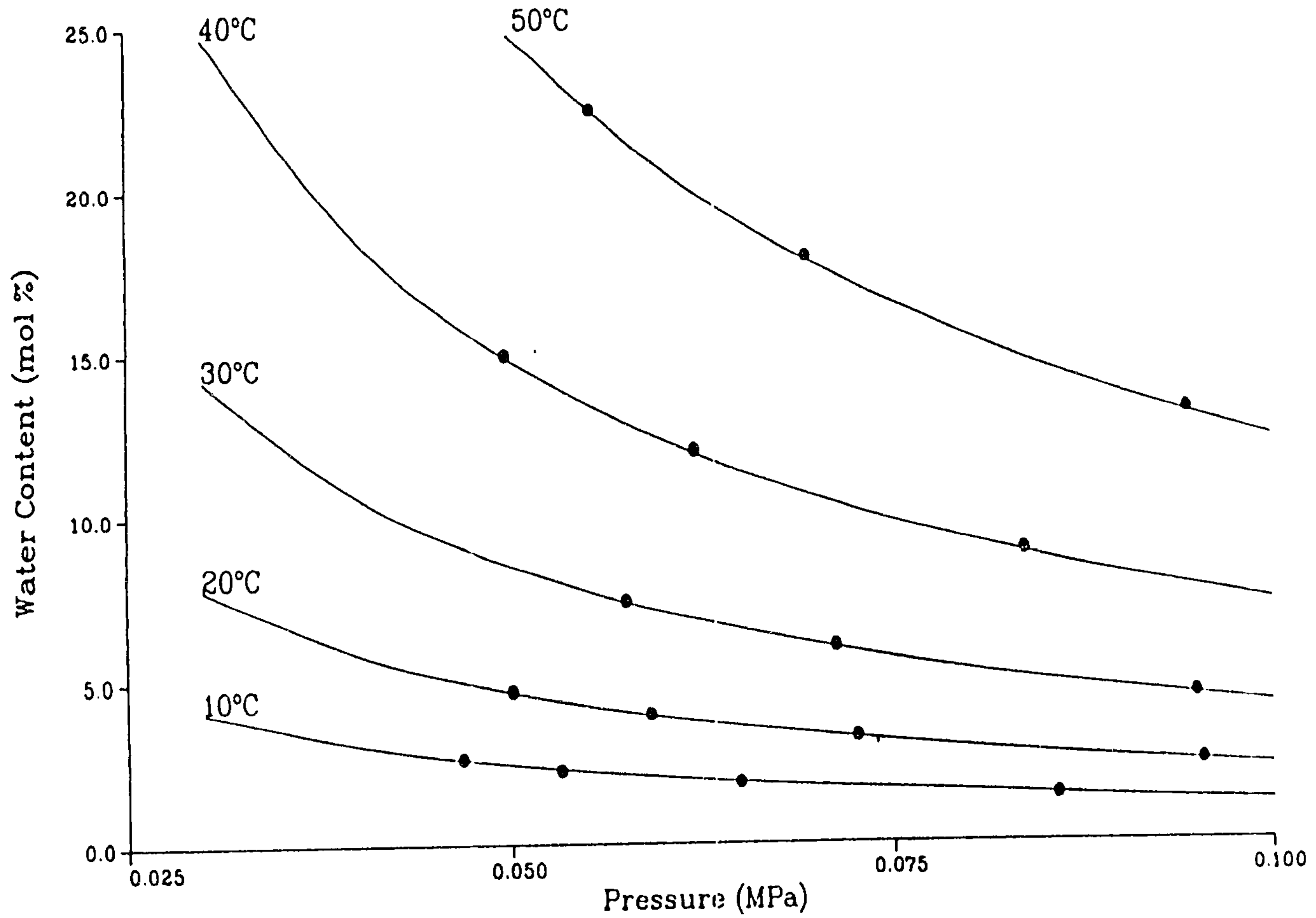

Fig. 6.6 Water Content of the Vapour at Pressure Below 100 kPa [Data from Clarke and Glew (1971)]

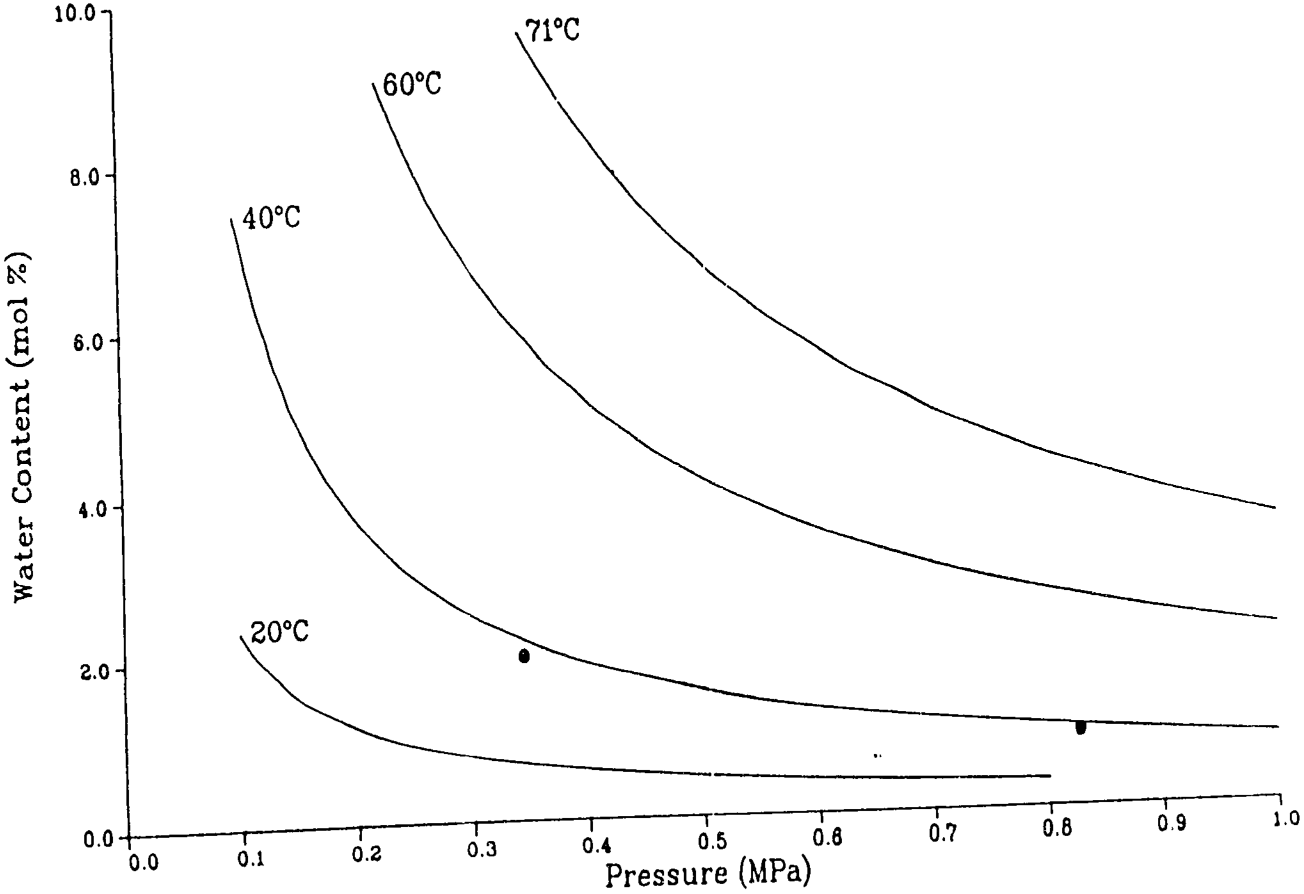

Fig. 6.7 Water Content of the Vapour at Pressure Below 1 MPa
[Data from Gillespie et al. (1984) at 37.8°C]

Fig. 6.8 compares the vapour compositions predicted by the model with the assumption of the strict Raoult's law for three isotherms. At atmospheric pressure, the difference is only about 1%. At 0.5 MPa the deviations have increased to about 5% and at 1 MPa they are about 10%. This observation is true for all temperatures.

Fig. 6.9 shows the fugacity coefficients for the hydrogen sulphide in the vapour as predicted by the Redlich-Kwong equation. The compositions at which these fugacities were calculated are the equilibrium vapour compositions at the given temperature and pressure. Above about 125 kPa the fugacity coefficients become less than 0.99. Thus, at lower pressures the strict Henry's law is accurate to within 1%.

C. Comments on the Low Pressure Calculations

Wilhelm et al. (1977) made a thorough review of the low pressure solubility of gases in water. In their review, they concluded that the data of Wright and Maass (1932a) and Clarke and Glew (1971) were the most reliable for hydrogen sulphide. Many other sets of data were rejected. Wright and Maass observed that the system water-hydrogen sulphide did not obey the strict Henry's law. However, this work shows that at and below atmospheric pressure, this system does obey the strict Henry's law. Thus, the older data may indeed be of some value. For example, some of the data of Winkler are at temperatures where no other data exist. Above about

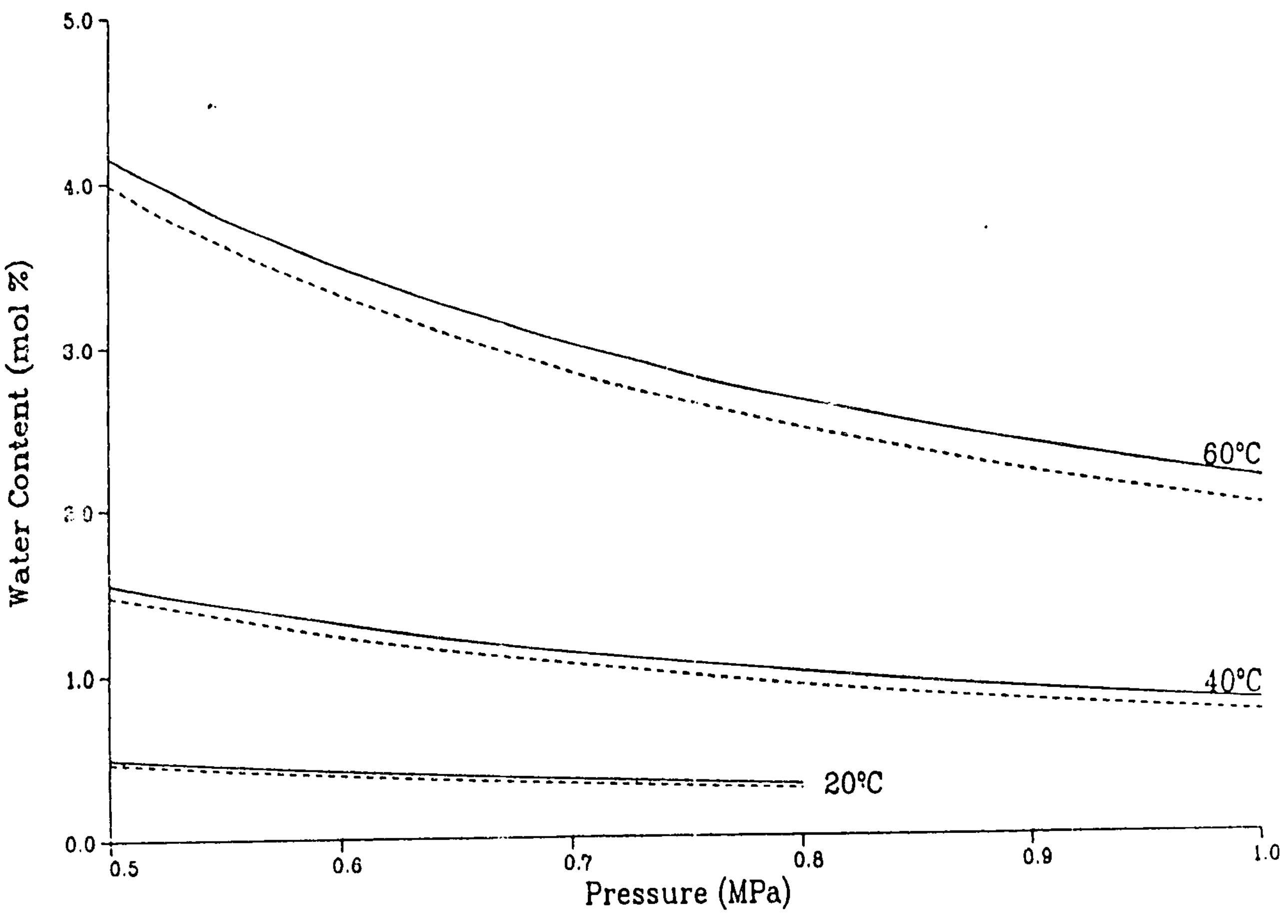

Fig. 6.8 A Comparison Between This Model (Solid Line) and the Simple Raoult's Law (Broken Line) for the Vapour Phase Composition

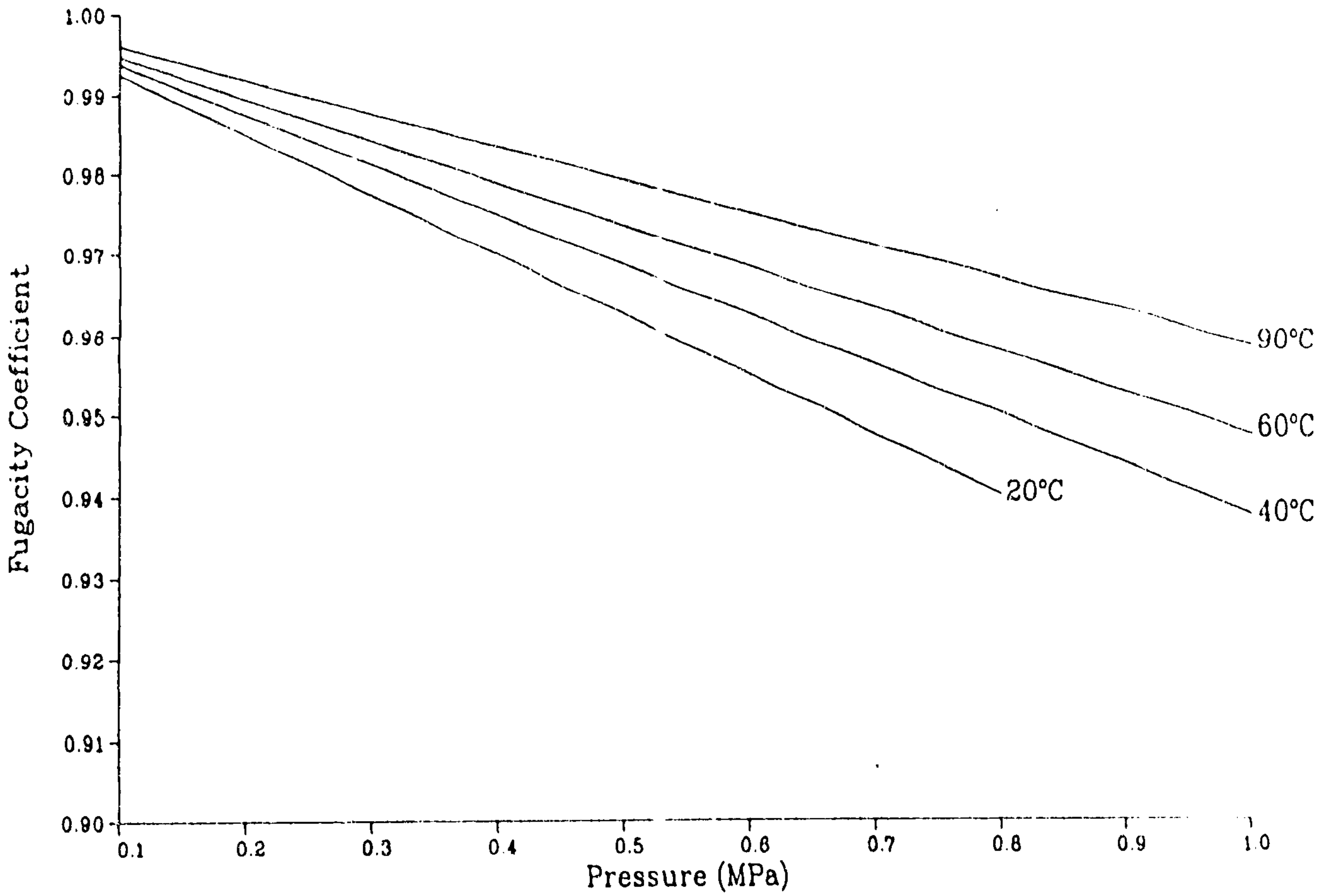

Fig. 6.9 Fugacity Coefficients of Hydrogen Sulphide as Predicted by the Redlich-Kwong Equation of State

125 kPa, the fugacity coefficients deviate significantly from unity. Their inclusion in the Henry's law model can adequately model the solubility up to 1 MPa. Thus the deviations observed by Wright and Maass can be accounted for by the vapour phase non-idealities.

It is ironic that Wright and Maass observed deviations from Henry's law, but assumed Raoult's law for the vapour. Deviations from both of these limiting laws can be explained by the same effect - non-ideality of the vapour phase.

At pressures above 1 MPa, the activity coefficients begin to deviate significantly from unity. Thus, to extend the model to higher pressures, some model for the activity coefficients must be included.

VII. Hydrate Forming Conditions

Up to this point, the discussion has been concerned with fluid phase equilibria. This chapter investigates the equilibria involving solid phases. It critically reviews the experimental investigations of the hydrate forming conditions for H_2S in water. Data from the literature and those presented in Chapter III are examined. Correlations are provided for the pressure and temperature along loci involving hydrates.

For the location of the various loci with respect to each other, refer to Fig. 1.2 (the pressure-temperature diagram).

A. The L_A-H-V Locus

As discussed in Chapter II there have been several investigations of the L_A-H-V locus. In order to compare the experimental values, all of the data were correlated using a Clausius-Clapeyron-type equation.

$$\ln P = A + B/T \tag{7.1}$$

Table 7.1 lists the constants for the individual sets of data and these values are for P in kPa and T in K. The stated ranges are the 95% confidence intervals. From this table and plots of pressure versus temperature it is concluded that the data of de Forcrand and Villard (1888), Scheffer (1913) and Scheffer and Meyer (1919a,b) are the

Table 7.1 Correlation of the L_A-H-V Locus for the System Hydrogen Sulphide-Water From Several Sources Via a Clausius-Clapeyron-Type Equation

Ref	NP	t_{min} (°C)	t_{max} (°C)	Slope	Intercept	r^2
1	12	0.5	29.0	-8071±614	34.18±2.13	0.9885
2	10	1.0	25.0	-7281±903	31.68±3.16	0.9774
3	16	0.0	5.2	-7790±116	33.10±0.42	0.9993
4	11	16.3	29.5	-9436±324	38.86±1.09	0.9979
5	4	1.0	7.1	-7776±127	33.07±0.46	1.0000
6	5	2.2	10.5	-8008±1863	33.74±6.64	0.9842
7	3	10.0	26.5	-8093±3264	34.33±11.22	0.9990
8	5	11.7	24.4	-8608±633	36.07±2.18	0.9984
9	13	25.5	27.7	-8659±1591	36.37±5.31	0.9288

1. de Forcrand (1882)
2. Cailletet and Bordet (1882)
3. de Forcrand and Villard (1888)
4. Scheffer (1913)
5. Scheffer and Meyer (1919a,b)
6. Wright and Maass (1932a)
7. Bond and Russell (1949)
8. Selleck et al. (1951)
9. This Work

best; they have the narrowest confidence intervals. Note, these data were selected in spite of their age. Over a narrow range of temperature the Clausius- Clapeyron-type equation provides an adequate fit of the data, especially for comparison purpose. Unfortunately, the Clausius-Clapeyron equation is not the best for correlating these data over the entire range of temperature. The following equation was significantly better:

$$\ln P = -26.8952 + 0.15139\ T + 2788.88/T - 3.5786 \ln T \quad (7.2)$$

where P is in kPa and T in K.

In their review of hydrates, van der Waals and Platteeuw (1959) misquote Selleck et al. (1952) by stating that the dissociation pressure of the H_2S hydrate at 0°C was 93.1 kPa (698 mm Hg). This is actually the pressure at -0.4°C, the H-I-V-L_A quadruple point. At 0°C, Selleck et al. give 97.5 kPa (731 mm Hg) whereas Equation (7.2) gives 98.6 kPa (739 mm Hg). de Forcrand and Villard (1888) measured a value of 97.5 kPa (731 mm Hg) at 0°C. Also, from Equation (7.2), the dissociation temperature at 101.325 kPa (1 atm) is 0.3°C.

The L_A-H-V locus is plotted on Fig. 7.1. This figure shows Equation (7.2) along with the data of de Forcrand and Villard, Scheffer, and Scheffer and Meyer. Fig. 7.2 shows the above correlation along with the remaining experimental data. Note the large amount of scatter on this plot. These

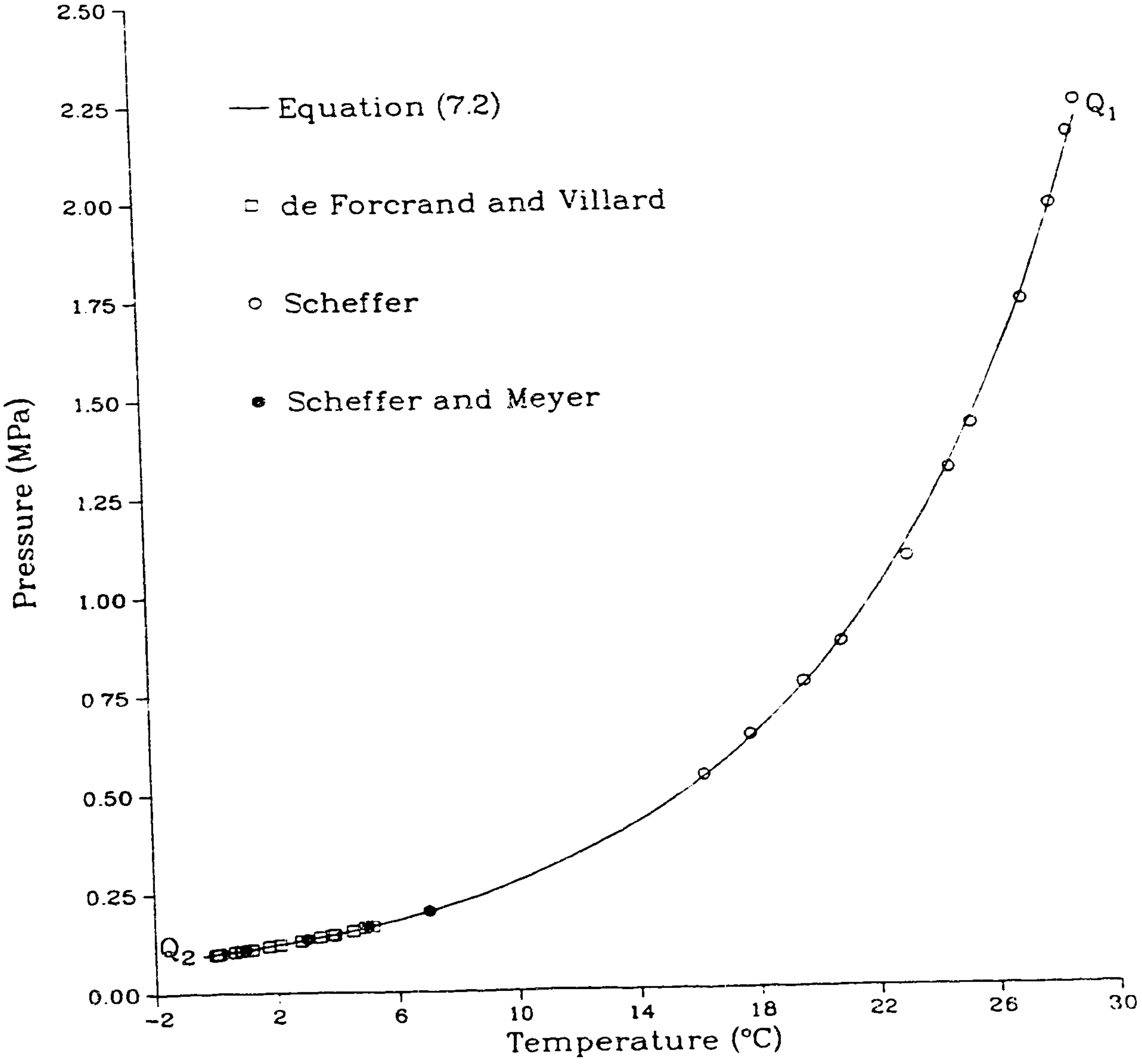

Fig. 7.1 The Aqueous Liquid-Hydrate-Vapour Locus for the System Hydrogen Sulphide-Water (Best Data)

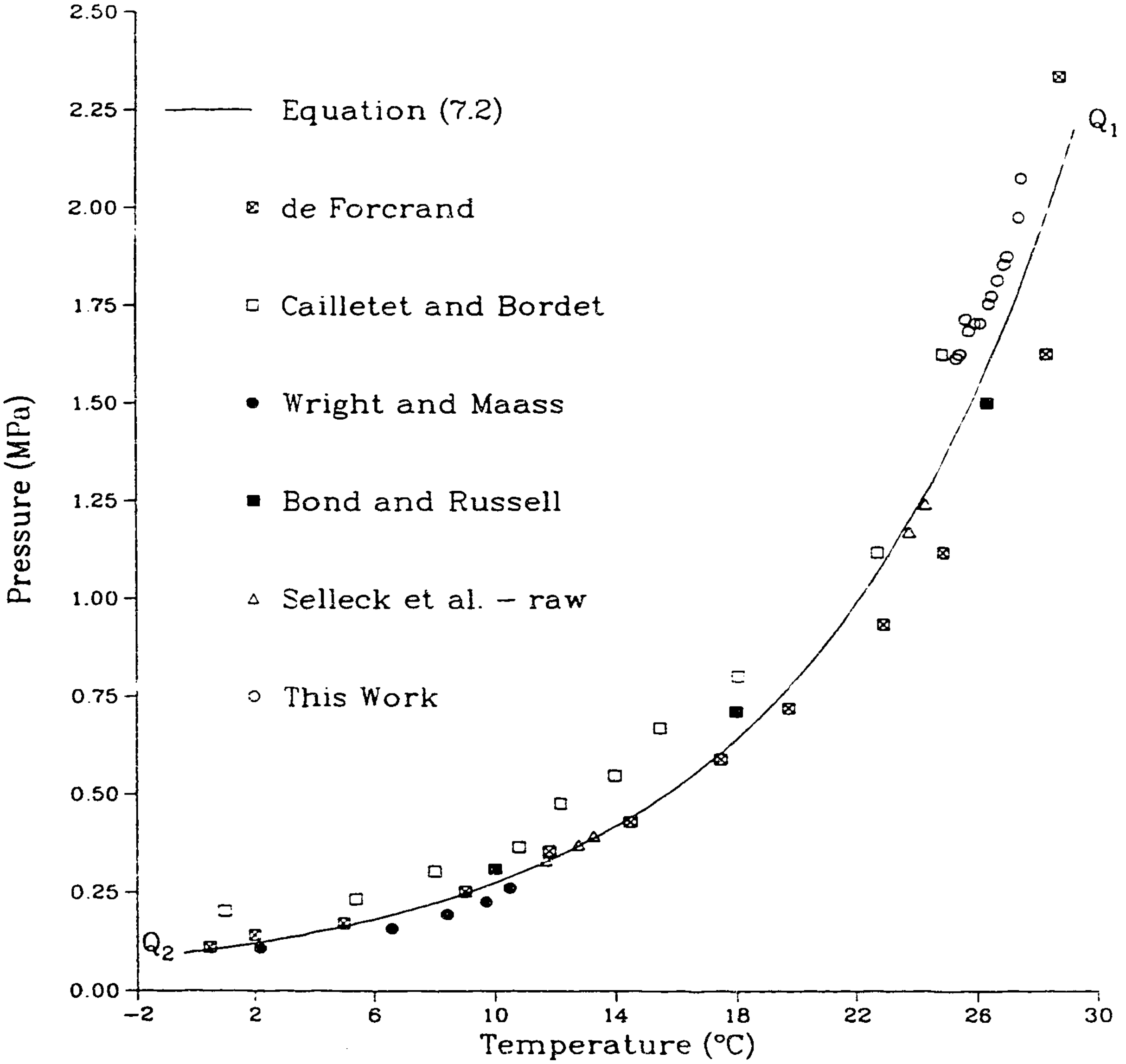

Fig. 7.2 The Aqueous Liquid-Hydrate-Vapour Locus for the System Hydrogen Sulphide-Water (Other Data)

figures reinforce the selection of the three sets of data as the best.

Even in the nineteenth century it was possible to measure the temperature to a fraction of a degree. Pressures below about 300 kPa could easily be measured to within 0.13 kPa (1 mm Hg) using a mercury manometer. Higher pressures could have been measured to ±1% (or better) using a bourdon tube gauge. Thus, the reason for the error is probably not due to the temperature or pressure measurements. The most likely reason for the errors is impurities in the samples. These impurities can cause both increases and decreases in the hydrate formation temperature.

One reason why the observed values for the L_A-H-V are at lower temperature (higher pressure) than the "true" value is the inhibitor effect. Bond and Russell (1949) observed the effect of several antifreeze agents (salts, alcohols, glycols and sugars). Ng and Robinson (1985) investigated the effect of methanol on the H_2S hydrate. In both of these investigations, the hydrate pressure at a given temperature was increased by the antifreeze. Noaker and Katz (1954) studied the hydrate for H_2S-CH_4 mixtures. They observed that the presence of CH_4 increased the hydrate forming pressure. Also, some impurities decrease the pressure at which the hydrate forms. For example, mixtures of H_2S-CH_2Cl_2, H_2S-CH_3Cl and H_2S-CCl_4 all form hydrates at lower pressures than pure H_2S (Stackelberg and Frühbuss, 1954). This may explain why some values are at lower pressures than expected. Of course, there is also experimental error. Some problems with the data of Selleck et al. (1951) were demonstrated in Chapter IV. Also, as noted earlier, the data from Chapter III are not of high quality because of the apparatus used. It is interesting to note that although the solubility data of Wright and Maass (1932a) are considered to be among the most reliable, their hydrate data are at significantly lower pressures than the other data and are concluded to be in error.

Composition of the Hydrate

One of the interesting features of gas hydrates is that they are non-stoichiometric. That is, a stable crystal forms without a guest molecule in each void. Thus the ratio of water to guest molecules is greater than the theoretical value. The lack of the correct crystal structure for the gas hydrate made estimation of the composition of the hydrate difficult. Most of the early investigators used a "synthetic" method to estimate the ratio of water to guest molecules rather than by direct measurement.

As noted in Chapter I, the theoretical formula for the hydrate is $H_2S \cdot 5.75\ H_2O$. There have been many attempts to determine the composition of the H_2S hydrate. Most were incorrect. From a simple analysis de Forcrand (1902a) concluded that at 0.35°C and 1 atm the hydrate was $H_2S \cdot 5.69\ H_2O$, but this is too low. Korvezee and Scheffer (1931) estimated that the ratio was 6.06±0.03. They obtained this value from the intersection of the L_A-H-V and H-I-V loci at the lower quadruple point (-0.4°C). Believing that the ratio should be an integer these values were rounded to 6. Even Selleck et al. (1952) report this ratio as six. Cady (1981) made some precise gravimetric measurements at 0°C for the hydrate composition as a function of pressure. His measurements show that the ratio is not an integer and not equal to the theoretical value. Cady (1983) discusses the history and problems associated with experimental measurements of hydrate compositions.

A modification of the method of van der Waals and Platteeuw (1959) was used to estimate the composition of the hydrate along the L_A-H-V locus. Essentially, the procedure of Munck et al. (1988) was used. Their model included the effect of the solubility of the hydrate forming gas in the aqueous phase. Although they included this effect for CO_2, they state that it was negligible for H_2S. However, the solubility of H_2S in water is larger than that of CO_2. The solubility of H_2S was not neglected in this application. The solubility of H_2S and the vapour properties were calculated using the low pressure model from Chapter VI. The pressures were calculated using Equation (7.2). According to Cady, it is a good assumption that the saturation for the two different cavities are equal. That is, there is an equal probability of there being an H_2S molecule in the small voids as there is in the large voids. (This was only true for H_2S.) This assumption was not made by Munck et al. Table 7.2 list the composition of the co-existing phases along the L_A-H-V locus. The composition of the hydrate was calculated using Cady's hypothesis. At 0°C and 98.6 kPa, this method gives n=5.98. Although Cady extrapolates his data to get 6.12 at this point, the value of 5.98 is in good agreement with his data. The composition of the hydrate at 0°C is plotted on Fig. 7.3.

B. The L_S-H-V Locus

Scheffer (1913) Selleck et al. (1951) and this work report values for pressures and temperatures along the L_S-H-V locus. As with the L_A-L_S-V locus, the L_S-H-V lies very close to the vapour pressure of H_2S. The agreement among the three sets of data is quite good - in spite of the relatively low quality of the data presented in Chapter III. The data were correlated with a Clausius-Clapeyron-type equation. A least squares regression yields

$$\ln P = 14.5229 - 2061.05/T \qquad (7.3)$$

where P is in kPa and T in K. The fit of the experimental data was sufficiently accurate. Fig. 7.4 shows the experimental data from the three sources and Equation (7.3). Also shown on this plot is the vapour pressure of H_2S which was calculated using the correlation of Goodwin (1982). At low temperatures, the L_S-H-V locus is at slightly higher

Table 7.2 Compositions of the Co-existing Phases Along the L_A-H-V Locus for the System Hydrogen Sulphide-Water

Temp (°C)	Press[1] (kPa)	Mole Per Cent Hydrogen Sulphide		
		Aqueous[2]	Hydrate[3]	Vapour[2]
0	98.6	0.366	14.3	99.373
5	163.9	0.511	14.4	99.458
10	274.7	0.725	14.5	99.539
15	463.6	1.053	14.6	99.613
20	787.9	1.525	14.6	99.676

1 - from Equation (7.2)
2 - from low pressure solubility model, Chapter VI
3 - from a modified van der Waals-Platteeuw (1959) model using the parameters from Munck et al. (1989) and the hypothesis of Cady (1983)

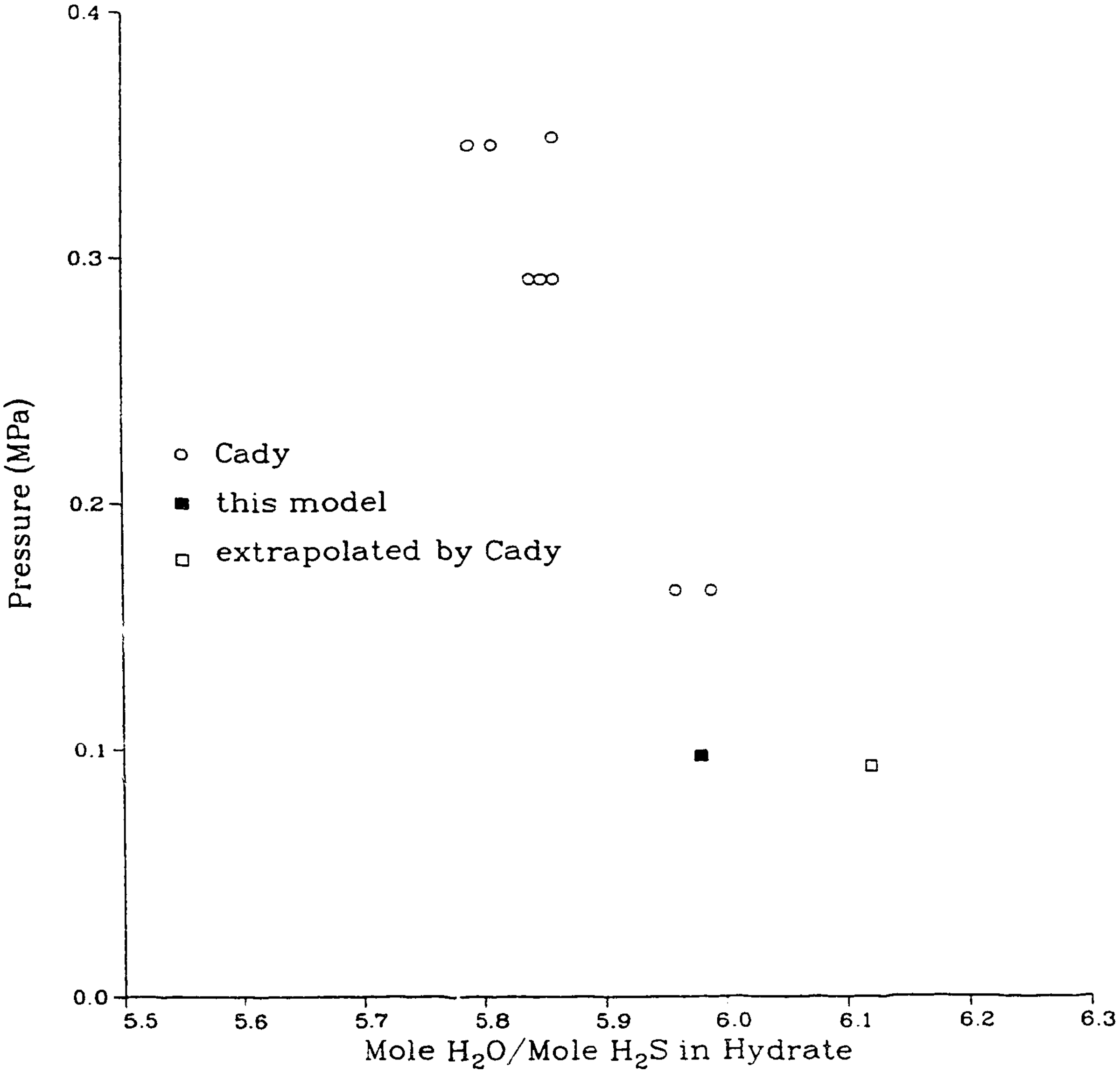

Fig. 7.3 Composition of the Hydrogen Sulphide Hydrate at 0°C

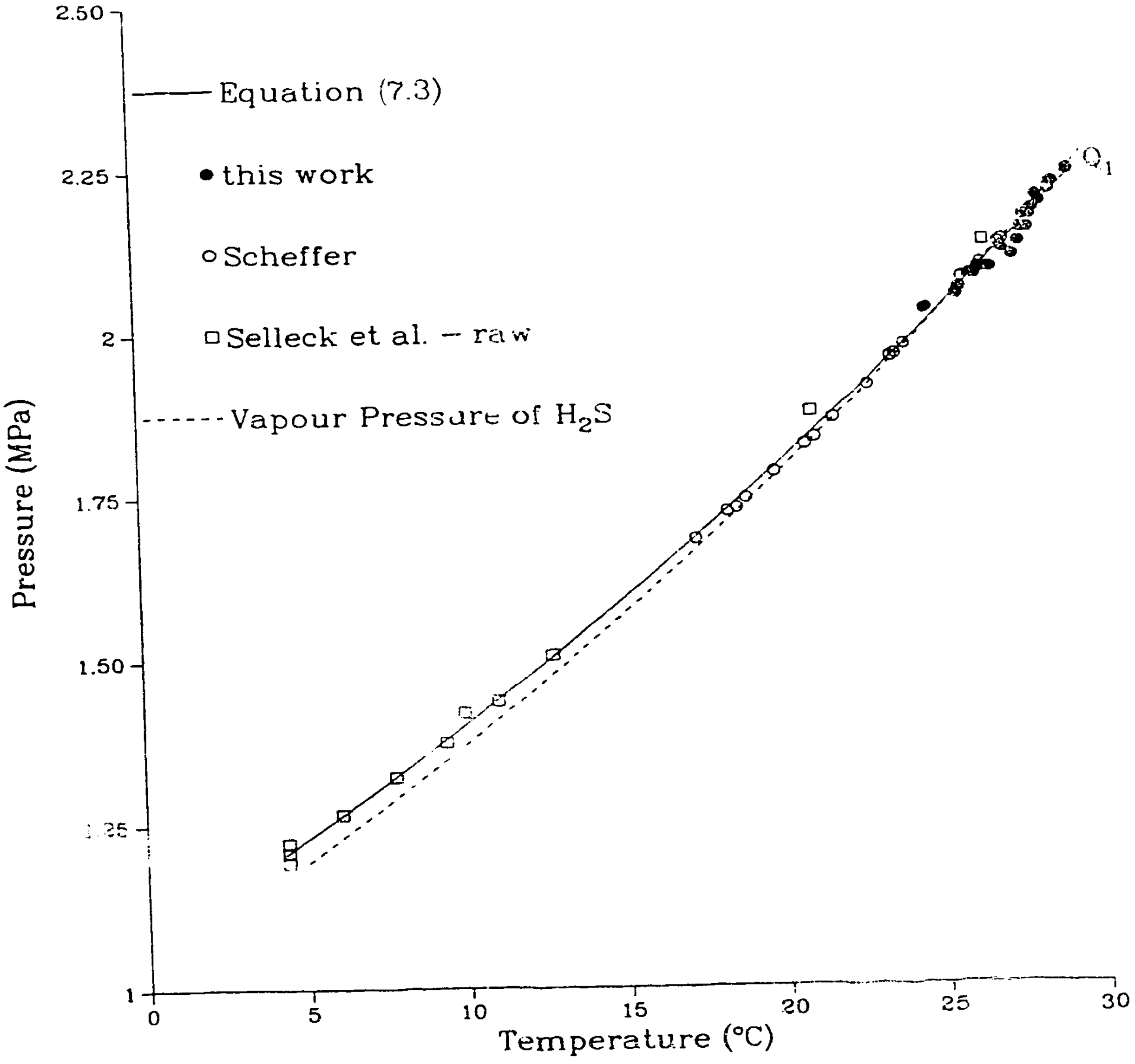

Fig. 7.4 The H_2S-Rich Liquid-Hydrate-Vapour Locus for the System Hydrogen Sulphide-Water

pressures than the H_2S vapour pressure. As the L_A-L_S-H-V quadruple point is approached the difference becomes smaller. At the quadruple point the L_S-H-V and the vapour pressure are essentially the same.

C. The L_A-L_S-H Locus

Scheffer (1913) and Selleck et al. (1951) both report points on the L_A-L_S-H locus. The total data set consists of only five points, two from Scheffer and three from Selleck et al. The data of the two sources were combined and correlated. The following equation was obtained.

$$P = 11.083\ T - 3352.515 \qquad (7.4)$$

where P is in MPa and T in K. Fig. 7.5 shows the L_S-L_A-H locus. This correlation looks deceptively poor because of the temperature scale used. As with other solid-liquid equilibria, this curve is very steep. Unlike the other correlations, this equation uses P and not ln P.

D. The H-I-V Locus

Although Selleck et al. (1952) report smoothed values along the H-I-V locus, the only experimental values in this region are those of Scheffer and Meyer (1919a,b). These data were fit with a Clausius-Clapeyron-type equation

$$\ln P = 15.8059 - 3070.13/T \qquad (7.5)$$

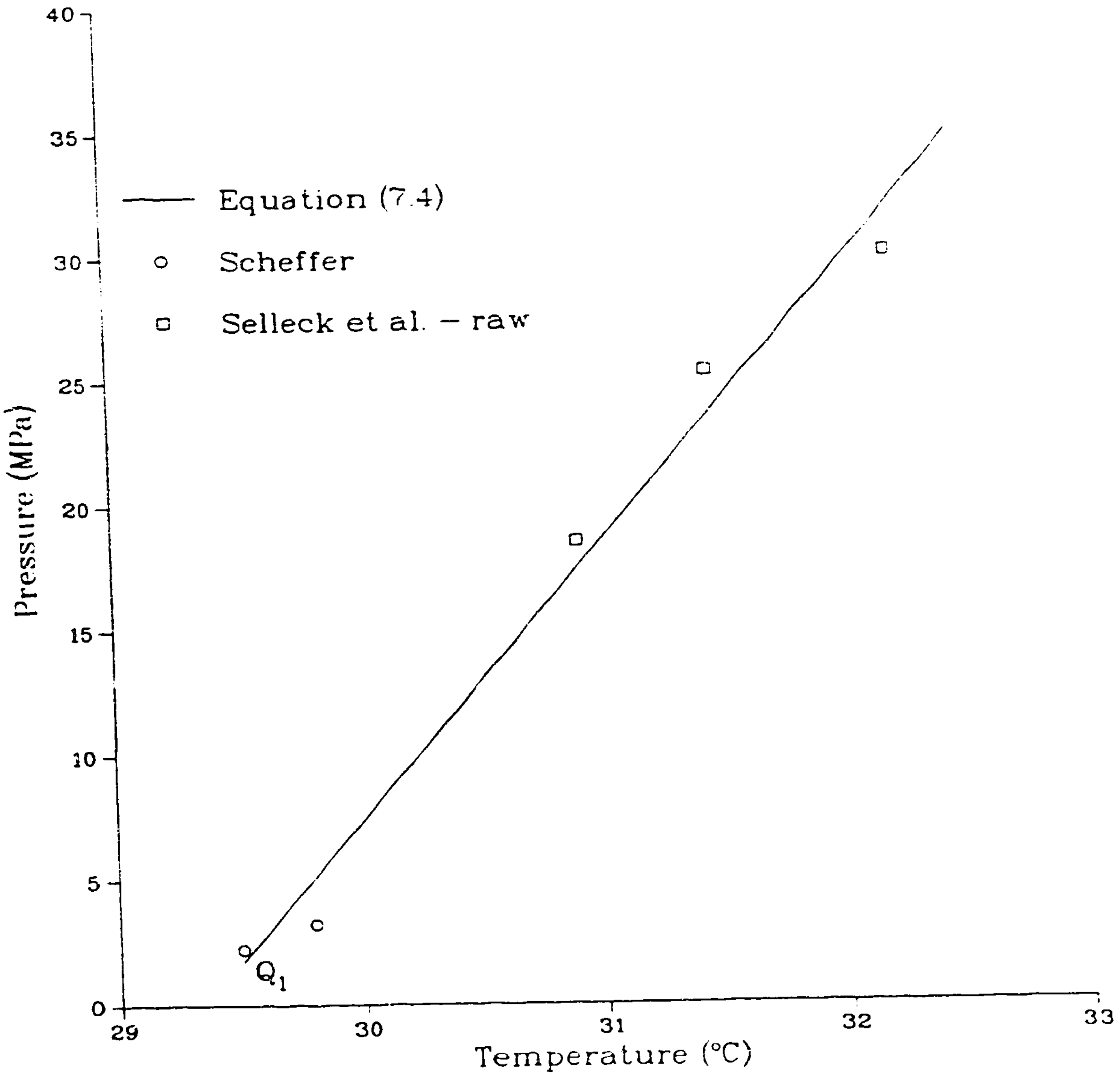

Fig. 7.5 The H_2S-Rich Liquid-Aqueous Liquid-Hydrate Locus for the System Hydrogen Sulphide-Water

where P is in kPa and T in K. Fig. 7.6 shows the experimental data and the correlation.

E. Summary

This chapter investigated the hydrate forming conditions for the system hydrogen sulphide-water. In particular, the pressure-temperature loci were correlated for the following equilibria: (1) L_A-H-V, (2) L_S-H-V, (3) L_A-L_S-H and (4) H-I-V. These correlations incorporated all of the data in the literature, regardless of their age. Errors in some of the studies were demonnstrated.

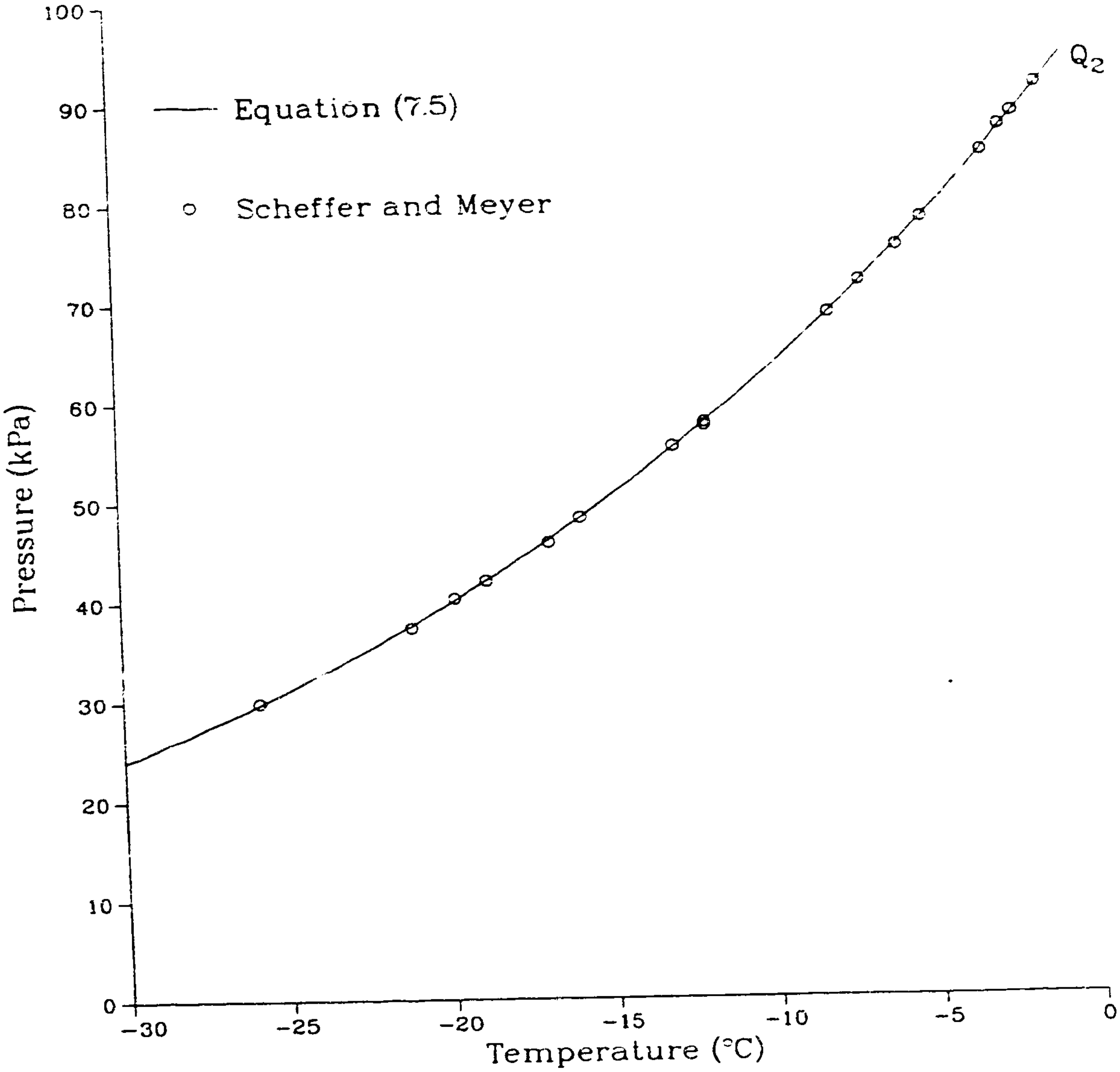

Fig. 7.6 The Hydrate-Ice-Vapour Locus for the System Hydrogen Sulphide-Water

VIII. Skeleton Tables

In Appendix C a series of tables of smoothed data are presented. These are neither experimental data nor a substitute for experimental data. Furthermore, it is not the author's intention to represent them as such. These tables are provided for rapid estimation of equilibrium properties.

The first table is the solubility at pressures below 1 MPa. The solubilities were calculated using the low pressure, Henry's law model presented in Chapter VI.

The next table is the vapour-liquid compositions at high pressures. These compositions were calculated using the PRSV equation of state. Below 200°C the values were calculated using the van Laar-type mixing rule. At 200°C and above, the calculations were performed using the original mixing rule. The pressures in this table are up to 100 MPa or until a third phase was encountered or to the critical pressure depending on the temperature. Thus, many of these entries represent extrapolations.

The final tables are the pressures and temperatures along the various three-phase . The L_A-L_S-V locus was calculated using the equation given in Chapter III. The other loci were calculated with the equations presented in Chapter VII.

IX. Concluding Remarks

A significant, new interpretation of the phase behavior of the system hydrogen sulphide-water was presented. It was developed using new experimental data as well as those from the literature

A thorough and critical review of the literature was presented. For almost forty years, the smoothed data of Selleck, Carmichael and Sage (1952) were considered to be the benchmark for this system. Notwithstanding, errors in their smoothed data have been discovered.

The major new observation of this thesis is that the LLV critical end point is 6°C higher than previously believed. By itself, this is a significant observation. However, the consequence of this observation is more important. Coupling this observation with the work of Selleck et al., one must conclude that the smoothing of Selleck et al. is wrong.

An equation of state (PRSV) was used to correlate fluid phase behavior in the system H_2S-H_2O. Data from many sources, including the raw data of Selleck et al. (1951) were examined. It was demonstrated that the smoothing and extrapolations of Selleck et al. are in error and in particular, the aqueous phase extrapolations are incorrect, possibly by up to a factor of three. Also, a new description of the 104.4°C isotherm is presented which is consistent with the raw data of Selleck et al. This isotherm is the keystone of the new analysis. The experimental data show a three-phase point at this temperature which the smoothing/extrapolations of Selleck et al. indicated did not exist.

Low pressure solubility data were correlated using a modified-Henry's law approach. An excellent fit of virtually all of the experimental data in this region was obtained. Since the model fit the vast majority of the data, it was concluded that experimental values which disagree with the model must be in error.

Finally, the various three-phase loci involving hydrates were examined. All of the data in the literature as well as new values were used to correlate the pressure and temperature along these loci.

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APPENDIX A The High Pressure Cell

As a part of this thesis a series of high temperature experiments was also proposed. These experiments were designed to measure dew points of hydrogen sulphide-water mixtures in the vicinity of the critical point of water. From these dew points the upper critical locus for the binary system would be established. Unfortunately the high pressure apparatus could not be made to work.

A. Equilibrium Cells

Many autoclaves have been utilized to investigate high pressure and high temperature phase behavior. Almost all of the cells proposed fall into one of two groups: (1) sampled cells and (2) dew/bubble point cells. Schneider (1977) classifies these two methods as (1) analytical and (2) synthetic. In his review of high temperature-high pressure apparatus he lists the advantages and disadvantages of both methods.

In sampled cells, once equilibrium has been achieved, the pressure and temperature are measured and samples are withdrawn. Care must be taken not to disturb the equilibrium when taking samples. The pressure drop must be kept to a minimum during sampling; thus large samples usually cannot be removed. To aid in the attainment of equilibrium, the sample is mixed. The type of mixing used allows the sampled cells to be subclassified into (1) flow and (2) static. In flow-type cells, the vapour is withdrawn from the top of the cell and recirculated through the bottom (the liquid). Static cells use some type of mechanical agitation, usually rocking or stirring. The cell used for the investigation of the three-phase locus was a flow-type, sampled cell.

In the dew/bubble point cells, a sample of known composition is injected into the cell; thus no composition measurements are required. Usually the cell is operated in one of two modes: (1) isothermally or (2) isochorically. In the isochoric method, the cell is heated (cooled) until the bubble (dew) point is reached. Detection of the phase change is often difficult to ascertain visually. To aid in its detection, the pressure and temperature should be monitored simultaneously. The phase transition occurs when there is a discontinuity in the slope of the P-T curve. In the isothermal method, a mixture of known composition is compressed (expanded) from the single phase region into the two phase region. A discontinuity in the slope of the P-v curve indicates the phase boundary. A major disadvantage of the synthetic method is that the composition of the second phase is unknown; it must be inferred. Another advantage of the dew/bubble point cell is that P-v-T data can be easily measured for the mixture.

B. The Dew-Point Cell

The synthetic method was to be used for the high temperature experiments. The two types of dew point cells were considered: (1) the variable volume cell of Lentz

(1968) and (2) the constant volume cell of Seward and Franck (1981). After an investigation of the autoclaves, it was concluded that the basic design of Lentz would be the best for the proposed study. However, there are differences between the cell described in the Lentz paper and the one proposed for this investigation.

A study of the corrosion of alloys for sour gas well environments performed by Watkins and Greer (1976) concluded that *Hastelloy C-276* was one of the best alloys for this application. Test conditions were severe: up to 260°C and 140 MPa. Thus *Hastelloy C-276* was used for the construction of the autoclave used in this study. *Hastelloy C-276* is a complex alloy containing nickel (55%), molybdenum (16%), chromium (15.5%), iron (5.5%), tungsten (3.75%), cobalt (2.5%) and other elements in amounts less than 1%. It is not ferromagnetic.

The cell was a thick-walled cylinder with a window at one end. The cell has an internal diameter of 12.7 mm (0.5 in) and an outside diameter of 50.8 mm (2.0 in) and a window diameter of 19.1 mm (0.75 in). Its length was 356 mm (14 in). Given that the yield strength of *Hastelloy C-276* at 450°C (the maximum temperature that the cell will be subjected to in this investigation) is 225 MPa, the Lamé equation (Popov, 1976) predicts that the cell should withstand an internal pressure of 135 MPa which is well above the maximum pressure of this investigation. A sample injection port and a themocouple well were located 76.2 mm

(3.0 in) from the end of the cell and were diametrically opposed.

Inside the cell was a piston. The piston was used to change the internal volume of the cell. The piston was 63.5 mm (2.5 in) in length and fit snugly inside the cell. The front face of the piston was polished which permitted the contents of the cell to be viewed. The location of the piston was determined by magnetic induction. A thin rod was welded to the free end of the piston (1.6 mm [1/16 in] in diameter and 280 mm [14 in] long). A small magnet was attached to the other end of the rod. This approach is similar to that of Gehrig (1980). An O-ring was placed near one end of the piston to prevent the pressure transmitting fluid (water) from entering the sample. In order for the O-ring to function properly, it must not be subjected to high temperatures. Thus a cooling jacket was required. Initially a copper coil was used. Unfortunately, this did not work. In order for the cooling to be large enough, the cooling water must come in contact with the exterior wall of the cell. A new cooling jacket was constructed with this in mind. No further problems were encountered due to overheating of the O-ring.

In order to obtain the the phase transition, the pressure and temperature must be monitored simultaneously. In this case, the temperature was measured using a Type J thermocouple and the pressure using a transducer. The transducer was a Druck Type PTX 150 (0-50 MPa) The thermocouple was calibrated using a platinum resistance thermometer. Pressure measuring devices were calibrated using a dead weight gauge. The output from the thermocouple and pressure transducer were read on a digital voltmeter (Hewlett Packard Model 3450A) and simultaneously on an X-Y plotter (F.L. Moseley Co. Model 2D). The pressure was also monitored using two sixteen-inch Heise bourdon tube gauges (0-30 MPa and 0-100 MPa) which allowed for an easier measurement of the pressure, especially in case of emergency.

A spindle press was used to inject water (the pressure transmitting fluid) into the manifold. Thus the position of the piston could be changed.

After examining many window seals, it was decided that the window of the proposed cell would be sealed using the Poulter-type seal (Spain and Paauwe, 1977). In this type of seal the touching faces of the sapphire window and the metal seal must be optically flat (that is, they must be smooth to within 0.5 μm). Seward and Franck (1981) used a similar seal that held at pressures up to 250 MPa. Cylindrical sapphire windows 19.1 mm (0.75 in) in diameter and 19.1 mm (0.75 in) in length were obtained from Crystal Systems Inc. The face of the seal was polished flat. The flatness of these surfaces was verified using certified optical flats.

The transducer malfunctioned and had to be returned to the manufacturer. A long delay was encountered getting the transducer repaired.

The internal volume of the cell cannot be calculated from geometrical methods. A geometrical appproach would not include the volume of the injection line and valve, the effect of the thermocouple well and the space between the piston and the cell wall. The volume of the cell is a function of the temperature, pressure and piston position. Because the wall of the cell is quite thick, the effect of pressure is believed to be quite small (less than 1%). The effect of temperature can be estimated from thermal expansion. Assuming *Hastelloy C-276* has a constant coefficient of thermal expansion of $1.1x10^{-5}$/°C, then a temperature increase of 425°C will result in an increase in the volume of the metal of approximately 1.5%. In order to calibrate the volume of the cell as a function of pressure, temperature and piston position, argon was to have been used. The P-v-T properties of argon are well known; thus by changing the three variables in a specified manner, the volume can be correlated.

In order to prevent any disasters due to the catastrophic failure of the cell, it was placed in an explosion-proof barricade. The barricade was a cube approximately one meter on each side constructed from three-millimeter-thick steel plate. The design of the barricade followed the guidelines of Moore (1967).

C. Problems With The Window

Initial pressure testing of the original design of the cell revealed that the seal around the window end of the cell did not work. Pressure testing was performed using a cylinder of nitrogen. Leak rates from the window were seemingly small. During a series of pressure tests the cell was submerged in a tank of water. A buret was set up to collect any gas that escaped from the window end of the cell. In one such test 5 cm^3 of gas (at room conditions) was collected over a period of 5 h. During that time the pressure fell from 12.125 MPa to 11.750 MPa ($\Delta P/\Delta t \approx -.075$ MPa/h). Although this seems like a small leak, any leak was deemed unacceptable. Tightening the bolts around the window did not decrease the leak rate.

The window housing was redesigned. A threaded cap, into which the window fit snuggly, was constructed. A new seal was made with a threaded end such that the cap and the seal could be connected. The face of the new seal was polished optically flat. Both the cap and the new seal were constructed from 316 stainless steel. A series of pressure tests was performed using the cap-seal arrangement. They were unsuccessful. Even at low pressure (less than 1 MPa) this seal leaked. A small amount of Canada balsam was then placed between the window and the seal. This time a seal was achieved at pressures up to 18.5 MPa (full pressure from a nitrogen bottle) for several hours. This was deemed a successful test.

The cell was removed from the pressure test apparatus and connected to the experimental equipment As a test of the equipment a series of experiments to measure the vapour pressure of pure water were proposed. The purpose of these experiments was to ensure that all of the auxiliary apparatus functioned properly. For example, there was some doubt that the heaters would be able to heat the cell and its contents to 400°C. A small amount of water was injected into the cell. The heaters were turned on and the temperature and pressure were monitored. During this test a temperature of 300°C was obtained before the heaters were turned off. In spite of the difficulties reading the pressure gauge and the voltmeter (the pressure and temperature were changing rapidly), the measured vapour pressure was reasonably accurate (maximum error of about 4%).

However, during the second attempt to measure the vapour preesure, the window end of the cell was clearly leaking. The pressure was very low, never exceeding 0.1 MPa. Steam could be seen escaping from the window.

The seal was modified slightly by placing a piece of gold foil (0.025 mm thick) between the window and the seal. With this arrangement, the window never sealed even at low pressure.

APPENDIX B Cubic Equations of State for Water

Pure water is well understood on the macroscopic level and for any application involving pure water, the tabulated data should be consulted. Unfortunately, in many situations, water is a component in a mixture. To evaluate the properties of these mixtures, the tabular data are less useful. Many multiconstant equations of state have been proposed which accurately describe the properties of pure water. These equations are much too complex to be used to predict mixture properties or multicomponent phase equilibrium. However, the cubic equations proposed were too simplistic to be expected to predict accurately all the thermophysical properties of pure water and aqueous systems but can be used with reasonable accuracy for correlating vapour-liquid equilibrium.

Since van der Waals demonstrated that a single equation could be applied to both the liquid and vapour phases, many cubic equations have been proposed. A major shortcoming of these equations is their inability to accurately represent the properties of both the liquid and vapour phases. However, the ease of application of the cubic-type equation has led to a lot of work to develop an equation which is accurate for a wide range of substances. With the

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A portion of this appendix was presented at a conference. Carroll, J.J. and Mather, A.E., "Cubic Equations of State for Water and Aqueous Systems", *Second International Conference on the Thermodynamics of Water and Aqueous Systems With Industrial Applications*, Airlie House, VA, May (1987). Publication pending.

introduction of the Soave equation, accurate prediction of phase behavior using a cubic equation for both phases was shown to be feasible. Peng and Robinson advanced the process with an equation which improved the prediction for the liquid phase properties. Although these two equations gave excellent results for hydrocarbons and a few associated inorganic compounds (carbon dioxide, carbon monoxide, nitrogen and hydrogen sulphide for example), water and other polar substances were not easily incorporated into this method of predicting vapour-liquid equilibrium. This appendix contains a review of a few of the better known cubic equations of state and how they have been modified for use on aqueous systems.

A. Introductory Discussion

There have been hundreds of equations of state proposed over the past century. Many of these equations had a similar algebraic structure. Abbott (1973) defined a generic cubic equation of state

$$P = \frac{RT}{v-b} - \frac{\theta}{v^2+\delta v+\epsilon} \tag{B.1}$$

This model represents the pressure of a fluid as the sum of a repulsive term (the first term) and an attractive term (the second tem). The repulsive pressure, the first term in Equation (B.1) was modelled using the van der Waals hard sphere equation. All equations examined in this paper utilized essentially the same repulsive term. Although several authors have proposed modifications of this term, they result in equations that are not cubic. None of these modifications will be discussed. The attractive term is a function of volume and usually temperature. In all of the equations studied in this review θ is temperature dependent. Equation (B.1) can be rearranged to

$$v^3 + (\delta-b-RT/P)v^2 + (\epsilon-\delta b-RT\delta/P+\theta/P)v - (\epsilon b+RT\epsilon/P+\theta b/P) = 0 \tag{B.2}$$

hence the term "cubic equation". For a fluid in the two phase region, the largest real root of Equation (B.2) would be the vapour volume. The smallest real root which is greater than the co-volume is the liquid volume. However, the deignation of the root to a specified phase is more difficult in practise, especially when dealing with mixtures.

The constants in a cubic equation are obtained from applying the criteria that the critical isotherm has a flat inflection point at the critical point. Mathematically

$$(\partial P/\partial v)_{T_c} = 0 \tag{B.3}$$

$$(\partial^2 P/\partial v^2)_{T_c} = 0 \tag{B.4}$$

For a two-parameter equation of state any the two of these three equations may be used to calculate two parameters. Equations (B.3) and (B.4) are used to obtain the constants and the critical compressibility, z_c, is obtained from the original equation.

If $\theta=a$, $\delta=0$ and $\epsilon=0$, then Equation (B.1) reduces to the simplest cubic equation of state

$$P = RT/(v-b) - a/v^2 \tag{B.5}$$

This is the van der Waals (1873) equation. Applying the criteria of inflection of the critical isotherms yields:

$$a = 27R^2T_c^2/64P_c \tag{B.6}$$

$$b = RT_c/8P_c \tag{B.7}$$

$$z_c = 3/8 \tag{B.8}$$

Reid, Prausnitz and Sherwood (1977) list the critical compressibilities for almost 350 organic and inorganic substances. Their table includes values obtained experimentally and from correlations. These values range from a low of 0.12 for hydrogen fluoride to a high of 0.480 for nitrogen dioxide. The mean of this data is 0.266 and the standard deviation is 0.028. Assuming a normal distribution, 68% of the values are in the range 0.238 to 0.294 and 95% in the range 0.211 to 0.321. Therefore over 97.5% of the substances listed in this table have a critical compressibility less than 3/8.

Although equations of state are correlations of pressure, temperature and volume, their great utility is in their application to vapour-liquid equilibrium calculations. For calculating phase behavior, the component fugacities are required. The fugacity of a pure component is evaluated using an equation of state and the following thermodynamic relation

$$\ln(\phi) = \ln(f/P) = -1/RT \int_{V}^{\infty} (v - RT/P)(\partial P/\partial v)_T \, dv \qquad (B.9)$$

When working with mixtures, the equation of state is coupled with an appropriate set of mixing rules. The fugacity of a component in the solution is obtained from

$$\ln(\hat{\phi}_i) = 1/RT \int_{V}^{\infty} [(\partial P/\partial n_i)_{T,v,nj} - RT/v] \, dv - \ln z \qquad (B.10)$$

There are analytical solutions to the above improper integrals for all equations studied in this review.

B. Redlich-Kwong Equations

Unfortunately, the van der Waals equation does not accurately represent fluid properties over a very wide range of pressure and temperature. A more accurate equation was proposed by Redlich and Kwong (1949). Their equation is

$$P = \frac{RT}{v-b} - \frac{a}{\sqrt{T}v(v+b)} \qquad (B.11)$$

where a and b are evaluated from the critical isotherm

$$a = 0.42748\ R^2T_c^{2.5}/P_c \tag{B.12}$$

$$b = 0.08664\ RT_c/P_c \tag{B.13}$$

$$z_c = 1/3 \tag{B.14}$$

Although the critical compressibility factor for this equation is less than van der Waals, it is still greater than the experimental value for most substances. Over 97.5% of the substances listed in Reid et al. have critical compressibilities less than 1/3.

van der Waals used kinetic theory to develop his equation. The basis for the Redlich-Kwong equation is an empirical extension of the van der Waals equation and is justified by the improvement in the property predictions.

For applications to mixtures, the following rules are used

$$a = \sum_i\sum_j x_i x_j\ (a_i a_j)^{1/2} \tag{B.15}$$

$$b = \sum_i x_i b_i \tag{B.16}$$

A more thorough discussion of mixing rules is presented later.

De Santis, Breedveld and Prausnitz (1974) varied the a for water, making it temperature dependent:

$$a = a^0 + a^1(T) \tag{B.17}$$

where a^0 represented the intermolecular attraction due to London forces and a^1 was to account for attraction due to hydrogen bonds, permanent dipole and quadrupole moments. To obtain a^0, a^1 and b tabulated steam densities were fit using a least-squares technique. It was found that $b = 14.6 \text{ cm}^3/\text{mol}$ (Equation (B.13) gives $21.1 \text{ cm}^3/\text{mol}$) and a was given as a table of values. Holloway (1977) recalculated a based on the fugacity of pure water and used a least-squares method to correlate the a^1 with the following

$$a^1 = 1.318\text{x}10^8 - 1.93080\text{x}10^5 t + 186.4t^2 - 0.071288t^3 \quad (\text{B}.18)$$

and $a^0 = 3.5\text{x}10^7 \text{ cm}^6 \text{ atm K}^{1/2} \text{ mol}^{-2}$. In Equation (B.18) t was in degrees Celsius. Holloway claimed that this equation reproduces the fugacity of pure water vapour from 20° to 1000°C and 0.05 to 10 MPa to within 1.3%. Flowers (1979) found errors in the mixture fugacity equations given by Holloway.

De Santis et al. also changed the mixing rules for aqueous systems. For a binary containing water and a non-polar component

$$a_{iw} = (a_i a_w^0)^{1/2} \quad (\text{B}.19)$$

For water-carbon dioxide

$$a_{wc} = (a_w^0 a_c^0)^{1/2} + R^2 T^{5/2} K_{eq}/2 \quad (\text{B}.20)$$

where K_{eq} is an equilibrium constant for the gas-phase reaction between water and carbon dioxide and is given by

$$\ln K_{eq} = -11.071 + 5953/T - 2.746\text{x}10^{6}/T^{2} + 4.646\text{x}10^{8}/T^{3} \qquad (B.21)$$

where T is in K. Note, the a^0 for carbon dioxide was obtained from experimental second-virial cross-coefficients data for carbon dioxide and simple non-polar gases. De Santis et al. give a^0=4.6x10^7 cm^6 atm $K^{1/2}$ mol^{-2} and a^1 is tabulated as a function of temperature (Equation (B.12) gives 6.37x10^7 cm^6 atm $K^{1/2}$ mol^{-2}).

Bowers and Helgeson (1985) further modified this equation for use on sodium chloride-water-carbon dioxide mixtures at high temperatures and pressures. The system is treated as a pseudobinary and the a for the water-sodium chloride pseudocomponent is a function of the weight fraction sodium chloride and temperature and the b is a function of the concentration of sodium chloride. These relations are quite long and will not be repeated here.

The Redlich-Kwong equation worked well for predicting the properties of light gases, but it did not work for liquids. Thus, it could not be used to predict vapour-liquid equilibrium. However, this equation did form the basis for other equations which have been used successfully for phase equilibrium calculations. As well, this equation has found use in the two-fluid approach to phase equilibrium. For example, Chao and Seader (1961) proposed a correlation where vapour phase fugacities are calculated using the Redlich-Kwong equation and liquid phase fugacities are obtained from a generalized correlation. This method was successfully applied to predict phase equilibria in hydrocarbon systems and is still widely used.

A complete review of all of the proposed modifications and applications of the Redlich-Kwong equation was beyond the scope of this chapter, but Horvath (1974) referenced many Redlich-Kwong papers.

Soave Equation

One of the first cubic equations of state to be successfully used for predicting phase equilibrium was the Soave (1972) modification of the Redlich-Kwong equation. Soave reasoned that for an equation to be applicable to a multicomponent mixture, it should accurately calculate the vapour pressure of the pure components. He replaced the $a/T^{1/2}$ term with a more general temperature dependence. Thus:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \tag{B.22}$$

The temperature dependence of the a was obtained from the pure component vapour pressure. Applying the classical criteria of inflection of the critical isotherm, the constants are

$$a(T_c) = 0.42748\ R^2T_c^2/P_c \tag{B.23}$$

$$b = 0.08664\ RT_c/P_c \tag{B.24}$$

$$z_c = 1/3 \tag{B.25}$$

The temperature dependence of a was found to be substance dependent, but for hydrocarbons Soave was able to correlate it using the acentric factor. The expression he derived is

$$a(T) = a(T_c)\cdot\alpha \tag{B.26}$$

$$\alpha = (1 + m\ [1-T_R{}^{1/2}])^2 \tag{B.27}$$

$$m = 0.480 + 1.574\omega - 0.176\omega^2 \tag{B.28}$$

For mixtures the following mixing rules are used

$$a = \sum_i\sum_j x_i x_j a_{ij} \tag{B.29}$$

$$a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij}) \tag{B.30}$$

$$b = \sum_i x_i b_i \tag{B.31}$$

Soave proposed the binary interaction parameter, k_{ij}, but found that it was unnecessary for mixtures of hydrocarbons.

Graboski and Daubert (1978a) used a larger and more accurate data base of vapour pressure and critical properties to recalculate m

$$m = 0.48508 + 1.55171\omega - 0.15613\omega^2 \tag{B.32}$$

For acentric factors in the range 0.0 to 0.8, this equation results in a maximum deviation in m of only about 1% over that of Soave. This seemingly small difference can have a dramatic effect on predicted vapour pressures.

Graboski and Daubert (1978b) also calculated interaction parameters for binary mixtures containing carbon dioxide, nitrogen, hydrogen sulphide and carbon monoxide. These interaction parameters were found by minimizing the deviation of experimental and predicted vapour-liquid equilibrium data. For the systems examined, the k_{ij} were found to be nearly independent of temperature, pressure and composition, and only a function of the binary pair. The k_{ij} ranged from 0.15 to -0.06 for the systems that were investigated.

The Soave-Redlich-Kwong equation is accurate for predicting equilibrium compositions in systems of hydrocarbons and a few associated non-hydrocarbons. It still did not accurately predict the physical properties of the liquid very well. As outlined above, the equation is not applicable to aqueous systems. The equation does a poor job of predicting the vapour pressure of water. It has been found that by varying the a the vapour pressure of water can be reproduced. Fig. B.1 shows the value of a required to do this along with the original-Soave a term, expressed as the ratio of a(T) to a(T_c). Correction of the a term formed a basis for modifications to the Soave equation for application to aqueous systems.

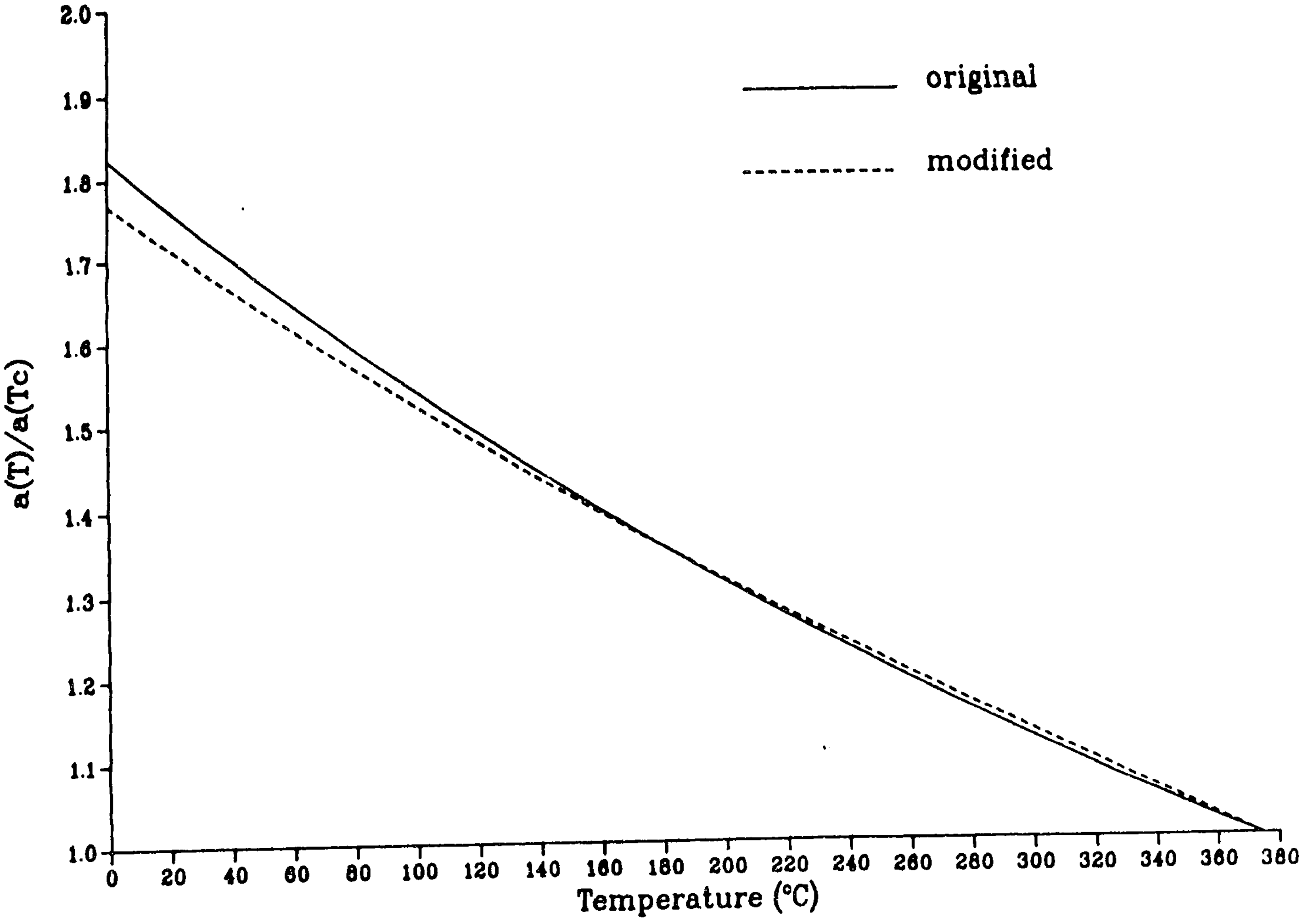

Fig. B.1 Modification of the Soave-Redlich-Kwong Equation for Water

Evelein, Moore and Heidemann (1976) proposed the following correction for the a for water

$$\hat{a}_{ii}/a_{ii} = 1 - k_{ii} \tag{B.33}$$

where $\hat{a}_{ii}$ is the value used to reproduce the vapour pressure, a_{ii} is from the original Soave method, and their table of k_{ii} values is well correlated by the following least-squares fit

$$k_{ii} = 0.11260 - 3.8705\text{x}10^{-4}T + 3.345\text{x}10^{-7}T^2 \tag{B.34}$$

where T is in K and ranged from 298 to 445 K (25° to 171°C). The values for k_{ii} were obtained by fitting the vapour pressure of pure water.

Won and Walker (1982) changed the Soave equation for polar substances. The a term was divided into two parts

$$a = a_n + a_p \tag{B.35}$$

where a_p is a polar contribution which is zero for non-polar substances. To obtain a

$$a_n = [a(T_c) - a_p(T_c)][1 + m(1 - T_R^{1/2})]^2 \tag{B.36}$$

$$a_p = a_p(T_c)/T_R^3 \tag{B.37}$$

$$a(T_c) = a_n(T_c) + a_p(T_c) = 0.42747\ R^2T_c^2/P_c \qquad (B.38)$$

For water: $a_n(T_c)$ = 2.93 atm L^2/mol^2, $a_p(T_c)$ = 2.59 atm L^2/mol^2 and m = -0.47. These values were found by minimizing the error in the predicted second virial coefficient, where the virial coefficient was calculated by

$$B = b - (a_n + a_p)/RT \qquad (B.39)$$

This equation was obtained by expanding the cubic equation into the virial form. Note, m is not the value given by either the Soave equation (m = 1.0006) or the Graboski-Daubert equation (m = 1.0004). This procedure did not ensure that the vapour pressure was accurately reproduced.

Mathias (1983) observed that for polar substances, the Soave α (actually he used the Graboski-Daubert) is too large for $T_R < 0.7$ and too small for $0.7 < T_R < 1$. This is demonstrated for water in Fig. B.1. He proposed the following modification

$$\alpha = [1 + m(1 - T_R^{1/2}) - p(1 - T_R)(0.7 - T_R)]^2 \qquad (B.40)$$

where p is a parameter that was determined from vapour pressure data. For water, p = 0.1277. Unfortunately it did not appear possible to correlate this parameter with any pure substance property (such as acentric factor or dipole moment). For a supercritical component α was changed to

$$\alpha = [\exp(c[1 - T_R^d]))]^2 \tag{B.41}$$

where

$$c = 1 + m/2 + 0.3p \tag{B.42}$$

$$d = (c-1)/c \tag{B.43}$$

Equations (B.42) and (B.43) were obtained by equating Equations (B.40) and (B.41) at the critical point. This modification was employed because it gave a better fit for the predicted second virial coefficients for pure substances at the higher temperatures.

Gibbons and Laughton (1984a,1984b) proposed the following modification

$$\alpha = 1 + X(T_R - 1) + Y(T_R^{1/2} - 1) \tag{B.44}$$

No generalization was given for X and Y but comparing Equations (B.44) and (B.27) gives:

$$X = m^2 \tag{B.45}$$

$$Y = -2m(m + 1) \tag{B.46}$$

For the materials examined, X and Y were obtained by fitting the pure component vapour pressure. For water X = 0.165 and

Y = -2.465.

Kabadi and Danner (1985) modified the α term for water

$$\alpha = [1 + c(1 - T_R^d)]^2 \tag{B.47}$$

The constants c and d were obtained by minimizing the error in the predicted vapour pressure, and c = 0.6620 and d = 0.80.

A summary of all the α terms where

$$\alpha = a(T)/a(T_c) \tag{B.48}$$

is given in Table B.1. The formulations of Mathias, Gibbons-Laughton and Kabadi-Danner accurately correlated the optimum α given in Fig. B.1. For water, there is only a small difference between the Soave and Graboski-Daubert and the error in the estimated α is shown in Fig. B.1. The method of Won and Walker is grossly in error. Below 100°C, the α's are greater than twice as large as the optimum. At the triple point, their value of α is 3.7 times too large. The error is smaller in the region of the critical point; however, the equation of Won and Walker does a poor job of reproducing the vapour pressure of water.

Table B.1 Summary of the α Modifications for the Soave Equation for Water

1. **Soave:**

$$\alpha = [1 + 1.00063(1 - T_R^{1/2})]^2$$

2. **Graboski and Daubert:**

$$\alpha = [1 + 1.00039(1 - T_R^{1/2})]^2$$

3. **Evelein, Moore and Heidemann:**

$$\alpha = [1 - k_{ii}(1 + - T_R^{1/2})]^2$$

$$k_{ii} = 0.11260 - 3.8705\text{x}10^{-4}T + 3.345\text{x}10^{-7}T^2$$

4. **Won and Walker:**

$$\alpha = 0.5308[1 - 0.47(1 - T_R^{1/2})]^2 + 0.4692/T_R^3$$

5. **Mathias:**

$$\alpha = [1 + 1.00039(1 - T_R^{1/2}) - 0.1277(1 - T_R)(0.7 - T_R)]^2$$

6. **Gibbons and Laughton:**

$$\alpha = 1 + 0.165(T_R - 1) - 2.465(T_R^{1/2} - 1)$$

7. **Kabadi and Danner:**

$$\alpha = [1 + 0.6620(1 - T_R^{0.8})]^2$$

C. Peng-Robinson Equation

A major shortcoming of the Redlich-Kwong-type equations is their inability to accurately predict the properties of the liquid phase (notably the density). Peng and Robinson (1976a) proposed a modification of the attractive term which resulted in the following equation

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) + b(v-b)} \tag{B.49}$$

The temperature dependence of the a term was obtained by fitting the pure component vapour pressure (in a similar fashion to Soave).

$$a(T) = a(T_c)\cdot\alpha \tag{B.50}$$

$$a(T_c) = 0.45724\ R^2T_c^2/P_c \tag{B.51}$$

$$\alpha = [1 + \kappa(1 - T_R^{1/2})]^2 \tag{B.52}$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{B.53}$$

$$b = 0.07780\ RT_c/P_c \tag{B.54}$$

$$z_c = 0.3074 \tag{B.55}$$

The critical compressibility for this equation is smaller than Redlich-Kwong equations, but still slightly larger than the experimental values for most substances.

This equation worked very well for light hydrocarbons, associated non-hydrocarbons (hydrogen sulphide, carbon dioxide, carbon monoxide and nitrogen for example) and mixtures of these substances. It did not work as well for water and aqueous systems. As with the Soave equation, this equation did not accurately predict the vapour pressure of water. However, by modifying the a, the equation could fit the saturation pressure. Fig. B.2 shows how the a should be modified to reproduce the vapour pressure of water.

Peng and Robinson (1980) suggested the following alteration of the a term for use with water

$$\alpha = [1.0085677 + 0.82153(1 - T_R^{1/2})]^2 \qquad T_R < 0.7225 \tag{B.56}$$

$$\alpha = [1 + 0.85964(1 - T_R^{1/2})]^2 \qquad T_R \geq 0.7225 \tag{B.57}$$

The second of these is the original equation. This now ensured that the vapour pressure of water would be accurately estimated.

Stryjek and Vera (1986a) proposed the following modification of the original-Peng-Robinson equation

$$\kappa = \kappa_0 + \kappa_1(1 + T_R^{1/2})(0.7 - T_R) \tag{B.58}$$

where

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.019655\omega^3 \tag{B.59}$$

and κ_1 is a empirical parameter and was obtained by fitting the pure component vapour pressure and was found to be uncorrelated with any pure component property, even for hydrocarbons. Even for nonpolar compounds $\kappa_1 \neq 0$. for

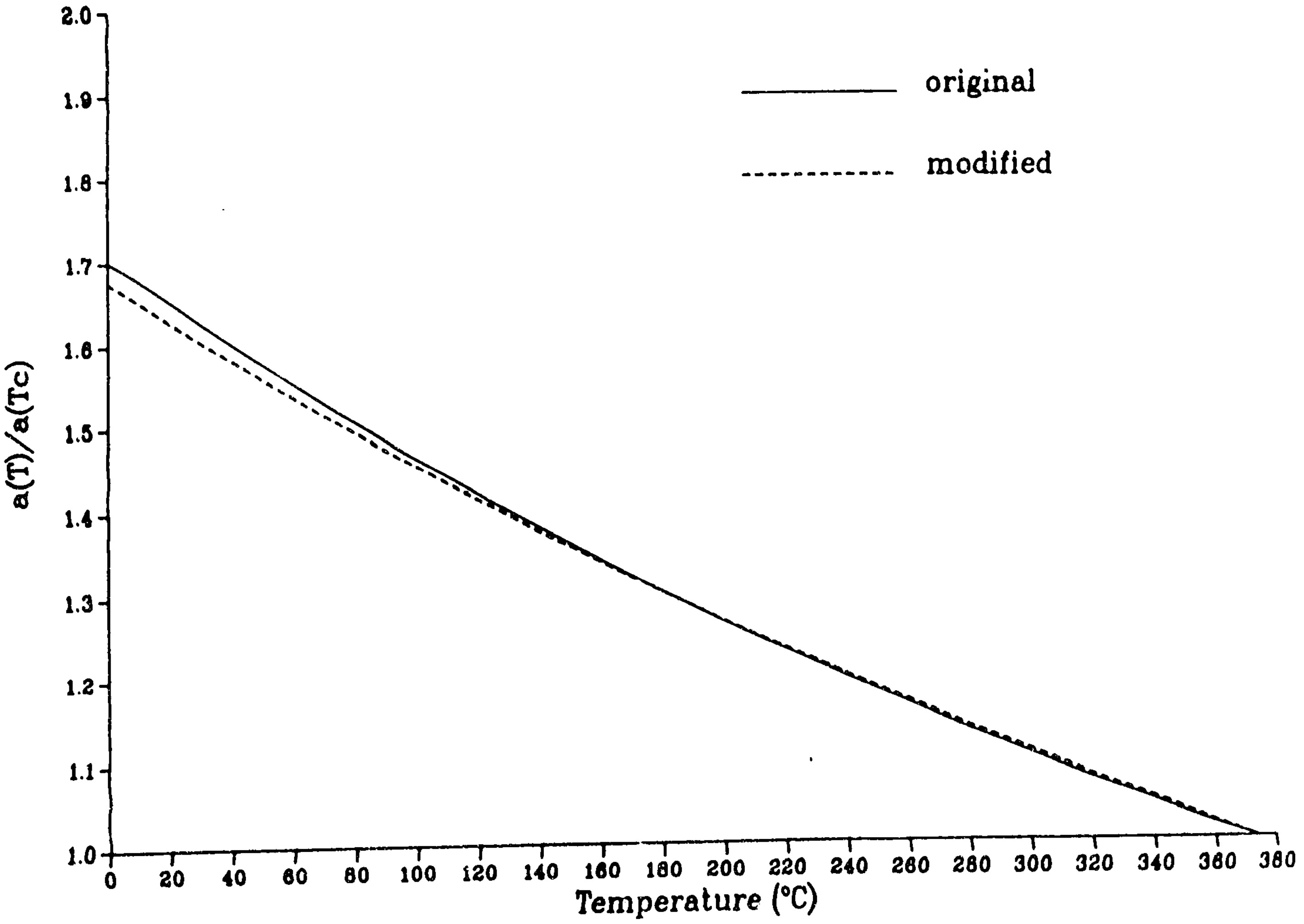

Fig. B.2 Modification of the Peng-Robinson Equation for Water example $\kappa_1 = -0.00159$ for methane, whereas for water $\kappa_1 = -0.06635$. For most substances, excluding water and alcohols, better results were obtained for $T_R > 0.7$ using $\kappa_1 = 0$ and for all substances in the supercritical region they recommend using $\kappa_1 = 0$.

D. Three-Parameter Equations

All the equations discussed to this point had two parameters: a and b. In all cases a was a function of temperature and b was a constant. Using this approach, the vapour pressure of a pure substance could be accurately reproduced, but the other thermophysical properties might not be. For the equations discussed so far, the vapour density was accurately predicted, except for the region close to the critical point. However, liquid densities were not as good. With the introduction of a third parameter, c, the liquid density prediction should be improved.

The first three-parameter equation was proposed by Clausius (1880) and has the following form

$$P = \frac{RT}{v-b} - \frac{a}{T(v+c)(v+c)} \tag{B.60}$$

From the inflection of the critical isotherm

$$a = 27R^2T_c^3/64P_c \tag{B.61}$$

$$b = v_c - RT_c/4P_c \tag{B.62}$$

$$c = 3RT_c/8P_c - v_c \tag{B.63}$$

For this equation, the critical compressibility is an input parameter.

Martin (1979) demonstrated that an equation with this form is the "best" cubic for predicting densities of pure fluids.

Heyen Equation

Heyen (1980) presented an equation with the following form

$$P = \frac{RT}{v-b(T)} - \frac{a(T)}{v[v+b(T)] + c[v-b(T)]} \tag{B.64}$$

where both a and b were functions of temperature. From the criteria of inflection of the critical isotherm he obtained

$$a(T_c) = \Omega_a R^2 T_c^2 / P_c \tag{B.65}$$

$$b(T_c) = \Omega_b R T_c / P_c \tag{B.66}$$

$$c = \Omega_c R T_c / P_c \tag{B.67}$$

where

$$\Omega_c = 1 - 3z_c \tag{B.68}$$

$$\Omega_a = 3z_c^2 + 2\Omega_b\Omega_c + \Omega_b + \Omega_c + \Omega_b^2 \tag{B.69}$$

and Ω_b was the smallest positive root of

$$\Omega_b^3 + (2 - 3z_c)\Omega_b^2 + 3z_c^2\Omega_b - z_c^3 = 0 \tag{B.70}$$

Note, if $z_c = 0.3047$ (or equivalently, if $c = b$), then the

Heyen equation has the same form as the Peng-Robinson equation. If $z_c = 1/3$ ($c = 0$), then it has the form of the Soave equation.

The temperature dependence of the a and b are given by

$$a(T) = a(T_c)\exp[k(1 - T_R^n)] \tag{B.71}$$

$$b(T) = b(T_c)(1 - m\tanh[\theta(T_R - 1)/2]) \tag{B.72}$$

The values of the four constants (k, m, n and θ) were obtained by fitting pure component vapour pressure and liquid density. For normal fluids, the constants were correlated with the acentric factor

$$k = 0.47614 + 0.51445\omega - 0.19072\omega^2 \tag{B.73}$$

$$n = 1.589 + 1.188\omega \tag{B.74}$$

$$m = 0.2311 - 0.0421\omega + 0.39068\omega^2 \tag{B.75}$$

$$\theta = 6.8635 + 13.982\omega + 7.8829\omega^2 \tag{B.76}$$

In a study of equations of state Trebble and Bishnoi (1986) demonstrated that for some regions the Heyen equation predicted negative heat capacities. This is physically impossible and thus the Heyen equation should be used with extreme caution.

Patel-Teja Equation

Teja and Patel (1981) and Patel and Teja (1982) presented an equation with a form similar to Heyen's

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) + c(v-b)} \qquad (B.77)$$

In this case only the a term was a function of temperature. The constants were given by

$$a(T_c) = \Omega_a R^2 T_c^2/P_c \qquad (B.78)$$

$$b = \Omega_b R T_c/P_c \qquad (B.79)$$

$$c = \Omega_c R T_c/P_c \qquad (B.80)$$

where

$$\Omega_c = 1 - 3\zeta_c \qquad (B.81)$$

$$\Omega_a = 3\zeta_c^2 + 2\Omega_b\Omega_c + \Omega_b + \Omega_c + \Omega_b^2 \qquad (B.82)$$

and Ω_b was the smallest, positive real root of the following equation

$$\Omega_b^3 + (2 - 3\zeta_c)\Omega_b^2 + 3\zeta_c^2\Omega_b - \zeta_c^3 = 0 \qquad (B.83)$$

From this analysis ζ_c should have been the critical compressibility factor, but instead it was treated as a substance dependent parameter. Several relations were examined for the temperature dependence of the a term. The following

$$a(T) = a(T_c)[1 + F(1 - T_R^{1/2})]^2 \qquad (B.84)$$

which was similar to those of Soave and Peng-Robinson was determined to be the best. The values for F and ζ_c were obtained by fitting the saturated liquid while simultaneously satisfying the criteria of equality of the fugacities along the vapour pressure curve. For non-polar substances, F and ζ_c were correlated with the acentric factor

$$F = 0.452413 + 1.30982\omega - 0.295937\omega^2 \tag{B.85}$$

$$\zeta_c = 0.329032 - 0.076799\omega + 0.0211947\omega^2 \tag{B.86}$$

However, for polar substances, such a generalization was not possible. For water, F = 0.689803 and $\zeta_c = 0.269$, thus $\Omega_a = 0.50455$, $\Omega_b = 0.065103$ and $\Omega_c = 0.193$.

To improve the density prediction in the critical region ($0.9 \leq T_R \leq 1$), they proposed the following modification

$$\zeta_c' = \zeta_c - 10(\zeta_c - z_c)(T_R - 0.9) \tag{B.87}$$

The cost of this modification is a decrease in the accuracy of the vapour pressure prediction and an increase in the computation time because Ω_a, Ω_b and Ω_c became functions of temperature. Equation (B.87) ensures that the equation of state reproduces the critical compressibility and hence improve the liquid and vapour densities predictions in this region. This is not the case for equations with an "artificial" z_c such as Redlich-Kwong and Peng-Robinson.

E. Other Equations of State

Research into equations of state is dynamic and ongoing. Over the decades since van der Waals proposed his equation, hundreds of new and modified equations have been proposed.

Recently, an equation was proposed by Trebble and Bishnoi (1988). The TB equation may become the prominent equation in the future. It is superior to both the SRK and PR equations for predicting the density of pure liquids. However, it has not yet been subjected to the thorough testing that the SRK and PR equations have.

The TB equations is a four constant equation. Each of the constants has a carefully formulated temperature dependence. Thus the problems with the negative heat capacities does not occur.

F. Prediction of the Properties of Pure Water

Six of the equations of state examined in this study were tested for their ability to predict the properties of pure, saturated water. The equations selected were: (1) Soave, (2) Mathias, (3) Peng-Robinson, (4) Stryjek-Vera (5) generalized-Patel-Teja (6) optimum-Patel-Teja. Four properties were calculated: (1) vapour pressure (2) vapour compressibility, (3) liquid density and (4) enthalpy of vapourization. Comparison was made with the tables of Keenan et al. (1978). Since the temperature dependence of a was virtually the same for Mathias, Gibbons-Laughton and Kabadi-Danner over the range of temperature investigated, these equations would have essentially the same error associated with them. For the generalized-Patel-Teja equations, F and ζ_c were calculated from Equations (B.85) and (B.86). Also, the suggested modification of ζ_c in the critical region [Equation (B.87)] was not implemented. Several of the equations are used to predict the second virial coefficient and these are compared with values in the literature.

In this analysis the following definitions are used to describe the accuracy of the selected equations. The relative error, RE_i, is

$$RE_i = (T_i - C_i)/T_i \tag{B.88}$$

where T_i is the value from the steam tables and C_i is the calculated value. The absolute average deviation, AAD, is

$$AAD = \sum_{i=1}^{N} |RE_i|/N \tag{B.89}$$

where N is the total number of points that were calculated. The bias is

$$BIAS = \sum_{i=1}^{N} RE_i/N \tag{B.90}$$

The root-mean-squared deviation, RMS, is

$$RMS = (\sum_{i=1}^{N} RE_i^2)^{1/2}/N \tag{B.91}$$

For all equations, thirty six points were used from 10° to 360°C at 10° intervals. This covers almost the entire range from the triple point to the critical point.

For all equations, the critical properties for water are $T_c = 647.3$ K and $P_c = 22.09$ MPa and the acentric factor is 0.344. Small variations in these quantities can have a significant effect on the predicted vapour pressure.

The procedure for finding the saturation pressure at a given temperature was an iterative one. The Newton-Raphson method was used to obtain successive estimates of the pressure. Given a good starting point, convergence occurred in about five iterations. The initial estimate of the saturation pressure was obtained from the generalized correlation of Lee and Kesler (Reid, Prausnitz and Sherwood, 1977). Iterations on the pressure continued until the natural logarithm of the ratio of the the liquid and vapour fugacity coefficients was sufficiently small (in this case 10^{-5}). As a byproduct of this procedure, the compressibility factors for the saturated states were obtained. To avoid numerical problems, the roots of the cubic equation were calculated using the analytic solution (Perry and Chilton, 1973).

Vapour Pressure

Table B.2 lists the errors associated with the predicted vapour pressure for seven of the equations of state discussed earlier. Included in this table is the Redlich-Kwong equation. Fig. B.3 shows the the relative errors for the Soave, Peng-Robinson and generalized-Patel-Teja equations and Fig. B.4 shows the errors for the Mathias, Stryjek-Vera and optimum-Patel-Teja. Note, the ordinates on these plots are significantly different.

From Fig. B.3, the error in the Soave equation that led to the Mathias modification is clearly shown. The vapour pressure was underestimated for temperatures below $T_R = 0.7$ (T = 180°C) and overestimated above. Of these six equations, the Soave equation did the worst job of predicting the vapour pressure. From Fig. B.1, the modification of the α term required to fit the vapour pressure appeared quite small, but this analysis showed that it was very important.

The Peng-Robinson equation was the next poorest. However, at temperatures above $T_R = 0.7225$ ($T \simeq$ 195°C) the relative error was quite small - hence the form of the 1980 modification of Peng and Robinson. As with the Soave equation, the required modification of the a seemed quite small (Fig. B.2), but it had a large effect on the predicted vapour pressure.

The Mathias, Stryjek-Vera and optimum-Patel-Teja equation did an excellent job of predicting the vapour pressure.

Saturated Vapour Compressibility Factor

On Figs. B.5 and B.6 are shown the relative error in the compressibility factor for saturated steam as a function of temperature. Table B.3 summarizes the errors associated with the six equations.

Table B.2 Errors in the Predicted Vapour Pressure of Water

	AAD (%)	BIAS (%)	RMS (%)
Redlich-Kwong	16.9	-16.9	49.9
Soave-Redlich-Kwong	6.94	4.85	1.811
Mathias-Soave	0.42	-0.11	0.083
Peng-Robinson	4.13	3.08	1.113
Stryjek-Vera	0.21	-0.08	0.047
generalized-Patel-Teja	5.01	4.43	1.338
optimum-Patel-Teja	0.84	0.63	0.161

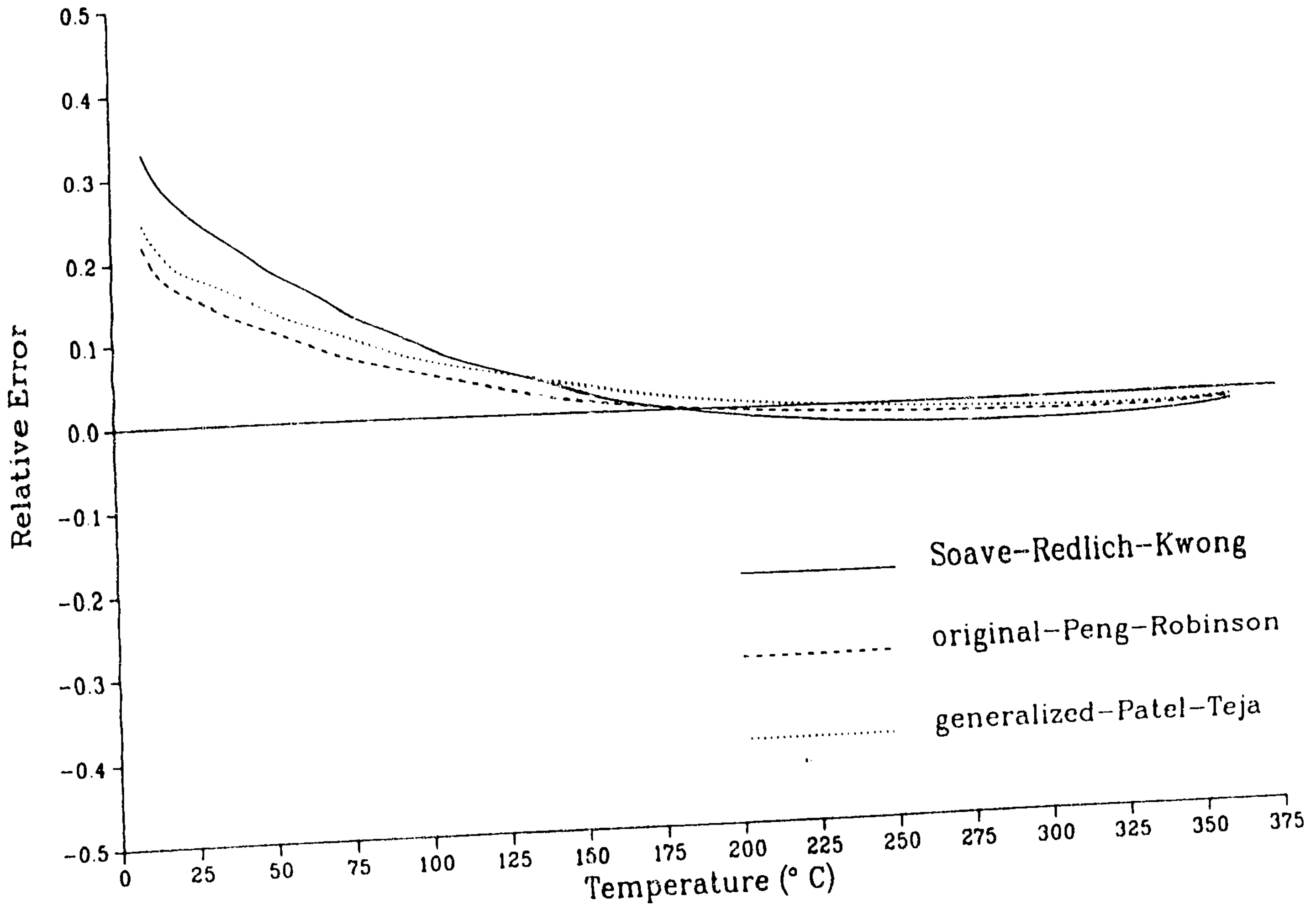

Fig. B.3 Errors in the Predicted Vapour Pressure of Water (Part I)

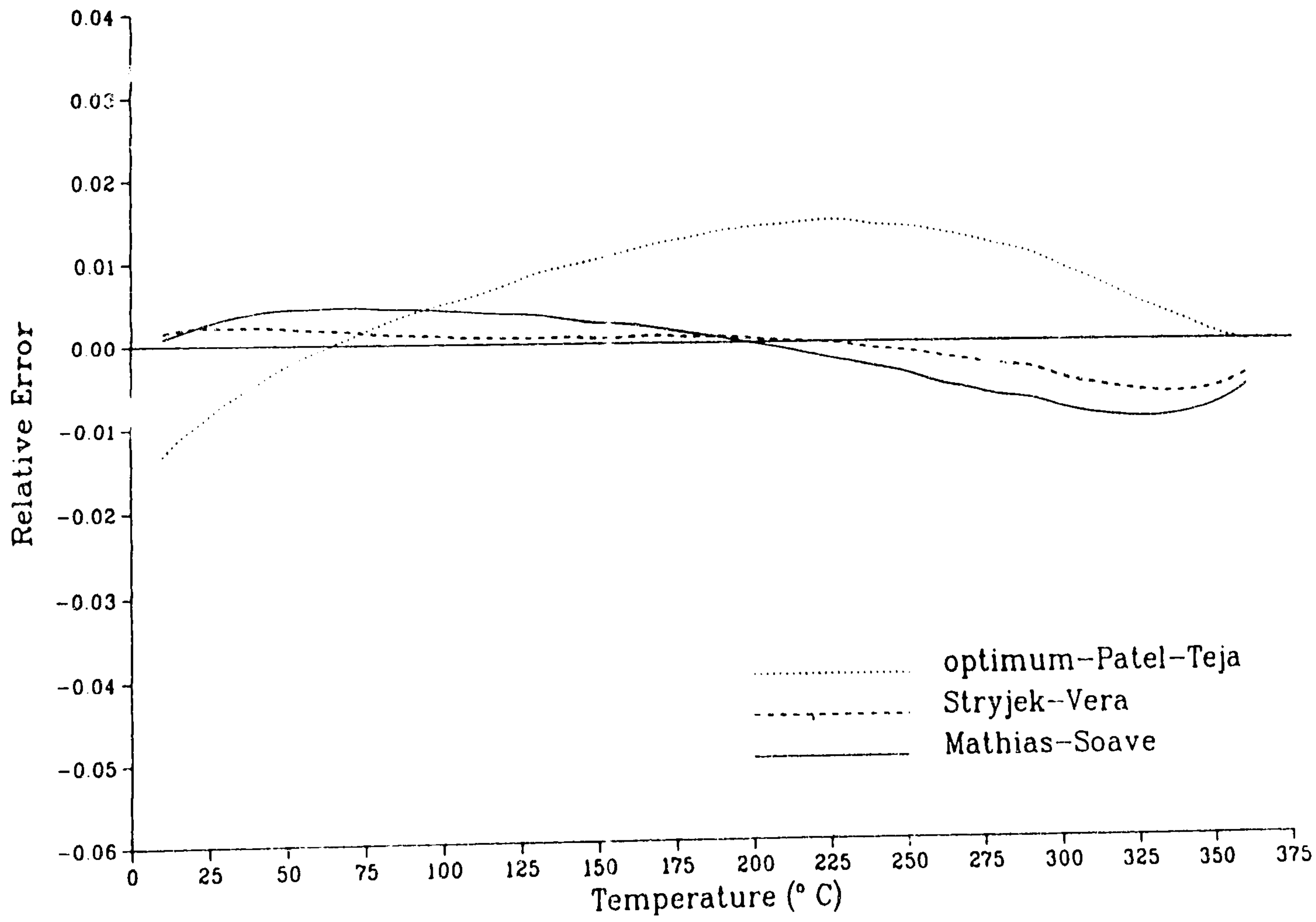

Fig. B.4 Errors in the Predicted Vapour Pressure of Water (Part II)

Table B.3 Errors in the Predicted Compressibility Factor of Saturated Steam

	AAD (%)	BIAS (%)	RMS (%)
Soave-Redlich-Kwong	3.23	-3.23	0.760
Mathias-Soave	3.44	-3.44	0.818
Peng-Robinson	2.38	-2.38	0.518
Stryjek-Vera	2.48	-2.48	0.548
generalized-Patel-Teja	2.37	-2.37	0.509
optimum-Patel-Teja	1.15	-1.15	0.224

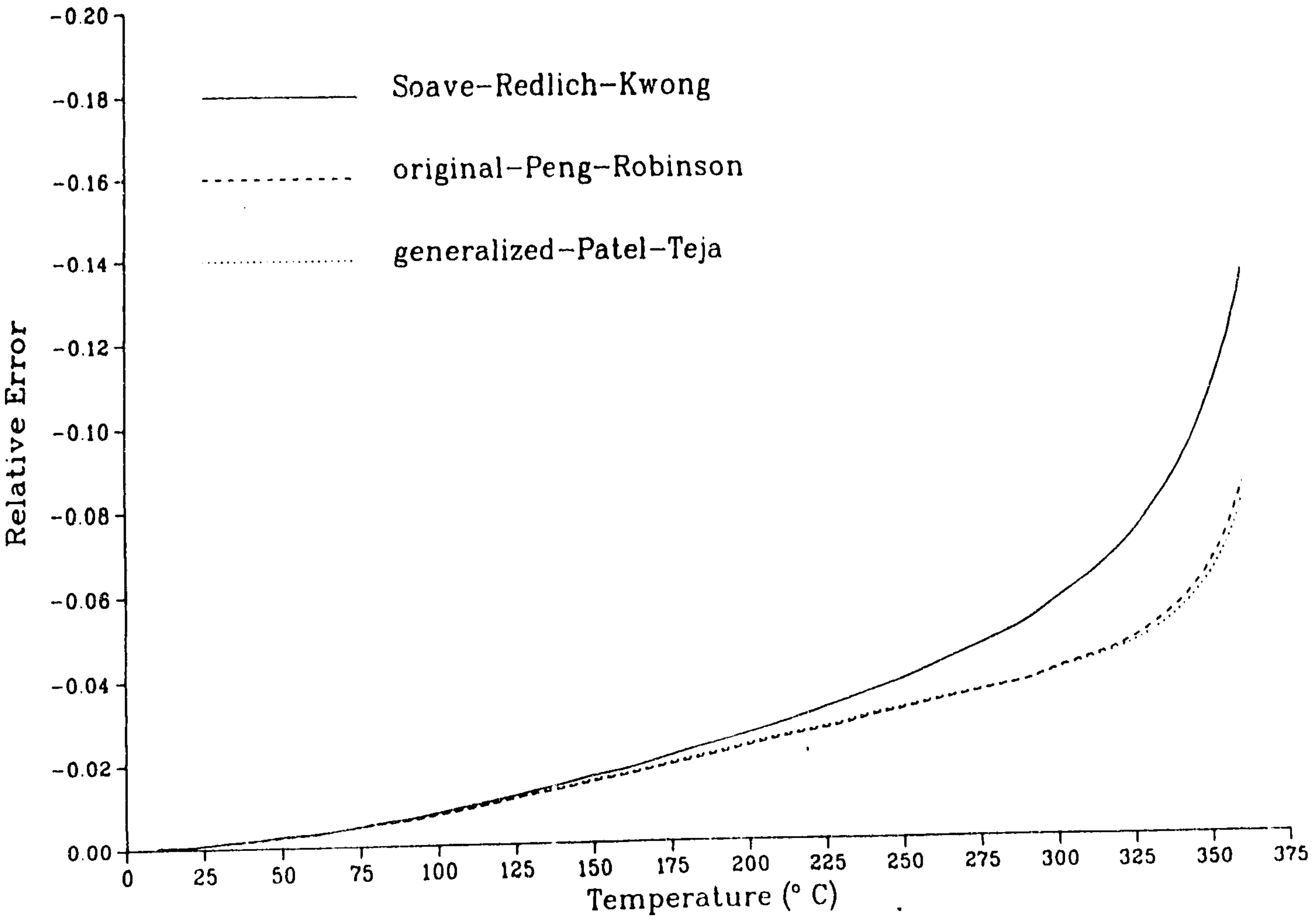

Fig. B.5 Errors in the Predicted Compressibility Factor of Saturated Steam (Part I)

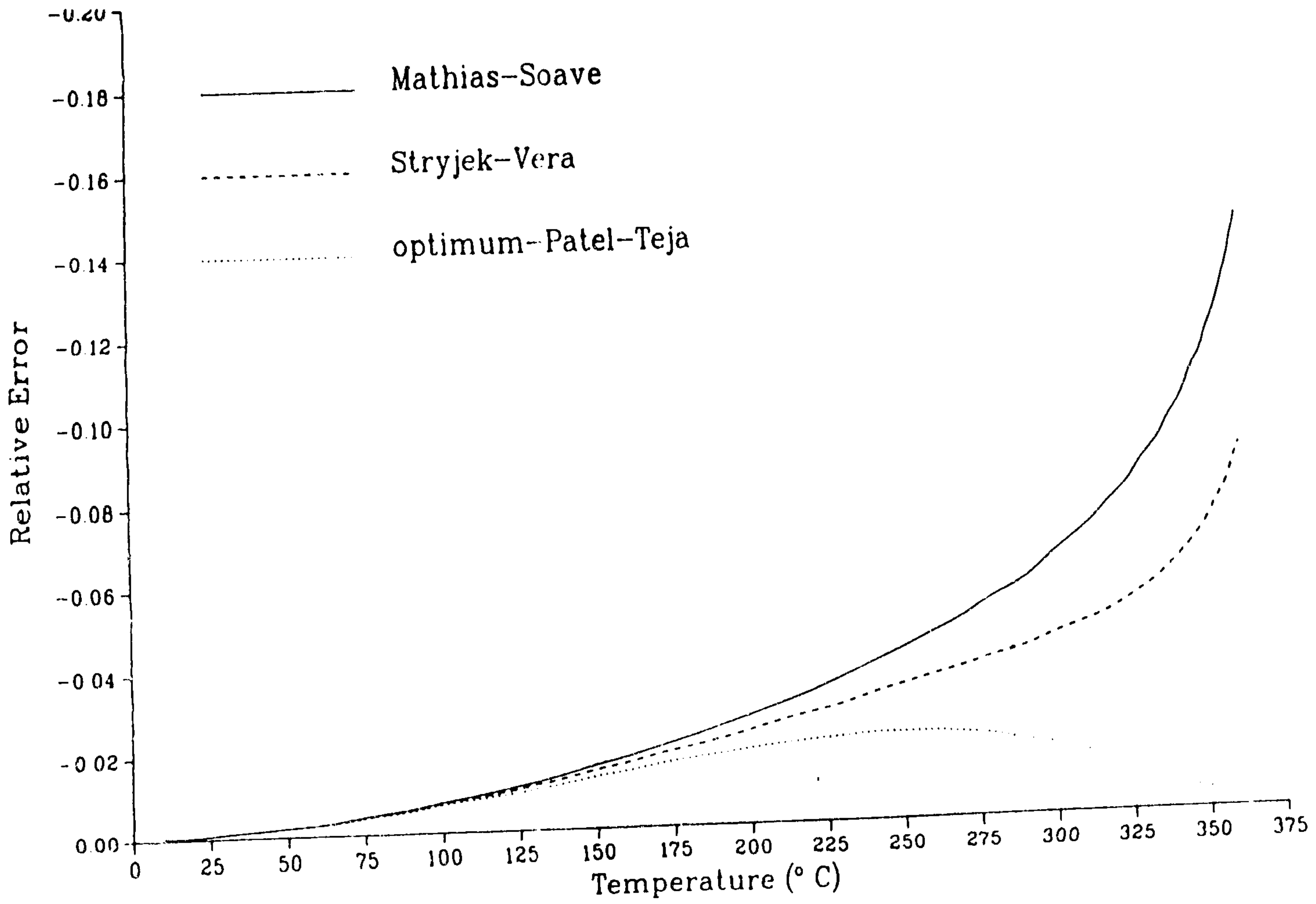

Fig. B.6 Errors in the Predicted Compressibility Factor of Saturated Steam (Part II)

The compressibility factor as opposed to the density, was selected for comparison because the density changed by five orders of magnitude over the temperature range studied whereas the compressibilities remained the same order of magnitude.

The predictions of all six equations are very good except in the region of the critical point. For five of the six equations, the maximum error in the predicted vapour compressibility occurred at the critical point. The exception to this was the optimum-Patel-Teja for which the maximum error occurred at about 250°C.

Saturated Liquid Density

Table B.4 summarizes the errors of the six equations for predicting the saturated liquid density. On Figs. B.7 and B.8 the relative error for each equation is plotted as a function of temperature.

Density was selected for analysis of the liquid data for the same reason that compressibility was selected for the vapour. The compressibility factor of the liquid changed by almost five orders of magnitude from the triple point to the critical point, whereas the density remained about the same order of magnitude. To calculate the density, first the compressibility factor is obtained. Then, using the estimated vapour pressure, the density is obtained from

$$\rho_L = MP^\circ / z_L RT \tag{B.92}$$

Table B.4 Errors in the Predicted Density of Saturated Water

	AAD (%)	BIAS (%)	RMS (%)
Soave-Redlich-Kwong	28.2	28.2	4.73
Mathias-Soave	28.1	28.1	4.71
Peng-Robinson	18.8	18.8	3.20
Stryjek-Vera	18.8	18.8	3.19
generalized-Patel-Teja	17.9	17.9	3.04
optimum-Patel-Teja	3.14	2.61	0.73

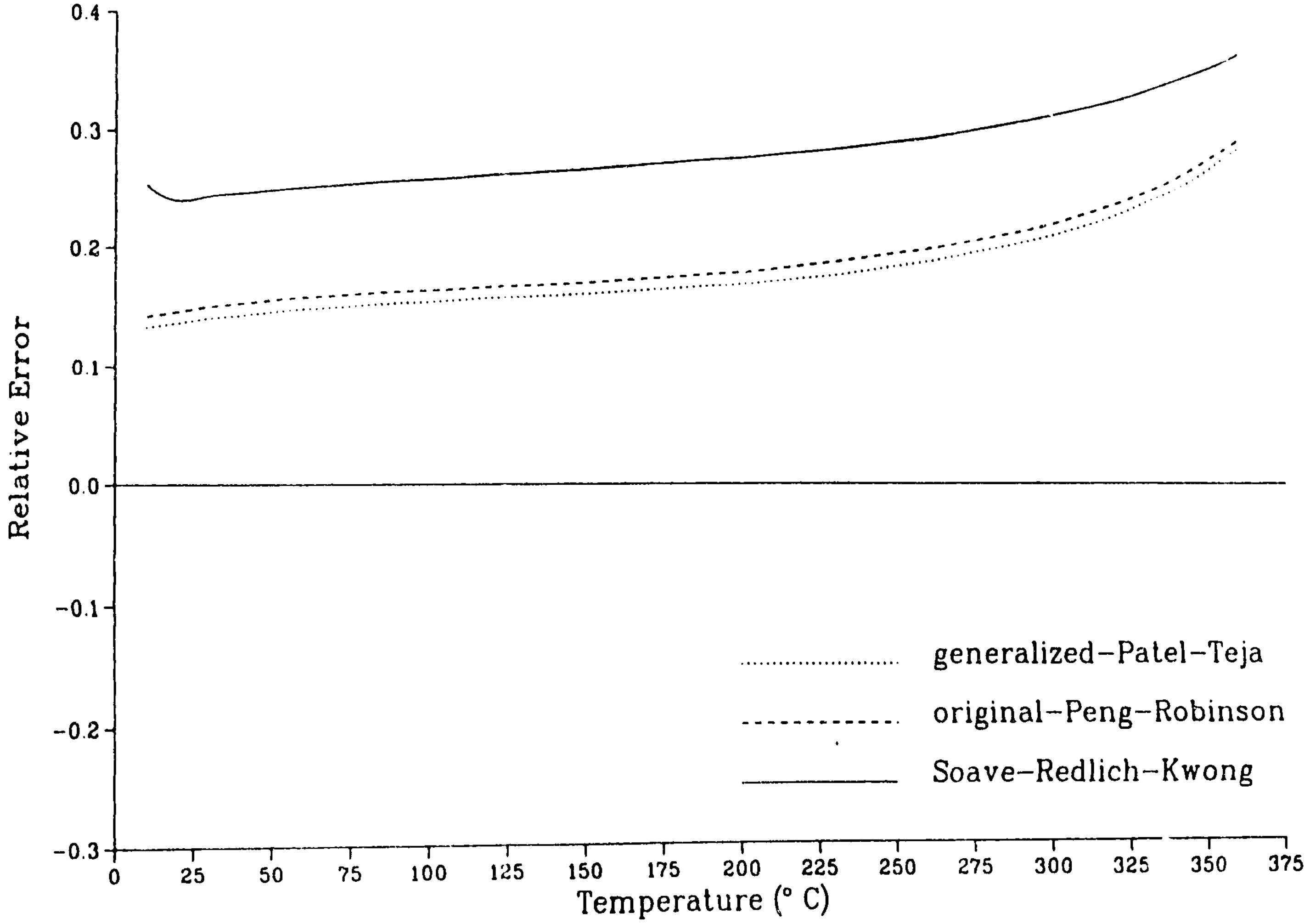

Fig. B.7 Errors in the Predicted Density of Saturated Liquid Water (Part I)

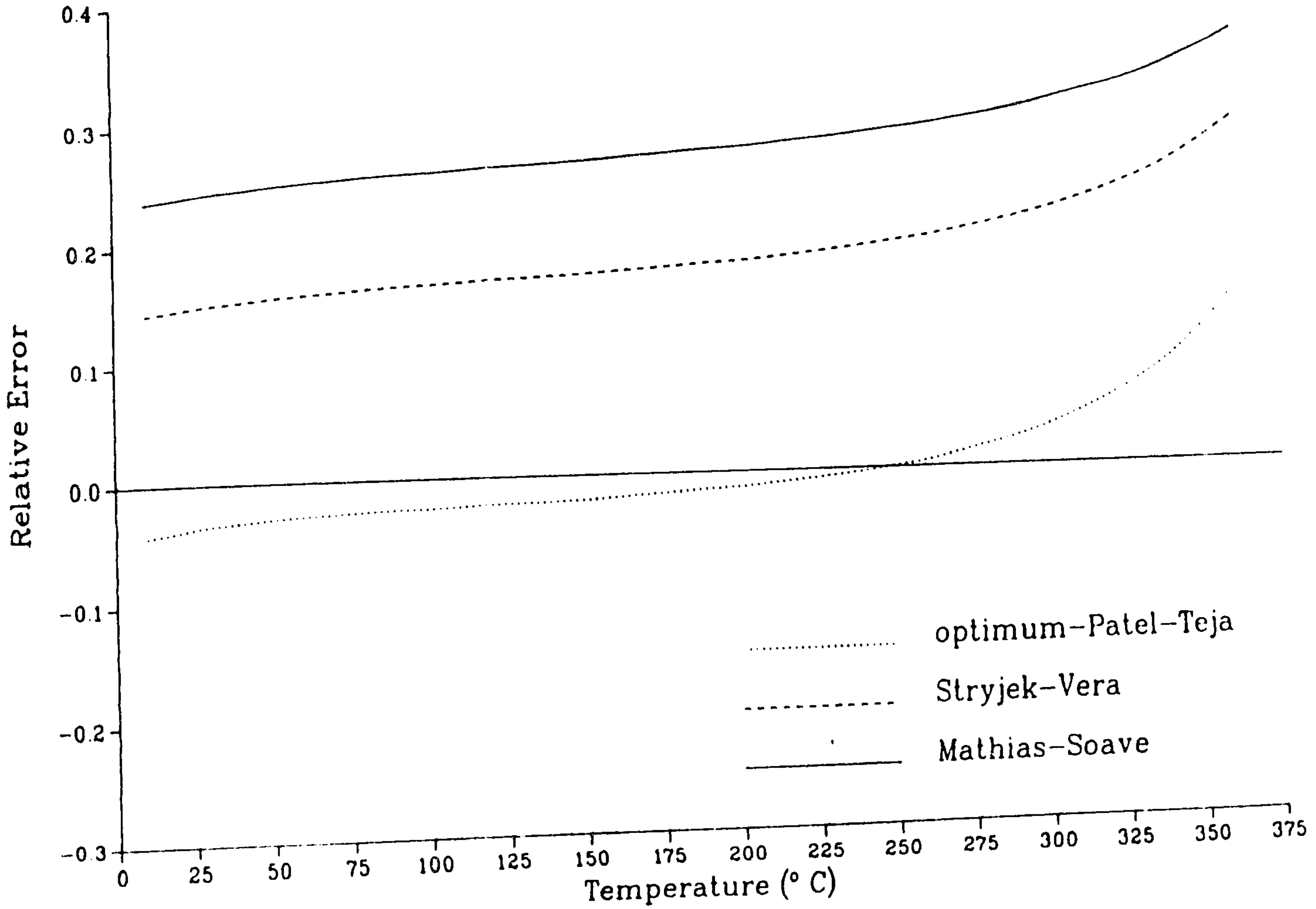

Fig. B.8 Errors in the Predicted Density of Saturated Liquid Water (Part II)

Thus it is unlikely that the equations which did a poor job of predicting the vapour pressure would give accurate values for the density unless there were compensating errors.

The optimum-Patel-Teja equation did the best job of predicting the liquid density. This is not unexpected since the parameters in this equation were obtained by minimizing the error in the predicted saturated liquid density along with the vapour pressure.

The Soave equation is the worst. This equation did not predict the liquid densities of hydrocarbons accurately, so this result was not unexpected. The Peng-Robinson equation did better than the Soave, but it was still very poor. Modifications of these equations which improved the vapour pressure predictions did not improve the liquid density predictions. As with the vapour density, the maximum error in the predicted liquid density occurred at the critical point. There was no exception this time.

G. Enthalpy of Vapourization

There are two methods for calculating the enthalpy of vapourization using an equation of state. The first involves calculating the enthalpy departure for each phase and taking the difference. Alternately, the Clapeyron equation could be used. The equation of state is used to predict the saturation pressure and the vapour and liquid specific volumes. The derivative of pressure with respect to temperature along the saturation curve is obtained numerically. Both of these procedures were used for a couple of the equations and there was not a significant difference. The results presented here were obtained using the departure method.

Figs. B.9 and B.10 show the relative error in the predicted enthalpy of vapourization as a function of temperature for the six equations. Table B.5 summarizes the errors for the six equations.

There is an improvement in the predictions for the equations which accurately predict vapour pressure over those which do not. However, even the worst of the equations is accurate to within about 10%. The errors for all of the equations tend towards infinity as if there were an asymptote through the critical point. However, the enthalpy of vapourization is zero at the critical point and the large relative error at the high temperatures is due to the smaller value of the enthalpy.

H. Application to Mixtures

The general mixing rule for a van der Waals-type equation is

$$\beta = \sum_i\sum_j x_i x_j \beta_{ij} \tag{B.93}$$

where β is a, b or for a three-parameter equation, c. For $i = j$, β_{ii} is the pure component parameter and for $i \neq j$, β_{ij} represents an interaction between the species i and j. Ternary and higher interactions are usually neglected.

Table B.5 Errors in the Predicted Enthalpy of Vapourization of Water

	AAD (%)	BIAS (%)	RMS (%)
Soave-Redlich-Kwong	4.62	-3.79	0.826
Mathias-Soave	2.02	-1.76	0.416
Peng-Robinson	3.21	-2.55	0.565
Stryjek-Vera	1.71	-1.36	0.352
generalized-Patel-Teja	3.57	-3.01	0.619
optimum-Patel-Teja	1.25	-0.59	0.274

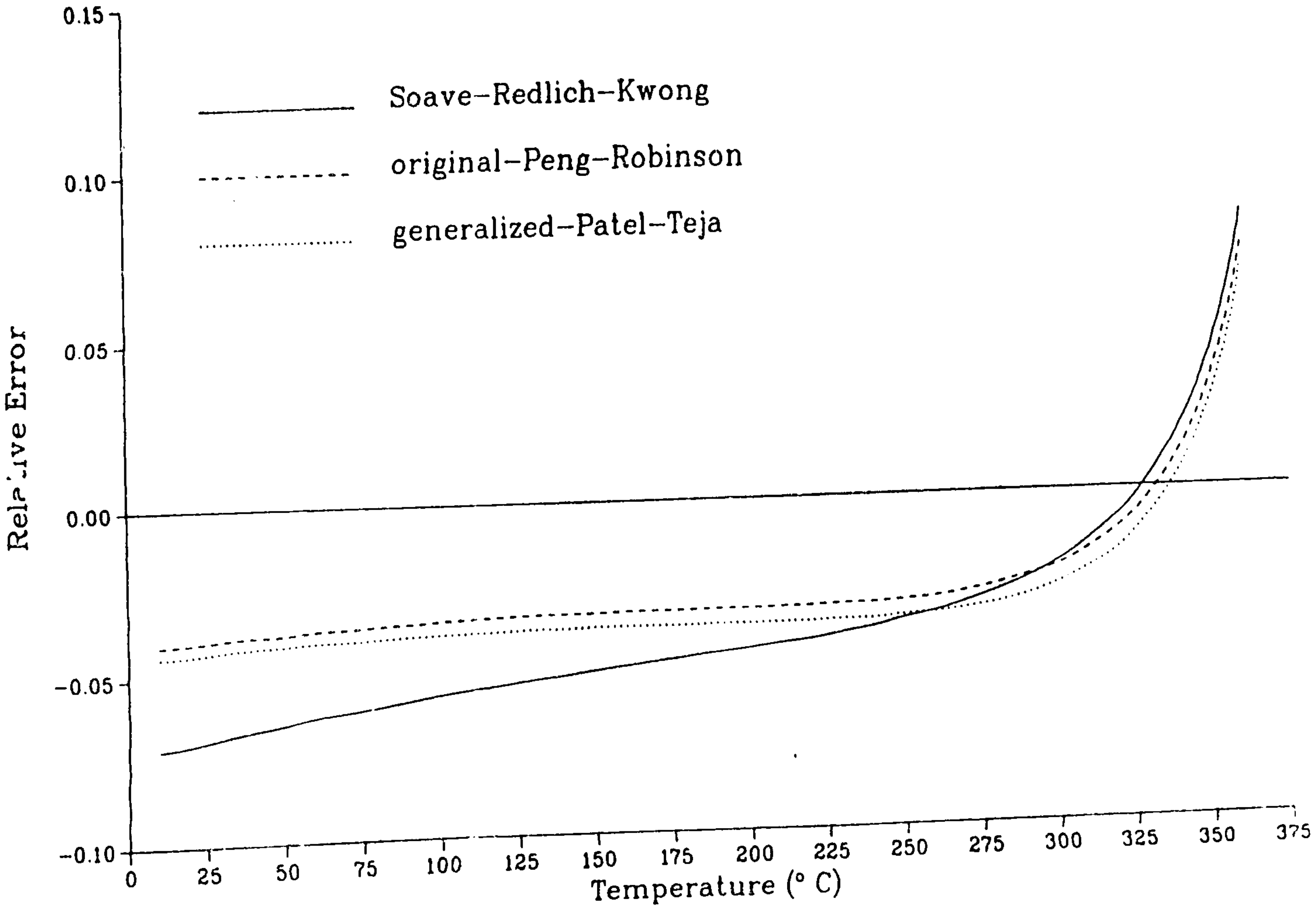

Fig. B.9 Errors in the Predicted Enthalpy of Vapourization (Part I)

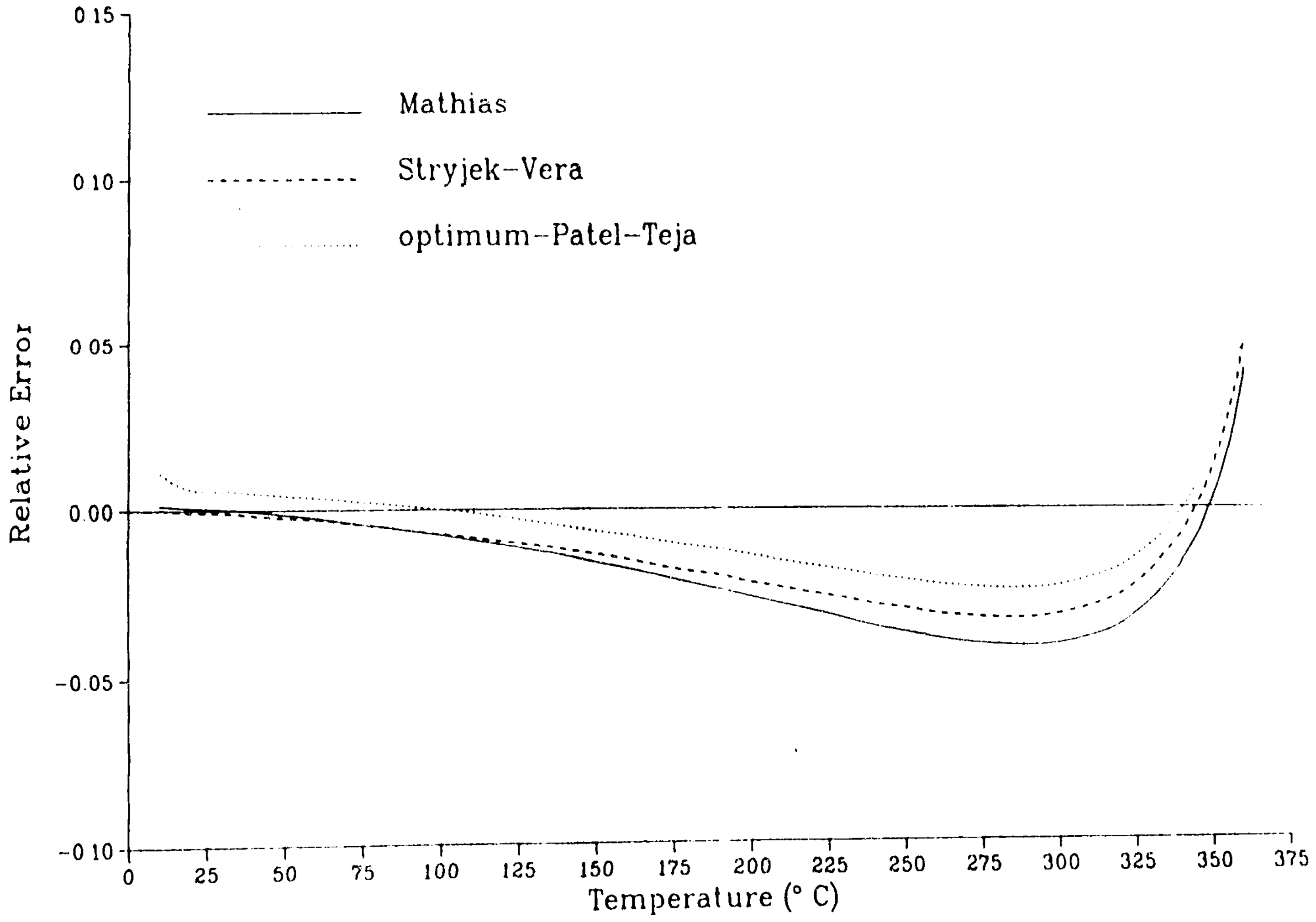

Fig. B.10 Errors in the Predicted Enthalpy of Vapourization (Part II)

For a, a geometric mean is usually used for the interaction term. Frequently an empirical parameter is included in the a term interaction.

$$a = \sum_i\sum_j x_i x_j a_{ij} \qquad (B.94)$$

$$a_{ij} = (a_i a_j)^{1/2}(1 - \delta_{ij}) \qquad (B.95)$$

The value of δ_{ij} is obtained from experimental data, usually vapour-liquid equilibria and $\delta_{ij} = \delta_{ji}$.

For b and c, β_{ij} are selected as the arithmetic mean, hence

$$b = \sum_i x_i b_i \qquad (B.96)$$

$$c = \sum_i x_i c_i \qquad (B.97)$$

These equations were used in the original Soave, Peng-Robinson, Heyen and Patel-Teja equations. With a single interaction parameter, they give excellent results for petroleum systems. Unfortunately, this approach is inadequate for aqueous systems. Several new mixing rules have been proposed. However, in the formulation of more complex mixing rules, it is important that in the limit as x_i approaches unity, β must approach β_{ii}. That is, as the solution becomes rich in one component the pure component parameters should be recovered. This is true for all rules presented here.

Evelein et al. (1976) applied the following mixing rules

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{B.98}$$

$$a_{ij} = (a_i a_j)^{1/2} (1 - k_{ij}) \tag{B.99}$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \tag{B.100}$$

$$b_{ij} = (b_i + b_j) (1 - c_{ij})/2 \tag{B.101}$$

Here a second interaction parameter, c_{ij}, was included. Note, the mixing rule for b reduces to the usual linear rule when $c_{ij} = 0$. When considering interactions between water and other components, the original-Soave a was used. Thus for water $k_{ii} \neq 0$ in Equation (B.99), but is given by Equation (B.34). For all other components, $k_{ii} = 0$ and for all components $c_{ii} = 0$. The parameters k_{ij} and c_{ij} were found by minimizing the the difference between the predicted and experimental liquid and vapour compositions.

For mixtures, Won and Walker (1979) applied the linear rule for b and for a the following is used

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{B.102}$$

$$a_{ij} = (a_{ni}(T_c) a_{nj}(T_c))^{1/2} m_i m_j + (a_{pi}(T_c) a_{pj}(T_c))^{1/2}/(T_{Ri} T_{Rj})^{3/2} \tag{B.103}$$

Mathias (1983) used the following mixing rules

$$a = \sum_{i}\sum_{j} x_i x_j a_{ij} \qquad (B.104)$$

$$a_{ij} = (a_i a_j)^{1/2}[1 - k_{a0} - k_{a1}T/1000] \qquad (B.105)$$

$$b = \sum_{i}\sum_{j} x_i x_j b_{ij} \qquad (B.106)$$

$$b_{ij} = (b_i + b_j)/2\ [1 - k_{b0} - k_{b1}T/1000] \qquad (B.107)$$

This method has an interaction parameter for both a and b and they have a linear temperature dependence. However, for all the systems he examined, he assumed $k_{a1} = 0$; that is, no temperature dependence of the interaction parameter for a.

Gibbons and Laughton (1984b) used the original combining rules with some success for aqueous systems. Dew point pressure predictions were quite good, but aqueous phase compositions were in error by more than an order of magnitude. They were also able to predict azeotropes in the system water-hydrogen chloride, but once again compositions were in error.

For predicting phase equilibrium in systems containing water and hydrocarbons Kabadi and Danner (1985) used the usual linear mixing rule was b, but for a

$$a = \sum_{i}\sum_{j} x_i x_j a_{ij} + \sum_{i} a''_{wi} x_w^2 x_i \qquad (B.108)$$

when i and j are both hydrocarbons then

$$a_{ij} = (a_i a_j)^{1/2} \qquad (B.109)$$

when i is water and j a hydrocarbon then

$$a_{ij} = a'_{wj}/2 \qquad (B.110)$$

$$a'_{wj} = 2(a_w a_j)^{1/2}(1 - k_{wi}) \qquad (B.111)$$

where k_{wi} is a binary interaction parameter which is a constant for hydrocarbons of the same homologous series. Finally, a''_{wi} is an empirical parameter given by

$$a''_{wi} = G_i[1 - (T/T_{cw})^{0.8}] \qquad (B.112)$$

where G_i was correlated via a group contribution technique.

Peng and Robinson (1976b) had some success modelling two and three phase equilibria in systems containing water and hydrocarbons using the original formulation of the equation and the original mixing rules. Interaction parameters were found to be quite large ranging from 0.500 for water-methane to 0.380 for water-1-butene. Typically for hydrocarbon-hydrocarbon binaries, $\delta_{ij} < 0.1$. Predicted compositions for the hydrocarbon-rich phase were in good agreement with the experimental values, but aqueous phase compositions were very low.

A second modification Peng and Robinson (1980) proposed for aqueous systems was a new mixing rule for the a. The aqueous phase was treated separately from the non-aqueous phase(s). Thus

$$a_{aq} = \sum_{i}\sum_{j} x_i x_j (a_{ij})_{aq} \tag{B.113}$$

$$(a_{ij})_{aq} = (a_i a_j)^{1/2}(1 - \tau_{ij}) \tag{B.114}$$

$$a_h = \sum_{i}\sum_{j} x_i x_j (a_{ij})_h \tag{B.115}$$

$$(a_{ij})_h = (a_i a_j)^{1/2}(1 - \delta_{ij}) \tag{B.116}$$

For all binaries they examined τ_{ij} was a monotonically increasing function of temperature. The δ_{ij}'s were found to be independent of temperature. For hydrogen sulphide-water τ_{ij} increased from -0.015 to 0.085 over the temperature range 30° to 175°C.

Huron and Vidal (1979) proposed a more complex set of mixing rules. For **b** the usual linear rule was used, but for **a** they proposed the following

$$a = b[\sum_{i} x_i a_i / b_i - g_{\infty}^{E} C] \tag{B.117}$$

where C is a numerical constant for a given equation of state and g_{∞}^{E} is the excess Gibbs energy at infinite pressure. This excess Gibbs function was modelled using the NRTL method of Renon and Prausnitz (1968). It is in this term that interaction parameters are introduced and each binary pair has two parameters.

Heyen (1981) proposed a new mixing rule for the a term which included two interaction parameters

$$a = \sum_i x_i \sum_j x_j^{(i)} a_{ij} \tag{B.118}$$

$$x_j^{(i)} = x_i \tau_{ij} / \sum_k x_k \tau_{ik} \tag{B.119}$$

$$\tau_{ij} \tau_{ji} = 1 \tag{B.120}$$

Note, the original mixing rule was recovered if $\tau_{ij} = 1$. This mixing rule was formulated to account for non-random mixing.

Stryjek and Vera (1986b) examined three mixing rules for highly non-ideal systems.

$$a_{ij} = (a_i a_j)^{1/2} (1 - x_i k_{ij} - x_j k_{ji}) \tag{B.121}$$

$$a_{ij} = (a_i a_j)^{1/2} [1 - k_{ij} k_{ji} / (x_i k_{ij} + x_j k_{ji})] \tag{B.122}$$

and the one proposed by Huron and Vidal (1979). The first of these is the same as that proposed by Panagiotopoulos and Reid (1986). By analogy to activity coefficient models, Stryjek and Vera called Equation (B.121) a Margules-type mixing rule and Equation (B.122) a van Laar-type. These rules were applied to several binary systems, including aqueous systems. They concluded that the van Laar method gave the best results.

Luedecke and Prausnitz (1985) proposed a density-dependent mixing rule for a.

$$a = \sum_i\sum_j x_i x_j (a_i a_j)^{1/2}(1 - k_{ij}) + (\rho/RT)\sum_i\sum_j x_i x_j (x_i c_{i(j)} + x_j c_{j(i)}) \qquad (B.123)$$

where $c_{i(j)} \neq c_{j(i)}$. The original mixing rule is recovered if $c_{i(j)} = c_{j(i)} = 0$. In this method, each binary pair has two interaction parameters. The use of this mixing rule make the equation of state quartic in volume. Also, the interaction parameters $c_{i(j)}$ and $c_{j(i)}$ are not dimensionless.

APPENDIX C Skeleton Tables

Table C.1 The Solubility of Hydrogen Sulphide in Water

Press (kPa)	Solubility of Hydrogen Sulphide in Water			
	mol%	wt%	molality	mole ratio (x100)
t=0°C				
0.6	0.0000	0.0000	0.0000	0.0000
10	0.0354	0.0669	0.0196	0.0354
20	0.0730	0.1380	0.0405	0.0730
30	0.1105	0.2089	0.0614	0.1106
40	0.1480	0.2796	0.0823	0.1482
50	0.1854	0.3501	0.1031	0.1857
60	0.2227	0.4205	0.1239	0.2232
70	0.2600	0.4907	0.1447	0.2607
80	0.2972	0.5607	0.1655	0.2981
90	0.3343	0.6306	0.1862	0.3354
98.6	0.3662	0.6905	0.2040	0.3675
t=5°C				
0.9	0.0000	0.0000	0.0000	0.0000
10	0.0290	0.0549	0.0161	0.0290
20	0.0607	0.1148	0.0337	0.0608
30	0.0924	0.1747	0.0513	0.0925
40	0.1240	0.2344	0.0689	0.1242
50	0.1556	0.2940	0.0865	0.1558
60	0.1871	0.3534	0.1041	0.1875
70	0.2186	0.4127	0.1216	0.2190
80	0.2500	0.4718	0.1391	0.2506
90	0.2813	0.5308	0.1566	0.2821
100	0.3126	0.5897	0.1741	0.3136
101.325	0.3167	0.5975	0.1764	0.3178
110	0.3438	0.6485	0.1915	0.3450
120	0.3750	0.7071	0.2090	0.3764
130	0.4061	0.7656	0.2264	0.4078
140	0.4372	0.8239	0.2438	0.4391
150	0.4682	0.8821	0.2611	0.4704
160	0.4992	0.9402	0.2785	0.5017
163.9	0.5112	0.9628	0.2852	0.5139
t=10°C				
1.2	0.0000	0.0000	0.0000	0.0000
10	0.0238	0.0449	0.0132	0.0238
20	0.0508	0.0961	0.0282	0.0508
30	0.0778	0.1471	0.0432	0.0779
40	0.1048	0.1980	0.0582	0.1049
50	0.1317	0.2488	0.0732	0.1319
60	0.1586	0.2995	0.0882	0.1588
70	0.1854	0.3501	0.1031	0.1857

80	0.2122	0.4006	0.1180	0.2126
90	0.2389	0.4510	0.1329	0.2395
100	0.2656	0.5012	0.1478	0.2663
101.325	0.2691	0.5079	0.1498	0.2699
110	0.2922	0.5514	0.1627	0.2931
120	0.3188	0.6015	0.1776	0.3199
130	0.3454	0.6514	0.1924	0.3466
140	0.3719	0.7012	0.2072	0.3733
150	0.3984	0.7510	0.2220	0.4000
160	0.4248	0.8006	0.2368	0.4266
170	0.4512	0.8501	0.2516	0.4532
180	0.4775	0.8995	0.2663	0.4798
190	0.5038	0.9488	0.2811	0.5064
200	0.5300	0.9980	0.2958	0.5329
210	0.5562	1.0471	0.3105	0.5594
220	0.5824	1.0961	0.3252	0.5858
230	0.6085	1.1449	0.3399	0.6122
240	0.6346	1.1937	0.3545	0.6386
250	0.6606	1.2424	0.3691	0.6650
260	0.6866	1.2909	0.3838	0.6913
270	0.7125	1.3394	0.3984	0.7176
274.7	0.7247	1.3621	0.4052	0.7300

t=15°C

1.7	0.0000	0.0000	0.0000	0.0000
10	0.0196	0.0371	0.0109	0.0196
20	0.0432	0.0817	0.0240	0.0432
30	0.0668	0.1262	0.0371	0.0668
40	0.0903	0.1706	0.0502	0.0904
50	0.1138	0.2150	0.0632	0.1139
60	0.1372	0.2592	0.0763	0.1374
70	0.1606	0.3034	0.0893	0.1609
80	0.1840	0.3475	0.1023	0.1843
90	0.2073	0.3915	0.1153	0.2078
100	0.2306	0.4354	0.1283	0.2312
101.325	0.2337	0.4412	0.1300	0.2343
120	0.2771	0.5229	0.1543	0.2779
140	0.3235	0.6101	0.1801	0.3245
160	0.3696	0.6970	0.2059	0.3710
180	0.4157	0.7835	0.2317	0.4174
200	0.4616	0.8696	0.2574	0.4637
220	0.5073	0.9554	0.2830	0.5099
240	0.5529	1.0408	0.3086	0.5560
260	0.5984	1.1260	0.3341	0.6020
280	0.6437	1.2107	0.3596	0.6478
300	0.6888	1.2951	0.3850	0.6936
320	0.7338	1.3792	0.4104	0.7392
340	0.7787	1.4629	0.4356	0.7848
360	0.8234	1.5463	0.4609	0.8302
380	0.8680	1.6293	0.4860	0.8755
400	0.9124	1.7120	0.5111	0.9208
420	0.9566	1.7944	0.5361	0.9659
440	1.0007	1.8764	0.5611	1.0109
460	1.0447	1.9581	0.5860	1.0558
463.6	1.0526	1.9728	0.5905	1.0638

t=20°C

2.3	0.0000	0.0000	0.0000	0.0000
10	0.0158	0.0299	0.0088	0.0158
20	0.0364	0.0688	0.0202	0.0364
30	0.0569	0.1076	0.0316	0.0569
40	0.0774	0.1464	0.0430	0.0775
50	0.0979	0.1851	0.0544	0.0980
60	0.1184	0.2237	0.0658	0.1185
70	0.1388	0.2623	0.0772	0.1390
80	0.1592	0.3007	0.0885	0.1595
90	0.1796	0.3391	0.0999	0.1799
100	0.1999	0.3775	0.1112	0.2003
101.325	0.2026	0.3826	0.1127	0.2030
120	0.2405	0.4539	0.1338	0.2410
140	0.2809	0.5301	0.1564	0.2817
160	0.3212	0.6060	0.1789	0.3223
180	0.3614	0.6816	0.2014	0.3628
200	0.4015	0.7569	0.2238	0.4031
220	0.4415	0.8319	0.2461	0.4434
240	0.4813	0.9066	0.2685	0.4836
260	0.5210	0.9811	0.2907	0.5238
280	0.5606	1.0553	0.3129	0.5638
300	0.6001	1.1292	0.3351	0.6037
320	0.6394	1.2028	0.3572	0.6435
340	0.6786	1.2761	0.3793	0.6833
360	0.7177	1.3491	0.4013	0.7229
380	0.7567	1.4219	0.4232	0.7625
400	0.7955	1.4944	0.4451	0.8019
420	0.8343	1.5666	0.4670	0.8413
440	0.8729	1.6385	0.4888	0.8806
460	0.9114	1.7102	0.5105	0.9197
480	0.9497	1.7815	0.5322	0.9588
500	0.9880	1.8526	0.5539	0.9978
520	1.0261	1.9235	0.5755	1.0367
540	1.0641	1.9940	0.5970	1.0755
560	1.1020	2.0643	0.6185	1.1142
580	1.1397	2.1343	0.6399	1.1528
600	1.1773	2.2040	0.6613	1.1913
620	1.2148	2.2735	0.6826	1.2297
640	1.2522	2.3426	0.7039	1.2680
660	1.2894	2.4116	0.7251	1.3062
680	1.3266	2.4802	0.7463	1.3444
700	1.3636	2.5486	0.7674	1.3824
720	1.4005	2.6167	0.7884	1.4204
740	1.4372	2.6845	0.8094	1.4582
760	1.4739	2.7520	0.8304	1.4959
780	1.5104	2.8193	0.8513	1.5336
787.9	1.5248	2.8458	0.8595	1.5484

t=25°C

3.2	0.0000	0.0000	0.0000	0.0000
10	0.0125	0.0236	0.0069	0.0125
20	0.0307	0.0580	0.0170	0.0307

30	0.0489	0.0924	0.0272	0.0489
40	0.0671	0.1268	0.0373	0.0671
50	0.0852	0.1611	0.0473	0.0852
60	0.1033	0.1953	0.0574	0.1034
70	0.1214	0.2295	0.0675	0.1216
80	0.1395	0.2636	0.0775	0.1397
90	0.1575	0.2976	0.0876	0.1578
100	0.1756	0.3316	0.0976	0.1759
101.325	0.1779	0.3361	0.0989	0.1783
120	0.2115	0.3994	0.1177	0.2120
140	0.2474	0.4669	0.1376	0.2480
160	0.2831	0.5342	0.1576	0.2839
180	0.3187	0.6013	0.1775	0.3198
200	0.3543	0.6681	0.1974	0.3555
220	0.3897	0.7347	0.2172	0.3912
240	0.4250	0.8010	0.2369	0.4269
260	0.4603	0.8672	0.2567	0.4624
280	0.4954	0.9330	0.2764	0.4979
300	0.5304	0.9987	0.2960	0.5332
320	0.5653	1.0641	0.3156	0.5685
340	0.6001	1.1293	0.3351	0.6038
360	0.6348	1.1942	0.3546	0.6389
380	0.6694	1.2589	0.3741	0.6739
400	0.7039	1.3234	0.3935	0.7089
420	0.7383	1.3876	0.4129	0.7438
440	0.7726	1.4516	0.4322	0.7786
460	0.8068	1.5154	0.4515	0.8134
480	0.8408	1.5789	0.4707	0.8480
500	0.8749	1.6422	0.4899	0.8826
520	0.9087	1.7053	0.5091	0.9171
540	0.9425	1.7681	0.5282	0.9515
560	0.9762	1.8308	0.5472	0.9858
580	1.0097	1.8931	0.5662	1.0200
600	1.0432	1.9553	0.5852	1.0542
625	1.0849	2.0327	0.6088	1.0968
650	1.1264	2.1097	0.6324	1.1392
675	1.1678	2.1864	0.6559	1.1816
700	1.2090	2.2627	0.6793	1.2238
725	1.2500	2.3386	0.7026	1.2658
750	1.2909	2.4142	0.7259	1.3077
775	1.3316	2.4895	0.7491	1.3495
800	1.3721	2.5644	0.7723	1.3912
825	1.4125	2.6389	0.7953	1.4328
850	1.4527	2.7131	0.8183	1.4742
875	1.4928	2.7869	0.8412	1.5154
900	1.5327	2.8604	0.8640	1.5566
925	1.5725	2.9336	0.8868	1.5976
950	1.6121	3.0064	0.9095	1.6385
975	1.6515	3.0788	0.9321	1.6792
1000	1.6907	3.1510	0.9547	1.7198

t=30°C

4.2	0.0000	0.0000	0.0000	0.0000
10	0.0094	0.0178	0.0052	0.0094
20	0.0258	0.0488	0.0143	0.0258

30	0.0422	0.0798	0.0234	0.0422
40	0.0585	0.1107	0.0325	0.0586
50	0.0749	0.1415	0.0416	0.0749
60	0.0911	0.1723	0.0506	0.0912
70	0.1074	0.2030	0.0597	0.1075
80	0.1237	0.2337	0.0687	0.1238
90	0.1399	0.2643	0.0778	0.1401
100	0.1561	0.2949	0.0868	0.1564
101.325	0.1583	0.2990	0.0880	0.1585
120	0.1885	0.3559	0.1048	0.1888
140	0.2207	0.4167	0.1228	0.2212
160	0.2529	0.4773	0.1407	0.2535
180	0.2850	0.5377	0.1586	0.2858
200	0.3169	0.5979	0.1765	0.3180
220	0.3489	0.6579	0.1943	0.3500
240	0.3807	0.7177	0.2121	0.3821
260	0.4124	0.7773	0.2299	0.4141
280	0.4440	0.8367	0.2476	0.4460
300	0.4758	0.8959	0.2652	0.4778
320	0.5070	0.9549	0.2829	0.5096
340	0.5384	1.0136	0.3005	0.5413
360	0.5697	1.0722	0.3180	0.5729
380	0.6009	1.1306	0.3355	0.6045
400	0.6320	1.1888	0.3530	0.6360
420	0.6630	1.2468	0.3705	0.6674
440	0.6939	1.3046	0.3879	0.6987
460	0.7247	1.3622	0.4052	0.7300
480	0.7554	1.4196	0.4225	0.7612
500	0.7861	1.4768	0.4398	0.7923
520	0.8167	1.5338	0.4571	0.8234
540	0.8471	1.5906	0.4723	0.8544
560	0.8775	1.6472	0.4914	0.8853
580	0.9078	1.7036	0.5085	0.9161
600	0.9380	1.7598	0.5256	0.9469
625	0.9757	1.8298	0.5469	0.9853
650	1.0132	1.8995	0.5682	1.0235
675	1.0505	1.9689	0.5893	1.0617
700	1.0877	2.0380	0.6104	1.0997
725	1.1248	2.1067	0.6315	1.1376
750	1.1618	2.1752	0.6525	1.1754
775	1.1986	2.2434	0.6734	1.2131
800	1.2352	2.3113	0.6942	1.2507
825	1.2717	2.3789	0.7150	1.2881
850	1.3081	2.4461	0.7358	1.3255
875	1.3444	2.5131	0.7564	1.3627
900	1.3805	2.5798	0.7770	1.3998
925	1.4165	2.6462	0.7976	1.4368
950	1.4523	2.7123	0.8180	1.4737
975	1.4880	2.7781	0.8384	1.5105
1000	1.5235	2.8435	0.8588	1.5471

t=35°C

5.6	0.0000	0.0000	0.0000	0.0000
10	0.0064	0.0121	0.0036	0.0064
20	0.0210	0.0398	0.0117	0.0210

30	0.0356	0.0674	0.0198	0.0356
40	0.0502	0.0949	0.0279	0.0502
50	0.0648	0.1225	0.0360	0.0648
60	0.0793	0.1500	0.0441	0.0794
70	0.0939	0.1774	0.0521	0.0939
80	0.1084	0.2048	0.0602	0.1085
90	0.1229	0.2322	0.0683	0.1230
100	0.1373	0.2595	0.0763	0.1375
101.325	0.1392	0.2631	0.0774	0.1394
120	0.1662	0.3140	0.0924	0.1665
140	0.1950	0.3685	0.1085	0.1954
160	0.2238	0.4224	0.1245	0.2243
180	0.2524	0.4764	0.1405	0.2531
200	0.2810	0.5302	0.1564	0.2818
220	0.3095	0.5839	0.1723	0.3105
240	0.3379	0.6373	0.1882	0.3391
260	0.3662	0.6906	0.2041	0.3676
280	0.3945	0.7438	0.2199	0.3961
300	0.4227	0.7967	0.2357	0.4245
320	0.4509	0.8495	0.2514	0.4529
340	0.4789	0.9021	0.2671	0.4812
360	0.5069	0.9546	0.2828	0.5095
380	0.5348	1.0069	0.2984	0.5377
400	0.5626	1.0590	0.3141	0.5658
420	0.5903	1.1109	0.3296	0.5938
440	0.6180	1.1627	0.3452	0.6218
460	0.6456	1.2143	0.3607	0.6498
480	0.6731	1.2656	0.3762	0.6777
500	0.7005	1.3170	0.3916	0.7055
520	0.7279	1.3681	0.4070	0.7332
540	0.7552	1.4191	0.4224	0.7609
560	0.7824	1.4699	0.4377	0.7886
580	0.8095	1.5205	0.4530	0.8162
600	0.8366	1.5709	0.4683	0.8437
625	0.8703	1.6338	0.4873	0.8780
650	0.9039	1.6963	0.5063	0.9122
675	0.9374	1.7586	0.5253	0.9374
700	0.9708	1.8207	0.5441	0.9803
725	1.0040	1.8825	0.5630	1 0142
750	1.0371	1.9440	0.5817	1.0480
775	1.0701	2.0053	0.6005	1.0817
800	1.1030	2.0663	0.6191	1.1153
825	1.1358	2.1271	0.6377	1.1489
850	1.1685	2.1876	0.6563	1.1823
875	1.2010	2.2479	0.6748	1.2156
900	1.2334	2.3079	0.6932	1.2488
925	1.2657	2.3677	0.7116	1.2819
950	1.2979	2.4272	0.7299	1.3150
975	1.3300	2.4865	0.7482	1.3479
1000	1.3619	2.5455	0.7664	1.3807

t=40°C

7.4	0.0000	0.0000	0.0000	0.0000
10	0.0034	0.0065	0.0019	0.0035
20	0.0167	0.0315	0.0092	0.0167

30	0.0298	0.0564	0.0166	0.0299
40	0.0430	0.0813	0.0239	0.0430
50	0.0562	0.1062	0.0312	0.0562
60	0.0693	0.1310	0.0385	0.0694
70	0.0824	0.1558	0.0458	0.0825
80	0.0955	0.1806	0.0531	0.0956
90	0.1086	0.2053	0.0604	0.1087
100	0.1217	0.2300	0.0676	0.1218
101.325	0.1234	0.2332	0.0686	0.1236
120	0.1478	0.2792	0.0822	0.1480
140	0.1738	0.3283	0.0967	0.1741
160	0.1998	0.3773	0.1111	0.2002
180	0.2257	0.4261	0.1256	0.2262
200	0.2515	0.4747	0.1400	0.2521
220	0.2773	0.5232	0.1543	0.2780
240	0.3030	0.5716	0.1687	0.3039
260	0.3286	0.6198	0.1830	0.3297
280	0.3542	0.6679	0.1973	0.3554
300	0.3797	0.7158	0.2116	0.3811
320	0.4051	0.7636	0.2258	0.4068
340	0.4305	0.8112	0.2400	0.4323
360	0.4558	0.8587	0.2542	0.4579
380	0.4810	0.9061	0.2683	0.4833
400	0.5062	0.9533	0.2824	0.5088
420	0.5313	1.0004	0.2965	0.5341
440	0.5563	1.0473	0.3105	0.5595
460	0.5813	1.0940	0.3246	0.5847
480	0.6062	1.1407	0.3386	0.6099
500	0.6311	1.1872	0.3525	0.6351
520	0.6559	1.2335	0.3665	0.6602
540	0.6806	1.2797	0.3804	0.6852
560	0.7052	1.3258	0.3942	0.7102
580	0.7298	1.3717	0.4081	0.7352
600	0.7543	1.4174	0.4219	0.7600
625	0.7849	1.4745	0.4391	0.7911
650	0.8153	1.5312	0.4563	0.8220
675	0.8457	1.5878	0.4734	0.8529
700	0.8759	1.6442	0.4905	0.8837
725	0.9061	1.7003	0.5075	0.9144
750	0.9361	1.7562	0.5245	0.9450
775	0.9661	1.8119	0.5415	0.9755
800	0.9959	1.8674	0.5584	1.0059
825	1.0256	1.9227	0.5752	1.0363
850	1.0553	1.9777	0.5920	1.0665
875	1.0848	2.0325	0.6088	1.0967
900	1.1142	2.0871	0.6255	1.1268
925	1.1434	2.1415	0.6421	1.1568
950	1.1728	2.1957	0.6587	1.1867
975	1.2019	2.2496	0.6753	1.2165
1000	1.2309	2.3034	0.6918	1.2463

t=45°C

9.6	0.0000	0.0000	0.0000	0.0000
20	0.0125	0.0237	0.0069	0.0125
30	0.0245	0.0464	0.0136	0.0245

40	0.0365	0.0690	0.0203	0.0365
50	0.0485	0.0917	0.0269	0.0485
60	0.0605	0.1143	0.0336	0.0605
70	0.0724	0.1369	0.0402	0.0725
80	0.0844	0.1595	0.0469	0.0844
90	0.0963	0.1820	0.0535	0.0964
100	0.1082	0.2045	0.0601	0.1083
101.325	0.1098	0.2074	0.0610	0.1099
120	0.1320	0.2493	0.0733	0.1321
140	0.1556	0.2941	0.0866	0.1559
160	0.1793	0.3387	0.0997	0.1797
180	0.2029	0.3832	0.1129	0.2034
200	0.2265	0.4276	0.1260	0.2270
220	0.2500	0.4719	0.1392	0.2506
240	0.2734	0.5160	0.1522	0.2742
260	0.2968	0.5600	0.1652	0.2977
280	0.3201	0.6038	0.1783	0.3211
300	0.3434	0.6476	0.1913	0.3445
320	0.3666	0.6912	0.2042	0.3679
340	0.3897	0.7347	0.2172	0.3912
360	0.4128	0.7781	0.2301	0.4145
380	0.4358	0.8213	0.2430	0.4377
400	0.4588	0.8644	0.2559	0.4609
420	0.4817	0.9074	0.2687	0.4841
440	0.5046	0.9503	0.2815	0.5071
460	0.5274	0.9930	0.2943	0.5302
480	0.5501	1.0356	0.3071	0.5532
500	0.5728	1.0781	0.3198	0.5761
520	0.5954	1.1205	0.3325	0.5990
540	0.6180	1.1627	0.3452	0.6219
560	0.6405	1.2049	0.3578	0.6447
580	0.6630	1.2468	0.3705	0.6674
600	0.6854	1.2887	0.3831	0.6901
625	0.7133	1.3409	0.3988	0.7184
650	0.7411	1.3929	0.4145	0.7467
675	0.7689	1.4447	0.4301	0.7749
700	0.7965	1.4962	0.4457	0.8029
725	0.8241	1.5477	0.4613	0.8310
750	0.8516	1.5989	0.4768	0.8589
775	0.8790	1.6499	0.4922	0.8868
800	0.9063	1.7007	0.5077	0.9146
825	0.9335	1.7514	0.5231	0.9423
850	0.9606	1.8018	0.5384	0.9699
875	0.9876	1.8521	0.5537	0.9975
900	1.0146	1.9022	0.5690	1.0250
925	1.0415	1.9520	0.5842	1.0524
950	1.0682	2.0017	0.5994	1.0798
975	1.0949	2.0513	0.6145	1.1070
1000	1.1215	2.1006	0.6296	1.1342

t=50°C

12.4	0.0000	0.0000	0.0000	0.0000
20	0.0084	0.0159	0.0047	0.0084
30	0.0195	0.0368	0.0108	0.0195

40	0.0305	0.0576	0.0169	0.0305
50	0.0415	0.0784	0.0230	0.0415
60	0.0525	0.0992	0.0291	0.0525
70	0.0634	0.1199	0.0352	0.0635
80	0.0744	0.1406	0.0413	0.0745
90	0.0853	0.1613	0.0474	0.0854
100	0.0963	0.1820	0.0535	0.0964
101.325	0.0977	0.1847	0.0543	0.0978
120	0.1181	0.2232	0.0656	0.1183
140	0.1399	0.2643	0.0778	0.1401
160	0.1616	0.3054	0.0899	0.1619
180	0.1833	0.3463	0.1020	0.1837
200	0.2050	0.3870	0.1140	0.2054
220	0.2266	0.4277	0.1260	0.2271
240	0.2481	0.4683	0.1381	0.2487
260	0.2696	0.5087	0.1500	0.2703
280	0.2910	0.5491	0.1620	0.2919
300	0.3124	0.5893	0.1739	0.3134
320	0.3337	0.6295	0.1859	0.3348
340	0.3550	0.6695	0.1978	0.3563
360	0.3762	0.7094	0.2096	0.3777
380	0.3974	0.7492	0.2215	0.3990
400	0.4186	0.7889	0.2333	0.4203
420	0.4396	0.8284	0.2451	0.4416
440	0.4607	0.8679	0.2569	0.4628
460	0.4816	0.9073	0.2687	0.4840
480	0.5026	0.9465	0.2804	0.5051
500	0.5235	0.9856	0.2921	0.5262
520	0.5443	1.0247	0.3038	0.5473
540	0.5651	1.0636	0.3154	0.5683
560	0.5858	1.1024	0.3271	0.5892
580	0.6065	1.1411	0.3387	0.6102
600	0.6271	1.1797	0.3503	0.6311
625	0.6528	1.2278	0.3648	0.6571
650	0.6785	1.2758	0.3792	0.6831
675	0.7040	1.3235	0.3936	0.7090
700	0.7295	1.3711	0.4079	0.7349
725	0.7549	1.4185	0.4222	0.7606
750	0.7802	1.4658	0.4365	0.7864
775	0.8055	1.5129	0.4507	0.8120
800	0.8306	1.5598	0.4649	0.8376
825	0.8557	1.6066	0.4791	0.8631
850	0.8807	1.6532	0.4932	0.8886
875	0.9057	1.6996	0.5073	0.9140
900	0.9305	1.7459	0.5214	0.9393
925	0.9553	1.7920	0.5354	0.9645
950	0.9800	1.8379	0.5494	0.9897
975	1.0148	1.8837	0.5633	1.0246
1000	1.0292	1.9293	0.5772	1.0399

t=55°C

15.8	0.0000	0.0000	0.0000	0.0000
20	0.0043	0.0081	0.0024	0.0043
30	0.0145	0.0274	0.0081	0.0145
40	0.0247	0.0467	0.0137	0.0247

50	0.0349	0.0660	0.0194	0.0349
60	0.0451	0.0852	0.0250	0.0451
70	0.0552	0.1044	0.0307	0.0552
80	0.0654	0.1236	0.0363	0.0654
90	0.0755	0.1427	0.0419	0.0756
100	0.0856	0.1619	0.0476	0.0857
101.325	0.0870	0.1644	0.0483	0.0870
120	0.1058	0.2000	0.0588	0.1060
140	0.1260	0.2381	0.0700	0.1262
160	0.1461	0.2761	0.0812	0.1464
180	0.1662	0.3140	0.0924	0.1665
200	0.1863	0.3518	0.1036	0.1866
220	0.2063	0.3895	0.1147	0.2067
240	0.2262	0.4271	0.1259	0.2267
260	0.2461	0.4646	0.1370	0.2467
280	0.2660	0.5020	0.1480	0.2667
300	0.2858	0.5393	0.1591	0.2866
320	0.3056	0.5764	0.1701	0.3065
340	0.3253	0.6136	0.1812	0.3263
360	0.3450	0.6506	0.1922	0.3462
380	0.3646	0.6875	0.2031	0.3659
400	0.3842	0.7243	0.2141	0.3857
420	0.4037	0.7610	0.2250	0.4054
440	0.4232	0.7977	0.2359	0.4250
460	0.4427	0.8342	0.2468	0.4447
480	0.4621	0.8706	0.2577	0.4643
500	0.4815	0.9070	0.2686	0.4838
520	0.5008	0.9432	0.2794	0.5033
540	0.5201	0.9793	0.2902	0.5228
560	0.5393	1.0154	0.3010	0.5422
580	0.5585	1.0513	0.3118	0.5616
600	0.5777	1.0872	0.3225	0.5810
625	0.6015	1.1319	0.3359	0.6052
650	0.6235	1.1764	0.3493	0.6293
675	0.6491	1.2208	0.3626	0.6533
700	0.6727	1.2650	0.3756	0.6773
725	0.6963	1.3091	0.3892	0.7012
750	0.7198	1.3531	0.4025	0.7251
775	0.7433	1.3969	0.4157	0.7489
800	0.7667	1.4405	0.4289	0.7726
825	0.7900	1.4840	0.4420	0.7963
850	0.8132	1.5274	0.4551	0.8199
875	0.8364	1.5706	0.4682	0.8435
900	0.8595	1.6137	0.4813	0.8670
925	0.8826	1.6566	0.4943	0.8904
950	0.9055	1.6993	0.5073	0.9138
975	0.9284	1.7420	0.5202	0.9371
1000	0.9513	1.7844	0.5331	0.9604

t=60°C

19.9	0.0000	0.0000	0.0000	0.0000
30	0.0095	0.0180	0.0053	0.0095
40	0.0190	0.0359	0.0106	0.0190
50	0.0285	0.0539	0.0158	0.0285
60	0.0379	0.0718	0.0211	0.0380

70	0.0474	0.0896	0.0263	0.0474
80	0.0568	0.1075	0.0316	0.0569
90	0.0663	0.1253	0.0368	0.0663
100	0.0757	0.1431	0.0421	0.0758
101.325	0.0770	0.1455	0.0428	0.0770
120	0.0945	0.1787	0.0525	0.0946
140	0.1133	0.2141	0.0630	0.1134
160	0.1321	0.2495	0.0734	0.1322
180	0.1508	0.2848	0.0838	0.1510
200	0.1694	0.3200	0.0942	0.1697
220	0.1880	0.3551	0.1046	0.1884
240	0.2066	0.3902	0.1149	0.2071
260	0.2252	0.4251	0.1253	0.2257
280	0.2436	0.4600	0.1356	0.2443
300	0.2621	0.4947	0.1459	0.2628
320	0.2806	0.5294	0.1562	0.2813
340	0.2989	0.5640	0.1664	0.2998
360	0.3173	0.5985	0.1767	0.3183
380	0.3356	0.6329	0.1869	0.3367
400	0.3538	0.6673	0.1971	0.3551
420	0.3721	0.7015	0.2073	0.3735
440	0.3902	0.7357	0.2175	0.3918
460	0.4084	0.7698	0.2276	0.4101
480	0.4265	0.8038	0.2378	0.4283
500	0.4446	0.8377	0.2479	0.4465
520	0.4626	0.8715	0.2580	0.4647
540	0.4806	0.9052	0.2680	0.4830
560	0.4985	0.9389	0.2781	0.5010
580	0.5164	0.9725	0.2882	0.5191
600	0.5343	1.0059	0.2982	0.5372
625	0.5566	1.0477	0.3107	0.5597
650	0.5788	1.0893	0.3231	0.5821
675	0.6009	1.1308	0.3356	0.6046
700	0.6230	1.1721	0.3480	0.6269
725	0.6451	1.2133	0.3604	0.6492
750	0.6670	1.2544	0.3727	0.6715
775	0.6889	1.2953	0.3851	0.6937
800	0.7108	1.3361	0.3974	0.7159
825	0.7326	[illegible]	0.4096	0.7380
850	0.7543	[illegible]	0.4219	0.7600
875	0.7759	[illegible]	0.4341	0.7820
900	0.7975	[illegible]	0.4463	0.8039
925	0.8191	[illegible]	0.4584	0.8258
950	0.8405	1.5783	0.4705	0.8477
975	0.8620	1.6182	0.4826	0.8694
1000	0.8833	1.6579	0.4947	0.8912

t=65°C

25.0	0.0000	0.0000	0.0000	0.0000
30	0.0044	0.0083	0.0024	0.0044
40	0.0133	0.0252	0.0074	0.0133
50	0.0233	0.0421	0.0124	0.0223
60	0.0312	0.0590	0.0173	0.0312
70	0.0401	0.0758	0.0223	0.0401
80	0.0490	0.0927	0.0272	0.0490

90	0.0579	0.1095	0.0322	0.0579
100	0.0668	0.1263	0.0371	0.0668
101.325	0.0680	0.1285	0.0377	0.0680
120	0.0845	0.1598	0.0470	0.0846
140	0.1022	0.1932	0.0568	0.1023
160	0.1199	0.2266	0.0666	0.1200
180	0.1375	0.2599	0.0764	0.1377
200	0.1551	0.2931	0.0862	0.1554
220	0.1727	0.3262	0.0960	0.1730
240	0.1902	0.3592	0.1058	0.1906
260	0.2077	0.3922	0.1155	0.2081
280	0.2252	0.4251	0.1253	0.2257
300	0.2426	0.4579	0.1350	0.2432
320	0.2600	0.4906	0.1447	0.2606
340	0.2773	0.5233	0.1544	0.2781
360	0.2946	0.5559	0.1640	0.2955
380	0.3119	0.5884	0.1737	0.3129
400	0.3291	0.6208	0.1833	0.3302
420	0.3463	0.6532	0.1929	0.3475
440	0.3635	0.6854	0.2025	0.3648
460	0.3806	0.7176	0.2121	0.3821
480	0.3977	0.7479	0.2217	0.3993
500	0.4148	0.7818	0.2312	0.4165
520	0.4318	0.8137	0.2407	0.4337
540	0.4488	0.8456	0.2502	0.4508
560	0.4657	0.8774	0.2597	0.4679
580	0.4827	0.9091	0.2692	0.4850
600	0.4995	0.9408	0.2787	0.5020
625	0.5206	0.9803	0.2905	0.5233
650	0.5416	1.0196	0.3023	0.5445
675	0.5625	1.0588	0.3140	0.5657
700	0.5834	1.0979	0.3257	0.5868
725	0.6042	1.1369	0.3374	0.6079
750	0.6250	1.1758	0.3491	0.6289
775	0.6457	1.2145	0.3607	0.6499
800	0.6664	1.2531	0.3724	0.6708
825	0.6870	1.2916	0.3840	0.6917
850	0.7075	1.3300	0.3955	0.7125
875	0.7280	1.3683	0.4071	0.7333
900	0.7484	1.4064	0.4186	0.7541
925	0.7688	1.4445	0.4301	0.7748
950	0.7891	1.4824	0.4415	0.7954
975	0.8094	1.5202	0.4530	0.816[illegible]
1000	0.8296	1.5579	0.4644	0.8365

t=70°C

31.2	0.0000	0.0000	0.0000	0.0000
40	0.0074	0.0139	0.0041	0.0074
50	0.0158	0.0299	0.0088	0.0158
60	0.0242	0.0458	0.0134	0.0242
70	0.0326	0.0617	0.0181	0.0326
80	0.0410	0.0776	0.0228	0.0410
90	0.0494	0.0935	0.0274	0.0494
100	0.0578	0.1093	0.0321	0.0578
101.325	0.0589	0.1114	0.0327	0.0590

120	0.0746	0.1410	0.0414	0.0746
140	0.0913	0.1725	0.0507	0.0914
160	0.1080	0.2040	0.0600	0.1081
180	0.1246	0.2355	0.0693	0.1248
200	0.1412	0.2668	0.0785	0.1414
220	0.1578	0.2981	0.0877	0.1581
240	0.1744	0.3294	0.0970	0.1747
260	0.1909	0.3605	0.1062	0.1913
280	0.2074	0.3916	0.1154	0.2078
300	0.2238	0.4226	0.1245	0.2243
320	0.2403	0.4536	0.1337	0.2408
340	0.2567	0.4844	0.1428	0.2573
360	0.2730	0.5152	0.1520	0.2738
380	0.2893	0.5459	0.1611	0.2902
400	0.3056	0.5766	0.1702	0.3066
420	0.3219	0.6072	0.1793	0.3229
440	0.3381	0.6377	0.1883	0.3393
460	0.3543	0.6682	0.1974	0.3556
480	0.3705	0.6985	0.2064	0.3719
500	0.3866	0.7289	0.2154	0.3881
520	0.4027	0.7591	0.2244	0.4043
540	0.4188	0.7893	0.2334	0.4205
560	4348	0.8194	0.2424	0.4367
580	0.4508	0.8494	0.2514	0.4528
600	4668	0.8794	0.2603	0.4690
625	.4867	0.9167	0.2715	0.4891
650	0.5065	0.9540	0.2826	0.5091
675	0.5264	0.9911	0.2937	0.5291
700	0.5461	1.0281	0.3048	0.5491
725	0.5658	1.0650	0.3159	0.5691
750	0.5855	1.1019	0.3269	0.5889
775	0.6051	1.1386	0.3379	0.6088
800	0.6247	1.1752	0.3489	0.6286
825	0.6442	1.2117	0.3599	0.6484
850	0.6636	1.2480	0.3708	0.6681
875	0.6830	1.2843	0.3818	0.6877
900	0.7024	1.3205	0.3927	0.7074
925	0.7217	1.3566	0.4035	0.7270
950	0.7410	1.3925	0.4144	0.7465
975	0.7602	1.4284	0.4252	0.7660
1000	0.7793	1.4641	0.4360	0.7854

t=80°C

47.4	0.0000	0.0000	0.0000	0.0000
50	0.0019	0.0036	0.0010	0.0019
60	0.0097	0.0183	0.0054	0.0097
70	0.0174	0.0329	0.0097	0.0174
80	0.0252	0.0476	0.0140	0.0252
90	0.0329	0.0622	0.0183	0.0329
100	0.0406	0.0769	0.0226	0.0407
101.325	0.0417	0.0788	0.0231	0.0417
120	0.0561	0.1061	0.0315	0.0561
140	0.0715	0.1352	0.0397	0.0716
160	0.0869	0.1643	0.0483	0.0870
180	0.1023	0.1934	0.0568	0.1024

200	0.1176	0.2223	0.0654	0.1178
220	0.1330	0.2512	0.0739	0.1331
240	0.1482	0.2801	0.0824	0.1485
260	0.1635	0.3089	0.0909	0.1638
280	0.1787	0.3376	0.0994	0.1791
300	0.1939	0.3663	0.1079	0.1943
320	0.2091	0.3949	0.1163	0.2096
340	0.2243	0.4234	0.1248	0.2248
360	0.2394	0.4519	0.1332	0.2400
380	0.2545	0.4803	0.1416	0.2551
400	0.2696	0.5087	0.1500	0.2703
420	0.2846	0.5370	0.1584	0.2854
440	0.2996	0.5653	0.1668	0.3005
460	0.3146	0.5935	0.1752	0.3156
480	0.3295	0.6216	0.1835	0.3306
500	0.3445	0.6497	0.1919	0.3457
520	0.3594	0.6777	0.2002	0.3607
540	0.3742	0.7056	0.2085	0.3756
560	0.3891	0.7335	0.2168	0.3906
580	0.4039	0.7613	0.2251	0.4055
600	0.4187	0.7891	0.2334	0.4205
625	0.4371	0.8238	[illegible]	0.4391
650	0.4555	0.8583	[illegible]	0.4576
675	0.4739	0.8927	[illegible]	0.4762
700	0.4922	0.927[illegible]	[illegible]	0.4947
725	0.5105	0.9614	0.2848	0.5131
750	0.5287	0.9955	0.2951	0.5315
775	0.5469	1.0296	0.3053	0.5499
800	0.5651	1.0636	0.3154	0.5683
825	0.5832	1.0975	0.3256	0.5866
850	0.6012	1.1313	0.3358	0.6049
875	0.6193	1.1650	0.3459	0.6231
900	0.6372	1.1987	0.3560	0.6413
925	0.6552	1.2322	0.3661	0.6595
950	0.6730	1.2656	0.3761	0.6776
975	0.6909	1.2990	0.3862	0.6957
1000	0.7087	1.3328	0.3962	0.7138

t=90°C

70.1	0.0000	0.0000	0.0000	0.0000
80	0.0070	0.0132	0.0039	0.0070
90	0.0143	0.0271	0.0080	0.0143
100	0.0217	0.0410	0.0120	0.0217
101.325	0.0226	0.0428	0.0126	0.0226
120	0.0363	0.0687	0.0202	0.0364
140	0.0510	0.0964	0.0283	0.0510
160	0.0656	0.1240	0.0364	0.0656
180	0.0802	0.1516	0.0445	0.0803
200	0.0948	0.1791	0.0526	0.0948
220	0.1093	0.2066	0.0607	0.1094
240	0.1238	0.2340	0.0688	0.1240
260	0.1383	0.2613	0.0769	0.1385
280	0.1528	0.2886	0.0849	0.1530
300	0.1672	0.3159	0.0930	0.1675
320	0.1817	0.3431	0.1010	0.1820

340	0.1961	0.3702	0.1090	0.1964
360	0.2104	0.3973	0.1171	0.2109
380	0.2248	0.4244	0.1251	0.2253
400	0.2391	0.4514	0.1330	0.2397
420	0.2534	0.4783	0.1410	0.2540
440	0.2677	0.5052	0.1490	0.2684
460	0.2819	0.5320	0.1569	0.2827
480	0.2962	0.5588	0.1649	0.2970
500	0.3104	0.5855	0.1728	0.3113
520	0.3245	0.6122	0.1807	0.3256
540	0.3387	0.6388	0.1886	0.3398
560	0.3528	0.6654	0.1965	0.3541
580	0.3669	0.6919	0.2044	0.3683
600	0.3810	0.7184	0.2123	0.3825
625	0.3986	0.7514	0.2221	0.4002
650	0.4161	0.7843	0.2319	0.4179
675	0.4336	0.8171	0.2417	0.4355
700	0.4511	0.8499	0.2515	0.4531
725	0.4685	0.8826	0.2613	0.4707
750	0.4859	0.9152	0.2710	0.4882
775	0.5032	0.9477	0.2807	0.5058
800	0.5205	0.9801	0.2904	0.5232
825	0.5378	1.0125	0.3001	0.5407
850	0.5550	1.0448	0.3098	0.5581
875	0.5720	1.0770	0.3195	0.5755
900	0.5894	1.1091	0.3291	0.5928
925	0.6065	1.1411	0.3387	0.6102
950	0.6236	1.1731	0.3483	0.6275
975	0.6406	1.2050	0.3579	0.6447
1000	0.6576	1.2368	0.3674	0.6619

Table C.2 Vapour-Liquid Equilibria in the System Water-Hydrogen Sulphide at High Pressure

Press	Mole Fraction H_2S	
(MPa)	Liquid	Vapour
t=75°C		
1	0.0064	0.9588
2	0.0130	0.9781
3	0.0196	0.9844
4	0.0259	0.9875
5	0.0318	0.9892
5.7^L	0.0355	0.9899
t=100°C		
1	0.0052	0.8926
2	0.0110	0.9431
3	0.0166	0.9597
4	0.0222	0.9678
5	0.0275	0.9725
6	0.0325	0.9753
7	0.0370	0.9770
8	0.0409	0.9776
8.6^L	0.0427	0.9768
t=125°C		
1	0.0039	0.7570
2	0.0090	0.8716
3	0.0141	0.9095
4	0.0190	0.9281
5	0.0238	0.9389
6	0.0285	0.9457
8	0.0371	0.9530
10	0.0441	0.9546
12.5	0.0495	0.9449
15	0.0522	0.9356
17.5	0.0541	0.9308
20	0.0558	0.9275
25	0.0588	0.9232
30	0.0613	0.9203
35	0.0636	0.9183
40	0.0657	0.9167
50	0.0694	0.9148
60	0.0726	0.9136
70	0.0755	0.9129
80	0.0781	0.9126
90	0.0804	0.9125
100	0.0825	0.9126
t=150°C		
1	0.0025	0.5100

2	0.0072	0.7419
3	0.0118	0.8188
4	0.0165	0.8568
5	0.0210	0.8790
6	0.0255	0.8933
8	0.0340	0.9094
10	0.0418	0.9165
12.5	0.0499	0.9169
15	0.0557	0.9076
17.5	0.0595	0.8951
20	0.0624	0.8858
25	0.0670	0.8739
30	0.0707	0.8662
35	0.0740	0.8607
40	0.0770	0.8565
50	0.0823	0.8506
60	0.0868	0.8467
70	0.0908	0.8442
80	0.0943	0.8424
90	0.0975	0.8413
100	0.1003	0.8403

t=175°C

2	0.0050	0.5288
3	0.0094	0.6704
4	0.0139	0.7405
5	0.0183	0.7819
6	0.0227	0.8086
8	0.0313	0.8400
10	0.0395	0.8557
12.5	0.0489	0.8632
15	0.0569	0.8603
17.5	0.0631	0.8483
20	0.0679	0.8320
25	0.0749	0.8054
30	0.0802	0.7876
35	0.0848	0.7747
40	0.0888	0.7647
50	0.0957	0.7502
60	0.1016	0.7401
70	0.1066	0.7328
80	0.1111	0.7273
90	0.1150	0.7232
100	0.1185	0.7201

t=200°C

2	0.0021	0.2071
3	0.0068	0.4474
4	0.0115	0.5670
5	0.0162	0.6380
10	0.0398	0.7698
15	0.0619	0.7939
20	0.0798	0.7744
25	0.0925	0.7348

30	0.1021	0.7017
35	0.1100	0.6767
40	0.1170	0.6570
50	0.1290	0.6273
60	0.1394	0.6054
70	0.1484	0,5884
80	0.1563	0.5749
90	0.1634	0.5639
100	0.1696	0.5549

t=225°C

5	0.0118	0.4376
10	0.0367	0.6552
15	0.0620	0.7092
20	0.0860	0.7103
25	0.1068	0.6800
30	0.1240	0.6402
35	0.1390	0.6048
40	0.1528	0.5749
50	0.1782	0.5267
60	0.2027	0.4874
70	0.2273	0.4525
80	0.2550	0.4183
90	0.2908	0.3781
94.6[c]	0.334	0.334

t=250°C

5	0.0051	0.1734
10	0.0313	0.5048
15	0.0593	0.5980
20	0.0887	0.6211
25	0.1186	0.6049
30	0.1481	0.5641
35	0.1779	0.5147
40	0.2104	0.4636
45	0.2521	0.4063
48.4[c]	0.325	0.325

t=275°C

7.5	0.0083	0.1629
10	0.0223	0.3180
15	0.0526	0.4602
20	0.0865	0.5092
30	0.1718	0.4709
35	0.2396	0.3919
36.9[c]	0.313	0.313

t=300°C

10	0.0081	0.0998
12.5	0.0235	0.2219
15	0.0401	0.2986
20	0.0775	0.3775

25	0.1242	0.3952
30	0.1941	0.3566
32.1^{c}	0.278	0.278
t=325°C		
15	0.0196	0.1210
17.5	0.0384	0.1883
20	0.0595	0.2322
22.5	0.0838	0.2582
25	0.1134	0.2678
28.9^{c}	0.213	0.213
t=350°C		
18	0.0111	0.0402
20	0.0288	0.0846
22	0.0494	0.1152
24	0.0755	0.1319
25.7^{c}	0.119	0.119

c - critical point
L - three-phase point

Table C.3 The Aqueous Liquid-H_2S-Rich Liquid-Vapour Locus for the System Hydrogen Sulphide-Water

Temp (°C)	Press (MPa)	Press (MPa)	Temp (°C)
29.4	2.23	2.23	29.4
30	2.25	2.5	34.5
35	2.53	3.0	42.7
40	2.83	3.5	50.0
45	3.15	4.0	56.6
50	3.50	4.5	62.6
55	3.88	5.0	68.2
60	4.28	5.5	73.4
65	4.71	6.0	78.4
70	5.17	6.5	83.0
75	5.66	7.0	87.4
80	6.17	7.5	91.6
85	6.72	8.0	95.6
90	7.31	8.5	99.5
95	7.92	9.0	103.2
100	8.57	9.39	106.2
105	9.25		
106.2	9.39		

Table C.4 The Aqueous Liquid-Hydrate-Vapour Locus for the System Hydrogen Sulphide-Water

Temp (°C)	Press (MPa)	Press (MPa)	Temp (°C)
-0.4	0.093	0.093	-0.4
0	0.099	0.25	9.1
5	0.164	0.50	15.7
10	0.275	0.75	19.5
15	0.464	1.00	22.2
20	0.788	1.25	24.3
25	1.35	1.50	26.0
29.4	2.23	1.75	27.4
		2.00	28.6
		2.23	29.4

Table C.5 The Aqueous Liquid-H_2S-Rich Liquid-Hydrate Locus for the System Hydrogen Sulphide-Water

Temp (°C)	Press (MPa)	Press (MPa)	Temp (°C)
29.4	2.23	2.23	29.4
30	7.30	5.0	29.8
31	18.38	10.0	30.2
32	29.46	15.0	30.7
		20.0	31.1
		25.0	31.6
		30.0	32.0

Table C.6 The H_2S-Rich Liquid-Vapour-Hydrate Locus for the System Hydrogen Sulphide-Water

Temp (°C)	Press (MPa)	Press (MPa)	Temp (°C)
5	1.23	1.25	5.7
10	1.40	1.50	12.7
15	1.59	1.75	19.0
20	1.79	2.00	24.6
25	2.02	2.23	29.4
29.4	2.23		

Table C.7 The Ice-Hydrate-Vapour Locus for the System Hydrogen Sulphide-Water

Temp (°C)	Press (kPa)	Press (kPa)	Temp (°C)
-0.4	93.1	93.1	-0.4
-5	78.0	90	-1.6
-10	62.7	80	-4.4
-15	50.1	70	-7.5
-20	39.6	60	-11.0
-25	31.0	50	-15.0
		40	-19.8
		30	-25.7