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IMPROVEMENT OF HYDROGEN SOLUBILITY AND ENTRAINMENT IN HYDROCRACKER FEEDSTOCKS

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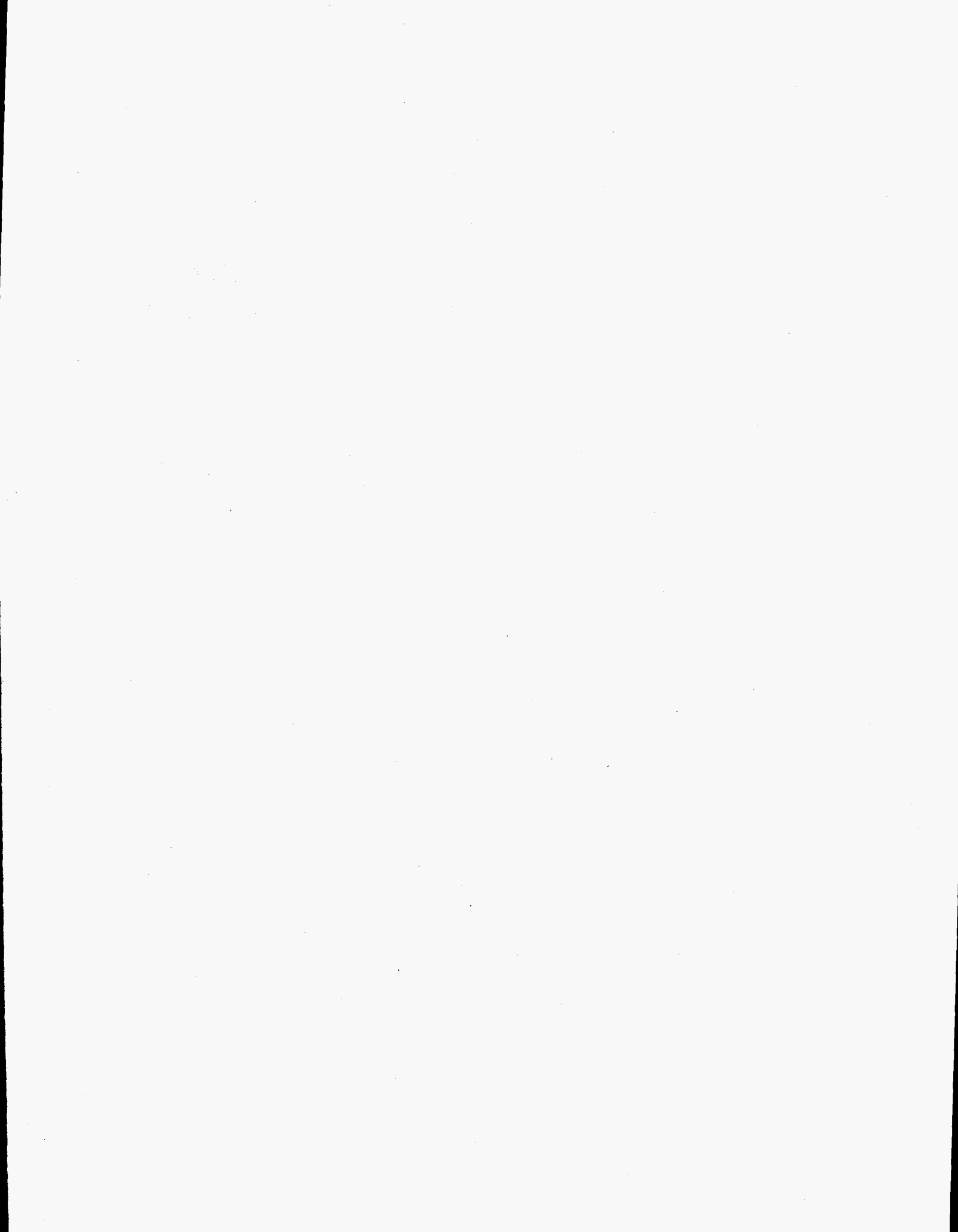
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The work on thermodynamic model for hydrogen solubility in hydrocarbons and in hydrocracker feedstocks was performed by the graduate student Mr. Junjie Luo, and the gas solubility apparatus to measure solubility of hydrogen in hydrocarbons was designed and constructed by the graduate student Mr. Michael McCormick with assistance from the undergraduate research assistant Ms. Ronica Sibert. Two manuscripts have been so far submitted for publication

1. J. J. Luo and V. N. Kabadi, "A Thermodynamic Model for Hydrogen Solubility in Hydrocarbons", Ind. Eng. Chem. Research, in Review.
2. J. J. Luo and V. N. Kabadi, "Estimation of Hydrogen Solubility in Hydrocracker Feedstocks at Process Conditions", Ind. Eng. Chem. Research, in Review.

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ABSTRACT

The work on this project was initiated on September 1, 1992. The project consisted of two tasks: 1. Development of a thermodynamic model for hydrogen solubility in hydrocarbons and extension of this model to predict solubility of hydrogen in hydrocracker feedstocks at conditions similar to those of hydrocracking operations, and 2. Design and construction of a gas solubility apparatus to measure solubility of hydrogen in hydrocarbons and in hydrocracker feedstocks.

The theoretical work proposed was fully accomplished by developing a sophisticated model for hydrogen solubility in hydrocarbons and in hydrocracker feedstocks at advanced temperatures and pressures. Two papers on this work have been submitted to the Journal, Industrial and Engineering Chemistry Research. Reviews of these articles are likely to be available shortly.

The proposed experimental work ran into a number of obstacles, especially to get the original and newly designed on-line sampling technique to function properly. A number of calibrations and tests for reproducibility were necessary to assure the accuracy of measured data. Although a very well designed gas solubility apparatus was built, not much time was left to generate significant hydrogen solubility data. The plans are to use the apparatus in future to measure hydrogen solubility data in liquid fuels to facilitate more efficient design of fuel conversion systems.

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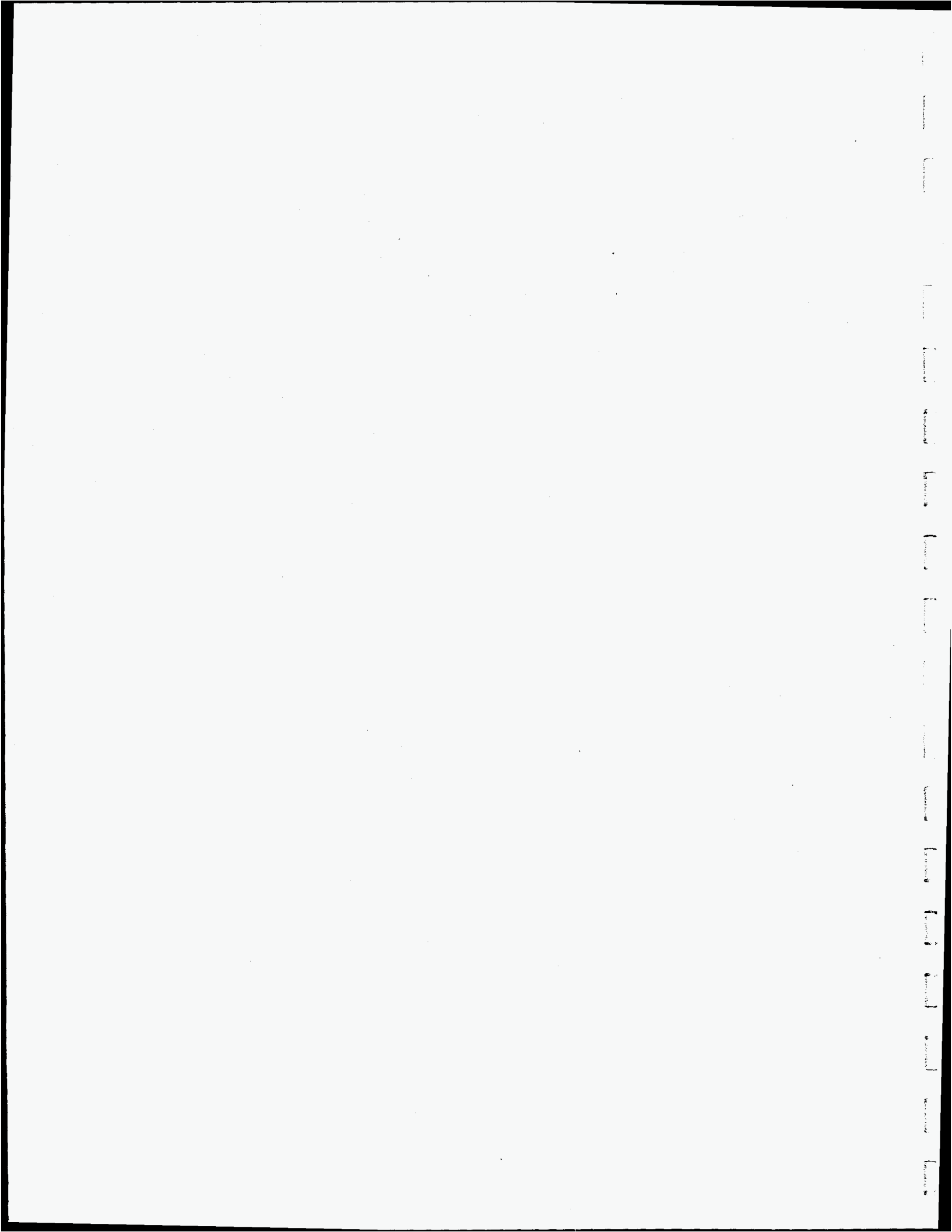
PROJECT OBJECTIVES AND SCOPE

The objective of this project is to determine the conditions for the hydrogen-heavy oil feed preparation so as to optimize the yield of hydrocracking reactions. Proper contacting of hydrogen with heavy oil on the catalyst bed is necessary to improve the yields of the hydrocracking reactions. It is most desirable to have the necessary amount of hydrogen available either in the dissolved or in entrained state, so that hydrogen diffusion to the reaction site does not provide rate controlling resistance to the overall rates of hydrocracking reactions. This project proposes to measure solubility and entrainment data for hydrogen in heavy oils at conditions such as in hydrocrackers, and investigate the improvement of these properties by usage of appropriate additives. Specifically, measurements will be carried out at temperatures up to 300 C and pressures up to 120 atmospheres. Correlations for solubility and entrainment kinetics will be developed from the measured data, and a method for estimating the yield of hydrocracking reactions using these correlations will be suggested. Exxon Research and Engineering Company will serve as private sector collaborator providing A&T with test samples and some technical expertise that will assure successful completion of the project.

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TECHNICAL HIGHLIGHTS AND MILESTONES

The detailed account of the progress on this project is divided into two parts. In the first part we present the thermodynamic model for hydrogen solubility in hydrocarbons and in petroleum fractions. In the second part, the solubility apparatus for hydrogen solubility measurements is described. Thermodynamic model development work has resulted in two papers. Plans are to prepare two more papers for publication from the experimental work completed.



PART 1

**A THERMODYNAMIC MODEL FOR HYDROGEN
SOLUBILITY IN PETROLEUM FRACTIONS**

Junjie Luo

and

V. N. Kabadi

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97
98
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100

TABLE OF CONTENTS

LIST OF TABLES	iv
LIST OF FIGURES	vi
NOMENCLATURE	vii
CHAPTER I INTRODUCTION	1
1.1 Project Objective and Scope	1
1.2 Introduction to Refining Hydroprocessing	1
1.3 Need for a New Correlation for Solubility	9
CHAPTER II REVIEW OF MODELS FOR GAS SOLUBILITY	11
2.1 Thermodynamics and Some GLE Calculation Methods	11
2.2 UNIFAC Group Contribution Method	19
2.3 Methods for Prediction of Hydrogen Solubility in Petroleum Fractions and Coal Liquids	21
CHAPTER III THE MODEL FOR HYDROGEN SOLUBILITY IN HYDROCARBON SOLVENTS	23
3.1 Overall Philosophy of the Model	23
3.2 Data Compilation	24
3.3 Model Development	25
3.3.1 Vapor Phase Fugacity	25
3.3.1.1 Estimation of the Second Virial Coefficients	28
3.3.1.2 Estimation of the Third Virial Coefficients	32
3.3.2 Liquid Phase Fugacity	36
3.3.2.1 Correlation for H_2 , r	38
3.3.2.2 Correlation for f_1^0	39
3.3.3 A Modified UNIFAC Methods	42
3.3.4 Estimation of Modified UNIFAC Group-Interaction Parameters	44
3.4 Results	47

CHAPTER IV	EXTENSION OF THE MODEL TO PETROLEUM FRACTIONS	81
4.1	Prediction of Functional Group in Petroleum Fractions	82
4.1.1	The Correlation for Pure Component Critical Properties and Acentric Factor by Using Group Contribution Method	84
4.1.1.1	Joback Modification of Lydersen's Method for T_c , P_c , and V_c	85
4.1.1.2	The Correlation for Acentric Factor	86
4.1.1.3	The Correlation for Boiling Point	87
4.1.2	Evaluation of Groups for Crude Oil Cuts	88
4.2	Prediction of Hydrogen Solubility in Petroleum Fractions	89
4.2.1	Comparison Between Predicted and Measured Solubilities	90
4.3	Application of the Model for the Hydrocracker Feedstocks at High Temperatures and Pressures	92
CHAPTER V	CONCLUSIONS AND RECOMMENDATIONS	117
REFERENCES		121

LIST OF TABLES

TABLE	PAGE
3.1 Constants for Calculation of Reference Henry's Constant According to $\ln(H_2, \text{atm}) = A + B/T + C\ln(T)$	58
3.2 Constants for Eqn. (3.44) to (3.45)	59
3.3 Pure Component Parameters for Hankinson-Brost-Thomson Correlation	60
3.4 Constants for Eqn. (3.47) to (3.49)	62
3.5 UNIFAC Group Volume and Surface-Area Parameters for Hydrogen Solubility Calculations	63
3.6 Summary of VLE Data Source for Regression of UNIFAC Group-Interaction Parameters	64
3.7 UNIFAC Binary Interaction Parameters $a_{(ij, n)}$ * Using Cubic Expression for Hydrogen-Hydrocarbon Systems	67
3.8 UNIFAC Binary Interaction Parameters $a_{(ij, n)}$ * Using Wagner's Expression For Hydrogen-Hydrocarbon Systems	68
3.9 Temperature Range for Binary Interaction Parameters Using Cubic Expression as a Function of Temperature	69
3.10 Temperature Range for Binary Interaction Parameters Using Wagner's Expression as a Function of Temperature	70
3.11 Error Analysis for Estimating Interaction Parameters Using Cubic Expression as a Function of Temperature	71
3.12 Error Analysis for Estimating Interaction Parameters Using Wagner's Expression as a Function of Temperature	73
3.13 Comparison of Hydrogen Solubilities in Hydrocarbon Solvents with Chao-Seader Correlation and Our Method	76

3.14	Comparison of Hydrogen Solubilities in Hydrocarbon Solvents with Chao-Seader Correlation with the Grayson-Streed New Coefficients and Our Method	78
3.15	Coefficients in Chao-Seader Correlation and in its Modification with the Grayson-Streed New Coefficients	80
4.1	Joback Group Contributions for Critical Properties and Normal Boiling Point [45]	95
4.2	Suggested Group Models for Crude Oil Fractions	96
4.3	The Value of n in Suggested Group	97
4.4	Comparison Between Experimental and Predicted Molar Mass	98
4.5	Experimental Mean Average Boiling Point of Model Compounds	99
4.6	Sensitivity of Concentration of Model Compounds to the Mid-Boiling Point of Crude Oil Cuts	102
4.7	Physical Properties of Crude Oil Fractions Determined by Mohamed, A.F and Elkilani, A.S [62]	103
4.8	Predicted Paraffins, Naphthenes and Aromatics Percent (PNA) in Crude Oil Cuts Determined by Mohamed, A.F. and Elkilani, A. S	104
4.9	Henry's Law Constant (kpa) for Hydrogen in Crude Oil Fractions at Different Temperatures	105
4.10	Physical Properties of "Coker Go" and "FCC LCGO"	106
4.11	Paraffins, Naphthenes and Aromatics Percent (PNA) in "Coker Go" and "FCC LCGO"	107
4.12	The Predicted Results for Hydrogen Solubility in 'Coker Go' and in 'FCC LCGO' at High Temperatures and High Pressures	108
4.13	Physical Properties of the Mixture of "Coker Go" and "FCC LCGO"	110
4.14	Paraffins, Naphthenes, and Aromatics Percent (PNA) in the Mixture of "Coker Go" and "FCC LCGO"	111
4.15	The Predicted Results for Hydrogen Solubility in the Mixture of "Coker Go" and "FCC LCGO" Using Two Different Methods	112

LIST OF FIGURES

FIGURE		PAGE
3.1	Experimental $H'_{2,r}$ (Eqn. 3.37) as a Function of Liquid Mole Fraction of Hydrogen at Isotherms for Hydrogen in n-Hexane Reference Solvent	51
3.2	Experimental $H'_{2,r}$ (Eqn. 3.37) as a Function of Liquid Mole Fraction of Hydrogen at Isotherms for Hydrogen in n-Decane Reference Solvent	52
3.3	Experimental $H'_{2,r}$ (Eqn. 3.37) as a Function of Liquid Mole Fraction of Hydrogen at Isotherms for Hydrogen in n-Hexadecane Reference Solvent	53
3.4	Experimental $H'_{2,r}$ (Eqn. 3.37) as a Function of Liquid Mole Fraction of Propane at Isotherms for Propane in Cyclohexane Reference Solvent	54
3.5	Temperature Dependency of UNIFAC Group Interaction Parameters Between Hydrogen and CH_3 - Using Cubic Expression and Wagner's Expression	55
3.6	Experimental and Calculated Solubilities of Hydrogen in n-Decane, Cyclohexane, and Benzene at 102 atm Partial Pressure as a Function of Temperature	56
3.7	Experimental and Calculated Solubilities of Hydrogen in n-Paraffins and Alkyl-benzene at 470 ^o K and 50 atm Partial Pressure	57
4.1	Experimental Mean Average Boiling Point of Model Compounds at different value of n	114
4.2	Pressure Dependency of Calculated Solubility of Hydrogen in "Coker Go" at Different Temperatures	115
4.3	Pressure Dependency of Calculated Solubility of Hydrogen in "FCC LCGO" at Different Temperatures	116

NOMENCLATURE

a_{ij}	Group-Interaction Parameters in UNIFAC
B	Second Virial Coefficient, $\text{cm}^3 \text{mole}^{-1}$
C	Third Virial Coefficient, $(\text{cm}^3 \text{mole}^{-1})^2$
D	Fourth Virial Coefficient, $(\text{cm}^3 \text{mole}^{-1})^3$
f_i^G	Fugacity of Component i in the Gas Phase, atm
f_i^L	Fugacity of Component i in the Liquid Phase, atm
f_i^0	Pure Component i Reference Fugacity in the Liquid State, atm
F	Objective Function
$H_{i,r}$	Reference Henry's Constant, atm
$K_{i,j}$	Characteristic Binary Constant
m	Molecular Weight
P	Pressure, atm
P_c	Critical Pressure, atm
P_i^{sat}	Saturated Vapor Pressure of Component i , atm
Q_K	Group Surface Area Parameters in UNIFAC
R_K	Group Volume Parameters in UNIFAC
R	Universal Gas Constant
T	Absolute Temperature, $^\circ\text{K}$
T_b	Temperature of Boiling Point, $^\circ\text{K}$
T_c	Critical Temperature, $^\circ\text{K}$
V_c	Critical Volume, $\text{cm}^3 \text{mole}^{-1}$
V^*	Pure Component Characteristic Volume, $\text{cm}^3 \text{mole}^{-1}$
V_s	Saturated Liquid Volume, $\text{cm}^3 \text{mole}^{-1}$
V^L	Compressed Liquid Volume, $\text{cm}^3 \text{mole}^{-1}$
x_i	Liquid Mole Fraction of Component i
y_i	Vapor Mole Fraction of Component i
Z_c	Critical Compressibility Factor
γ_i	Activity Coefficient of Component i
$\gamma_{i,r}^\infty$	Activity Coefficient of Component i in Infinite Dilution Reference Solvent
ϕ_i	Fugacity Coefficient of Component i in Vapor Phase
ρ	Specific Density, mole cm^{-3}
ω	Acentric Factor

CHAPTER I

INTRODUCTION

1.1 Project Objective and Scope

The objective of this project is to determine the conditions for the hydrogen - heavy oil feed preparation so as to optimize the yield of hydrocracking reactions. Proper contacting of hydrogen with heavy oil on the catalytic bed is necessary to improve the yields of the hydrocracking reactions. It is most desirable to have the necessary amount of hydrogen available either in the dissolved or in entrained state, so that hydrogen diffusion to the reaction site does not provide rate controlling resistance to the overall rates of hydrocracking reactions. This project will develop the new correlations for solubility from the experimental data and tested by measured data.

1.2 Introduction to Refining Hydroprocessing

The use of hydrogen in thermal processes is perhaps the single most significant advance in refining technology during the twentieth century [8]. The process uses the principle that the presence of hydrogen during a thermal reaction of a petroleum feedstock terminates many of the coke-forming reactions and enhances the yields of the lower boiling components, such as gasoline, kerosene, and jet fuel.

There is a rough correlation between the quality of petroleum products and their hydrogen content. It happens that desirable aviation gasolines, kerosenes, diesel fuels, and steam turbine and most other good lubricating oils are made up of hydrocarbons containing high proportions of hydrogen. In addition, it is usually possible to convert olefins

and polycyclics to paraffins and monocyclic hydrocarbons by hydrogen-adding processes. These facts have for many years encouraged attempts to employ hydrogenation for refining operations; despite considerable technical success, such processes were not economically possible until low-priced hydrogen became available as result of the rise of hydroreforming, which converts naphthenes to aromatics with the release of hydrogen.

Hydrogenation process for the conversion of petroleum fractions and petroleum products may be classified as destructive and nondestructive. Destructive hydrogenation (hydrogenolysis) or hydrocracking is characterized by the cleavage of carbon-carbon linkages accompanied by hydrogen saturation of the fragments to produce lower boiling products. Such treatment requires severe processing conditions and the use of high hydrogen pressures to minimize polymerizations and condensations leading to coke formation. Many other reactions, such as isomerization, dehydrogenation, and cyclization, occur under the drastic conditions employed. In fact hydrocracking is perhaps the single most significant advance in petroleum refining technology over the last several decades. It is essentially an efficient thermal catalytic method of converting refractory material to gasoline. However, hydrocracking should not be regarded as a competitor for catalytic cracking. Catalytic cracking units normally use virgin gas oils as feedstocks; hydrocracking feedstock usually consists of refractive gas oils derived from cracking and coking operations. Hence, hydrocracking is a supplement to, rather than a replacement for, catalytic cracking.

Nondestructive or simple hydrogenation is generally used for the purpose of improving product quality without appreciable alteration of the boiling range. Mild processing conditions are employed so that only the more unstable materials are attacked. Thus nitrogen, sulfur, and oxygen compounds undergo hydrogenolysis to split out ammonia, hydrogen sulfide, and water, respectively. Olefins are saturated and unstable

compounds, such as diolefins, which might lead to the formation of gums or insoluble materials, are converted to more stable compounds. Heavy metals present in the feedstock are also usually removed during hydrogen processing [1,87].

If high-molecular-weight petroleum fractions are pyrolyzed, that is, if no hydrogenation occurs, progressive cracking and polymerization generally lead to the final products, which are usually (1) gaseous and low-boiling liquid compounds of high hydrogen content, (2) liquid material of intermediate molecular weight with a hydrogen-carbon atomic ratio differing more or less from that of the original feedstock, depending on the method of operation, and (3) material of high molecular weight, such as tar and petroleum coke, possessing a lower hydrogen-carbon atomic ratio than the starting material. Highly aromatic or refractory cycle stocks or gas oils that contain varying proportions of highly condensed aromatic structures (naphthalene, phenanthrene, and pyrene types) usually crack, in the absence of hydrogen, to yield tar and coke.

An essential difference between pyrolysis and hydrogenolysis of petroleum is that in pyrolysis a certain amount of polymerized heavier products, like tar and coke, is always formed along with the light products, such as gas and gasoline, but during hydrogenolysis (destructive hydrogenation) polymerization may be partly or even entirely prevented so that only light products are formed. The prevention of tar and coke formation usually results in an increased gasoline yield. The condensed type of molecule, such as naphthalene or anthracene, is one that is closely associated with the formation of tar and especially coke, but in an atmosphere of hydrogen and in contact with catalysts, these condensed molecules are converted in lower molecular weight saturated compounds that boil within the gasoline range.

Hydrotreating is carried out by charging the feed to the reactor, together with a portion of all the hydrogen produced in the catalytic reformer. Suitable catalysts are tung-

estennickel sulfide, cobalt-molybdenum-alumina, nickel oxide-silica-alumina, and platinum-alumina. Most processes employ cobalt-molybdena catalysts, which generally contain about 10% molybdenum oxide and less than 1% cobalt oxide supported on alumina. The temperatures employed are in the range of 300-345°C (570-850°F), and the hydrogen pressures are about 500-1000 psig.

The reaction generally takes place in the vapor phase but, depending on the application, may be a mixed-phase reaction. The reaction products are cooled in a heat exchanger and led to a high-pressure separator where hydrogen gas is separated for recycling. Liquid products from the high-pressure separator flow to a low-pressure separator (stabilizer) where dissolved light gases are removed. The product may then be fed to a reforming or cracking unit if desired. Generally, it is more economical to hydrotreat high-sulfur feedstocks before catalytic cracking than to hydroheat the products from catalytic cracking. The advantages are (1) the products require less finishing, (2) sulfur is removed from the catalytic cracking feedstock, and corrosion is reduced in the cracking unit, and (3) carbon formation during cracking is reduced and higher conversions result, and (4) the catalytic cracking quality of the gas oil fraction is improved.

The mechanism of hydrocracking is basically similar to that of catalytic cracking, but with concurrent hydrogenation. Carbonium ions are produced via olefin intermediates and are quickly hydrogenated under the high-hydrogen partial pressures employed in hydrocracking. The rapid hydrogenation prevents adsorption of olefin on the catalyst and, hence, prevents their subsequent dehydrogenation, which ultimately leads to coke formation so that long on-stream times can be obtained without the necessity of catalyst regeneration.

One of the most important reactions in hydrocracking is the partial hydrogenation of polycyclic aromatics followed by rupture of the saturated rings to form substituted

monocyclic aromatics,. The side chains may then be split off to give isoparaffins. It is desirable to avoid excessive hydrogenation activity of the catalyst so that the monocyclic aromatics become hydrogenated to naphthenes; furthermore, repeated hydrogenation leads to loss in octane number, which increases the catalytic reforming required to process the hydrocracked naphtha.

Side chains of three or four carbon atoms are easily removed from an aromatic ring during catalytic cracking, but the reaction of aromatic rings with shorter side chains appears to be quite different. For example, hydrocracking single-ring aromatics containing four or more methyl groups produces largely isobutane and benzene. It may be that successive isomerization of the feed molecule adsorbed on the catalyst occurs until a four-carbon side chain is formed, which then breaks off to yield isobutane and benzene.

Paraffin wax decomposes at about equal rates in the presence and absence of hydrogen with and without catalyst, but both gas oils and heavier tars high in polynuclear aromatics have been found to form gasoline faster in the presence of hydrogen and a suitable catalyst than when cracked thermally. Coke formation is very low in such hydrocracking; secondary reactions, such as polymerization and condensation, ordinary precursors to coke production, are suppressed, progressively so as hydrogen pressure is increased.

When applied to crude oil residues the hydrocracking process can be used for several operations:

1. Fuel oil desulfurization
2. Residue conversion to lower boiling distillates
3. Production of high-quality synthetic crude oil from heavy residues

The products from hydrocracking are composed of either saturated or aromatic compounds; no olefins are found. In making gasoline, the lower paraffins formed have

high octane numbers; for example, the 5- and 6-carbon number fractions have led to search octane numbers of 00-100. The remaining gasoline has excellent properties as a feed to catalytic reforming, producing a highly aromatic gasoline that with added lead, easily attains a 100 octane number. Both gasolines are suitable for premium-grade motor gasoline. Another attractive feature of hydrocracking is the low yield of gaseous components, such as methane, ethane, and propane, which are less desirable than gasoline. When making jet fuel, more hydrogenation activity of the catalysis is used, since jet fuel contains more saturates than gasoline.

The hydrocracking process is being applied in other areas, notably to produce lubricating oils and to convert very asphaltic and high-boiling residues to lower boiling fuels. Its use will certainly increase greatly in the future, since it accomplishes two needed functions in the petroleum fuel economy: large, unwieldy molecules are cracked, and the needed hydrogen is added to produce useful, high-quality fuels.

The problems encountered in hydrocracking heavy feedstocks can be directly equated to the amount of complex, higher boiling constituents that may require pretreatment [81,94]. Processing these feedstocks is not merely a matter of applying know-how derived from refining "conventional" crude oils but requires a knowledge of composition. The materials are not only complex in terms of the carbon number and boiling point ranges but also because a large part of this "envelope" falls into a range of model compounds about which very little is known. It is also established that the majority of the higher molecular weight constituents produce liquids (with some coke). It is to both of these trends that hydrocracking is aimed.

The choice of processing schemes for a given hydrocracking application depends upon the nature of the feedstock as well as the product requirements [2, 69,70,102]. The process can be simply illustrated as a single-stage or as a two-stage operation. The single-

stage process can be used to produce gasoline but is more often used to produce middle distillate from heavy vacuum gas oils; the two-stage process was developed primarily to produce high yields of gasoline from straight-run gas oils, and the first stage may actually be a purification step to remove sulfur-containing (as well as nitrogen-containing) organic materials. Both processes use an extinction-recycling technique to maximize the yields of the desired product. Significant conversion of heavy feedstocks can be accomplished by hydrocracking at high severity [42]. For some applications, the products boiling up to 650°F (340°C) can be blended to give the desired final product.

Attention must also be given to the coke mitigation aspects. For example, in the hydrogen addition options particular attention must be given to hydrogen management, thereby promoting asphaltene fragmentation to lighter products rather than to the production of coke. The presence of a material with good solvating power to diminish the possibility of coke formation is preferred. In this respect it is worth noting the reappearance of donor solvent processing of heavy oils [59,100], which has its roots in the older hydrogen donor diluent visbreaking process [7,10,52].

Hydrocracking is an extremely versatile process that can be utilized in many different ways. One of the advantages of hydrocracking is its ability to break down high-boiling aromatic stocks produced by catalytic cracking or coking. This is particularly desirable when maximum gasoline and minimum fuel oil must be made. For example, in the early days of the process, a particular type of feedstock was used to provide limited distribution of lower boiling products. However, it must be forgotten that product distribution and quality vary considerably depending upon the nature of the feedstock constituents as well as on the process. In modern refineries, hydrocracking is one of several process options that can be applied to the production of liquid fuels from the heavier feedstocks. A most important aspect of the modern refinery operation is the desired prod-

uct slate, which dictates the matching of a process with any particular feedstock to overcome differences in feedstock composition.

Hydrogen consumption is also a parameter that varies with feedstock composition, thereby indicating the need for a thorough understanding of the feedstock constituents if the process is to be employed to maximum efficiency. A convenient means of understanding the influence of feedstock on the hydrocracking process is through a study of the hydrogen content (H/C atomic ratio) and molecular weight (carbon number) of the various feedstocks or products. Such data show the extent to which the carbon number and/or the relative amount of hydrogen that must be added to generate the desired lower molecular weight, hydrogenated products must be reduced. In addition, it is also possible to use data for hydrogen usage in residuum processing, where the relative amount of hydrogen consumed in the process can be shown to be dependent upon the sulfur content of the feedstock.

The purpose of hydrocracking is to convert high-boiling feedstocks to lower boiling products by cracking the hydrocarbons in the feed and hydrogenating the unsaturated materials in the product streams. The polycyclic aromatics are first partially hydrogenated before cracking of the aromatic nucleus takes place. The sulfur and nitrogen atoms are converted to hydrogen sulfide and ammonia, but a more important role of the hydrogenation is probably to hydrogenate the coke precursors rapidly and prevent their conversion to coke.

The petroleum industry often employs two-stage processes in which the feed stock undergoes both hydrotreating and hydrocracking. In the first, or pretreating, stage the main purpose is conversion of nitrogen compounds in the feed to hydrocarbons and to ammonia by hydrogenation and mild hydrocracking. Typical conditions are 650-740°F (340-390°C), 150-2500 psig (1-17 MPa), and a catalyst contact time of 0.5-1.5 h; up to 1.5 wt% hydro-

gen is absorbed, partly by conversion of the nitrogen compounds but chiefly by aromatic compounds that are hydrogenated. It is most important to reduce the nitrogen content of the product oil to less than 0.001 wt% (10 parts per million). This stage is usually carried out with a bifunctional catalyst containing hydrogenation promoters, for example, nickel and tungsten or molybdenum sulfides, on an acid support, such as silica-alumina. The metal sulfides hydrogenate aromatics and nitrogen compounds and prevent deposition of carbonaceous deposits; the acid support accelerates nitrogen removal as ammonia by breaking carbon-nitrogen bonds.

Most of hydrocracking is accomplished in the second stage, which resembles the first but uses a different catalyst. Ammonia and some gasoline are usually removed from the first-stage product, and then the remaining oil, which is low in nitrogen compounds, is passed over the second-stage catalyst. Again, typical conditions are 600-700°F (300-370°C), 1500-2500 psig (10-17 MPa) hydrogen pressure, and 0.5-1.5 h contact time; 1-1.5 wt % hydrogen may be absorbed. Conversion to gasoline or jet fuel is seldom complete in one contact with the catalyst, so the lighter oils are removed by distillation of the products and the heavier, higher-boiling product combined with fresh feed and recycled over the catalyst until it is completely converted.

1.3 Need for a New Correlation for Solubility

Hydrogen solubility is a major factor in the design of crude oil hydrocracking process. In most current hydrocracking process, crude oil fractions undergo catalytically hydrogenated reactions to increase the hydrogen-to-carbon ration of the fuel. In these reactions, proper contact of hydrogen with heavy oil on the catalytic bed is necessary to improve the yields of the hydrocracking reactions. It is most desirable to have the necessary amount of hydrogen available either in the dissolved or in entrained state, so that

hydrogen diffusion to the reaction site does not provide rate controlling resistance to the overall rates of hydrocracking reactions. At the same time, hydrogen traces in the product streams may affect the quality of the final product. Thus reliable estimates of hydrogen solubility in hydrocarbons and crude oil fractions are necessary. Hydrocracking reactions normally carried out at average catalyst temperatures between 550 and 750 ° F and at reactor pressures between 1,200 and 2,000 psig. A good method of correlating the solubility of hydrogen at such high temperatures and pressures is still not available.

A number of correlations (explained in detail in chapter II) have been developed for the solubility of hydrogen in hydrocarbon solvents. Most of these are limited to low pressures and room temperatures. The other methods are cannot be recommended for general applications. There is a clear need for a new correlation for hydrogen solubility.

In this work, we present a correlation of the solubility of hydrogen based on all available phase equilibrium data for hydrogen-containing mixtures of identifiable components at temperature up to 700 K and pressures up to 600 bar. The correlation for hydrogen - hydrocarbon systems has been developed and is discussed in detail in chapter III. This model has been extended for hydrogen solubility prediction in petroleum fractions using an approximate method for petroleum fraction characterization into molecular weigh distributions and functional group compositions, which is explained in chapter IV.

CHAPTER II

REVIEW OF MODELS FOR GAS SOLUBILITY

The solubility of hydrogen in hydrocarbon solvents is of interest in hydrofining of oil and coal where it is basic to engineering design of the processes and to analysis of reaction kinetics. Recent intensified development of coal liquefaction has amplified this interest. Accurate description of phase equilibria in systems containing subcritical as well as supercritical components has recently attained much attention.

A number of correlations have been developed for the calculation of gas solubilities. The regions of pressure and temperature which are of interest in gas-liquid equilibrium (GLE) calculations range from low temperature and pressure up to the critical point of the system under consideration. The liquid solvents are often complex mixtures and may contain polar as well as nonpolar substances.

Experimental data are scarce in this field. It is therefore desirable to develop models for GLE which do not need specific information concerning the system in question but only certain information concerning the behavior of the constituent parts of the molecules, i.e., the groups they contain. In this way it is possible to cover a variety of solvents using only a few group parameters.

2.1 Thermodynamics and Some GLE Calculation Methods

The solubility of gases in liquids has been under quantitative investigation since the beginning of the nineteenth century. The last decade has seen some remarkable advances in theory, empirical correlations, systems studied, and apparatus. Much of the earlier work

was more qualitative than quantitative. Gas solubilities have become increasingly more important for both the theoretical understanding of the liquid state and solutions. A rigorous method for the prediction of gas solubilities requires a valid theory of solutions. Such a theory is unfortunately, not available, but for a semiempirical description of nonpolar systems the theory of regular solutions can serve as the basis of a correlating scheme. Previous attempts to use regular solution theory for gas-liquid solutions [11,22,28,51,76] have been quite successful. However these earlier studies were concerned either with a particular class of solutions (such as hydrocarbons), or were limited to a particular temperature, or were chiefly interested in the theoretical aspects of the problem.

The Krichevsky-Kasarnovsky equation [49] gives an excellent representation of the solvent at high pressure. This equation can be expected to hold for cases which conform to the two assumptions on which the equation rests. One of these is that the activity coefficient of the solute does not change noticeably over the range of x_2 (mole fraction of gas in liquid phase) being considered; in other words, x_2 must be small. The other assumption states that the infinitely dilute solution must be essentially incompressible, which is approximately true at temperatures far removed from the critical temperature of the solution.

Chao and Seader [12] developed a correlation of vaporization-condensation equilibria of hydrocarbon mixtures to apply at more general conditions. They included the solubility of hydrogen in the correlation. The data base for the hydrogen correlation was limited mainly to paraffin solvents with benzene, toluene, m-xylene, and cyclohexane and methylcyclohexane the only naphthenic solvents. The temperature range of the data base was also quite limited. As a result, the correlation was specifically restricted to temperatures not to exceed 530 K.

Grayson and Streed [33] modified the correlation of Chao and Seader on the basis of proprietary data on hydrogen + oil systems. The upper temperature limit was extended to about 740 K.

Both the Chao-Seader correlation and the basic Chao-Seader relations with the Grayson-Streed numerical values of the coefficients can give us the good results for solubility predictions at high temperatures and pressures. They need specific information concerning the system in question, such as solubility parameters and liquid mole volume of the pure compounds including in the system. Since the general correlations for these two thermodynamic properties are still not available, they can not be recommended for predictions of gas solubility in undefined compounds, such as petroleum fractions. The comparison with these two correlations and our method developed in this work will be discussed in chapter III.

In the following description of the thermodynamic background for gas solubility calculations we focus on expressions for the liquid phase fugacity of supercritical components. It may be assumed that the gas phase fugacities of subcritical as well as supercritical components can be calculated from an equation of state. The liquid phase fugacity of subcritical species can be calculated using the same procedures as in the case of vapor-liquid equilibrium (VLE) calculations; that is, either by means of an activity coefficient approach (as indicated in eqn. 2.1) or by means of an equation of state (as indicated in eqn. 2.3).

The isofugacity criterion for a supercritical component in a GLE system may be written in three basically different ways:

$$\hat{f}_i^G = \hat{f}_i^L = x_i \cdot \gamma_i \cdot f_i^0 \quad (2.1)$$

$$= x_i \cdot \gamma_i^* \cdot H_{i,s} \quad (2.2)$$

$$= x_i \cdot \hat{\phi}_i^L \cdot P \quad (2.3)$$

where f_i^G and f_i^L are the fugacities of component i in the gas (G) and liquid (L) phase, x_i is the liquid mole fraction of component i , f_i^0 is the pure-component reference fugacity in the liquid state at system temperature T and pressure P , and γ_i and γ_i^* are the activity coefficients in the symmetric and unsymmetric conventions. $H_{i,s}$ is Henry's constant for gas i in a pure solvent, or solvent mixture s , at the system T and P ; ϕ_i^L is the fugacity coefficient in the liquid phase at T and P .

The activity coefficient γ_i^* in eqn. (2.2) is a function of pressure P :

$$\gamma_i^* = \gamma_i^*(P^+) \exp \int_{P^+}^P [(\bar{v}_i - \bar{v}_i^\infty)/RT] dP \quad (2.4)$$

where P^+ is a reference pressure, \bar{v}_i is the partial molar volume of component i at the given composition (x_1, x_i, x_N), \bar{v}_i^∞ is the partial molar volume of component i at infinite dilution, and $\gamma_i^*(P^+)$ is the activity coefficient at the reference pressure P^+ . Equation (2.4) is based on the assumption that $H_{i,s}$ is measured at pressure P .

Henry's constant is itself a function of pressure:

$$H_{i,s} = H_{i,s}^+ \exp \int_{P^+}^P (\bar{v}_i^\infty/RT) dP \quad (2.5)$$

This means that if Henry's constant is referred to pressure P^+ , combination of eqns. (2.2), (2.4) and (2.5) yields

$$\hat{f}_i^L = x_i \cdot \gamma_i^{**} \cdot H_{i,s}^+ \quad (2.6)$$

where

$$\gamma_i^{**} = \gamma_i^*(P^+) \exp \int_{P^+}^P (\bar{v}_i/RT) dP \quad (2.7)$$

Equation (2.1) requires the knowledge of a pure-component reference fugacity in the liquid state. Such a state is hypothetical for supercritical components, and the calculation of this quantity must therefore be based on some kind of extrapolation of information concerning the pure-component fugacity (vapor pressure) as a function of temperature into the supercritical region.

Prausnitz and Shair [79] have described a method for establishing a generalized plot of reduced reference fugacity versus reduced temperature for low-pressure gas solubilities. The plot covers most of the industrially important gases except H₂, Ne, and He for reduced temperatures below 3.2. The model for activity coefficients used by Prausnitz and Shair is based on regular-solution theory and requires no binary parameters. The plot of reduced reference fugacity versus temperature is independent of solvent, at least in principle. However, the plot will reflect the inherent deficiencies of the model used for the activity coefficient, and any reference fugacity plot should therefore be combined exclusively with the activity coefficient model on which it is based. Regular-solution theory cannot describe mixtures of, for example, associated and inert components. Activity coefficient models which can represent complex systems (e.g., UNIQUAC, Wilson, NRTL) contain at least one parameter per pair of components. Low-pressure gas solubility data often cover a very narrow concentration range. It is therefore possible to estimate only one parameter from each new binary system. A reference fugacity plot for low-pressure gas solubilities using one of the more sophisticated activity coefficient models can hence not

be established. The reference fugacity approach of Prausnitz and Shair is therefore useful only for relatively simple systems.

Equation (2.2) requires a Henry's constant for the system considered. Henry's constant is a limiting property. It requires a few isothermal experimental solubility data points in the diluted region to obtain $H_{i,s}$ at the pure-solvent vapor pressure. Henry's constant is defined as

$$H_{i,s} = \lim (\hat{f}_i/x_i)_{P,T,n_j} \quad (2.8)$$

where n_j is the number of moles of component i . The limit is taken at constant P and T and at constant numbers of moles of all components except component i .

An experimental isothermal data set will, for example consist of the solubilities of a gas (2) in a solvent (1) as a function of the partial pressure of 2 in the gas phase. Such data cannot be used directly together with eqn. (2.8) to estimate $H_{2,1}$, since the phase rule prevents P from being kept constant if the f_2 's are calculated along the phase boundary where $f_2^G = f_2^L$. The following arguments may be used to solve the problem.

If there is equilibrium at pressure P' between a gas and a liquid, then

$$\hat{f}_2' = \hat{f}_2^G = \hat{f}_2^L \quad (2.9)$$

At any pressure $P \geq P'$,

$$\hat{f}_2 = \hat{f}_2' \exp \int_{P'}^P (\bar{v}_2/RT) dP \quad (2.10)$$

Henry's constant is given by eqn. (2.8) as

$$H_{2,1} = \lim_{n_2 \rightarrow 0} [(\hat{f}_2/x_2) \exp \int_{P'}^P (\bar{v}_2/RT)/dP]_{P,T,n_j} \quad (2.11)$$

For $n_2 \rightarrow 0$, $P' \rightarrow P_1^{\text{sat}}$ and $\bar{v}_2 \rightarrow \bar{v}_2^\infty$. Equation (2.11) may therefore be written as

$$H_{2,1} = \lim_{n_2 \rightarrow 0} (\hat{f}_2/x_2)_{T,\sigma,n_j} \exp \int_{P_1^{\text{sat}}}^P (\bar{v}_2^\infty/RT)dP \quad (2.12)$$

where σ indicates that f_2' is taken on the phase boundary. Setting $P = P_1^{\text{sat}}$.

$$H_{2,1}(P_1^{\text{sat}}) = \lim_{n_2 \rightarrow 0} (\hat{f}_2/x_2)_{T,\sigma,n_j} \quad (2.13)$$

Equation (2.13) shows that experimental phase equilibrium data at varying pressure P' may be used to calculate $H_{2,1}(P_1^{\text{sat}})$, even though this quantity is defined as a limiting value at fixed pressure, P_1^{sat} .

In the Krichevsky-Ilinskaya procedure [50], the two-suffix Margules equation is used for the activity coefficient in eqn. (2.2). This procedure works for simple (nonpolar) solvents up to relatively high pressures, provided that a good estimate can be supplied for the partial molar volume of the gas at infinite dilution (see eqn. 2.5). This equation is similar to the Krichevsky-Kasarnovsky equation (mentioned before) except that this equation takes into account deviations from Henry's Law due to the effect of composition in addition to the effect of total pressure, and has a wider applicability. It is especially useful for solutions of light gases in liquid solvents where the solubility is appreciable.

Orentlicher and Prausnitz [76] represented the thermodynamic model of hydrogen solubility in cryogenic solvents at high pressure. Solubility data for hydrogen in liquids at low temperature and high pressure have been reduced by a thermodynamic relation similar to the Krichevsky-Kasamovsky equation, but allowing for the variation of activity coefficients with the hydrogen concentration. The parameters appearing in this relation have been partially correlated on the basis of a very simple solution model.

Mathias and O'Connell [60] used the Henry's constant concept in applying their direct-correlation-function approach. The idea of a Henry's constant for a reference solvent, as used by Mathias and O'Connell, is further explained in the following section.

The approaches according to eqn (2.1) and (2.2) have common weakness. The use of one model for the gas phase and another model for the liquid phase inevitably leads to difficulties near the critical point. The critical point described by the equation of state for the gas phase will not in general agree with the critical point described by the reference fugacity and activity coefficient models. These last models may exhibit no critical point at all. Furthermore, application of these two approaches to high pressure GLE requires fairly accurate description of the volumetric properties of the liquid phase. A solution to the above-mentioned problems is the application of a suitable equation of state for both phases, i.e., eqn. (2.3). Simple equations of state, for example the Soave-Redlich-Kwong equation, describe phase equilibria in systems containing simple nonpolar substances with high accuracy over wide ranges of temperature and pressure. Several attempts have been made to extend the applicability of the equation-of-state approach to complex mixtures. Baumgaertner et al. [6] combined chemical theory with Redlich-Kwong equation for components with strong specific interactions (water, organic acids, etc). Although this procedure leads to substantial improvements in the representation of phase equilibria, it cannot be recommended for general applications. The use of chemical theory leads to a

considerable increase in the number of model parameters, and the solution of the mass balances leads to a severe increase of computational effort.

The work of Huron and Vidal [43]), Mollerup [63] and Whiting and Prausnitz [101] presents some interesting new ideas about mixing rules in equations of state. These new equations are based on a combination of simple equations of state, such as the Soave Redlich-Kwong or the Van der Waals equation, with the very successful local-composition models for the Gibbs excess function, such as the Wilson, NRTL or UNIQUAC equations. Such equations may prove useful for high-pressure GLE calculations for systems containing relatively complex solvents.

The "parameters from group contributions" equation of state [17] is based on a combination of the Wilson model for excess properties and an empirical description of liquid expansion [102]. As indicated by the name, this equation combines the advantages of an equation of state with the advantage of describing a variety of substances by means of relatively few group parameters. The results obtained by Cunningham [17] and Moshfeghian et al. [65] indicate that it is possible to apply the group-contribution concept to equations of state.

2.2 UNIFAC Group Contribution Method

The UNIFAC (UNIQUAC Functional Group Activity Coefficients) group-contribution method has a number of years been applied to predict activity coefficients for non-electrolytic liquid mixtures. The method has thereby become a fast and reliable tool for prediction liquid-phase activity coefficients in nonelectrolyte mixture at low to moderate pressures and temperatures between 300 and 425 K. It has become widely used in practical chemical engineering applications, most notably in phase equilibrium calculations in cases where little or no relevant experimental information is available.

The UNIFAC method was originally developed by Fredenslund et al [24]. Later the method was revised and its range of applicability considerably extended [26, 27, 92]. The parameters needed for the use of UNIFAC are group volumes (R_K), group surface areas (Q_K), and group-interaction parameters (a_{mn} and a_{nm}). The uses and shortcomings of UNIFAC is that the built-in temperature dependence is not good enough for simultaneous prediction of vapor-liquid equilibria (VLE) and excess enthalpies (H^E).

The modified UNIFAC model [53] for predicting activity coefficients presented in this work is based on the well-known UNIFAC model. Two changes are introduced in modified UNIFAC: (1) the group-interaction-parameters have been made temperature-dependent and (2) the combinatorial term is slightly modified according to the ideas of Kikic et al [48]. It is shown that modified UNIFAC gives somewhat better predictions of vapor-liquid equilibria than does UNIFAC, while the predictions of excess enthalpies are much improved. Hence, modified UNIFAC has a better built-in temperature dependence than UNIFAC. It was concluded that good VLE results including a successful description of the temperature dependency of group interaction parameters were obtained.

Sander and his coworker [86] reviewed the fundamental thermodynamics needed for the calculation of gas solubilities. It is shown that the UNIFAC group-contribution method can be applied to predict the solubility of some gases of industrial importance (methane, ethane, ethylene, acetylene, hydrogen, oxygen, nitrogen, hydrogen sulphide, carbon monoxide and carbon dioxide in pure solvent and solvent mixtures. The method is applicable at low pressures (up to ~10 bar) and low solubilities (up to a mole fractions of ~0.1), and to both nonpolar and polar nonelectrolytic solvents.

The UNIFAC method is fully described in those references we mentioned before and we do not here repeat the description. It is the aim of this work to predict the solubility of hydrogen in hydrocarbon solvents and petroleum fractions at advanced temperatures

and pressures. The extensions and revisions of the UNIFAC parameters tables which can be used at high temperatures will be reported in chapter III.

2.3 Methods for Prediction of Hydrogen Solubilities in Petroleum Fractions and Coal Liquids

Petroleum crude oil and coal liquids are complex mixtures of mainly paraffins, naphthenes, and aromatic compounds. For oil fractions of molecular weight higher than about 100, it is unpractical to list all of the compounds present. Hence, one of the major problems in phase equilibrium calculations involving such fractions is the representation of the many different hydrocarbons in terms of a few properly averaged characteristic.

The work presented by Ruzicka et al [85] describes a new method of characterizing heavy petroleum fractions. In this work, the UNIFAC group-contribution method for predicting vapor-liquid equilibria has been used as a basis for describing complex petroleum fraction in terms of model compounds. Standard procedures may be used to estimate critical properties, acentric factors, and molecular weights for the model compounds. This allows the inclusion of complex petroleum fractions in already available generalized methods for phase equilibrium calculations, based on equation of state or the UNIFAC group-contribution method. Good results are obtained for lower and medium molecular weight petroleum fractions at temperatures up to 600 K. At higher temperatures, the method may fail due to present limitations of the UNIFAC method.

Hartoumian and Allen [37] has proposed a method for estimating the solubility of hydrogen in Wilsonville ITSL coal derived liquid using the UNIFAC group contribution method. Functional group concentrations estimated from analytical data were combined with literature values of group contribution parameters to provide reasonable estimates of hydrogen solubility.

The method of Mohamed and Elkilani [61] has been known to work well for prediction of the solubilities of hydrogen in the naphtha reformat cut (423-473 K) by using modified UNIFAC group contribution method. It has been shown that the predicted solubility data were compared favorably with experimental values obtained by the pulse response technique using gas chromatography within 10% error at one atmosphere.

Mohamed and Elkilani [62] also presented the use of the modified UNIFAC group contribution method for estimating hydrogen solubility in different crude oil fractions. Functional group concentration were estimated from suggested group model structures. An optimization technique was carried out on critical properties to test the group model structure. The validity of this approach was verified by comparing the predicted and experimental hydrogen solubilities at temperatures up to 473 K, and pressures up to one atmosphere. The experimental hydrogen solubilities were measured by means of pulse response techniques.

In summary, there are number of methods available for the prediction of gas solubilities. Though, no one method is applicable to estimate the hydrogen solubility in hydrocarbon solvents and petroleum fractions at advanced temperatures and pressures, many of the methodologies and approaches are very sound at it would be wise to take advantage of these concepts and ideas for the development of a new method for hydrogen solubility in petroleum fractions. The further extensions and revisions of these methods will be reported in detail in chapter III and IV.

CHAPTER III

THE MODEL FOR HYDROGEN SOLUBILITY IN HYDROCARBON SOLVENTS

3.1 Overall Philosophy of the Model

As we discussed in chapter I, recent intensified development of hydrofining processes, particularly hydrocracking reactions, has increased the need for knowledge of hydrogen solubilities in petroleum fractions at advanced temperatures and pressures. This information is required for engineering design and analysis of reaction kinetics of hydrofining process.

Petroleum fractions are mixtures of different hydrocarbons, mainly paraffins, naphthenes, and aromatic compounds, from different homologous groups. It is believe that any model for predicting the hydrogen solubility in petroleum fractions must in the first place work well for the compounds that are characteristic of those found in petroleum fractions. Hence, as a first step it was necessary to develop an accurate model to predict the hydrogen solubilities in hydrocarbon solvents at high temperatures and pressures.

The models used by various researchers for the prediction of gas solubilities were discuss in detail in chapter II. Since the objective of this work was to develop a thermodynamic model for predicting hydrogen solubility in hydrocarbon solvents, and moreover finally extend the model to petroleum fractions so as to optimize the yield of hydrocracking reactions, it is clear that there is no method available now which appears to be useful. Some methods can only be used at room temperatures and low pressures. Some methods

have some common weaknesses. The use of one model for the gas phase and another model for the liquid phase inevitably leads to difficulties near the critical point.

After reviews of various correlation methods in the literature which considered for gas solubility calculations, the method of Sander et al [86] seems most attractive. Central to this method is an expression for Henry's Law constants for hydrogen in a reference solvent at supercritical temperature and modified UNIFAC group contribution method for activity coefficients of hydrogen in the solution. Our method varies some what from the correlation for vapor phase fugacity calculation, and UNIFAC group-interaction parameters have been made different temperature dependent. It is shown that the model we presented in this work provides the way which gives better prediction of vapor-liquid equilibria for hydrogen - hydrocarbon systems at high temperatures and pressures. New interaction parameters between hydrogen and hydrocarbon groups are predicted in this work as a function of temperature and are used to apply the modified UNIFAC method for solubility prediction. In the following sections, we will discuss our method in detail and present the results.

3.2 Data Compilation

In this work, we have extended the UNIFAC group-interaction parameter by including experimental vapor - liquid equilibrium data for hydrogen - hydrocarbon and hydrocarbon - hydrocarbon systems published until the middle of 1950. As a first step towards the development of a model, the experimental hydrogen solubility data for 29 hydrogen - hydrocarbon systems at high temperatures and pressures were compiled. The data set had 1345 vapor - liquid equilibrium data points in the temperature range from 277 K to 623 K, and pressure up to 680 atmosphere. These experimental data are automatically retrieved from the data bank and used directly in the UNIFAC group - interaction parameter estimation procedures.

3.3 Model Development

As discussed in chapter II, the UNIFAC group-contribution method has for a number of years been applied to predict activity coefficients or nonelectrolytic liquid mixtures. The method has thereby become a fast and reliable tool for the prediction of VLE data [30] for systems for which little or no experimental information is available.

The fundamental equations for calculation of GLE are the same as for VLE, and hence it should also be possible to predict the solubility of a gas in a solvent or a solvent mixture by means of the UNIFAC method.

The isofugacity criterion for hydrogen dissolved in a hydrocarbon solvent may be represented in the following way:

$$f_1^G = f_1^L \quad (3.1)$$

$$f_2^G = f_2^L \quad (3.2)$$

where subscript 1 refers to hydrocarbon solvent,; subscript 2 refers to hydrogen, and G and L correspond to gas and liquid phase. f_1^G and f_2^G are the fugacity of hydrocarbon and hydrogen in the vapor phase respectively, and will be calculated from the virial equation of state by the following procedure.

3.3.1 Vapor Phase Fugacity

The fugacity of a component in a mixture depends on the temperature, pressure and composition of that mixture. In principle, any measure of composition can be used. For the vapor phase, the composition is nearly always expressed by the mole fraction y . To relate f_i^G to temperature, pressure, and mole fraction, it is useful to introduce the fugacity

coefficient ϕ_i . It is defined as the ration of that component's fugacity in the mixture to its partial pressure [80]. In our case, it may be represented by

$$f_1^G = P \cdot y_1 \cdot \phi_1 \quad (3.3)$$

$$f_2^G = P \cdot y_2 \cdot \phi_2 \quad (3.4)$$

ϕ_1 and ϕ_2 in the above equations are the fugacity coefficients of hydrocarbon and hydrogen in a vapor phase. It is given precisely by:

$$\ln \phi_i = \ln \frac{\bar{f}_i}{y_i \cdot P} = \frac{1}{RT} \int_0^P \left(\bar{V}_i - \frac{RT}{P} \right) dP \quad (3.5)$$

Numerous equation of state have been proposed for pure gas [21]. As almost all are empirical or at best semiempirical in nature, it has not been possible to make an accurate assessment of physical meaning which is associated with the various constants. It is this deficiency of equations of state for pure gases which has made it difficult to extend them to gas mixtures. Various empirical rules have been suggested for predicting the constants of a mixture from the constants of the pure components, but while some of these give good results in specific cases, they are generally not reliable. All mixing rules which relate the constants of a mixture to those of the pure components must in some way reflect the nature of the intermolecular forces acting between unlike molecules. These forces are sufficiently complex to render any particular mixing rule valid for only a restricted class of mixtures.

In this work, we use the virial equation of state to calculate the fugacity coefficients proposed by Prausnitz [78]. It indicates that for the vast majority of chemical engineering problems the virial equation is the most suitable equation of state for fugacity calculations in mixtures. At very high densities the virial equation is not useful, since a large number

of virial coefficients are required, but at pressures and temperatures commonly encountered in chemical engineering work the virial equation is both adequate and convenient. This equation can be written in either a pressure - or a volume - explicit form. In this work we use pressure - explicit form which is more suitable for this work, since it requires a smaller number of terms and its coefficients have theoretical significance. It is given by

$$Z = \frac{Pv}{RT} = 1 + B\rho + C\rho^2 + D\rho^3 \dots \quad (3.6)$$

B, C, and D are respectively the second, third, and fourth virial coefficients, which are functions of temperature and composition, but not of density or pressure. When terminated after the third virial coefficient, Equation (3.6) is valid up to almost the critical density and frequently beyond it. Since much information [35] is available on the second virial coefficients of numerous gases and the correlation for the third virial coefficient is available now, almost nothing is known about the fourth and higher virial coefficients, for all practical purposes therefore the series in Equation (3.6) must be cut off after the third term. The final correlation for fugacity coefficient using virial equation of state is:

$$\ln \phi_i = 2\rho \sum_j^n y_j \cdot B_{ij} + \frac{3}{2}\rho^2 \sum_j^n \sum_k^n y_j y_k C_{ijk} - \ln Z \quad (3.7)$$

Equation (3.7) is an exact expression for the fugacity coefficient subject only to the restriction that the density be sufficiently small to permit neglect of terms involving the fourth and higher virial coefficients. For our case, Equation (3.7) is the most suitable now available.

For the hydrogen - hydrocarbon binary system, Equation (3.7) can be expressed as follow

$$\ln \phi_1 = 2\rho(y_1 B_{11} + y_2 B_{12}) + \frac{3}{2}\rho^2(y_1^2 C_{111} + 2y_1 y_2 C_{112} + y_2^2 C_{122}) - \ln Z \quad (3.8)$$

$$\ln \phi_2 = 2\rho(y_1 B_{12} + y_2 B_{22}) + \frac{3}{2}\rho^2(y_1^2 C_{112} + 2y_1 y_2 C_{122} + y_2^2 C_{222}) - \ln Z \quad (3.9)$$

Methods of estimating the second and third virial coefficient are proposed in following section. The principle of these methods lies in an extension of the theorem of corresponding states to mixtures. This extension consists of the definition of parameters, which characterizes the interactions responsible for the cross coefficients and which, with suitable rearrangements of Pitzer's results for pure components are sufficient to estimate the cross coefficients. Because of its small masses, the properties of hydrogen can not be described by classical statistical mechanics. It is possible to write an expression for the second and third virial coefficients of light gases, such as hydrogen, based on quantum mechanics. All of these ideas can best be summarized by the equations below.

3.3.1.1 Estimation of the Second Virial Coefficients

Reliable volumetric studies have been reported for only a limited number of mixtures. However a considerable body of results is available for pure gases, and with the help of existing theory of intermolecular forces it is possible in many cases to make good estimates of the second virial coefficients for mixture. Most experimental and theoretical work [99] has been concerned with the second virial coefficient, and at present much more is known about the third. Though Equation (3.7) is such that the fugacity coefficient is much more sensitive to the various B terms than to the C terms, in this work due to the high pressure, it is necessary to keep the third virial coefficient to calculate the fugacity coefficients using Equation (3.7). The correlation for the third virial coefficients will be proposed in the next section.

The Goodwin Correlation [32] for the Second Virial Coefficient of Pure Hydrogen (B_{22})

As we discussed before, the configurational properties of low molecular - weight gases (hydrogen, helium, and neon) must be described by quantum, rather than classical statistical mechanics. As a result, the properties of these gases do not follow the same corresponding state behavior as that for other gases when the true critical constants are used as the reducing parameter. Goodwin and his coworkers [32] have established empirical correlations for second and third coefficients of hydrogen over a wide temperature range. For the second virial coefficient, their results are given in the form:

$$B_{22} = \sum_{i=1}^4 b_i \cdot X^{(2i-1)/4} \quad (3.10)$$

where

$$X = 109.83 / T$$

T in ° K

$$b_1 = 42.464$$

$$b_2 = -37.1172$$

$$b_3 = -2.2982$$

$$b_4 = -3.0484$$

The Pitzer - Curl - Tsonopoulos Correlation for the Second Virial Coefficients of Pure Hydrocarbon and Mixture of Hydrogen and Hydrocarbon:

For a pure hydrocarbon, the generalized correlation for the second virial coefficient suggested by Pitzer and Curl [75] is given below

$$B_{11} = \frac{RT_{c1}}{P_{c1}} (\Gamma^{(0)} + \omega_1 \Gamma^{(1)}) \quad (3.11)$$

The function $\Gamma^{(0)}$ gives the reduced second virial coefficients for simple fluid ($\omega = 0$) while $\Gamma^{(1)}$ is a correction function which, when multiplied by ω , gives the effect of

acentricity on the second virial coefficient. As modified by Tsonopoulos [99]. These functions are

$$\Gamma^{(0)}(T_R) = 0.1445 - \frac{0.330}{T_R} - \frac{0.1385}{T_R^2} - \frac{0.0121}{T_R^3} - \frac{0.000607}{T_R^8} \quad (3.12)$$

$$\Gamma^{(1)}(T_R) = 0.0637 + \frac{0.331}{T_R^2} - \frac{0.423}{T_R^3} - \frac{0.008}{T_R^8} \quad (3.13)$$

where $T_R = T/T_c$

Equation (3.11), (3.12), and (3.13) provide a good correlation for the second virial coefficients of normal fluids. A normal fluid, such as hydrocarbons is one whose molecules are of moderate size, are nonpolar or else slightly polar, and do not associate strongly; further, it is a fluid whose configurational properties can be evaluated to sufficiently good approximation by classical rather than quantum, statistical mechanics.

Methods of estimating the second virial cross coefficients have been proposed by Guggenheim and McGlashan [35] and Prausnitz and Gunn [77] have shown how these methods can be modified to handle complex mixtures of a variety of nonpolar or slightly polar compounds. The principle of these methods lies in an extension of the theorem of corresponding states to mixtures. This extension consists of the definition of parameters which characterize the interactions and which characterize the interactions responsible for the cross coefficients and which, with a suitable rearrangement of Pitzer's results for pure compounds, are sufficient to estimate to estimate the cross coefficients. These ideas can best be summarized by the modified Pitzer - Curl - Tsonopoulos correlation discussed below.

To estimate the cross - coefficient B_{12} , we use the same correlation presented in Equation (3.12) given below

$$B_{12} = \frac{RT_{c12}}{P_{c12}} (\Gamma^{(0)} + \omega_{12}\Gamma^{(1)}) \quad (3.14)$$

In above equation, $\Gamma^{(0)}$ and $\Gamma^{(1)}$ are given by Equation (3.12) and (3.13). For mixtures containing one or more of the quantum gas, such as hydrogen, the effective critical constants are given by the mixing rules of Chueh [13] as below.

$$T_{cij} = \frac{(T_{ci}^0 \cdot T_{cj}^0)^{1/2}(1 - k_{ij})}{1 + (C_1/m_{ij} \cdot T)} \quad (3.15)$$

$$P_{cij} = \frac{P_{cij}^0}{(1 + C_2/m_{ij} \cdot T)} \quad (3.16)$$

where

$$P_{cij}^0 = \frac{Z_{cij}^0 \cdot R(T_{ci}^0 \cdot T_{cj}^0)^{1/2}(1 - k_{ij})}{V_{cij}^0} \quad (3.17)$$

$$(V_{cij}^0)^{1/3} = \frac{1}{2} [(V_{ci}^0)^{1/3} + (V_{cj}^0)^{1/3}] \quad (3.18)$$

$$\frac{1}{m_{ij}} = \frac{1}{2} \left(\frac{1}{m_i} + \frac{1}{m_j} \right) \quad (3.19)$$

m in the Eq. (3.19) is the molecular weight.

In above equations, the critical properties of hydrogen are adjusted in the mixing rules for better agreement with experimental data. The values of classifiable critical constants for hydrogen are $T_{c2}^0 = 43.6$ °K, $P_{c2}^0 = 20.23$ atm, and $V_{c2}^0 = 51.50$ cm³ mole⁻¹. The

constants C_1 , C_2 , and C_3 in the above equations are the same for all quantum gases. They are (in $\text{g mole}^{-1} \text{K}$): $C_1 = 21.8$, $C_2 = 44.2$, and $C_3 = -9.91$.

The characteristic binary constant k_{ij} represents the deviation from the geometric mean for T_{cij} ; when attention is limited to the vapor phase, it is, to a good approximation, a molecular constant independent of temperature, composition, and density. Since k_{ij} is characteristic of $i - j$ interaction, it must be obtained from some experimental data for the $i - j$ mixture. A good correlation for k_{ij} suggested by Tarakad and Danner [96] is shown as below.

$$k_{ij} = 1 - \frac{8\sqrt{V_{ci} \cdot V_{cj}}}{(V_{ci}^{1/3} + V_{cj}^{1/3})^3} \quad (3.20)$$

In the following section, we will discuss about the correlation for the third virial coefficients.

3.3.1.2 Estimation of the Third Virial Coefficients

Experimental information on third virial coefficients is scarce and the discrepancy between reported values for the same compound is, in most case, considerable. Observation of the data of third virial coefficients plotted versus reduced temperature for different fluids by Chueh and Prausnitz [14] suggested that the curves for different compounds will almost coincide if the values of the third virial coefficients for each compound were divided by the values of the third virial coefficient of the same compound at its critical temperature, T_c .

In addition, it was found that the third virial coefficient at the critical temperature of each fluid, reduced using critical temperature and critical pressure as parameters, could be well correlated as a function of the acentric factor. Based on these points, a generalized

empirical correlation using in this work for vapor phase fugacity calculation was developed by Hasan and Vera [38].

The correlation is similar to the successful empirical correlations for second virial coefficient we discussed before [75,99]. It requires a knowledge of the critical temperature critical pressure and acentric factor of the compounds for the prediction of third virial coefficients in the absence of experimental data. The use of the correlation for mixtures of non polar gases, including quantum gases, required one binary parameter for each binary interaction. This fact allows the use of the density using the same information that previously did not allow one to go beyond 0.5 the critical density. Within the accuracy of the experimental information on the third virial coefficients, the new correlation performs as well as the more complex expressions existing in the literature. The detailed the procedures are represented as below

An Empirical Correlation for the Third Virial Coefficients of Pure Hydrocarbons:

The generalized correlation for third virial coefficient developed by Hasan and Vera [38] can be expressed by following equations:

$$C_{111} = \left(\frac{RT_{c1}}{P_{c1}} \right)^2 \left(f^{(0)} + \omega_1 f^{(1)} \right) \quad (3.21)$$

with

$$f^{(0)}(Tr) = 0.01407 + 0.02432/Tr^{2.8} - 0.00313/Tr^{10.5} \quad (3.22)$$

$$f^{(1)}(Tr) = -0.02676 + 0.01770/Tr^{2.8} + 0.040/Tr^{3.0} - 0.003/Tr^{6.0} - 0.00228/Tr^{10.5} \quad (3.23)$$

In general there is a good agreement which can be used at high temperature. The reason for this is that in the generalized correlation presented in this work, the high tem-

perature limit of the third virial coefficient has been allowed to vary with the acentric factor of the compound. The flexibility of this correlation usually results in a better agreement with reported experimental data in the high temperature.

The Goodwin Correlation for the Third Virial Coefficient of Pure Hydrogen:

As we discussed before, the Goodwin correlation for the third virial coefficient [32] of hydrogen can be written by following equation.

$$C_{222} = C_0 X^{1/2} [1 + CX^3] [1 - \exp(1 - X^{-3})] \quad (3.24)$$

where

$$X = T_0/T$$

$$T_0 = 20.615^\circ \text{K}$$

$$C = 2.1486^*$$

$$C_0 = 1310.5 (\text{cm}^3 \text{gmole}^{-1})^2$$

Extension Correlation to Gas Mixtures:

The correlation for the third virial coefficient presented in this work may be extended to mixtures using exactly the same method proposed by Chuech and Prausnitz [14] and used by De Santis and Grande [14].

The third virial coefficient of a mixture is given by the following rigorous expression

$$C = \sum_i \sum_j \sum_k (C_{ij} C_{ik} C_{jk})^{1/3} \quad (3.25)$$

where Chuech and Prausnitz [20] have proposed to evaluate C_{ijk} as

$$C_{ijk} = (C_{ij} C_{ik} C_{jk})^{1/3} \quad (3.26)$$

and terms of form C_{ij} are obtained with Eqn (3.21) using the Equations from (3.15) to (3.20) for the values of T_c , P_c , and ω .

Recall, for the hydrogen - hydrocarbon binary system, the second and third virial coefficient of mixture may be written as

$$B_{mix} = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \quad (3.27)$$

and

$$C_{mix} = y_1^3 C_{111} + 3y_1^2 y_2 C_{112} + 3y_1 y_2^2 C_{122} + y_2^3 C_{222} \quad (3.28)$$

We use a volume - explicit form, truncated after the third virial coefficient to express the virial equation of state. It is more suitable for this work, since it requires a smaller number of terms and its coefficients have theoretical significance.

$$Z_{mix} = \frac{Pv}{RT} = 1 + B_{mix}\rho + C_{mix}\rho^2 \quad (3.29)$$

we rearranged Equation (3.29) and get

$$\rho^3 C_{mix} RT + \rho^2 B_{mix} RT + \rho RT - P = 0 \quad (3.30)$$

By using experimental VLE data and suitable correlations for the second and third virial coefficients we discussed before, the specific density ρ may be obtained with the above cubic equation.

Once ρ , B_{11} , B_{12} , B_{22} , C_{111} , C_{222} , C_{112} , C_{122} and Z_{mix} are computed, ϕ_1 and ϕ_2 may be determined from Equation (3.8) and (3.9) and used in Equation (3.3) and (3.4) to obtain f_1^G and f_2^G .

In the following description of the thermodynamic background for hydrogen solubility calculations, we focus on expression for the liquid phase fugacity. The detailed procedures will be discussed in following section.

3.3.2 Liquid Phase Fugacity

The liquid phase fugacity is a function of temperature, pressure and composition, and can be calculated by means of an activity coefficient approach. It may be written as:

$$f_1^L = x_1 \cdot \gamma_1 \cdot f_1^0 \quad (3.31)$$

$$f_2^L = x_2 \cdot \gamma_2 \cdot f_2^0 \quad (3.32)$$

The UNIFAC group-contribution method has for a number of years been applied to predict activity coefficients for nonelectrolytic liquid mixtures. The method has thereby become a fast and reliable tool for the prediction of VLE (vapor - liquid - equilibria) data [27] for systems for which little or no experimental information is available.

The fundamental equations for calculation of GLE (gas - liquid - equilibria) are the same as for VLE, and hence it should also be possible to predict the solubility of a gas in a solvent or solvent mixture by means of the UNIFAC method. The problem is the reference fugacity f_i^0 in eq. (3.31) and (3.32). For every component i , f_i^0 is the fugacity of pure liquid i at system temperature and pressure; i.e., the arbitrarily chosen pressure is the total pressure P , and the arbitrarily chosen composition is $x_i=1$. Frequently, this standard-state fugacity refers to a hypothetical state, since it may happen that component i can not physically exist as pure liquid at system temperature and pressure. Fortunately, for hydrocarbon solvents, since liquid phase properties remote from the critical region are not sensitive to pressure, it is possible to calculate this standard-state fugacity from experimental data and then extrapolated into the hypothetical liquid region. If the difference between T and

T_{ci} is great, such an extrapolation will be most uncertain. For the gaseous component, such as hydrogen, the value of f_i^0 represents a property of a hypothetical pure liquid whenever T is greater than the critical temperature T_{ci} for the gas.

Following Mathias and O'Connell [60], the problem may be changed into one of estimating a Henry's constant for a reference solvent. In general, for a gas (2) dissolved in a solvent or solvent mixture S ,

$$f_2^0 = H_{2,s} / \gamma_{2,s}^\infty \quad (3.33)$$

In this equation, $H_{2,s}$ is Henry's constant as defined in eq. (2.8), and $\gamma_{2,s}^\infty$ is the activity coefficient at infinite dilution in the symmetric convention.

For a reference solvent, similarly,

$$f_2^0 = H_{2,r} / \gamma_{2,r}^\infty \quad (3.34)$$

Introduction of eq.(3.34) into the eq. (3.32) leads to

$$f_2^L = x_2 \cdot H_{2,r} \cdot \gamma_2 / \gamma_{2,r}^\infty \quad (3.35)$$

The activity coefficients $\gamma_1, \gamma_2, \gamma_{2,r}^\infty$ are calculated from the modified UNIFAC which will be discussed later. The reference Henry's constants $H_{2,r}$ was calculated as a function of temperature from the suitable relation which has been developed and is discussed below.

3.3.2.1 Correlation for $H_{2,r}$

In choosing a reference solvent for a given gas it is crucial to find a solvent for which reliable experimental solubility data for the gas are available. The data should cover as broad a temperature range as possible.

In this work, four hydrocarbon solvents have been chosen as a reference solvent because of the data availability and the types of systems that we plan to apply to the correlation to . n-Hexane has been used as a reference solvent for the hydrocarbon solvents containing 2 to 6 carbon atoms; n-decane has been used for the solvents containing 7 to 12 carbon atoms; and for the hydrocarbon solvents which contain more than 12 carbon atoms, we chose n-hexadecane as a reference solvent. For propane - cyclohexane binary system, since the system temperature is greater than the critical temperature of propane, we chose cyclohexane as a reference solvent to obtain the reference Henry's constant of propane.

Each gas solubility data in reference hydrocarbon solvent were compiled as isotherms. The reference Henry's constant $H_{2,r}$ is calculated as a function of temperature from the following relation which has been found appropriate for this work.

$$\ln H_{2,r} = A + \frac{B}{T} + C \ln T \quad (3.36)$$

A, B, C are estimated from experimental solubility data for components 2 (gas) in the reference solvent by means of the equation,

For the estimation of $H_{2,r}'$ (and hence A, B, C), it is thus assumed that $\gamma_{2,r}/\gamma_{2,r}^\infty = 1$. $H_{2,r}$ would be equal to $H_{2,r}'$ in the limit as $x_{2,r}$ tends to zero. f_2^G in equation (3.37) was computed using the virial equation of state discussed before and experimental data. $H_{2,r}'$ was plotted against $x_{2,r}$ at isotherms. The plots are shown in figure 3.1 to 3.4. In each case, the curve was extrapolated to $x_2=0$ to obtain $H_{2,r}$ as the intercept on y-axis.

Furthermore, a correlation for $H_{2,r}$ was obtained as a function of temperature by using least square regression.

Table 3.1 presents the chosen reference solvents for hydrogen and propane and the estimated parameters A, B and C for calculating the reference Henry's constants. Very good fit was obtained with errors of less than 0.1%. This expression for $H_{2,r}$ is now ready to be used in solubility calculations.

3.3.2.2 Correlation for f_1^0

To calculate the fugacity of a pure hydrocarbon solvent at a specified temperature and pressure, we required two primary thermodynamic properties: the saturation (vapor) pressure, which depends only on temperature, and the liquid density, which depends primarily on temperature and to a lesser extent on pressure.

The fugacity of pure liquid i at temperature T and pressure P is given by

$$f_1^{0L}(T, P, x_1 = 1) = P_{vp,1}(T) \cdot \phi_1^s(T) \cdot \exp \int_{P_{vp,1}}^P \frac{V_1^L(T, P)}{RT} dP \quad (3.38)$$

where $P_{vp,1}$ is the vapor pressure and may be calculated by the Pitzer expansion [74] as following.

$$\ln(P_{vp,r}) = f^{(0)}(T_r) + \omega f^{(1)}(T_r) \quad (3.39)$$

where $P_{vp,r} = P_{vp}/P_c$, and in this work the function $f^{(0)}$ and $f^{(1)}$ have been expressed by Lee and Kesler [54].

$$f^{(0)} = 5.92714 - \frac{6.09648}{T_r} - 1.28862 \ln(T_r) + 0.169347T_r^6 \quad (3.40)$$

$$f^{(1)} = 15.2518 - \frac{15.6875}{T_r} - 13.4721 \ln(T_r) + 0.43577T_r^6 \quad (3.41)$$

The fugacity coefficient ϕ_1^s (superscript s stands for saturation) is calculated from virial equation.

$$\phi_1^s = \exp\left(\frac{B_{11} \cdot P_{vp,1}}{RT}\right) \quad (3.42)$$

where B_{11} can be calculated from Eq. (3.11), (3.12) and (3.13), and P_1^s can be obtained from Eq. (3.39), (3.40), (3.41).

The molar liquid volume V_1^L is the ratio of the molecular weight to the density where the latter is expressed in units of mass per unit volume. The exponential term in Eq. (3.38) called the Poynting factor which can be calculated by HBT technique.

Hankinson - Brobst - Thomson (HBT) Technique:

Hankinson and Thomson [36] present the following correlation for saturated densities of liquids.

$$\frac{V_s}{V^*} = V_R^{(0)} [1 - \omega_{SRK} \cdot V_R^{(1)}] \quad (3.43)$$

$$V_R^{(0)} = 1 + a(1 - T_r)^{1/3} + b(1 - T_r)^{2/3} + c(1 - T_r) + d(1 - T_r)^{4/3} \quad (3.44)$$

$$V_R^{(1)} = [e + f \cdot T_r + g \cdot T_r^2 + h \cdot T_r^3] / (T_r - 1.00001) \quad (3.45)$$

In above equations, T_r should be large than 0.25 and less than 1.0, and values of constants in above equations are listed in Table 3.2.

V^* is a pure component characteristic volume generally within 1 to 4 percent of the critical volume; ω_{SRK} is the acentric factor which forces the Soave equation to give a best fit of existing vapor pressure data. Values of V^* and ω_{SRK} for the compounds presenting in this work are listed in Table 3.3.

If no data are available for a compound, ω_{SRK} should be replaced by the true acentric factor; V^* may be replaced by the true critical volume. The resulting error will often be less than 1 percent but can be as high as 4 percent.

More recently, Thomson et al [97] have extended the HBT method to allow prediction of compressed liquid volumes by generalizing the constants in the Tait equation. Thus

$$V^L = V_s \left(1 - C \ln \frac{\beta + P}{\beta + P_{vp}} \right) \quad (3.46)$$

V_s , the saturated liquid volume at the vapor pressure P_{vp} , should be obtained from Eq.(3.43), β and C are obtained from

$$\beta/P_c = -1 + a(1 - T_r)^{1/3} + b(1 - T_r)^{2/3} + d(1 - T_r) + e(1 - T_r)^{4/3} \quad (3.47)$$

where

$$e = \exp(f + g \cdot \omega_{SRK} + h \cdot \omega_{SRK}^2) \quad (3.48)$$

and

$$C = j + k \cdot \omega_{SRK} \quad (3.49)$$

The constants a through k for eq. (3.47) to (3.49) are given in Table 3.4. By using Eq. (3.38) to (3.49), we can obtain the pure fugacity of hydrocarbon (f_1^0) as a liquid phase.

3.3.3 Modified UNIFAC Method

The fundamental idea of a solution - of - groups is to utilize existing phase equilibrium data for predicting equilibria of system for which no experimental data are available. In concept, the UNIFAC method follows the ASOG (the analytical solution of groups) method, where in activity coefficients in mixtures are related to interactions between structural groups. The essential features are:

1. Suitable reduction of experimentally obtained activity coefficient data to yield parameters characterizing interactions between pairs of structural groups in non-electrolyte systems.
2. Use of those parameters to predict activity coefficients for other systems which have not been studied experimentally but which contain the same functional groups.

The molecular activity coefficient is separated into two parts: one part provides the contribution due to differences in molecular size, and the other provides the contribution due to molecular interactions. In this work, we use modified UNIFAC model for predicting activity coefficients which is based on the well-known UNIFAC model. Two changes are introduced in the modified UNIFAC: (1) the group - interaction parameters have been made temperature-dependent and (2) the combinatorial term is slightly modified. It is shown that modified UNIFAC gives somewhat better predictions of vapor liquid equilibria than does UNIFAC, hence, modified UNIFAC has a better built-in temperature dependence than UNIFAC.

For hydrogen (2) dissolved in hydrocarbon solvents, the activity coefficient of component *i* may be expressed as

$$\ln(\gamma_i) = \ln(\gamma_i^c) + \ln(\gamma_i^r) \quad (3.50)$$

where the combinatorial activity coefficients expression used in modified UNIFAC is

$$\ln(\gamma_i^c) = \ln\left(\frac{\omega_i}{x_i}\right) + 1 - \frac{\omega_i}{x_i} \quad (3.51)$$

with modified volume fractions following Kikic et al [48]

$$\omega_i = \frac{x_i \cdot r_i^{2/3}}{\sum_j x_j \cdot r_j^{2/3}} \quad (3.52)$$

where x_i is the mole fraction of component i in liquid phase

The residual contribution term is given by

$$\ln(\gamma_i^r) = \sum_k \nu_{ki} (\ln \Gamma_k - \ln \Gamma_k^i) \quad (3.53)$$

where ν_{ki} is the number of groups of type k in molecule i , Γ_k is the activity coefficient of group k at mixture composition, and Γ_k^i is the activity coefficient of group k at a group composition corresponding to pure component i . Γ_k and Γ_k^i are given by:

$$\ln \Gamma_k = \frac{Z}{2} Q_k \left(- \left[\ln \left(\sum_m \theta_m \tau_{mk} \right) \right] + 1 - \sum_i \frac{\theta_i \tau_{ki}}{\sum_j \theta_j \tau_{ji}} \right) \quad (3.54)$$

In modified UNIFAC

$$\tau_i = \sum_k \nu_{ki} R_k \quad (3.55)$$

$$\theta_k = \frac{n_k \frac{Z}{2} Q_k}{\sum_m n_m \frac{Z}{2} Q_m} \quad (3.56)$$

$$\tau_{mk} = \exp\left(-\frac{a_{mk}}{T}\right) \quad (3.57)$$

The total number of group (k) in the mixture is n_k . The structural parameters, such as group volume (R_k) and surface-area (Q_k) required in the modified UNIFAC method have been values from Gmehling et al [31]. Table 3.5 shows the R_k and Q_k values applied. It should be noted that the quantity $(Z/2)Q$ in Table 3.5 for all practical purposes is completely equivalent to the quantity Q in the original UNIFAC model.

The estimation of temperature-dependent group-interaction parameters (a_{mk}) are described as follows.

3.3.4 Estimation of Modified UNIFAC Group-Interaction Parameters

The UNIFAC parameter tables published to date (e.g., [31]) do not contain parameters for the interaction between hydrogen molecules and hydrocarbon solvent groups at high temperature and pressure. It has therefore been necessary to estimate such parameters.

For the estimation of group-interaction parameters, the VLE data bank for hydrogen-hydrocarbon binary systems at high temperatures and pressures has been established. Table 3.6 shows the summary of experimental data sources for estimation of UNIFAC group-interaction parameters. The objective function, which is minimized by the parameter estimation program, is a sum of squared deviations between experimental and

calculated properties. The properties included in this sum of squares (SSQ) are the directly measured data; i.e., for hydrogen - hydrocarbon binary VLE data it is the temperature (T), the pressure (P), the liquid mole fraction of hydrogen (x_2), and the vapor mole-fraction of hydrogen (y_2). The mole fraction of hydrocarbon solvent is not included, as they are obtained directly from the mole fraction of hydrogen. The following objective function has been minimized for the estimation of UNIFAC interaction parameters between hydrogen and hydrocarbon solvent groups.

$$F = \sum_n [(P_{exp} - P_{clc})/P_{exp} + (y_{exp} - y_{clc})/y_{exp}]^2 \quad (3.58)$$

where n is the number of data points and subscripts exp and clc indicate the experimental data and the calculated VLE values, respectively.

Recalling, for hydrogen dissolved in a hydrocarbon solvent, the gas-liquid equilibrium may be represented by

$$P \cdot y_1 \cdot \phi_1 = \gamma_1 \cdot f_1^0 \cdot x_1 \quad (3.59)$$

$$P \cdot y_2 \cdot \phi_2 = \gamma_2 \cdot H_{2,r} \cdot x_2 / \gamma_{2,r}^\infty \quad (3.60)$$

where ϕ_1 , ϕ_2 , f_1^0 and $H_{2,r}$ can be calculated from experimental VLE data by using suitable correlations discussed before, γ_1 , γ_2 and $\gamma_{2,r}^\infty$ may be obtained from the modified UNIFAC method. Therefore, the values of P_{clc} and y_{cls} in Eq. (3.58) can be calculated by means of the technique for bubble point calculations and used in above objective function to estimate the group-interaction parameters. In this work, two expressions have been suggested to describe the temperature dependent of the group-interaction parameters, the first suggestion is cubic expression and the further suggestion is Wagner's expression.

For cubic expression, four coefficients are used to describe the temperature dependence of the interaction parameters given by

$$a_{ji} = a_{ji,1} + a_{ji,2}(T - T_0) + a_{ji,3}(T - T_0)^2 + a_{ji,4}(T - T_0)^3 \quad (3.61)$$

where T_0 is an arbitrary reference temperature, here 298.15 K.

The temperature dependence shown in Eq. (3.61) was chosen from considering a_{ji} as related to the excess enthalpy of the mixture. It may give the better results for excess enthalpy prediction.

The Wagner's expression for temperature-dependent group-interaction parameters is

$$a_{ji} = T_0 (a_{ji,1} \cdot X + a_{ji,2} \cdot X^{1.5} + a_{ji,3} \cdot X^3 + a_{ji,4} \cdot X^6) \quad (3.62)$$

where $T_0 = 750$ °K; $X = (1-T/T_0)$.

The expression shown in Eq. (3.62) was chosen from considering a_{ji} as related to vapor pressure. It has been generalized by a number of researchers that Wagner's equation is one of the most accurate forms to represent vapor pressure data and may provide the best method for vapor pressure computation.

It is possible to use the objective function showing above to obtain the binary group interaction parameters required in the modified UNIFAC correlation by regression as function of temperatures using experimental solubility data over a wide range of temperature and pressure. Two expressions of temperature-dependent group interaction parameters are used respectively. Up to eight coefficients of each expression shown in Eq. (3.60) and (3.61) can totally be determined for the two temperature-dependent interaction parameters (a_{ji} and a_{ij}) characterizing a binary group combination. As a consequence, it is necessary to establish the values for interaction parameters between hydrogen molecules

and paraffinic CH_3 group before any other parameters can be determined. Then the parameters between hydrogen and benzene, hydrogen and naphthenic $\text{CH}_{2, \text{cyc}}$, and naphthenic $\text{CH}_{2, \text{cyc}}$ and benzene have been simultaneously determined on the basis of experimental data including these groups. At last, the interaction parameters between paraffinic CH_3 and naphthenic $\text{CH}_{2, \text{cyc}}$, and paraffinic CH_3 and benzene are determined respectively (see Table 3.6). The results of this work are reported below.

3.4 RESULTS

The database for the UNIFAC parameter between hydrogen molecule and hydrocarbon solvent groups estimations consist of ~ 1230 high-temperature high-pressure GLE data points. The results of an error analysis using the present model as compared to experimental values from the literature are expressed by the absolute average deviation (AAD) in all cases defined as:

$$AAD(\%) = \frac{1}{N} \sum_i^N \frac{|(\text{calculated} - \text{experimental})|}{\text{experimental}} \times 100 \quad (3.63)$$

where N is the number of experimental points and i denotes the data point.

In Table 3.7 and Table 3.8, the estimated binary interaction parameters using the cubic expression and Wagner's expression as functions of temperature between hydrogen and hydrocarbon subgroups are presented, respectively. The two expressions for UNIFAC group interaction parameters as functions of temperature are shown in figure 3.5. For the interaction parameters between hydrogen molecule and hydrocarbon solvent groups are estimated from experimental hydrogen solubility in pure hydrocarbon solvents. The other interaction parameters between hydrocarbon solvent groups, themselves have been estimated from experimental VLE data of hydrocarbon binary systems.

Table 3.9 and Table 3.10 present the temperature range for the experimental solubility data used for parameter estimation using cubic expression and Wagner's expression for group-interaction parameters. In general, application of the UNIFAC equation outside the temperature range of the solubility data used to obtain the group interaction parameters is not recommended.

Table 3.11 and Table 3.12 show the deviations between the experimental and calculated VLE data for hydrogen - hydrocarbon binary systems which are used to regress the interaction parameters by using the cubic expression and Wagner's expression as functions of temperature.

The accuracy of the proposed method is illustrated in figure 3.6-3.7. Figure 3.6 shows experimental and calculated solubilities as a function of temperature for hydrogen in n-decane, cyclohexane and in benzene. Figure 3.7 shows experimental and calculated solubilities for hydrogen in the homologous series of n-paraffins and n-aromatics at 470°K for a partial of the gas of 50 atm. It can be found from the Figure 3.7 that for the same molecule size of paraffins and aromatics, the solubility of hydrogen in paraffins is considerably more than that in aromatics at the same conditions of temperature and pressure. Because of the deficiency of the experimental solubility data, we can not show the same curve for hydrogen in naphthenes in Figure 3.7. In generally, the solubility of hydrogen in naphthenes will lie some place between that in paraffins and aromatics. The experimental data show us that the hydrogen solubility in cyclohexane is more than that in benzene and less than that in n-hexane.

Table 3.13 and Table 3.14 present a comparison of Chao-Seader correlation and its modification with the Grayson-Streed new coefficients with our method which use Wagner's expression for interaction parameters with experimental VLE data for hydrogen in various binary and ternary solutions. 1 refers to our method and 2 refers to Chao-Seader

correlation and its modification. Included in the Tables are the temperature and pressure range, the number of experimental data points, experimental data sources, and the absolute average deviation of the predicted from the experimental VLE data for two methods.

The AAD values in Table 3.13 and Table 3.14 indicate that all of the correlations predict hydrogen solubility in hydrocarbon solvents quite well for almost all the systems tested. The overall error for our method is smaller (13 %) than that of Chao-Seader correlation (17 %) and its modification with the Grayson-Streed new coefficients (15 %). On the other hand, our method does not need specific information concerning the system in question, i.e., solubility parameters and liquid mole volume required by Chao-Seader correlation, but only certain information concerning the behavior of the constituent parts of the molecules, i.e., the groups they contain. Therefore, the new model we developed here provides us a much easier and more valuable way to cover a variety of solvents including undefined compounds such as petroleum fractions using only a few group parameters than any other correlations. The values of the coefficients for the correlation of pure-liquid fugacity coefficients used by Chao-Seader correlation and its modification with the Grayson-Streed new coefficients are given in Table 3.15.

It has been shown that this model which has been developed here can be applied to predict the solubility of hydrogen in pure hydrocarbon solvents for the temperatures up to 620 K and pressures up to 680 atmosphere and provide a more generalized method for accurate description of phase equilibria in both liquid and vapor phase than any other available model. Two expressions of interaction parameters as functions of temperature presented above yield the errors which are equally well and in most cases, the errors are small enough to meet the requirements in the prediction of hydrogen solubilities in hydrocarbon solvents at high temperatures and pressures. Of these two expressions for group-interaction parameters, Wagner's expression seems much more attractive to be ex-

tended to petroleum fractions. As we know, petroleum crude oil are mixtures of different hydrocarbons from different homologous groups and can be divided into several cuts depending upon the mid-boiling points. Because of the limitation of experimental VLE data, for prediction the hydrogen solubility in petroleum fractions at the conditions of hydrocracking reaction, inevitably, we have to extrapolated the interaction parameters to much higher temperatures, which exceed the temperature range of experimental hydrogen solubility data in pure hydrocarbon solvents. In this case, as shown in figure 3.5, Wagner's expression may provide much better results, since it provides a better temperature-dependent expression at high temperature in which the change of temperature has less influence on the group-interaction parameters. The detailed procedures for extending the model to prediction of hydrogen solubility in petroleum fractions will be discussed in chapter IV.

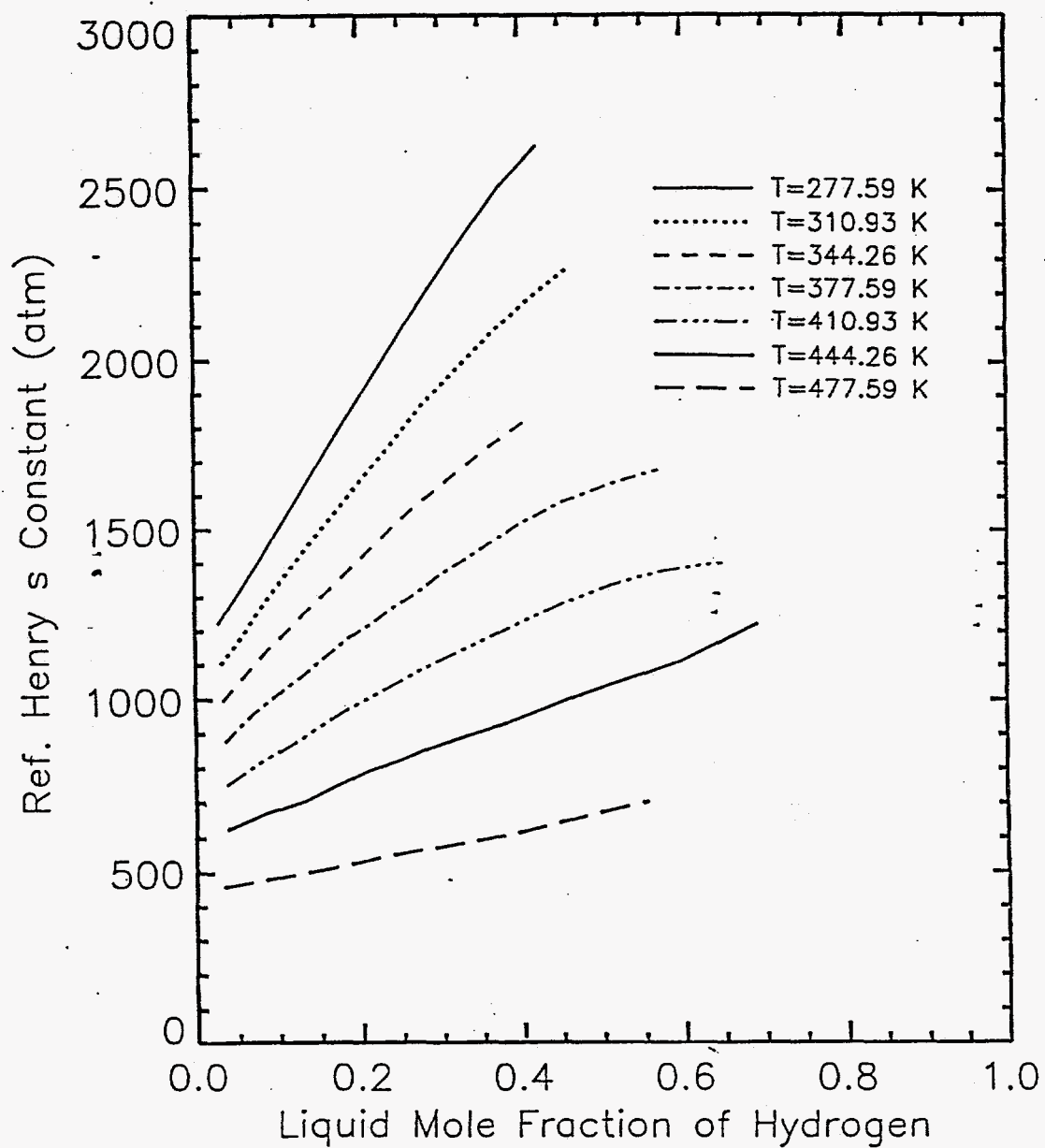


Fig. 3.1 Experimental $H_{2,r}$ ' (Eq. 3.37) as a function of liquid mole fraction of hydrogen at isotherms for hydrogen in the n-hexane reference solvent.

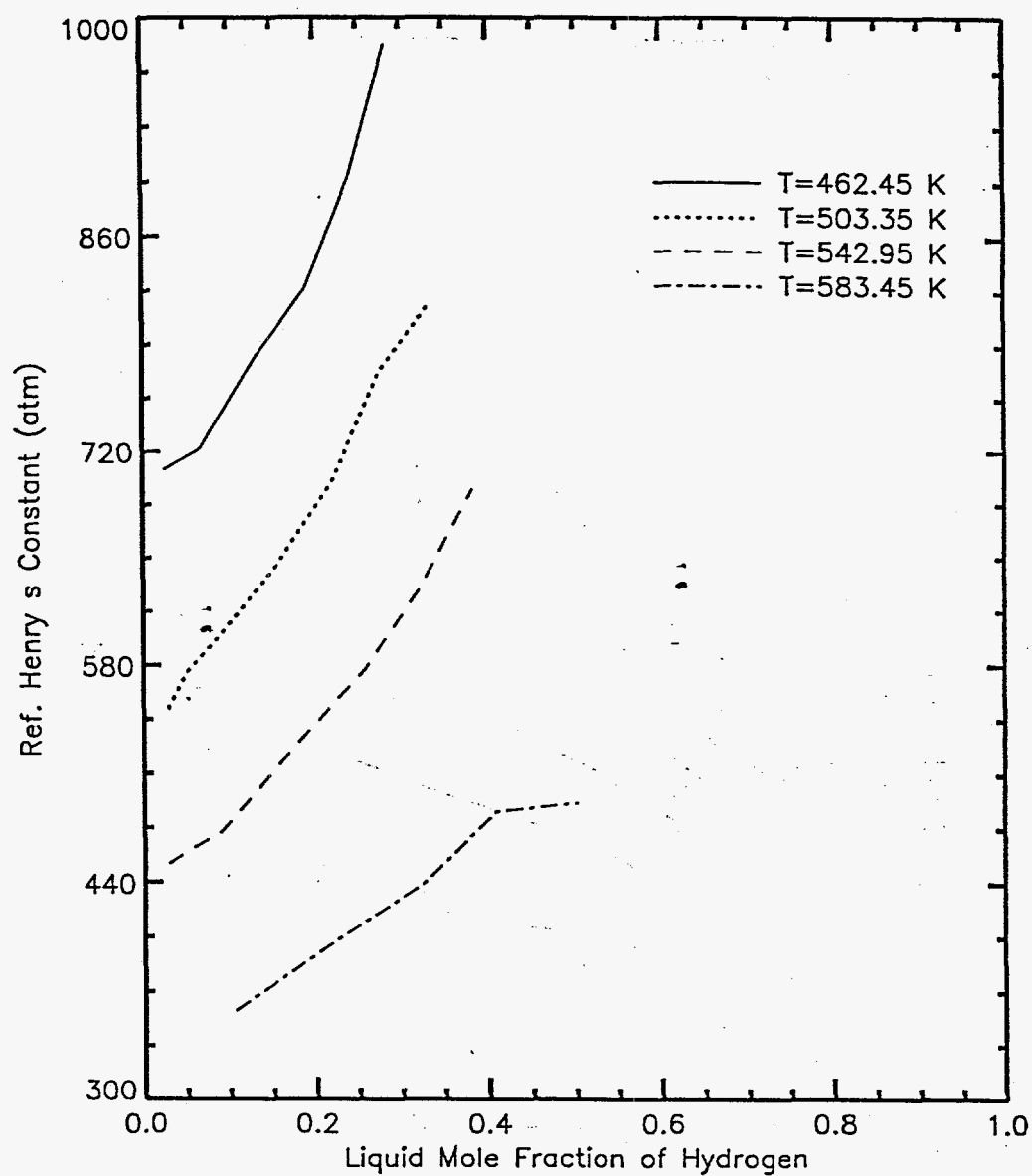


Fig. 3.2 Experimental $H_{2,r}$ ' (Eq. 3.37) as a function of liquid mole fraction of hydrogen at isotherms for hydrogen in the n-decane reference solvent.

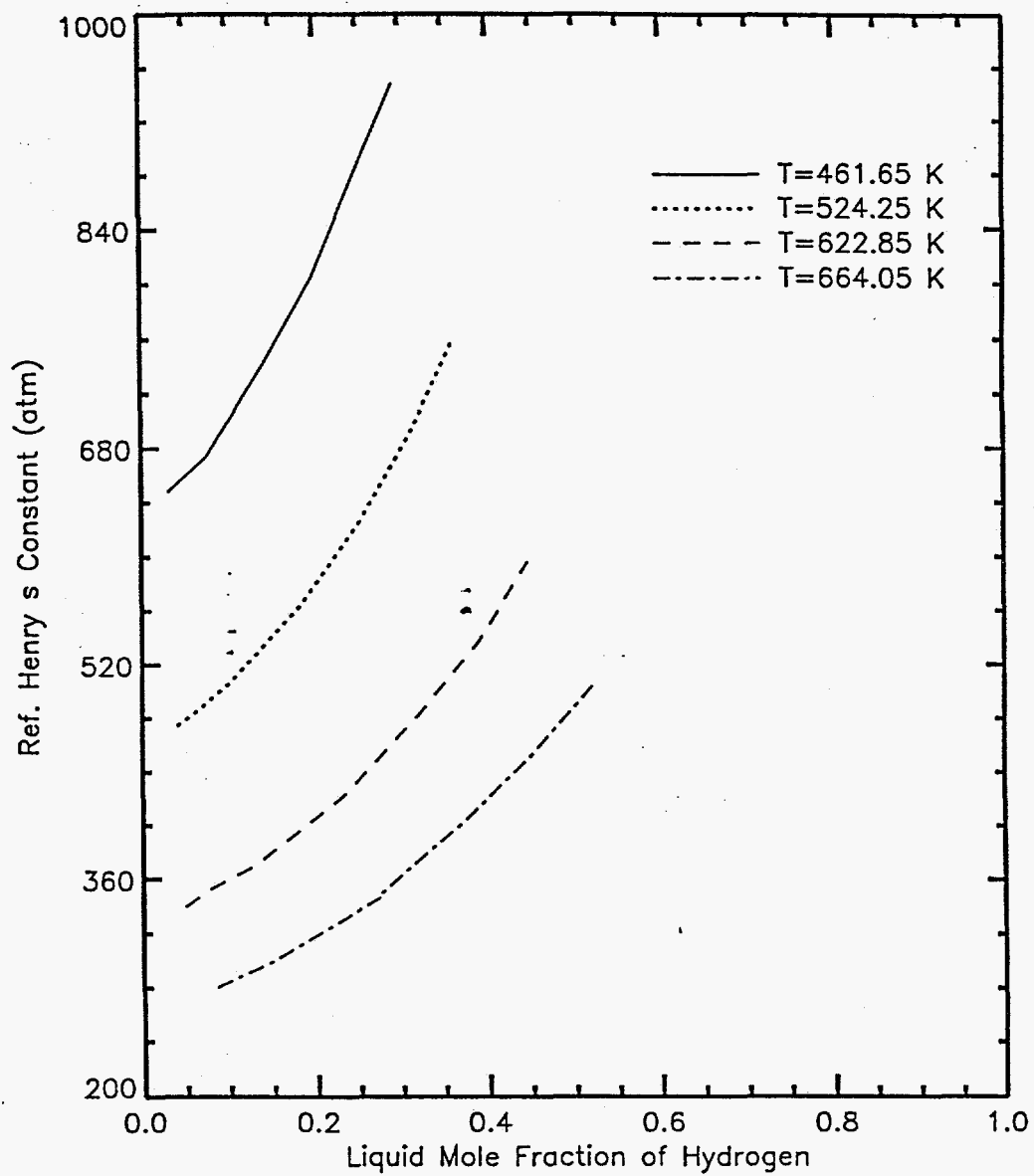


Fig. 3.3. Experimental $H_{2,r}'$ (Eq. 3.37) as a function of liquid mole fraction of hydrogen at isotherms for hydrogen in the n-hexadecane reference solvent.

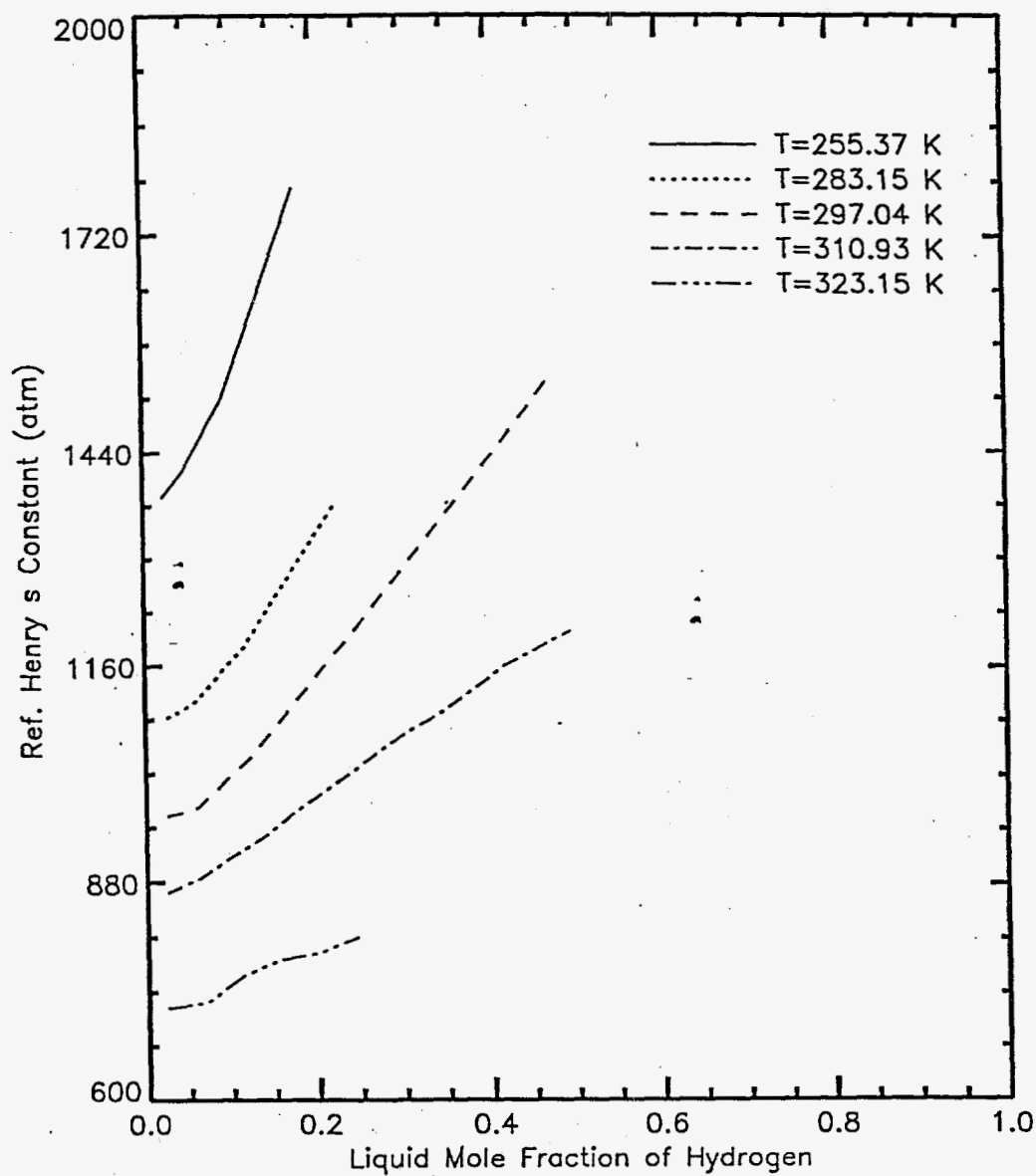


Fig. 3.4 Experimental $H_{2,r}$ ' (Eq. 3.37) as a function of liquid mole fraction of propane at isotherms for propane in the cyclohexane reference solvent.

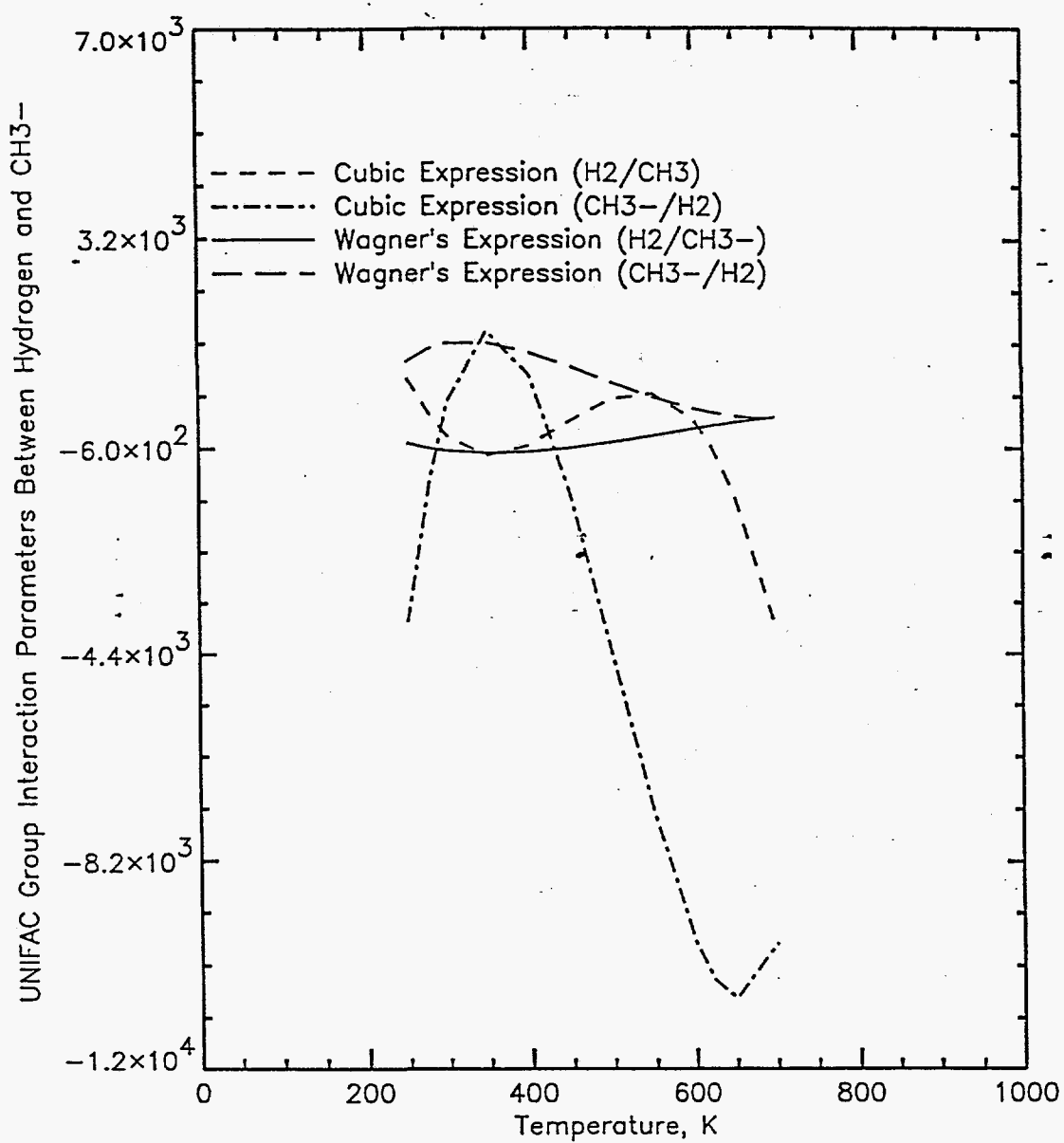


Fig. 3.5 Temperature Dependency of UNIFAC Group Interaction Parameters Between Hydrogen and CH₃- Using Cubic Expression and Wagner's Expression

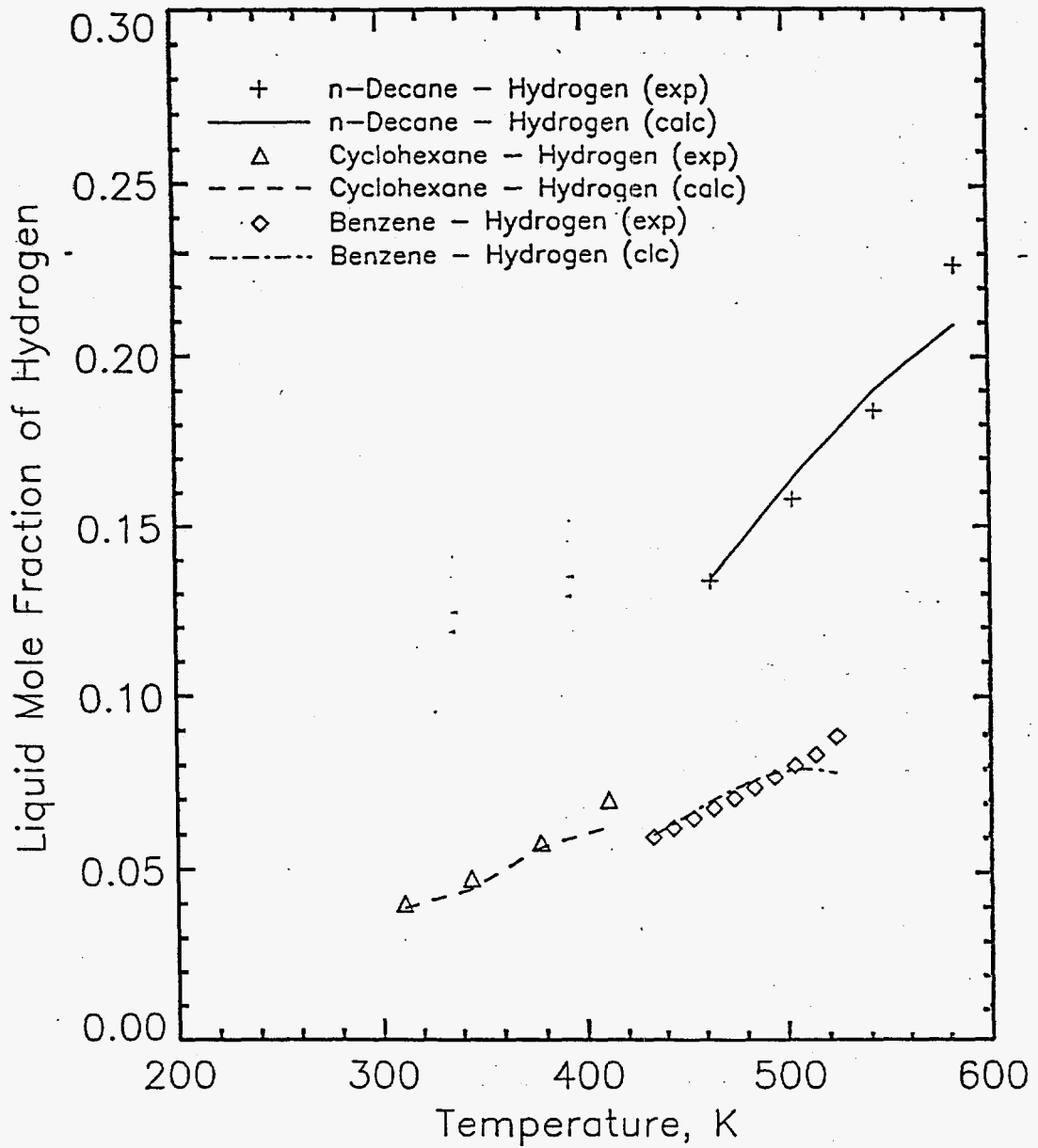


Fig. 3.6 Experimental and Calculated Solubilities of Hydrogen in n-Decane, Cyclohexane, and Benzene at 102 atm Partial Pressure as a Function of Temperature

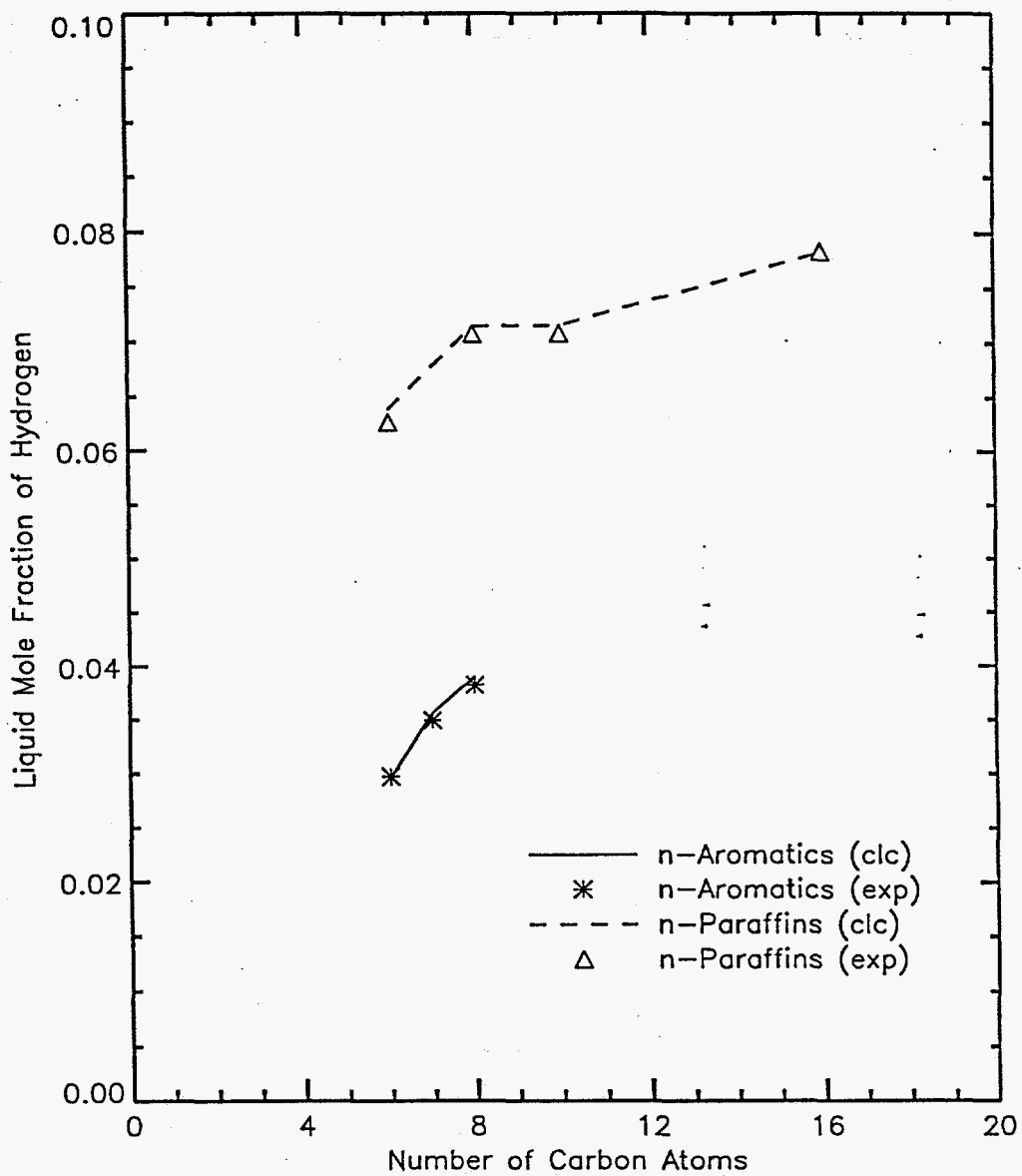


Fig. 3.7 Experimental and Calculated Solubilities of Hydrogen in n-Paraffins and Alkyl-benzene at 470°K and 50 atm Partial Pressure

Table 3.1

Constants for Calculation of Reference Henry's Constant
According to $\ln (H_{2,r}/\text{atm}) = A + B/T + C \ln T$

Gas	A	B	C	Reference Solvents
H ₂	30.841476	-814.371094	-3.709661	n-hexane
H ₂	5.582315	1312.302490	-0.365635	n-decane
H ₂	67.537529	-3440.442871	-8.743119	n-hexadecane
C ₂ H ₆	6.596310	-1190.588501	0.204263	cyclohexane

Table 3.2

Constants for Eqn (3.44) to (3.45)

a	-1.52816	b	1.43907
c	-0.81446	d	0.190454
e	-0.296123	f	0.386914
f	-0.0427258	h	-0.0480645

Table 3.3

Pure Component Parameters for the Hankinson - Brobst - Thomson Correlation

Paraffins	ω_{SRK}	V^* , L/mol
Ethane	0.0983	0.1458
Propane	0.2532	0.2001
n-Butane	0.2008	0.2544
Isobutane	0.1825	0.2568
n-Pentane	0.2522	0.3113
Isopentane	0.2400	0.3096
n-Hexane	0.3007	0.3682
2-Methylpentane	0.2791	0.3677
n-Heptane	0.3507	0.4304
3-Ethylpentane	0.3118	0.4163
2,2,4-Trimethylpentane	0.3144	0.4689
n-Octane	0.3998	0.4904
4-Methylheptane	0.3708	0.4841
3,4-Dimethylhexane	0.3376	0.4722
2,3-Dimethylheptane	0.3848	0.5383
n-Decane	0.4916	0.6192
n-Dodecane	0.5807	0.7558
n-Tetradecane	0.6821	0.9022
n-Hexadecane	0.7667	1.0539
Cycloparaffins		
Cyclopentane	0.1969	0.2600
Methylcyclopentane	0.2322	0.3181
Cyclohexane	0.2128	0.3090
Methylcyclohexane	0.2371	0.3709
Aromatics		
Benzene	0.2137	0.2564
Toluene	0.2651	0.3137
m-Xylene	0.3270	0.3731

Table 3.3 (continued)

Ethylbenzene	0.3048	0.3702
Cumene	0.3277	0.4271
Naphthalene	0.3000	0.3834
1-Methylnaphthalene	0.3422	0.4504
2-Methylnaphthalene	0.3669	0.4591
Tetralin	0.3209	0.4304

Table 3.4

Constants for Eqn. (3.47) to (3.49)

a	-9.070217	b	62.45326
d	-135.1102	f	4.79594
g	0.250047	h	1.14188
j	0.0861488	k	0.0344483

Table 3.5

**UNIFAC Group Volume and Surface-Area Parameters for Hydrogen
Solubility Calculations**

	<u>Main Group</u>		<u>Subgroup</u>		<u>Structural Parameters</u>	
	no	name	no	name	R	(Z/2)Q
Alkane	1	"CH ₂ "	1	CH ₃	0.9011	0.848
			2	CH ₂	0.6744	0.540
			3	cyclic CH ₂	0.6744	0.540
			4	CH	0.4469	0.228
			5	C	0.2195	0.000
Benzene	2	"C ₆ H ₆ "	6	C ₆ H ₆	3.1878	2.400
			7	C ₆ H ₅	3.0217	2.120
			8	C ₆ H ₄	2.8556	1.840
			9	C ₆ H ₃	2.6895	1.560
Naphthalene	3	"C ₁₀ H ₈ "	10	C ₁₀ H ₈	4.9808	3.440
			11	C ₁₀ H ₇	4.8147	3.160
			12	C ₁₀ H ₆	4.6486	2.880
Triaromatic	4	"C ₁₄ H ₉ "	13	C ₁₄ H ₁₀	6.7738	4.480
			14	C ₁₄ H ₉	6.6077	4.200
			15	C ₁₄ H ₈	6.4416	3.920
Hydrogen	5	"H ₂ "	16	H ₂	0.4160	0.571

Table 3.6

Summary of VLE Data Source for Regression of UNIFAC Group- Interaction Parameters

UNIFAC Group	System	Temperature K	Pressure atm	Data Source
H ₂ - CH ₃	Hydrogen - Propane	223-298	34-204	[34]
	Hydrogen - i-Butane	310-366	34-204	[19]
	Hydrogen - n-Butane	327-378	30-166	[55]
	Hydrogen - n-Hexane	277-477	34-680	[69]
	Hydrogen - n-Octane	463-553	6.8-136	[15]
	Hydrogen - 2,2,4-Trimethylpentane	310-423	12-345	[19]
	Hydrogen - n-Decane	462-583	19-251	[40]
H ₂ - Benzene H ₂ - CH _{2, cyc} CH _{2, cyc} - Benzene	Hydrogen - Benzene	433-523	13-204	[15]
	Hydrogen - Cyclohexane	310-410	34-612	[68]

Table 3.6 (continued)

	Hydrogen - Tetralin	463-622	20-250	[90]
	Benzene - Cyclohexane	298-343	0.13-0.8	[3], [70], [71]
	Benzene - Cyclopentane	323-350	1.00	[9]
CH ₃ - CH ₂ , cyc	Cyclohexane Ethane	283-505	6.8-68	[46]
	Cyclohexane n-Hexane	308	0.2-0.3	[5]
	Cyclohexane n-Heptane	313-370	0.13-1.0	[16], [88]
	Cyclohexane Methylcyclohexane	308-373	0.1-1.0	[71], [83]
	Cyclohexane n-Octane	308	0.06-0.18	[57]
	Cyclohexane 2,2,4-Trimethylpentane	308-348	0.11-0.82	[5], [57]
	Cyclohexane 3,4-Dimethylhexane	308	0.07-0.19	[57]
	Cyclohexane 4-Methylheptane	308-373	0.1-1.00	[57]

Table 3.6 (continued)

Benzene - CH ₃	Hydrogen - Toluene	462-575	20-271	[90]
	Hydrogen - m-Xylene	462-580	20-251	[91]
	Benzene - Propane	310-344	1.4-23.8	[30]
	Benzene - Toluene	343-393	0.54-2.8	[34], [39] [48], [84]
	Benzene - n-Heptane	383-488	1.6-16.8	[9]
	Benzene - m-Xylene	298-323	0.04-0.3	[93]
	Benzene - Ethylbenzene	354-393	1.00	[47], [58]

Table 3.7

UNIFAC Binary Interaction Parameters $a(ij, n)^0$ Using Cubic Expression for Hydrogen ~ Hydrocarbon Systems

Group Name	H ₂	CH ₃	-CH ₂ -	Benzene
H ₂	0.0	-364.9760	-59.2080	1012.0922
		-14.4821	-14.8597	-2.6972
		0.1625 E+00	0.6784 E-01	-0.4919 E-01
		-0.3694 E-03	0.9553 E-03	0.1224 E-03
CH ₃	154.4521 53.0974 -0.5580 E+00 0.9079 E-03	0.0	-24.3436	-37.6387
			-1.2244	4.3628
			-0.2295 E-03	-0.1100
			-0.3584 E-04	0.2777 E-03
-CH ₂ -	-123.9720 33.3412 -0.3578 E+00 0.4623 E-03	115.5466	0.0	849.9684
		1.0772		4.3030
		0.4230 E-02		-0.1318 E+00
		0.7813 E-04		-0.4833 E-03
Benzene	1190.3585 2.037 -0.9902 E-01 -0.4841 E-04	360.3341	-322.2550	0.0
		-23.9494	2.0030	
		0.5887 E +00	0.4000 E+00	
		-0.3314 E-02	0.5626 E-02	

* -i, j Correspond to group i and group j and four numbers in each entry correspond to n=1, 2, 3, 4 as in equation (3.61)

Table 3.8

UNIFAC Binary Interaction Parameters $a_{(ij, n)}$ * Using Wagner's
Expression for Hydrogen-Hydrocarbon systems

Group Name	H ₂	CH ₃	-CH ₂ -	Benzene
H ₂	0.0	0.3251	7.2136	19.6928
		-5.0133	-4.2569	-5.8521
		5.1891	-19.7264	188.2786
		3.4035	26.3902	3009.1099
CH ₃	-5.0483 13.0097 0.2735 -28.4965	0.0	-0.8418	7.2705
			-0.5119	-3.7508
			1.6807	-15.4791
			2.8823	12.3222
-CH ₂ -	15.1144 -19.2729 -25.4371 137.9856	3.1854	0.0	0.0888
		0.0011		-0.0135
		-9.1881		-0.0158
		10.4907		-0.0202
Benzene	4.3920 -16.6041 42.8989 -157.6755	-1.1572	0.0885	0.0
		-3.4716	-0.0247	
		12.3204	-0.0171	
		-0.6128	0.0592	

* -i, j correspond to group i and group j and four numbers in each entry correspond to n=1, 2, 3, 4 as in equation (3.62)

Table 3.9

Temperature Range for the Binary Interaction Parameter Using Cubic
Expression as a Function of Temperature

Groups	Temperature Range (K)
H ₂ - CH ₃	277.59 ~ 622.85
H ₂ ~ -CH ₂ -	310.92 ~ 621.75
H ₂ ~ Benzene	433.15 ~ 621.75
CH ₃ ~ Benzene	310.94 ~ 582.10
-CH ₂ - Benzene	462.75 ~ 621.75
-CH ₂ - CH ₃	283.15 ~ 505.37

Table 3.10

Temperature Range for the Binary Interaction Parameters Using Wagner's
Expression as a Function of Temperature

Groups	Temperature Range (K)
H ₂ ~ CH ₃	277.29 ~ 622.85
H ₂ ~ -CH ₂ -	310.92 ~ 621.75
H ₂ ~ Benzene	433.15 ~ 621.75
CH ₃ ~ Benzene	298.15 ~ 582.10
-CH ₂ - Benzene	298.15 ~ 621.75
-CH ₂ - CH ₃	283.15 ~ 505.37

Table 3.11
Error Analysis for Estimating Interaction Parameters Using Cubic
Expression as a Function of Temperature

No.	Systems	No. Pts.	Temperature Range (°K)	Pressure Range (atm)	dev P (%)	dev Y (%)
1.	Propane- Hydrogen	64	223.15~360.93	17.01~272.7	15.4	0.4
2.	n- Butane Hydrogen	48	327.65~377.55	27.42~165.2	11.4	2.8
3.	i-Butane Hydrogen	18	310.93~366.48	34.02~204.1	16.2	5.1
4.	n-Hexane Hydrogen	96	277.59~477.59	34.02~680.5	15.3	3.4
5.	n-Octane Hydrogen	71	463.15~553.15	6.80~136.1	10.6	9.1
6.	2,2,4-Trimethyl- pentane~Hydrogen	31	310.93~423.43	11.91~363.2	30.8	1.0
7.	n-Decane - Hydrogen	26	462.45~583.45	19.01~251.8	4.8	3.1
8.	n-hexadecane- Hydrogen	29	461.65~622.85	19.69~250.5	3.6	0.3
9.	Tetralin- Hydrogen	19	462.75~621.75	20.00~250.0	5.5	0.4
10.	Cyclohexane- Hydrogen	64	310.92~410.93	34.02~544.37	6.0	9.6

Table 3.11 (continued)

No.	Systems	No. Pts.	Temperature Range (°K)	Pressure Range (atm)	dev P (%)	dev Y (%)
11.	Benzene - Hydrogen	130	433.15~533.15	13.61~204.1	2.3	4.4
12.	Benzene-Toluene	9	343.15~393.15	0.54~2.46	1.7	0.9
13.	Benzene-Ethylbenzene	11	353.24~408.46	1.00	3.7	10.8
14.	Benzene-Propane	16	310.94~344.27	1.36~23.8	2.0	0.9
15.	Toluene-Hydrogen	47	461.85~575.15	20.0~322.7	7.6	11.6
16.	M-xylene-Hydrogen	27	462.4~582.10	19.6~251.0	10.2	5.5
17.	Cyclohexane-Ethane	47	283.15~505.37	6.8~88.46	1.9	4.0
Overall Error					9.1	4.73

Table 3.12

**Error Analysis for Estimating Interaction Parameters Using
Wagner's Expression as a Function of Temperature**

No.	Systems	No. Pts.	Temperature Range (°K)	Pressure Range (atm)	dev P (%)	dev Y (%)
1.	Propane- Hydrogen	64	223.15-360.93	17.01-272.7	12.5	1.36
2.	n- Butane Hydrogen	48	327.65-377.55	27.42-165.5	16.3	2.17
3.	i-Butane Hydrogen	18	310.93-366.48	34.02-204.1	11.1	3.17
4.	n-Hexane Hydrogen	96	277.59-477.59	34.02-680.5	17.6	3.25
5.	n-Octane Hydrogen	71	463.15-553.15	6.80-136.1	11.7	12.2
6.	2,2,4-Trimethyl- pentane-Hydrogen	31	310.93-423.43	11.91-363.2	33.2	1.12
7.	n-Decane - Hydrogen	26	462.45-583.45	19.01-251.8	5.1	2.30
8.	n-hexadecane- Hydrogen	29	461.65-622.85	19.69-250.5	5.0	0.25
9.	Tetralin- Hydrogen	19	462.75-621.75	20.0-250.0	10.6	1.13
10.	Cyclohexane- Hydrogen	64	310.92-410.93	34.02-544.37	5.9	0.10

Table 3.12 (continued)

No.	Systems	No. Pts.	Temperature Range (°K)	Pressure Range (atm)	dev P (%)	dev Y (%)
11.	Benzene - Hydrogen	130	433.15~533.15	13.61~204.1	3.1	1.45
12.	Benzene- Cyclohexane	57	298.15~343.15	0.13~1.0	0.48	1.64
13.	Cyclopentane- Benzene	19	323.15~349.85	1.00	1.04	1.61
14.	Benzene- M-Xylene	34	298.15~323.15	0.04~0.30	3.00	3.32
15.	Benzene- Propane	16	310.93~344.26	1.36~23.8	6.42	1.75
16.	Benzene- Toluene	45	343.15~393.15	0.54~2.81	1.45	1.07
17.	Benzene- Ethylbenzene	8	354.24~393.14	1.00	1.38	0.42
18.	Benzene~ Heptane	74	383.15~488.15	1.57~16.8	5.24	9.22
19.	Toluene~ Hydrogen	47	461.85~575.15	20.0~271.4	14.2	14.4
20.	M-Xylene~ Hydrogen	27	462.40~582.10	19.6~251.1	23.7	7.74
21.	Cyclohexane~ 3,4-Dimethylpentane	17	308.15	0.07~0.19	2.10	2.17

Table 3.12 (continued)

No.	Systems	No. Pts.	Temperature Range (°K)	Pressure Range (atm)	dev P (%)	dev Y (%)
22.	Cyclohexane~ 4-Methylpentane	17	308.15	0.07~0.19	2.36	2.13
23.	Cyclohexane~ n-Octane	17	308.15	0.06~0.18	3.24	1.54
24.	Cyclohexane~ n-Hexane	19	308.15	0.20~0.30	1.81	4.21
25.	Cyclohexane~ 2,2,4-Trimethylpentane	114	308.15~348.15	0.11~0.82	2.04	2.29
26.	Cyclohexane~ Methylcyclohexane	38	308.15~372.55	0.10~1.00	1.94	1.50
27.	Cyclohexane~ n-Heptane	38	313.15~370.45	0.13~1.00	0.0007	0.003
28.	Cyclohexane Ethane	47	283.15~505.37	6.80~88.5	6.02	4.55
Overall Error					7.62	3.53

Table 3.13

Comparison of Hydrogen Solubilities in Hydrocarbon Solvents with
Chao- Seader Correlation and Our Method

Systems	T, K	P, atm	No.of Points	AAD% X2		AAD% Y1		Source
				1	2	1	2	
n-Propane (1) / Hydrogen (2)	223-360	17-223	64	10.9	5.1	6.9	19.8	[34]
i-Butane(1) / Hydrogen (2)	310-394	34-204	18	10.5	4.7	34.7	28.3	[19]
n-Butane (1) / Hydrogen (2)	328-394	27-165	48	15.2	4.9	4.8	3.3	[55]
n-Hexane (1) / Hydrogen (2)	277-477	34-680	96	17.5	10.9	32.8	49.0	[69]
n-Octane (1) / Hydrogen (2)	463-553	6-136	71	17.1	12.4	6.0	6.1	[15]
2,2,4-Trimethyl- pentane(1) / Hydrogen(2)	310-423	12-363	31	45.9	19.0	8.5	9.5	[19]
n-Decane (1) / Hydrogen (2)	462-583	19-252	26	4.7	10.0	14.1	19.9	[40]
n-Hexadecane (1) /Hydrogen(2)	462-664	20- 250	29	4.5	7.5	7.1	36.3	[55]
Cyclohexane (1) /Hydrogen (2)	310-410	34-544	64	6.3	35.9	4.9	32.3	[68]
Benzene (1) / Hydrogen (2)	433-533	13-204	130	5.9	18.0	2.4	5.2	[15]

Table 3.13 (continued)

Systems	T, K	P, atm	No. of Points	AAD% X2		AAD% Y1		Source
				1	2	1	2	
Toluene(1) / Hydrogen (2)	462-575	20-272	47	15.6	19.5	17.2	19.3	[90]
m-Xylene (1) / Hydrogen (2)	462-580	20-251	27	35.5	29.3	13.8	11.4	[91]
Tetralin (1) / Hydrogen (2)	462-621	20-250	19	12.8	42.6	6.6	9.5	[90]
Tetralin (1) / Hydrogen (2) / Diphenylmethane (3)	462-701	20-250	31	7.2	---	12.7(1) 3.5(3)	---	[103]
Tetralin (1) / Hydrogen (2) / m-Xylene (3)	462-582	20-250	30	9.4	38.4	5.5(1) 1.5(3)	12.2(1) 10.8(3)	[103]
Total			658	13.5	17.5	10.9	19.0	

* 1 refers to our method and 2 refers to Chao-Seader Correlation.

Table 3.14

Comparison of Hydrogen Solubilities in Hydrocarbon Solvents with Chao-Seader Correlation with the Grayson-Streed New Coefficients and Our Method

Systems	T, K	P, atm	No. of Points	AAD% X2		AAD% Y1		Source
				1	2	1	2	
n-Propane (1) / Hydrogen (2)	223-360	17-223	64	10.9	6.8	6.9	9.5	[34]
i-Butane(1) / Hydrogen (2)	310-394	34-204	18	10.5	6.0	34.7	17.4	[19]
n-Butane (1) / Hydrogen (2)	328-394	27-165	48	15.2	6.4	6.4	3.3	[55]
n-Hexane (1) / Hydrogen (2)	277-477	34-680	96	17.5	9.1	32.8	44.5	[69]
n-Octane (1) / Hydrogen (2)	463-553	6-136	71	17.1	26.7	6.0	6.4	[15]
2,2,4-Trimethyl- pentane(1) / Hydrogen(2)	310-423	12-363	31	45.9	16.5	8.5	20.3	[19]
n-Decane (1) / Hydrogen (2)	462-583	19-252	26	4.7	9.4	14.1	15.4	[40]
n-Hexadecane (1) /Hydrogen(2)	462-664	20- 250	29	4.5	13.2	7.1	26.2	[55]
Cyclohexane (1) /Hydrogen (2)	310-410	34-544	64	6.3	33.4	4.9	26.7	[68]
Benzene (1) / Hydrogen (2)	433-533	13-204	130	5.9	10.9	2.4	5.6	[15]

Table 3.14 (continued)

Systems	T, K	P, atm	No. of Points	AAD% X2		AAD% Y1		Source
				1	2	1	2	
Toluene(1) / Hydrogen (2)	462-575	20-272	47	15.6	20.0	17.2	14.3	[90]
m-Xylene (1) / Hydrogen (2)	462-580	20-251	27	35.5	16.5	13.8	7.5	[91]
Tetralin (1) / Hydrogen (2)	462-621	20-250	19	12.8	19.0	6.6	10.2	[90]
Tetralin (1) / Hydrogen (2) / Diphenylmethane (3)	462-701	20-250	31	7.2	----	12.7(1) 3.5(3)	----	[103]
Tetralin (1) / Hydrogen (2) / m-Xylene (3)	462-582	20-250	30	9.4	18.1	5.5(1) 1.5(3)	5.8(1) 7.3(3)	[103]
Total			658	13.5	15.4	10.9	16.4	

* 1 refers to our method, and 2 refers to Chao-Seader Correlation with the Grayson-Streed numerical values of the coefficients.

Table 3.15

**Coefficients in Chao-Seader Correlation and in its Modification with the
Grayson-Streed New Coefficients**

	Simple Fluid		Hydrogen	
	1	2	1	2
A ₀	5.75748	2.05135	1.96718	1.50709
A ₁	-3.01761	-2.10899	1.02972	2.74283
A ₂	-4.98500	0	-0.054009	-0.02110
A ₃	2.02299	-0.19396	0.0005288	0.00011
A ₄	0	0.02282	0	0
A ₅	0.08427	0.08852	0.008585	0.008585
A ₆	0.26667	0	0	0
A ₇	-0.31138	-0.00872	0	0
A ₈	-0.02655	-0.00353	0	0
A ₉	0.02883	0.00203	0	0

* 1 refers to Chao-Seader Correlation; 2 refers to Chao-Seader Correlation with the Grayson-Streed numerical values of the coefficients.

CHAPTER IV

EXTENSION OF THE MODEL TO PETROLEUM FRACTIONS

Hydrogen solubility is a major factor in the design of crude oil hydrocracking process. In most current hydrocracking process, hydrogenation reactions take place to increase the hydrogen - to - carbon ratio of the fuel. Thus, reliable estimates of hydrogen solubility in petroleum fractions are necessary. As we discussed in chapter III, the UNIFAC group contribution method can be used for predicting hydrogen solubility in hydrocarbons at advanced temperatures and pressures with activity coefficient calculations. It was concluded that good results for hydrogen solubility predictions including a successful description of the temperature dependency of reference Henry's Law constant and UNIFAC group interaction parameters were obtained with a typical accuracy of $\pm 13\%$.

Previous papers have provided some methods for prediction hydrogen solubility in coal derived liquids and crude oil cuts at low temperatures (300-473 K) and at atmospheric pressure which discussed in chapter II. In order to apply the UNIFAC model for the prediction of hydrogen solubility, the functional groups present in each cut have to be identified first, then the interaction parameters between these groups and hydrogen can be used later for solubility predictions. Although there are some interaction parameters that were obtained by Hartounian and Alien [36] between hydrogen and some main groups at low temperatures and pressures, new interaction parameters were predicted in chapter III as a function of temperature and are used to apply the modified UNIFAC method for solubility predictions at high temperatures and pressures.

For light crude oil cuts such as naphtha (423-473 K), analytical approach could be used to determine functional group concentrations [61]. In the case of heavy cuts, analytical techniques are significantly more difficult and their analysis to individual components is almost impossible. In this work, attempts will be made to describe the complex petroleum fractions in terms of model compounds based on Ruzicka's method [85].

4.1 Prediction of Functional Group in Petroleum Cuts

Petroleum fractions are complex mixtures of mainly paraffins, naphthenes, and aromatic compounds. For oil fractions of molecular weight higher than about 100, it is unpractical to list all of the compounds present. Hence, one of the major problems in phase equilibrium calculations involving is the representation of the many different hydrocarbons in terms of few properly average characteristic parameters. When the pseudo-compound method is used for prediction of hydrogen solubility in undefined petroleum fractions, knowledge of the paraffins, naphthenes and aromatics (PNA) content of each fraction is required. If the experimental values of PNA content of each fraction are not available other properties could be used for their prediction. Riazi and Daubert [82] developed a set of correlations for molecular-type analysis which required density, refractive index and viscosity measurements. The fractions were divided into light and heavy molar mass range.

A few methods of characterizing heavy petroleum fractions are available in the literatures. The method suggested by Ruzicka et al [85] is based on the UNIFAC group-contribution model for predicting vapor-liquid equilibria [26] and pure-component vapor pressures [44]. It requires a complete TBP-analysis (boiling point temperature vs. liquid volume percent boil-off), a PNA analysis preferably for each subfraction, and density, preferably for each subfraction. In contrast to real components, the model compounds may be described by non-integer value of v_k^i , which is defined as the number of UNIFAC

group k in molecule i . The UNIFAC group compositions of each pseudo-component are expressed by functions of a parameter n by satisfying two conditions: (1) the Equation (4.1) expressed as follows should be satisfied.

$$\sum_i^3 X_i \cdot \gamma_i \cdot P_i^0 = 1 \quad (4.1)$$

assuming that the operating pressure is one atmosphere, where X_i is the mole fraction of paraffins, naphthenes, or aromatics, i.e. (PNA). γ_i is the activity coefficient calculated by UNIFAC, and P_i^0 is the pure component vapor pressure calculated also by UNIFAC [44]. (2) The pure-component vapor pressure of the three pseudo-components for a given subfraction should be closed together so that their boiling points are equal to the mid-boiling point of the subfraction at atmospheric pressure. The functional forms for UNIFAC group compositions are altered until the above two conditions are satisfied as closely as possible. Thus, each fraction is represented by three pseudo-components each of which consists of UNIFAC groups given by expressions of a quantity n which has a unique value as determined by satisfying the two conditions stated above.

Fahim and Elkilani [24] use exactly the same method as Ruzicka [85], and they furthermore check the model by requiring that the critical properties (T_c , P_c , V_c), acentric factors and molar mass predicted using a group contribution method [56] from the proposed model structure agree with those calculated from experimental mid-boiling point and specific gravity using the correlation of Riazi and Daubert [82].

These two methods discussed above have a common weakness. They use different group model for each crude oil cut and arbitrarily try the group assignment for obtaining the structure of model components in each cut. Naturally it is too cumbersome to assign the groups "by hand" for each oil mixture.

The new method for evaluation of functional groups in model compounds developed in this work followed the procedures suggested by Ruzicka et al [85] except for the way of group assignments for model compounds and the pure component vapor pressure calculations. It entails the following steps (1) division of the TBP curve into a number of subfractions; (2) definition of model compounds for each subfraction in terms of UNIFAC group such as CH_3 -, CH_2 ,_{cyc}- and aromatic group; (3) using the same group assignments for model compounds in each crude oil cut and adjustment of the number of groups by a fitted continuous parameter n so as to match the mid-boiling point for each subfraction; (4) establishment the correlation for n as a function of mid-boiling point from light to heavy petroleum fractions.

Comparing with the Ruzicka et al [85] and Fahim and Elkilani [24] methods, the most distinguished advantage of our method is that the group assignments of model compounds in each crude oil cut are fixed and adjusted by a fitted continuous parameter n . No matter changed in n , the proposed structure model always bring the vapor pressure of model compounds closed together to match the mid-boiling point of each subfraction. Furthermore, a correlation for n as a function of mid-boiling point was obtained. In this way, it is possible to evaluate the group concentration for a variety of crude oil cuts by only using mid-boiling point as a parameter. In the following sections, we will discuss about the correlation for undefined pure compound critical properties required by Lee and Kesler correlation for pure component vapor pressure calculations [54] and the new method for evaluation of groups for crude oil in detail.

4.1.1 The Correlation for Pure Component Critical Properties and Acentric Factor by Using Group Contribution Method

Critical temperature, pressure, and volume represent three widely used pure component constants. Yet, recent experimental measurements are almost nonexistent. In most

cases, the values given were measured. An excellent computation of critical properties is available in a National Physical Laboratory report by Ambrose [4]. Earlier reviews were given by Kudchadker et.al. [51] for organic compounds and Mathews [59] for inorganic compounds. The Design Institute for Physical Property Data [18] also presents a detailed discussion of critical properties and their estimation. In this work, we use Joback modification of Lydersen's method to estimate the critical properties of three model compounds in petroleum fractions.

4.1.1.1 Joback Modification of Lydersen's Method for T_c , P_c , and V_c

One of the first very successful group contribution methods to estimate critical properties was developed by Lydersen [56] in 1955. Since that time, more experimental values have been reported and efficient statistical techniques have been developed to determine the optimum group contributions. Joback [44] reevaluated Lydersen's scheme, added several functional groups and determined the values of the group contributions. His proposed relations are:

$$T_c = T_b \cdot [0.584 + 0.965 \sum \Delta_T - (\sum \Delta_T)^2]^{-1} \quad (4.3)$$

$$P_c = (0.113 + 0.0032 \cdot n_A - \sum \Delta_P)^{-2} \quad (4.4)$$

$$V_c = 17.5 + \sum \Delta_c \quad (4.5)$$

As with this method, the units are Kelvin's, bars, and cubic centimeters per mole, n_A is the number of atoms in the molecule. The Δ values are given in table 4.1.

4.1.1.2 The Correlation for Acentric Factor

One of the more common pure component constants is the acentric factor [73,74] which is defined as

$$\omega = -\log P_{vpr} \text{ (at } T_r = 0.7) - 1.000 \quad (4.6)$$

As originally proposed, ω represented the acentricity or non-sphericity of a molecule. It also rises with polarity. At present, ω is very widely used as a parameter which in some manner is supposed to measure the complexity of a molecule with respect to both the geometry and polarity.

If acentric factors are needed for a material, here for model compounds, the usual technique is to locate (or estimate the critical constants T_c and P_c and then determine the vapor pressure at $T_r = 0.7$. The reduced vapor pressure correlations are below:

$$\omega = \frac{\alpha}{\beta} \quad (4.7)$$

where

$$\alpha = -\ln P_c - 5.97214 + 6.09648\theta^{-1} + 1.28862 \ln \theta - 0.169347\theta^6 \quad (4.8)$$

$$\beta = 15.2518 - 15.6875\theta^{-1} - 13.47211 \ln \theta + 0.43577\theta^6 \quad (4.9)$$

$$\theta = \frac{T_b}{T_c} \quad (4.10)$$

and P_c is in atmospheres, Lee and Kesler [54] reported the Eqn (4.7) yields values of ω very close to those selected by Passut and Danner [72] and Henry and Danner [41] in their critical reviews.

In many instances, in the literature, one finds ω related to Z_c by

$$Z_c = \frac{P_c \cdot V_c}{R \cdot T_c} = 0.291 - 0.080 \cdot \omega \quad (4.11)$$

This equation results from applying a PVT correlation that employs ω at the critical point, where $Z = Z_c$. Eqn (4.11) is only very approximate as the reader can readily show from the values in the literature.

4.1.1.3 The Correlation for Boiling Point

A number of methods to estimate the normal boiling point have been proposed. More recent techniques are usually specific for a given homologous series.

To obtain a very approximate guess of T_b , one may use the group contributions by T_b in Table 4.1 with the relation:

$$T_b = 198 + \sum \Delta_b \quad (4.12)$$

where T_b is in Kelvin's. The group increments were developed by Joback [45], and with Equation (4.12) were tested on 438 diverse organic compounds. The average absolute error found was 12.9 K, and the standard deviation of the error was 17.9 K. The average of the absolute percent errors was 3.6%. Whereas these errors are not small, this simple technique may be useful as a guide in obtaining approximate values of T_b should no experimental value be available.

For each cut, once the critical properties (T_c , P_c , V_c) and acentric factor of model compounds were predicted using the proposed group contribution model showing above, the pure component vapor pressure may be determined by Lee and Kesler [54] correlation and used in Equation(4.1) to obtain the group model in petroleum fractions.

4.1.2 Evaluation of Groups for Crude Oil Cuts

The petroleum crude oil was fractionated into three temperature-ranged fractions based on their mean molecular weights. The first fraction (400 - 500 K) is assumed to be composed of three equimolar pseudo-compounds (paraffins, naphthenes and monoaromatics). For the second fraction (500 - 600 K), we assume that the cut is composed of paraffins, naphthenes and two equimolar aromatics (monoaromatics and diaromatics). We represent the third fraction (600 - 750 K) in terms of paraffins, naphthenes, and three equimolar aromatics (monoaromatics, diaromatics, and triaromatics). The structures of these compounds are fixed and adjusted by a fitted continuous parameter, so that their boiling points are equal to the mid-boiling points of the cut at atmospheric pressure. For each cut, a characteristic value of the parameter n completely defines the cut in terms of the three kinds of equimolar model compounds (paraffins, naphthenes and aromatics). The proposed model and the assumed values of n could be regarded as correct when the condition in equation (4.1) was satisfied.

The results of suggested group for crude oil fractions and the value of n in different mid-boiling point are given in Table 4.2 and Table 4.3. Comparison of the molar mass obtained from the proposed group model and that predicted from Riazi and Daubert correlations [82] which are based on the experimental values of mid-boiling point and specific gravity is shown in Table 4.4. Table 4.5 presented the experimental mean average boiling point of model compounds which come from the proposed group model. It shows that our method for evaluation of group concentration for crude oil cuts gives us very closed boiling point of model compounds at the same value of n from light hydrocarbons to heavy hydrocarbons ($C_8 - C_{20}$). Figure 4.1 shows the same results clearly.

As we discussed before, this method does have some advantages. One of the features of this approach is that it does not need specific properties of each petroleum fraction,

such as specific gravity and mole concentration of model compounds other than mid-boiling point. It allows the sensitivity of the mole concentrations of model compounds to the functional group concentrations to be small enough to be neglected. Table 4.6 shows that if we keep the same model structure and the value of n as those predicted from equimolar concentrations of model compounds, the change in molar concentration of model compounds in mid-boiling point is very small. The biggest deviations of mid-boiling point are within ± 6 K for n varied from 0.3333 to 5. It indicates that the assumption for model structure unrelated to the concentration of model compounds is reasonable.

Furthermore, a correlation for the characteristic value of n in each cut was obtained as a function of mid-boiling point from the following relation which has been found appropriate for this work..

$$n = a_0 + a_1 \cdot T_b + a_2 \cdot T_b^2 + a_3 \cdot T_b^3 \quad (4.13)$$

where T_b is the mid-boiling points of crude oil cuts. The estimated parameters in eqn. (4.13) are obtained by using least square regressions and are given below:

$$a_0 = -0.438268, \quad a_1 = -0.157568E-01, \quad a_2 = 0.570183E-04, \quad a_3 = -0.343543E-07$$

Very good fit was obtained with errors of less than 0.2%. This expression for n is now ready to be used in solubility calculations.

4.2 Prediction of Hydrogen Solubility in Petroleum Fractions

As we discussed in chapter III, the hydrogen solubility is predicted by equating the gas phase hydrogen fugacity to the liquid phase fugacity. In same way, the following equation could be used for prediction hydrogen solubility in petroleum fractions which came from eq (3.60).

$$X_{H_2} = \frac{Y_{H_2} \cdot \phi_{H_2} \cdot P}{H_{2,r} \cdot \gamma_{H_2} / \gamma_{H_2,r}^{\infty}} \quad (4.14)$$

where X_{H_2} is the mole fraction of hydrogen in liquid phase, and Y_{H_2} is the mole fraction of hydrogen in the gas phase. In Equation (4.14) P is the total pressure of the system, ϕ_{H_2} is the fugacity coefficient of hydrogen in vapor phase, which can be obtained by the virial equation of state described in chapter III, γ_{H_2} and $\gamma_{H_2,r}^{\infty}$ are the activity coefficient of hydrogen in the crude oil fraction and in the infinite dilution reference solvent respectively, and $H_{2,r}$ is Henry's law constant of hydrogen in the reference solvent. Use of a reference solvent is required since the standard state fugacity for hydrogen in crude oil fractions is not available. In this work, n-hexane, n-decane, and n-hexadecane are used as reference solvents corresponding to the number of carbon atoms in model compounds.

By using the new interaction parameters estimated from chapter III, the hydrogen solubility in petroleum fractions can be calculated from eq (4.14). The activity coefficient γ_{H_2} was calculated by modified UNIFAC for the functional group concentrations present in crude oil cuts. These group concentrations were calculated from the new method we discussed above by correlation the n as a function of mid-boiling points of crude oil cuts.

4.2.1 Comparison between Predicted and Measured Solubilities

As discussed before, hydrogen solubility data must be available experimentally to compare them with the predicted values to show the applicability of the UNIFAC model. Since the experimental hydrogen solubility in petroleum fractions at high temperatures and pressures are not available in the literatures, we use the experimental hydrogen solubility data at one atmosphere which was measured by Mohamed and Elkilani [62] to verify the validity of our model. Reported by Mohamed and Elkilani [62], the petroleum crude oil

was fractionated into five fractions where the specific gravity and mid-boiling point of each cut were determined and shown in table 4.7. These data were used to predict the PNA, using the Riazi and Daubert correlations [82]. The results are shown in Table 4.8.

Hydrogen solubility in each crude oil fraction which expressed as Henry's constant was determined experimentally by means of the pulse method [23] described by Mohamed and Elkilani [62].

Hydrogen solubility in each crude oil fraction was also predicted by means of Equation (4.14). The activity coefficients were calculated from UNIFAC for a mixture of pseudo model compounds, paraffin, naphthene and aromatic. The molecular structure of each compound was composed of UNIFAC groups with non-integer number n correlated as a function of mid-boiling point.

Since the gas phase may be considered ideal ($\phi_{H_2} = 1$) and the mole fraction of hydrogen in vapor phase to be equal to unity for nonvolatile liquids at atmospheric pressure then the eq (4.14) can be changed into following expression for solubility predictions:

$$X_{H_2} = (P / H_{H_2,r}) (\gamma_{H_2,r}^{\infty} / \gamma_{H_2}) \quad (4.15)$$

Furthermore, the mole fraction of hydrogen in liquid petroleum fraction which obtained from eq (4.17) is used to calculate the Henry's constant by means of Henry's law.

Recalling, for very small X_{H_2} , Henry's Law can be expressed as follows

$$f_{H_2}^G = P \cdot Y_{H_2} \cdot \phi_{H_2} = X_{H_2} \cdot H_{H_2} \quad (4.16)$$

Since the X_{H_2} is very small and the gas phase may be considered ideal at one atmosphere, Henry's constant of hydrogen in each crude oil cut could be calculated by $H_{H_2} = P / X_{H_2}$. The results of the experimental value of Henry's constant are compared with those pre-

dicted as shown in Table 4.9. The deviations shown in this table confirmed that the model including the new method for evaluation of the group concentrations in crude oil cuts can be used to predict hydrogen solubility in petroleum fractions successfully with 7 % average error at low temperature (308-473 K) and atmospheric pressure.

4.3 Application of the Model for the Hydrocracker Feedstocks at High Temperatures and Pressures

In this section we will discuss about using the model for predicting hydrogen solubility in petroleum fractions to work on some specific hydrocracker feedstocks, such as 'Coker Go' , 'FCC LCGO', and their mixture at the hydrocracking reaction operating conditions. "Coker Go" is a gas oil product obtained by delayed coking operations. In recently years, this process has been used to prepare hydrocracker feedstocks with minimizing refinery yields of residual fuel oil by severe thermal cracking of stocks such as vacuum residuals and thermal tars. The other very important and widely used refinery process is catalytic cracking which is used for converting heavy oils into more valuable gasoline and lighter products. The light cycle gas oil (LCGO) obtained from the fluid catalytic cracker (FCC) of the fluidized bed units is called FCC LCGO. As we discussed before, hydrogen solubility in different crude oil fractions was predicted using modified UNIFAC group contribution method. A new procedure for characterizing crude oil fractions has been established. Functional group concentrations were estimated by means of suggested group models with non integer number n correlated as a function of mid-boiling point of petroleum fractions. Due to the deficiency of experimental hydrogen solubility data in petroleum fractions at high temperatures and pressures, we can only represent the calculated results as follows

The crude oil properties of "Coker Go" and "FCC LCGO" cuts are reported by Gary and Handwerk [29]. The $^{\circ}$ API Gravity of these two fractions are obtained from this book

[29,page 156] and are used to determine the mid-boiling point of each cut by the TBP and gravity curves [29, page 29]. The Watson characterization factor is a widely used correlation between yield and the aromaticity and paraffinicity of crude oil cut and can be defined as following Equation.

$$K_w = (T_B)^{1/3} / G \quad (4.17)$$

where T_B is mean average boiling point, $^{\circ}R$, and G is specific gravity at $60^{\circ}F$ and can be calculated from $^{\circ}API$ gravity by the following relationship shown as follows

$$G = 141.5 / (^{\circ}API + 131.5) \quad (4.18)$$

Therefore, The Watson characterization factor (K_w) can be calculated by the expressions shown above. Table 4.10 shows the mid-boiling point, $^{\circ}API$ gravity and Watson characterization factor. These data are used to roughly estimate PNA and determine the functional group concentrations of model compounds. Since the saturated Hydrocarbons show a narrower range of K_w and vary from 9.8 for a pure aromatic compound to 13 for a pure paraffinic material, the crude oil cut could be considered containing more paraffins if the K_w closed to 13, or more aromatic compounds if K_w closed to 9.8. The rough PNA analysis for these two crude oil cuts are obtained by the information described above and shown in Table 4.11 where P, N, A_1 , A_2 , A_3 are pseudo-compounds (paraffin, naphthene, one-ring aromatic, two-ring aromatic, and three-ring aromatic)

The results of the predicted hydrogen solubility in 'Coker Go' and in 'FCC LCGO' at high temperatures and pressures are presented in Table 4.12. Figure 4.2 and 4.3 show solubilities as a function of temperature and pressure for hydrogen in "Coker Go" (Fig. 4.2)

and in "FCC LCGO" (Fig. 4.3). We find that the hydrogen solubility increases with increasing the temperatures and pressures.

For the mixture of 'Coker Go' and 'FCC LCGO', we use two different PNA analysis methods. Method 1 is that we use the average mid-boiling point over a wide range of true boiling and API° gravity to determine the functional group concentration of model compounds, the results are given in Table 4.13 and Table 4.14

Method 2 is that the wide range of true boiling point is broke into two subfractions, Coker Go and FCC LCGO. For each subfraction, we use its own mid-boiling point and API gravity for PNA analysis respectively to determine the functional group concentration. The results have been given in Table 4.10 and Table 4.11.

The predicted hydrogen solubility in mixture of Coker Go and FCC LCGO using these two methods are presented in Table 4.15 as isotherms

In Table 4.15, it is shown that there is no significant difference between these two methods for calculating the hydrogen solubility in crude oil cuts. It can be concluded that for a wide range of true boiling point, we don't need to divide a TBP curve into a number of subfractions, using the average mid-boiling point and API gravity over a wide range of boiling point for a petroleum fraction will give us almost the same results.

Table 4.1

Joback Group Contributions for Critical Properties, the Normal Boiling Point [45]

Nonring Increments	Δ			
	Δ_T	Δ_P	Δ_V	Δ_b
-CH ₃	0.0141	-0.0012	65	23.58
>CH ₂	0.0189	0	56	22.88
>CH-	0.0164	0.0020	41	21.74
>CH<	0.0067	0.0043	27	18.25
Ring Increments				
-CH ₂ -	0.0100	0.0025	48	27.15
>CH-	0.0122	0.0004	38	21.78
>C<	0.0042	0.0061	27	21.32
=CH-	0.0082	0.0011	41	26.73
=C<	0.0143	0.0008	32	31.01

Table 4.2
Suggested Group Models for Crude Oil Fractions

UNIFAC GROUPS	400 -- 750 K				
	P	N	A ₁	A ₂	A ₃
CH ₃	2+n	1	1+n	1	1
CH ₂	6+n	3n	n	3n-5	3n-12
CH	n	0	n	0	0
CH ₂ ,cyc	0	5	0	0	0
CH, cyc	0	1	0	0	0
C ₆ H ₅ (Benzene Ring)	0	0	1	0	0
C ₁₀ H ₇ (Naphthalene Ring)	0	0	0	1	0
C ₁₄ H ₉ (Triaromatic Ring)	0	0	0	0	1

P : Paraffin

N : Napthene

A₁ : MonoaromaticA₂ : DiaromaticA₃ : Triaromatic

Table 4.3
The Value of n in Suggested Group

Mid-Boiling Point T_b (K)	n	$\Sigma X_i \gamma_i P_i^0$
400	0.183	1.0001
410	0.319	0.9993
420	0.457	0.9998
430	0.598	0.9998
440	0.741	1.0008
450	0.888	0.9995
460	1.036	1.0000
470	1.187	0.9990
480	1.338	1.0005
490	1.492	0.9991
500	1.645	1.0007
510	1.786	1.0006
520	1.946	1.0006
530	2.106	1.0004
540	2.266	0.9995
550	2.424	1.0003
560	2.581	1.0008
570	2.737	1.0008
580	2.892	1.0000
590	3.045	0.9999
600	3.196	1.0004
620	3.555	1.0001
640	3.850	1.0003
660	4.131	0.9996
680	4.403	0.9998
700	4.671	1.0000
720	4.940	1.0000
740	5.212	0.9999

Table 4.4

Comparison Between Experimental and Predicted Molar Mass

Fraction K	Molar Mass g/mole	
	A	B
448	142.5	144.12
509	191.6	201.16
569	229.2	235.42
647	317.7	323.27
712	403.7	412.54

A: Experimental molar mass from Riazi and Daubert correlations [82]

B: Predicted Molar mass calculated from proposed structures

Table 4.5

Experimental Mean Average Boiling Point of Model Compounds

n	Model Compounds	MW	B.P. (K)
0.0	P (C ₈ H ₁₈)	114.23	386.04
	N (C ₇ H ₁₄)	96.188	374.08
	A1 (C ₇ H ₈)	92.141	383.78
0.3333	P (C ₉ H ₂₀)	128.26	410.00
	N (C ₈ H ₁₆)	112.21	404.93
	A1(C ₈ H ₁₀)	106.17	412.68
0.6666	P (C ₁₀ H ₂₂)	142.29	447.30
	N (C ₉ H ₁₈)	126.24	427.70
	A1 (C ₉ H ₁₂)	120.19	436.96
1.0000	P (C ₁₁ H ₂₄)	156.31	469.10
	N (C ₁₀ H ₂₀)	140.26	449.00
	A1 (C ₁₀ H ₁₄)	134.22	457.19
1.3333	P (C ₁₂ H ₂₆)	170.34	489.50
	N (C ₁₁ H ₂₂)	-----	479.30
	A1 (C ₁₁ H ₁₆)	148.25	479.85
	A2 (C ₁₀ H ₈)	128.17	491.14
1.6666	P (C ₁₃ H ₂₈)	184.37	508.60
	N (C ₁₂ H ₂₄)	-----	----
	A1 (C ₁₂ H ₁₈)	162.27	499.25
	A2 (C ₁₁ H ₁₀)	142.20	514.30
2.0000	P (C ₁₄ H ₃₀)	198.39	526.70
	N (C ₁₃ H ₂₆)	-----	----
	A1 (C ₁₃ H ₂₀)	-----	----
	A2 (C ₁₂ H ₁₂)	156.23	531.20

Table 4.5 (continued)

n	Model Compounds	MW	B.P. (K)
2.3333	P (C ₁₅ H ₃₂)	212.42	543.80
	N (C ₁₄ H ₂₈)	-----	-----
	A1 (C ₁₄ H ₂₂)	-----	-----
	A2 (C ₁₃ H ₁₄)	170.25	545.65
2.6666	P (C ₁₆ H ₃₄)	226.45	560.00
	N (C ₁₅ H ₃₀)	-----	-----
	A1 (C ₁₅ H ₂₄)	-----	-----
	A2 (C ₁₄ H ₁₆)	184.28	562.39
3.0000	P (C ₁₇ H ₃₆)	240.48	575.20
	N (C ₁₆ H ₃₂)	-----	-----
	A1 (C ₁₆ H ₂₆)	-----	-----
	A2 (C ₁₅ H ₁₈)	-----	-----
3.3333	P (C ₁₈ H ₃₈)	254.50	589.50
	N (C ₁₇ H ₃₄)	-----	-----
	A1 (C ₁₇ H ₂₈)	-----	-----
	A2 (C ₁₆ H ₂₀)	-----	-----
3.6666	P (C ₁₉ H ₄₀)	268.53	603.10
	N (C ₁₈ H ₃₆)	-----	-----
	A1 (C ₁₈ H ₃₀)	-----	-----
	A2 (C ₁₇ H ₂₂)	-----	-----
	A3 (C ₁₄ H ₁₀)	178.23	611.55
4.000	P (C ₂₀ H ₄₂)	282.56	617.00
	N (C ₁₉ H ₃₈)	-----	-----
	A1 (C ₁₉ H ₃₂)	-----	-----
	A2 (C ₁₈ H ₂₄)	-----	-----
	A3 (C ₁₅ H ₁₂)	192.26	636.00

Table 4.5 (continued)

5.000	P (C ₂₃ H ₄₈)	----	----
	N (C ₂₂ H ₄₄)	----	----
	A1 (C ₂₂ H ₃₈)	----	----
	A2 (C ₂₁ H ₃₀)	----	----
	A3 (C ₁₈ H ₁₈)	334.34	667.00

Table 4.6

Sensitivity of Concentration of Model Compounds to the Mid-Boiling Points of Crude Oil Cuts

Mole Fraction of Model Compound	Value of n	Mid-Boiling Point T_b (K)
0.3333 (P)	0.3333	411.20
0.3333 (N)		
0.3333 (A)		
0.1000 (P)	0.3333	414.70
0.4000 (N)		
0.5000 (A)		
0.9000 (P)	0.3333	406.30
0.0500 (N)		
0.0500 (A)		
0.3333 (P)	5.0000	724.58
0.3333 (N)		
0.1111 (A1)		
0.1111 (A2)		
0.1111 (A3)		
0.0500 (P)	5.0000	728.50
0.0500 (N)		
0.3000 (A1)		
0.3000 (A2)		
0.3000 (A3)		
0.9000 (P)	5.0000	724.40
0.0500 (N)		
0.0166 (A1)		
0.0167 (A2)		
0.0167 (A3)		

Table 4.7
**Physical Properties of Crude Oil Fractions Determined by Mohamed, A.F.,
and Elkilani, A.S [62]**

Fraction K	Mid. B.P T_b, K	Specific Gravity	Molar Mass g/mole
423-473	448.15	0.76228	142.46
473-544	508.65	0.80820	181.60
544-594	569.15	0.83950	229.18
594-700	647.15	0.88540	317.67
700-724	712.15	0.91330	403.65

Table 4.8

Predicted Paraffins, Napthenes and Aromatics Percent (PNA) in Crude Oil Cuts
Determined by Mohamed, A.F., and Elkilani, A.S [62]

Fraction K	Paraffins P%	Napthenes N%	Aromatics A%
423-473	71.90	4.75	23.35
473-544	42.23	32.80	24.97
544-594	33.78	39.13	27.09
594-700	17.52	49.18	33.30
700-724	10.35	54.55	35.10

Table 4.9
Henry's Law Constant (Kpa) for Hydrogen in Crude Oil Fractions at
Different Temperatures

Crude Fractions	Temperature K	Predicted H(kpa)	*Experimental H(kpa)	% Deviation
423-473 K	308	91890.5	81971.9	12.1
	318	73750.8	72092.7	2.3
	328	55068.4	59792.0	7.9
	338	43156.8	47217.5	8.6
473-544	298	122398.9	112602.5	8.7
	323	103847.1	91737.7	13.2
	348	83280.2	78344.5	6.3
	373	62016.7	59346.1	4.5
544-594	323	167139.1	147519.1	13.3
	373	146211.1	133526.1	9.5
	398	126061.3	115865.2	8.8
	423	104250.3	100048.3	4.2
594-700	323	229651.3	197634.5	16.2
	398	297313.1	276313.3	7.6
	423	271692.3	264549.5	2.7
	448	245318.9	242410.0	1.2
	473	243653.2	239816.1	1.6
700-724	373	305982.3	275411.6	11.1
	398	292339.5	276313.3	5.8
	423	270369.6	264549.5	2.2
	448	245803.7	242410.0	1.4
	473	238137.4	239816.1	0.7
average error(%)				6.81

* Experimental H(Kpa) measured by Mohamed and Elkilani [61]

Table 4.10

Physical Properties of Coker Go and FCC LCGO

Fraction	Mid B. P. T _b , K	°API Gravity	K _w
Coker Go	653.15	24.0	11.60
FCC LCGO	916.50	10.7	11.88

Table 4.11
Paraffins, Naphthenes and Aromatics Percent (PNA) in Coker Go
and FCC LCGO

Fraction	Paraffins	Naphthenes	Aromatics		
	P %	N %	A ₁ %	A ₂ %	A ₃ %
Coker Go	0.500	0.200	0.100	0.100	0.100
FCC LCGO	0.600	0.160	0.080	0.080	0.080

Table 4.12

The Predicted Results for Hydrogen Solubility in 'Coker Go' and in
'FCC LCGO' at High Temperatures and High Pressures

Temperature T, °K	Pressure P, atm	Liquid Mole Fraction of Hydrogen in	
		Coker Go	FCC LCGO
500	60	0.100	0.122
	70	0.115	0.141
	80	0.130	0.158
	90	0.145	0.176
	100	0.159	0.193
	110	0.174	0.209
	120	0.187	0.225
	130	0.201	0.241
	140	0.214	0.256
	150	0.227	0.270
550	60	0.119	0.145
	70	0.137	0.166
	80	0.154	0.187
	90	0.171	0.206
	100	0.188	0.226
	120	0.220	0.262
	130	0.235	0.279
	140	0.250	0.296
	150	0.265	0.312
	600	60	0.147
70		0.169	0.204
80		0.190	0.228
90		0.210	0.251
100		0.230	0.274
110		0.249	0.295
120		0.267	0.315
130		0.285	0.335
140		0.302	0.353
150		0.319	0.372

Table 4.12 (continued)

Temperature T, °K	Pressure P, atm	Liquid Mole Fraction of Hydrogen in	
		Coker Go	FCC LCGO
650	60	0.185	0.224
	70	0.211	0.254
	80	0.237	0.282
	90	0.261	0.309
	100	0.284	0.335
	110	0.306	0.359
	120	0.328	0.381
	130	0.348	0.403
	140	0.368	0.424
	150	0.387	0.443
700	60	0.234	0.283
	70	0.266	0.318
	80	0.297	0.351
	90	0.325	0.381
	100	0.353	0.410
	110	0.378	0.436
	120	0.403	0.461
	130	0.426	0.484
	140	0.448	0.508
	150	0.469	0.529

Table 4.13

Physical Properties of the Mixture of Coker Go and FCC LCGO

Fraction	Mid B. P. T _b , K	API ^o Gravity	K _w
Coker Go (61.8 %) / FCC LCGO (38.2 %)	717.59	18.9	11.71

Table 4.14

Paraffins, Naphthenes, and Aromatics Percent (PNA) in the Mixture of
Coker Go and FCC LCGO

Fraction	Paraffins	Naphthenes	Aromatics		
	P %	N %	A ₁ %	A ₂ %	A ₃ %
Coker Go (61.8 %) / FCC LCGO (38.2 %)	0.5618	0.1753	0.0876	0.0876	0.0877

Table 4.15

The Predicted Results for Hydrogen Solubility in the Mixture of "CokerGo"
and "FCC LCGO" Using Two Different Methods

Temperature T, K	Pressure P, atm	Predicted Hydrogen Solubility	
		Method 1	Method 2
500	60	0.106	0.108
	70	0.123	0.125
	80	0.139	0.141
	90	0.154	0.157
	100	0.169	0.172
	110	0.184	0.188
	120	0.199	0.202
	130	0.213	0.217
	140	0.227	0.231
	150	0.241	0.245
550	60	0.127	0.129
	70	0.146	0.148
	80	0.164	0.167
	90	0.182	0.185
	100	0.199	0.203
	110	0.216	0.220
	120	0.233	0.237
	130	0.249	0.253
	140	0.265	0.269
	150	0.280	0.284
600	60	0.157	0.160
	70	0.180	0.183
	80	0.202	0.205
	90	0.223	0.226
	110	0.263	0.267
	120	0.282	0.286
	130	0.301	0.305

Table 4.15 (continued)

Temperature T, K	Pressure P, atm	Predicted Hydrogen Solubility	
		Method 1	Method 2
700	140	0.388	0.391
	150	0.407	0.410
	60	0.252	0.254
	70	0.285	0.287
	80	0.316	0.318
	90	0.345	0.348
	100	0.373	0.376
	110	0.399	0.402
	120	0.423	0.427
	130	0.446	0.450
	140	0.468	0.472
	150	0.488	0.493

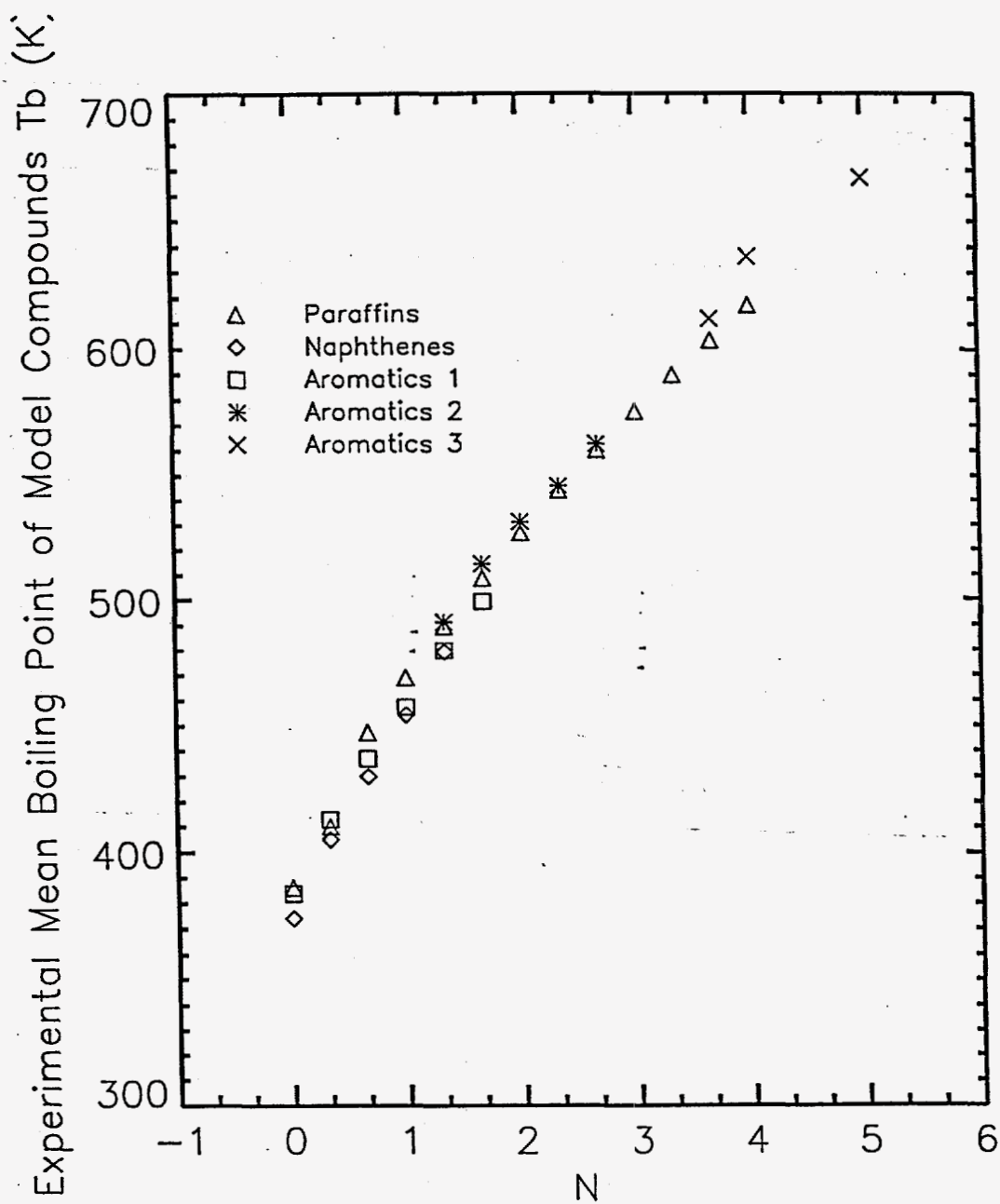


Fig. 4.1 Experimental Mean Average Boiling Point of Model Compounds at different value of n

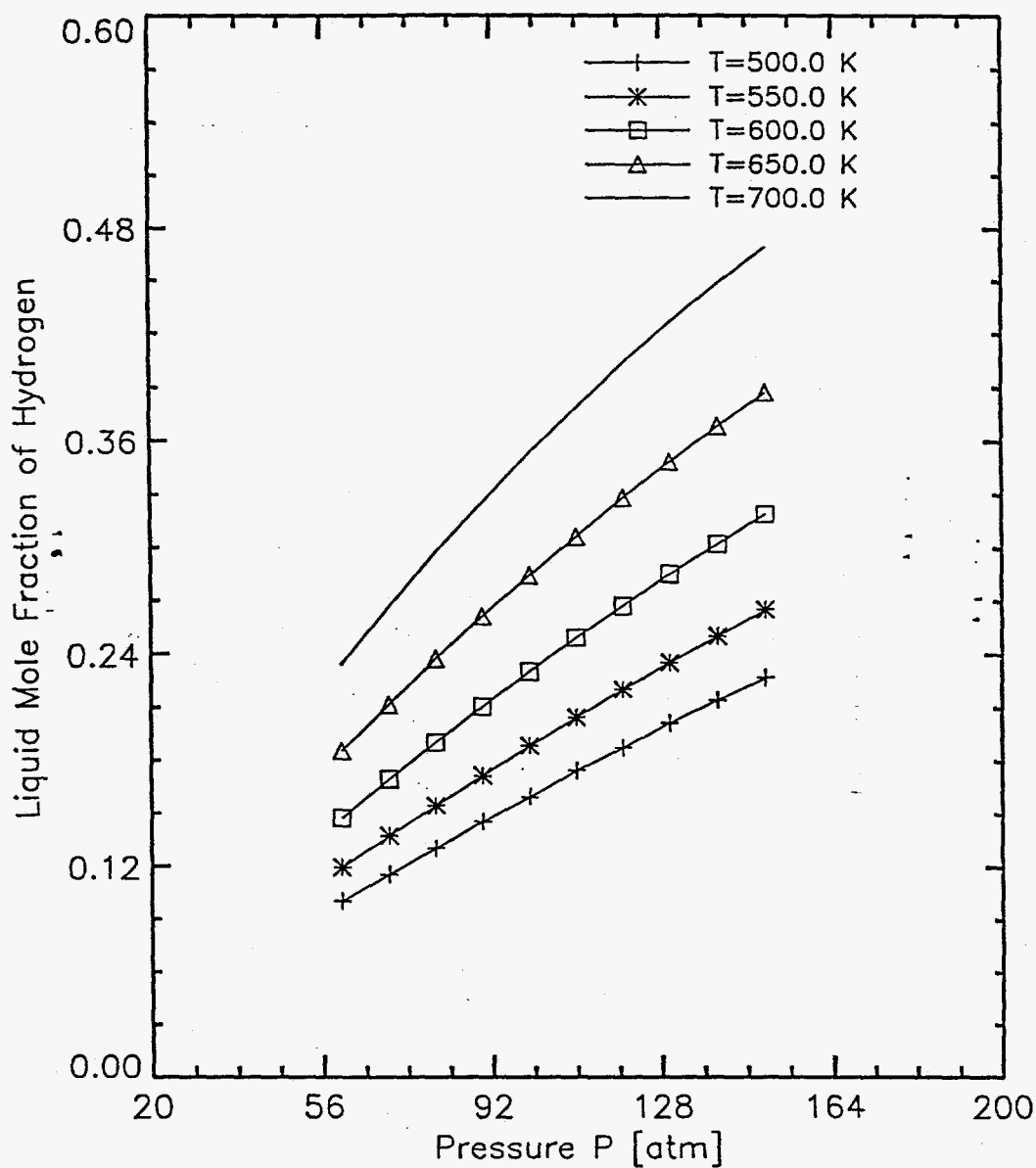


Fig. 4.2 Pressure Dependency of Calculated Solubility of Hydrogen in Coker Go at Different Temperatures

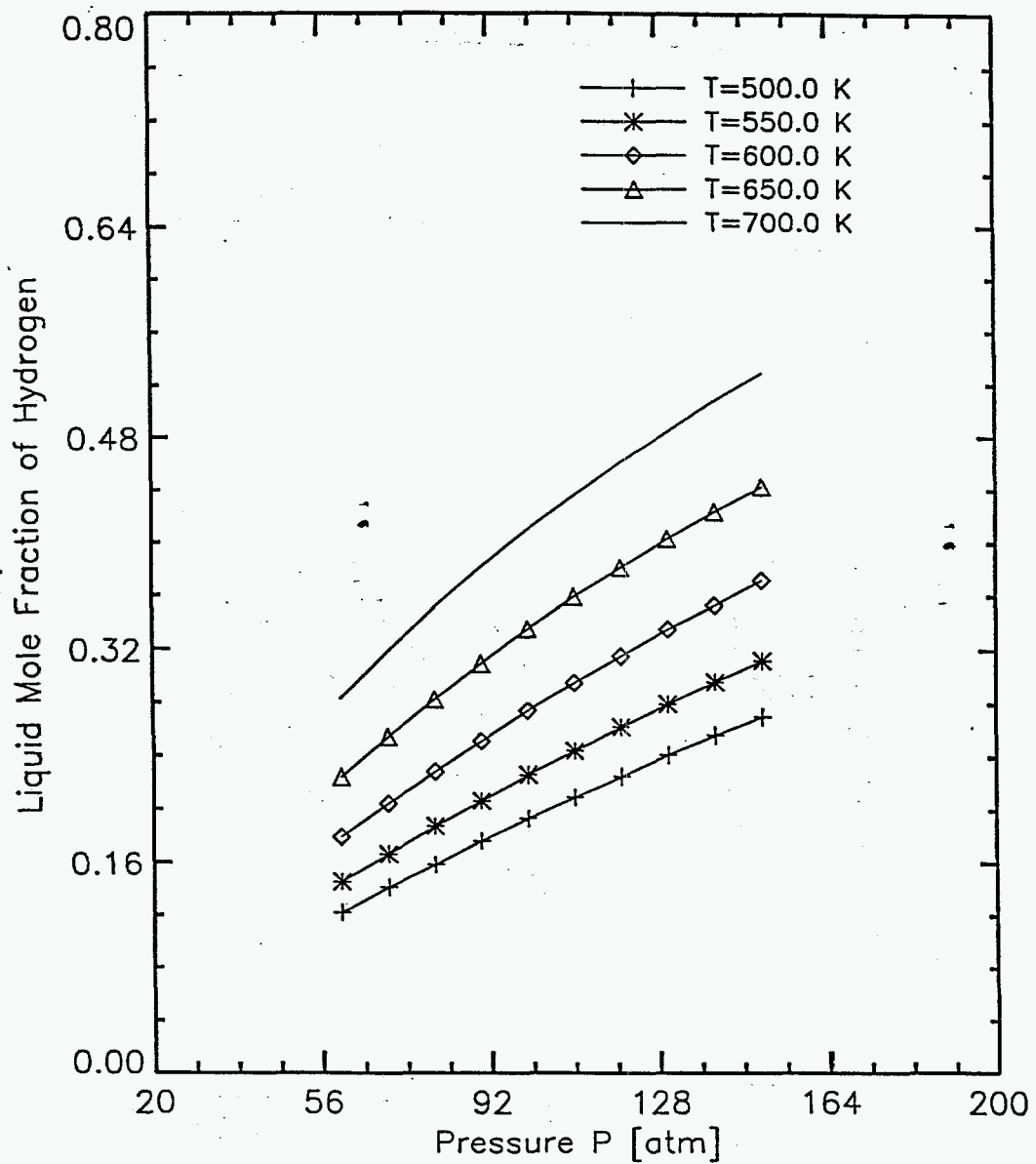


Fig. 4.3. Pressure Dependency of Calculated Solubility of Hydrogen in FCC LCGO at Different Temperatures

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

It was seen from chapter III that a new model for the prediction of solubility of hydrogen in pure hydrocarbon solvents at advanced temperatures and pressures has been developed. The method uses the virial equation of state for the vapor phase fugacity and modified UNIFAC group contribution correlation for activity coefficients in the liquid phase. An expression for Henry's law constant for hydrogen in a reference solvent as a function of temperature has been used to evaluate the supercritical fugacity of the pure hydrogen as a hypothetical liquid whenever T is greater than the critical temperature for hydrogen.

It has been shown that the UNIFAC group contribution method can be applied to predict the solubility of hydrogen in pure hydrocarbon solvents. The necessary parameters have been presented for calculations of hydrogen solubilities in hydrocarbon solvents for pressures up to 680 atm. and for temperature up to 600 °K. The average errors to be expected in the predicted solubilities are smaller than 13 %, if the temperature lies within the ranges indicated in Table 3.8 and in Table 3.9. In general it cannot be recommended to apply the UNIFAC method at temperatures outside the temperature range for which the experimental solubility data considered.

The method has certain features that made it elegant. In this work, we introduce the correlation for the third virial coefficients to calculate the vapor phase fugacity coefficients at high pressure. A Wagner's expression for group-interaction parameters suggested in UNIFAC model has been proven to be more suitable for prediction hydrogen solubility in

petroleum fractions. Moreover, three hydrocarbon solvents have been used as a reference solvent to evaluate the reference Henry's law constant of hydrogen which are shown to work well for prediction of hydrogen solubility in a variety of hydrocarbon solvents.

Since gas-liquid equilibrium calculations at high pressures and high temperatures are more difficult than those at low or modest pressures and temperatures, the model has certain limitations also. Firstly, our method for calculating the reference fugacity of pure hydrogen in the liquid state (f_2^0) is changed into one of estimating a Henry's constant for a reference solvent which is only a function of temperature ($f_2^0 = H_{2,r} \gamma_{2,r}^\infty$). The effect of pressure on f_2^0 is neglected. This expression for f_2^0 may lead to some error at high pressure. But so far the pressure dependency of reference Henry's law constant at constant temperature is still not available.

Secondly, the effect of pressure on liquid phase properties is significant only at high pressure. At low or modest pressures this effect can often be neglected or approximated; the common approximation made in this work is to assume that the standard-state fugacity depends on pressure (as given by the Poynting factor) but the activity coefficient is independent of pressure at constant composition and temperature. Since the assumption that activity coefficient γ_i is independent of pressure is equivalent to assuming that in the liquid phase the partial molar volume \bar{V}_i^L is equal to the molar volume of pure liquid i . At high pressure, especially in the critical region, this assumption can lead to serious error. But, so far the pressure dependence of the activity γ_i at constant temperature and composition is somewhat uncertain.

Thirdly, the vapor phase fugacity coefficient ϕ_i may be found from the virial equation of state suitable for high pressures, as discussed in sec. 3.3.1. Such equation tends to be complex. By contrast, at low pressures we can often set $\phi_i = 1$, and at modest pressures we can often calculate ϕ_i with the virial equation truncated after the second term. In

this work, we introduced the third virial coefficients to evaluate the vapor phase fugacity coefficients at high pressures. Due to the limitation of experimental data source, the correlations for the fourth and higher virial coefficients are still not available.

The model for hydrogen solubility in pure hydrocarbon solvents has been applied to petroleum fractions. A new procedure for characterizing crude oil fractions has been established. Functional group concentrations were estimated by means of suggested group models with a non-integer number n as a function of the mid-boiling point of the cut.

The validity of the model structure was tested by calculating the deviations between predicted and experimental molecular mass. The procedure has been found to work well for different petroleum fractions.

The hydrogen solubility in petroleum fractions was calculated by modified UNIFAC model with the new group-interaction parameters as a function of temperature obtained from chapter III. The comparison between predicted and experimental solubilities confirms the suggested model structure of crude oil cuts validity. It was found that hydrogen solubility could be reasonably predicted by using the model we have already developed with 7 % average error at one atmosphere.

Many attempts have been made to correlate gas solubilities, but success has been severely limited because, on the one hand, a satisfactory theory for gas-liquid solutions has not been established and on the other, reliable experimental data are not plentiful, especially at high pressures and high temperatures. Hydrogen solubility data in petroleum fractions at modest temperature and one atmosphere has been measured and published by various researchers over a period of time. However, at high pressures and high temperatures, data is scarce. Any effort towards the generation of data for those conditions would be worthwhile. Besides, the attempt to establish pressure dependence of activity coefficient in UNIFAC model will be much helpful to describe the phase behavior at high

pressures precisely, and will be expected to obtain the much better results for gas solubility calculations.

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PART 2

**AN APPARATUS FOR MEASUREMENT OF
HYDROGEN SOLUBILITY IN HYDROCARBONS**

Michael McCormick

and

V. N. Kabadi

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TABLE OF CONTENTS

I.	INTRODUCTION	1
II.	BACKGROUND	1
III.	EXPERIMENTAL PROCEDURES	10
	3.1 Experimental Setup	10
	3.2 Solubility Cell	13
	3.3 Sampling Valves	13
	3.4 Gas Chromatograph	17
IV.	REFERENCES	25

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
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I. INTRODUCTION

Gas solubilities measured at high temperatures and pressures are used for calculation of the derived thermodynamic quantities. The determination consists essentially of bringing the solvent in equilibrium with the gas at known temperature and pressure, withdrawing the vapor and liquid samples under the same conditions and analyzing it for its composition. Sampling is the most critical operation in this experiment and devising an appropriate sampling method is important. The difficulties arise due to lack of visual control and the large concentration gradients that occur during the withdrawal of the sample. The equilibrium apparatus consists of a solubility cell in which the solvent is saturated with a gas. After attainment of equilibrium, a sample of the liquid and vapor phase are withdrawn under identical conditions of temperature and pressure.

Vapor-liquid equilibrium data in hydrogen/solvent systems has been the subject of investigation by several researchers owing to their industrial importance and scientific interest. Such information is useful not only for the engineering design of gas-liquid contacting and separation equipment but also for the study of reaction kinetics in coal liquefaction mixtures (Simnick et al., 1977; Sebastian et al., 1978). Gas-solubility information at elevated temperatures and pressures is also an important parameter in high pressure processes such as coal liquefaction (Matsumoto and Satterfield, 1985) and for the design of gas absorption and stripping columns in chemical industries.

In this work, we are building a semi-flow type of equipment where the hydrogen gas will flow through a static solvent placed in a solubility cell. Simnick et al. (1977) have found that equilibrium can be attained at short residence times at high temperatures using a flow type of equipment. They have also found that the thermal decomposition that would normally occur at high temperatures is minimized due to the short residence times. A static type of equipment has been used for determining hydrogen solubility in coal liquids by Harrison et al., (1985).

II. BACKGROUND

i. *Experimental apparatus*

a. Flow type system proposed by Simnick et al. (1977): Simnick et al. (1977) adopted a flow type of design for their equilibrium cell to reduce the residence time of the sample at high temperatures that in turn reduced the thermal decomposition of the hydrocarbon/solvent. All the parts in the equipment used was made of 316 type stainless steel. A similar experimental design has been used by Sebastian et al. (1980) in their studies on a hydrogen/n-decane system, as well by Simnick et al. (1980) in their studies on a ternary system of hydrogen + methane + tetralin.

The basic design used by these researchers to study the vapor-liquid equilibrium data consisted of the following parts. Figure 1 is a schematic diagram of the vapor-liquid equilibrium apparatus used by Simnick et al. All parts exposed to the high temperature and pressure are made of stainless steel type 316.

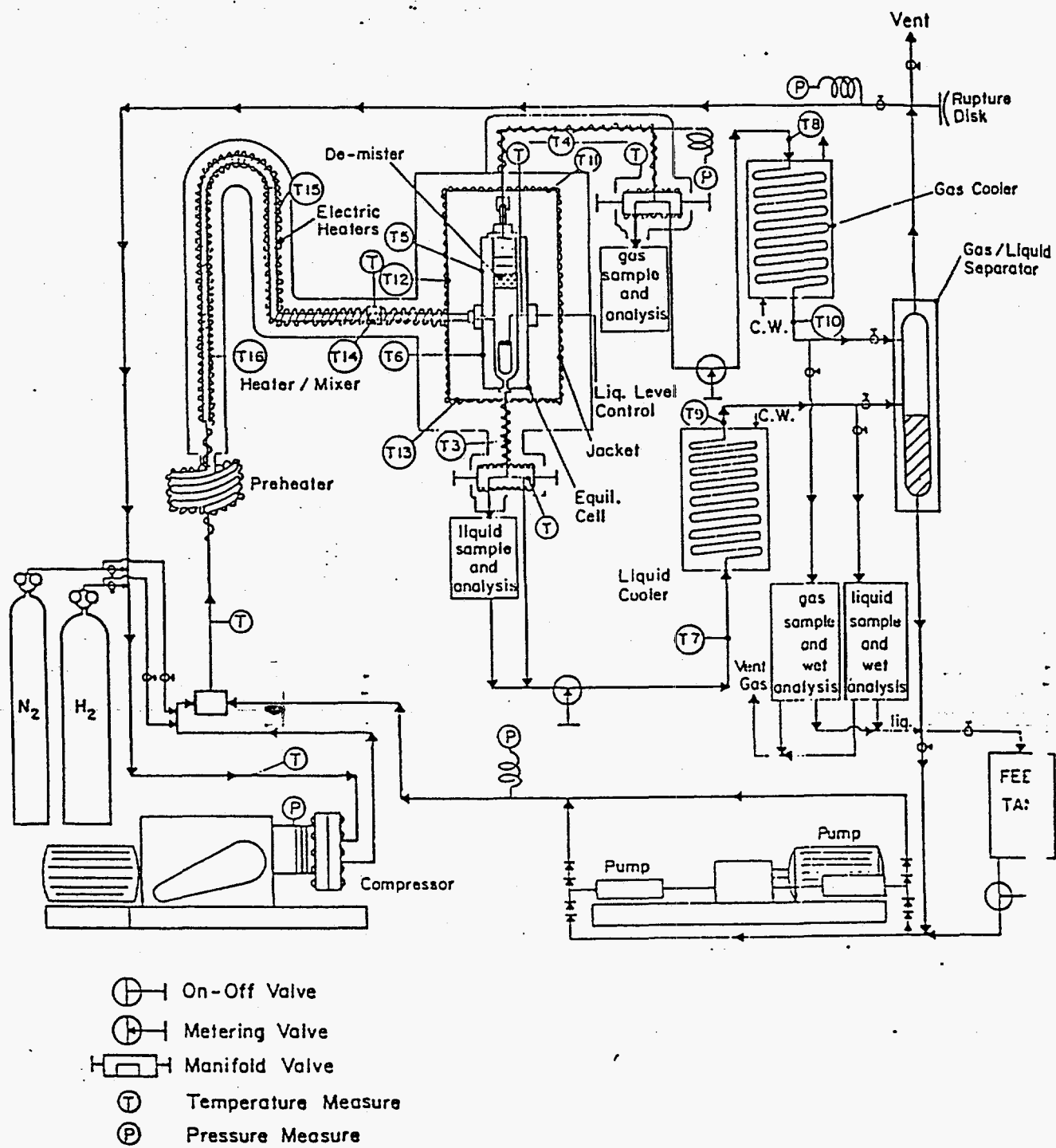


Figure 1. Vapor-liquid equilibrium apparatus (Simnick et al., 1977)

Hydrogen is supplied to the system from a high pressure cylinder through a pressure regulator. The experiments conducted by Simnick et al., were conducted at a pressure of 120 atm. or less. A compressor was used for the higher pressure. The fluctuations in pressure caused by the compressor was greatly reduced by a 500 ml pressure vessel equipped with a pressure regulator on the output line of the vessel, which is downstream from the compressor.

The liquid feed is delivered either from a Ruska pump (syringe type, 1000 ml contents) or a Hills-McCanna U type metering pump at rates of 500 to 2000 ml/hr. The flow from a Ruska pump is even, while that from the Hills-McCanna type, quite uneven. To reduce these fluctuations, a cylindrical vessel of 75 ml is installed in a vertical portion of the liquid line. The liquid flow is through the lower part of the vessel, while the hydrogen flow is through a valve connected to the top of the vessel. A teflon boat floats on the surface of the liquid to reduce depletion of the gas by absorption.

The hydrogen gas and the liquid feed are joined at a tee. The two-phase mixture is heated in a tube, initially in a small size tubing (2.11 mm ID) and finally in a larger size tubing (5.15 mm ID). The larger size tubing is fitted with an internal notched and twisted ribbon along its length to promote mixing of the flowing fluids. Heating is by means of electrical heating tapes wound on the outside surface of the tubings. The rate of heating is controlled so that the temperature of the feed stream is within 1°C of the equilibrium cell temperature.

The mixture is then fed into the equilibrium cell, where the gas and liquid phases are separated. The equilibrium cell is approximately 90 ml in volume. Two nozzles are welded to opposite sides of the cell. One nozzle is for the gas/liquid feed stream, while the other nozzle is for a liquid level detector. The electrical insulation is rated for a temperature of 430°C that sets the maximum temperature that can be reached by this apparatus. A pool of liquid is always maintained in the cell to avoid entrainment of gas in the liquid withdrawn from the cell. The liquid level is sensed by a capacitor in the cell and displayed on an oscilloscope screen as a horizontal line. By adjusting the metering valve at the bottom of the cell, the liquid level is always maintained and the capacitor is always kept half immersed. The entrained liquid droplets are prevented from escaping by a demistor pad in the equilibrium cell.

A copper jacket 32 mm thick encloses the entire cell to ensure uniform temperature in the equilibrium cell. Heating wires insulated in fishspine ceramic beads placed in grooves cut on the outside surface of the copper jacket provides adiabatic heating. A 76 mm thick insulation surrounds the entire copper jacket to maintain high temperature and promote isothermal conditions within.

The liquid stream from the bottom of the equilibrium cell is reduced in pressure, cooled and fed to a separator to separate the dissolved gas, which is vented to the atmosphere. The separated liquid is recharged to the liquid pump after purification. The gas stream from the top of the equilibrium cell is similarly reduced in pressure, cooled and fed to the same separator as the liquid stream.

The temperature of the equilibrium cell is measured by calibrated type K chromel-alumel thermocouples inserted in the wall of the cell. The thermocouples kept on opposite sides gave similar readings, indicating close approach to isothermal conditions in the cell jacket. The temperature of the feed stream to the cell is measured with a sheathed thermocouple housed in a valve body like block. The feed fluid flows through the block and around the sheath. The block is kept adiabatic by means of insulation and heating outside the insulation. A bare couple is attached to the outside surface of the block. Isothermal and adiabatic conditions for the thermocouple block is indicated by similar readings for the bare couple and sheathed couple.

This is achieved by adjusting the heater.

Lin et al., (1981) have used a similar experimental apparatus in their investigation of solubilities of hydrogen and methane in coal liquids. Simnick et al. (1980) modified the above apparatus in one of their later studies. Changes were made in the gas-feed system and in the sampling and analysis systems. In this modified system, a Matheson gas mixer was installed to provide a mixed gas stream at a set composition from individual cylinders of gases. Downstream from the blender, two vessels of 1L each were placed in series in front of the compressor to reduce pressure fluctuations and to promote mixing. This method is the most suitable for our type of application that involves both high temperature and pressure.

b. Static type system suggested by Harrison et al., (1985): Static systems have also been used for the determining hydrogen solubilities (Harrison et al., 1985). The authors claim that the static type of system is most suitable for study of coal liquids and complex systems containing water, ammonia, hydrogen sulfide and hydrogen. This method, though simple to

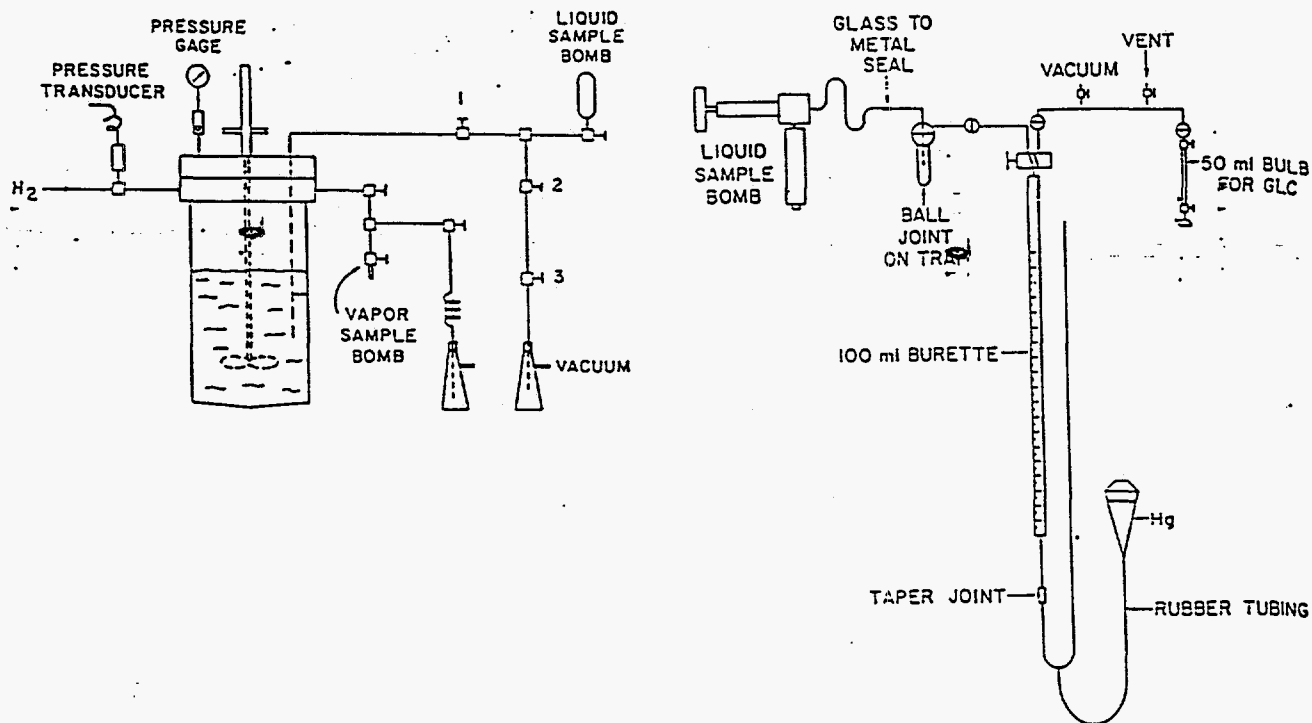


Figure 2. Equilibrium vessel cell and sampling system (Harrison et al., 1985).

operate, reasonably accurate and relatively low in cost, suffered due to the increased probability of sample reactions at high temperatures due to the long exposure times (Harrison et al., 1985). This system essentially consisted of a 2-L autoclave and sampling system, most parts being made out of 316 type stainless steel. The gases, compressed to 3700 psi, were mixed with 1300 cc of solvent in the autoclave, using a stirrer. A schematic description is given in Figure 2. Mixing and contact between the gas and liquid phases were effected by a hollow shaft mixer that drew the gas down the tube and dispersed it into the liquid. The seal for the stirrer into the cell has to be good enough to retain the high pressure.

c. Static type system suggested by Laugier et al., (1980): The experimental apparatus used by Laugier et al., (1980) consisted of sampling both the liquid phases that are in equilibrium. This was a static method.

d. Static type system suggested by Brunner (1979, 1980): A static system was used by Brunner (1979, 1980) which consists of three sections, i.e., gas supply, gas saturation, and degassing. In this method, Brunner used a thermostatted high-pressure equilibrium cell equipped with an electromagnetic reciprocating stirrer and the solvent is substantially degassed by prolonged evacuation. In this method, the pressure is measured by a strain-gage pressure transducer that is calibrated with the aid of a pressure balance before and after each series of experiments. The reproducibility of these pressure-transducer calibrations is better than 0.1 percent. A schematic diagram for measuring the gas solubilities used by Brunner (1980) is given in Figure 3. The solvent is saturated with hydrogen in the autoclave with intense stirring (approximately 30 minutes). For higher viscosity liquids, higher stirring times are necessary to effect complete saturation (up to 60 minutes). A sample of liquid is then drawn from the cell and let down to atmospheric pressure at constant temperature. The gas solubility being sought is calculated from the amount of gas that is liberated. The major disadvantage of this method is that the amount of the soluble hydrogen can change during the degassing operation. Moreover, the author has not considered the solvent vapor pressures into consideration that might condense in the glass burette during the degassing operation.

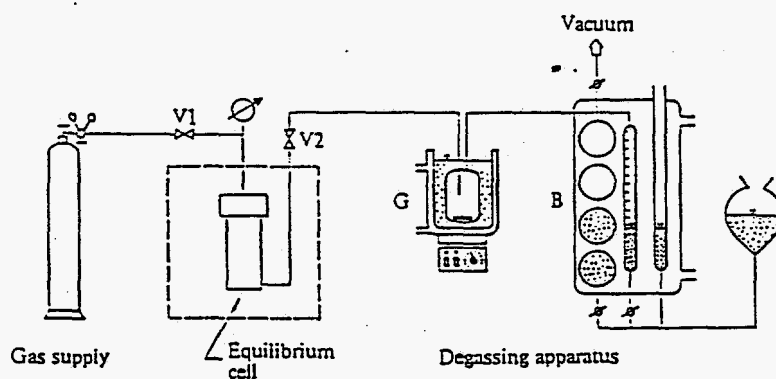


Figure 3. Schematic diagram for measuring gas solubilities (Brunner, 1980)

e. Static type system suggested by Ding et al., (1985): A similar system was used by Ding et al., (1985) which consisted of a high pressure equilibrium cell with two in situ hydrogen probes, with temperature and pressure measuring devices. The cell is also equipped with sampling tubes for rapidly withdrawing gas and liquid samples and thermocouples for monitoring and controlling temperature. A schematic diagram of the experimental set up is given in Figure 4. Liquid samples are withdrawn from the bottom of the cell into a low-pressure sampling section that consists of expansion cylinders, a Toepler pump and sampling tubes. A Hewlett-Packard chromatograph system is used to determine the compositions of the sample. The in situ hydrogen probes are used to find out if equilibrium is reached before the samples are drawn.

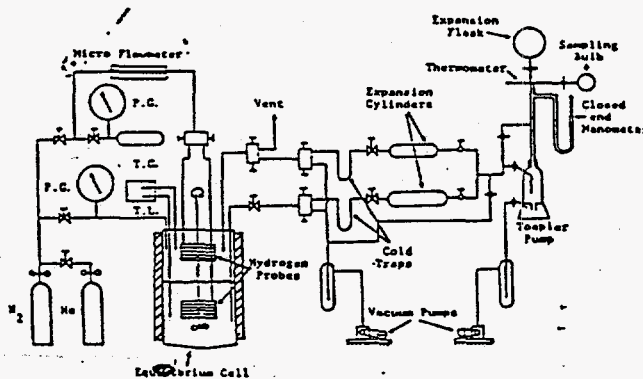


Figure 4. Schematic diagram of the experimental set up (Ding et al., 1983)

The various other methods used for the determination of gases in liquids has been reviewed by Markham and Kobe (1941). One of the methods used to determine the solubility of gases in liquids is the saturation method (Kruger and Nobel, 1961). This method measures the amount of gas taken up by the liquid after it has been degassed. The saturation method is time consuming. The gas in a closed system has to be brought into intimate contact with the liquid to achieve saturation within a reasonable length of time. Intimate contact between gas and liquid was achieved by passing the gas through the liquid as small bubbles (the dissolved hydrogen is expelled from the saturated solution by passing argon). To achieve good liquid-gas contact, the diameter of the solvent container must not be too large. Since solubility of hydrogen is low, a large amount of solvent is required. To keep the pressure difference between the top and the bottom of the cell as small as possible, Kruger and Nobel chose a helical shape for their saturator (Kruger and Nobel, 1961).

ii. Sampling and analysis techniques

a. Sampling technique suggested by Simnick et al. (1977, 1980): There are two sampling and analysis systems available for flow type of equipments (Simnick et al., 1977). In one system, the effluents from the cell at high temperature and high pressure are diverted by means of a manifold valve, sampled, and analyzed in a gas chromatograph. In the second system used by Simnick et al., (1977) the cell effluents are sampled after the temperature and pressure are reduced. In this system, the diverted stream enters a trap where the heavy component is retained as a liquid at ambient conditions and later weighed with an analytical balance. The quantity of hydrogen gas coming out of the trap is determined volumetrically, while the gas liberated from the liquid phase samples is collected in a graduated cylinder over water. A wet test meter is used to measure the larger quantities of hydrogen in the gas phase samples. The volume determinations are accurate to 0.5%.

Quantitative separation is achieved at the liquid trap due to the enormous differences in volatilities between hydrogen and tetralin. The quantity of solvent in the sample is calculated to be the sum of the weighed liquid and that vaporized into the gas volume (which is very minute). The quantity of hydrogen in the sample is the sum of that in the gas and liquid, which is calculated from Henry's law.

To determine the extent of thermal decomposition, the cell effluent was analyzed from selected runs using liquid chromatography (Simnick et al. 1977; Sebastian et al., 1980; Simnick et al., 1980). In a later study by the same group of researchers (Sebastian and Simnick et al., 1980) on a hydrogen/n-decane system, no decomposition products were obtained at any of the conditions.

In the system used by Simnick et al., (1977, 1980), the liquid and gas streams are cooled and reduced in pressure and then fed to a common separator to remove the hydrogen, which is then vented to the atmosphere. Samples are diverted from the cell effluents after they are reduced in temperature and pressure before they enter the separator. The diverted stream enters a trap where the condensate is retained and removed for weighing. The quantity of gas leaving the traps is calculated volumetrically. Due to the enormous differences in volatilities of hydrogen and the solvent, nearly complete separation is achieved by the liquid trap. The amount of hydrogen in a sample is the sum of that in the gas phase plus that dissolved in the liquid. The hydrogen dissolved in the liquid is found from Henry's law using the Henry's constant values from literature (Sebastian et al., 1978).

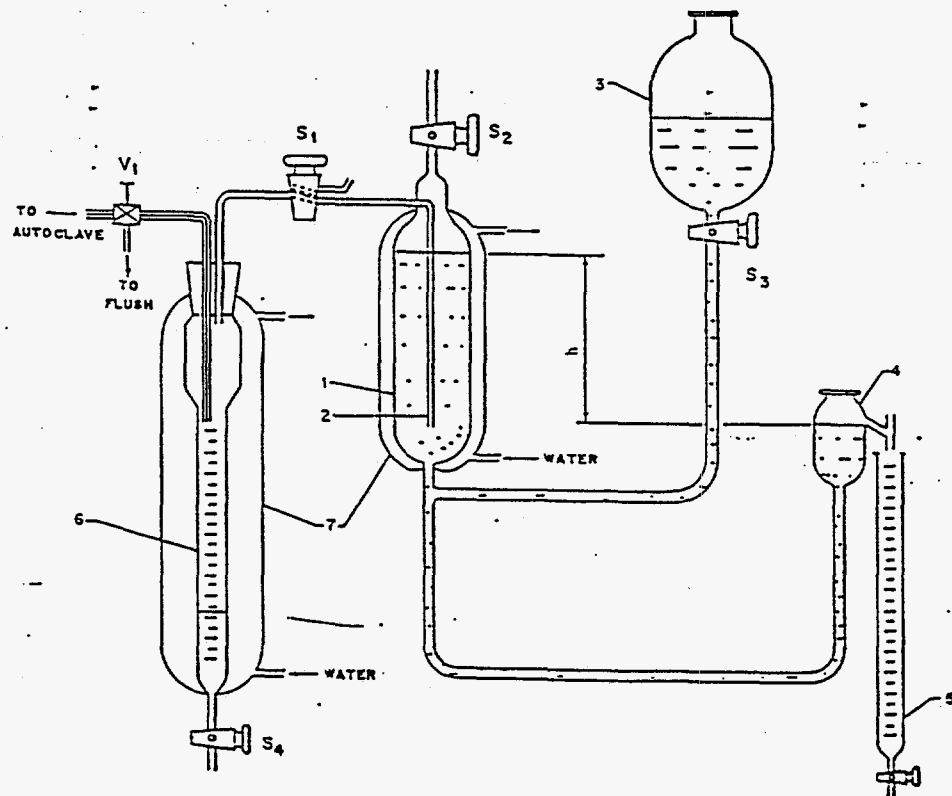
b. Sampling technique suggested by Harrison et al. (1985): In the system used by Harrison et al., (1985), the vapor samples were drawn into an evacuated bomb (see Figure 2). In this system, the volume of the tube from the bottom of the dip tube to valve 1 was minimized to reduce holdup and was about 1.5 cm³. The liquid in this tube was first drawn off and isolated between valves 2 and 3. Liquid samples were then taken into the sample bomb while maintaining the autoclave at constant pressure. The autoclave was subsequently repressured with hydrogen and reequilibrated before withdrawing the liquid sample. The liquid sample was withdrawn while maintaining the autoclave at constant pressure. The gas volume was measured by their in-house apparatus and analyzed using a GLC. The remaining liquid sample was analyzed using mass spectrometry.

c. Sampling technique suggested by Laugier et al. (1980): Laugier et al., (1980) used gas liquid chromatography for their analysis and mention that it is best suited for hydrogen-hydrocarbon concentrations. The method consisted of drawing a sample from the liquid and

vapor phases by means of a valve. When the valve is opened for a very short time (10^{-2} seconds), a sample of about $1 \mu\text{L}$ of each phase is automatically injected from a 50 cc cell into a chromatographic circuit. The maximum temperature for which these researchers conducted experiments was about 400°C . The temperature was maintained to within 0.2°C and measured with an accuracy of 0.5°C . They also mention that the thermal conductivity detector is the most suited to analyze hydrogen-hydrocarbon mixtures. Selective sensitivity with a thermal conductivity detector depends on the nature of the carrier gas. To maximize the sensitivity of measurement, it was found necessary to use a carrier gas such as neon with a thermal conductivity coefficient value that lies between that of hydrogen (highest thermal conductivity coefficient) and hydrocarbon (small thermal conductivity coefficient). To properly use the detectors, the polarity of electrical signal between hydrogen and hydrocarbon measurement needs to be changed (Laugier et al., 1980).

d. Sampling technique suggested by Brunner (1979, 1980): Brunner (1979, 1980) measured the volume of dissolved hydrogen gas using a degassing apparatus. However, the temperature range used in his experiments are 298 K, 323 K, and 373 K and pressures up to 10 MPa. The Kesler-Lee method was used for estimating molecular weights because of its applicability to a wide range of hydrocarbons by Ding et al., (1985).

e. Sampling technique suggested by Choudhary et al., (1982): A simple sampling and analysis technique for determining the solubility of gases in liquids at high temperatures and pressures has been suggested by Choudhary et al., (1982). A schematic of the apparatus is given in Figure 5. It essentially consists of two parts. In the first part, the desorption of the gas occurs



Solubility apparatus: (1) gas collector; (2) gas inlet tube; (3) water reservoir; (4) pressure adjusting device; (5) graduated buret; (6) sample buret; (7) water jacket.

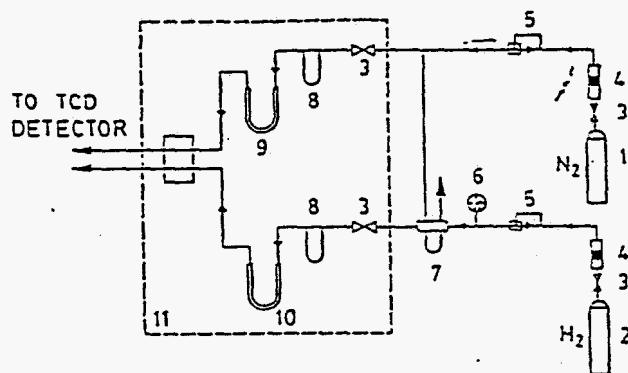
Figure 5. Solubility apparatus (Choudhary et al., 1982)

at atmospheric pressure and the volume of the sample is measured quantitatively. The authors have found out the effectiveness of the apparatus for water but it is to be expected that the apparatus could work as well with any other liquid. The liquid (in the paper cited, the liquid is water) is equilibrated with hydrogen at a known temperature and pressure for 1 h in an autoclave using a stirrer speed of 1000 rpm. The water in the gas collector and the reservoir was also saturated with hydrogen. The apparatus was prepared for the solubility measurement by adjusting the water level of the gas collector to a level close to that of the gas inlet tube.

Once the equipment was prepared for the solubility measurement, the stirring of the liquid in the autoclave was stopped and the outlet tube of the autoclave was flushed. After flushing, the inlet valve was opened and the liquid sample was introduced into the sample burette at a slow rate. The volume of the desorbed gas was measured by determining the volume of water displaced from the gas collector into the graduated burette. All the solubility experiments were repeated four times to ensure the reproducibility of the data.

The above work has been used to determine the solubility of hydrogen in water. The present apparatus may not be suitable for measurement of hydrogen solubility in petroleum fractions because of its density and viscous nature.

f. Sampling technique suggested by Fahim and Elkilani (1991, 1992): Recently, a pulse technique has been used by Fahim and Elkilani (1991,1992) to measure the solubility of hydrogen in different crude cuts, based upon methods suggested by Yow et al., (1983) and Mousa (1984) (cited in Fahim and Elkilani, 1991). In this method, a Varian Vista 6000 gas chromatograph connected to a six-way valve with a 1 mL sample loop was used to measure the hydrogen solubility of the crude oil fractions. The carrier gas used was nitrogen, with different flow rates. A schematic of the experimental apparatus for this technique is shown in Figure 6. Solid inert particles of red firebrick was used as the packing material. The ratio of initial weight of-liquid to weight of liquid plus solid is defined as liquid loading. A liquid loading of 0.5 was used in these experiments. The liquid loaded column was used to record and analyze the response signal, while the input signal was recorded by using a column, with the same dimensions, packed with solid material only. The maximum experimental temperature used was 328 K, to avoid the volatilization of the naptha cut during the runs.



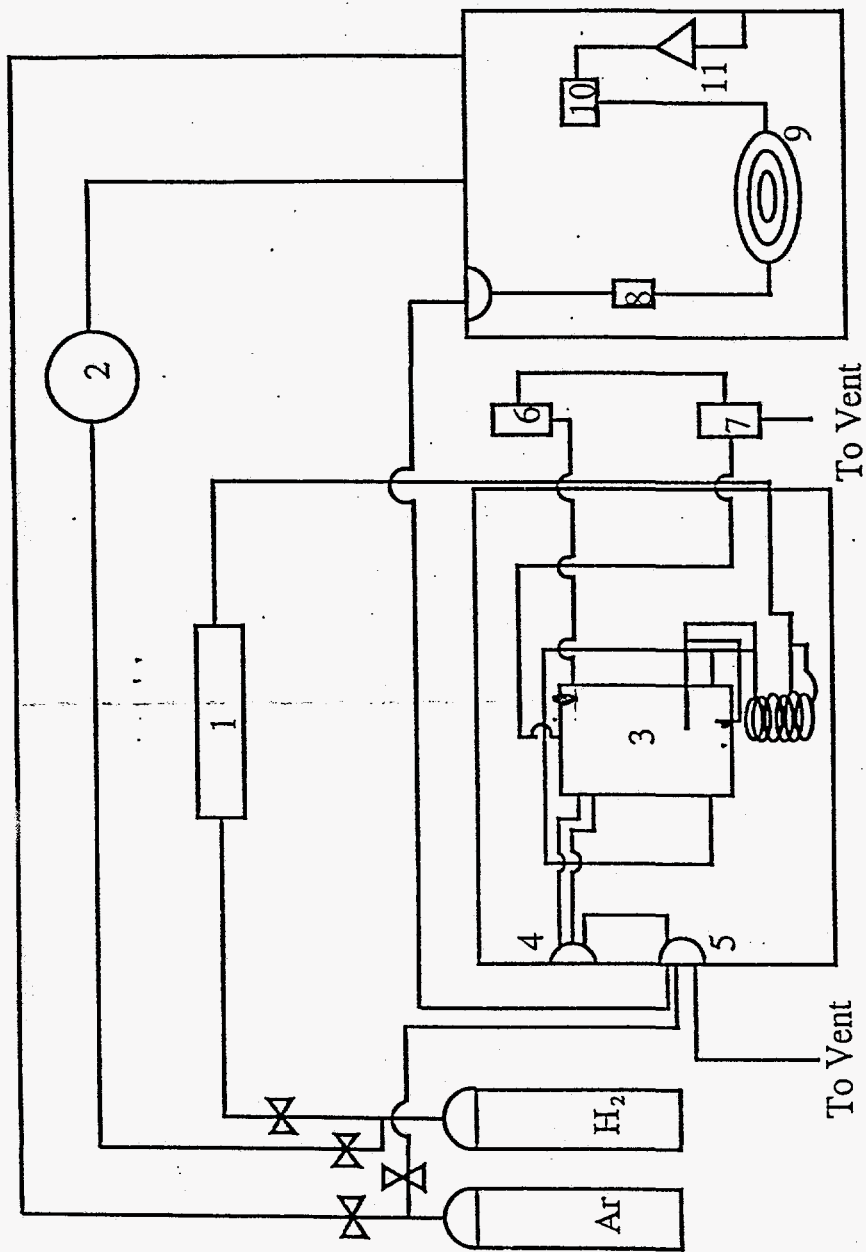
— Experimental apparatus for pulse technique:
 1. Nitrogen cylinder (carrier gas); 2. Hydrogen cylinder (solute gas); 3. Needle valve; 4. Rotameters; 5. Flow regulator;
 6. Pressure gauge; 7. Six-way valve; 8. Flow meters;
 9. Reference column (for TCD); 10. Tested column (crude oil cut-loaded); 11. Varian 6000 GC.

Figure 6. Experimental apparatus for the pulse technique (Fahim and Elkilani, 1991, 1992)

III. EXPERIMENTAL PROCEDURES

3.1 Experimental Setup

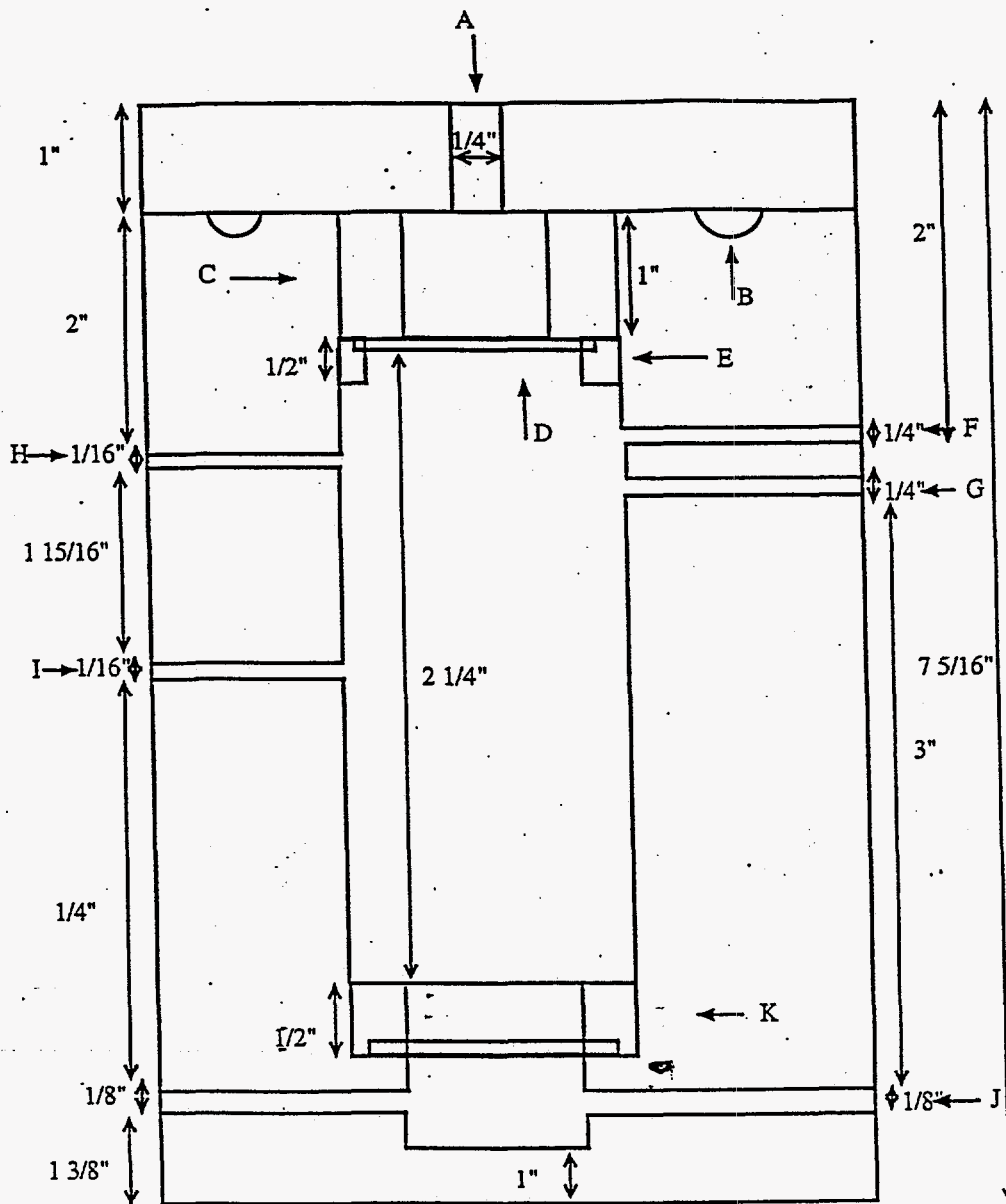
The apparatus for measuring the solubility of hydrogen in hydrocarbon feedstocks at high temperatures and pressures is illustrated in Figure 3.1. It is a combination of a flow type apparatus and a sampling method all in one package. Of all the methods described above, the flow type proposed by Simnick et al. (1977) was the most suitable fit for the type of research involved. The reason being was a flow-type apparatus would minimize the residence time to attain equilibrium which in turn would minimize the possible thermal decomposition and side reactions that might occur at the high temperatures and pressures that will be applied during the study. The proposed sampling technique is a combination of the methods indicated by Laugier et al., (1980) and Fahim and Elkilani (1991, 1992). The major advantage of this combination is that there is a gas chromatograph capable of analyzing both the hydrogen and hydrocarbons. This method has been modified to suit research requirements by incorporating an on-line gas chromatograph with a six-port valve within the oven so that the sample is an exact representation of the saturated liquid present in the solubility cell. The major reason for using gas chromatography as an analytical tool for the quantification of hydrogen gas present in the saturated liquid is because of its simplicity, speed, and reproducibility of measurements.



Legend:

- 1. Mass flowmeter
- 2. Step-Down Regulator
- 3. Solubility Cell
- 4. Three-port Valve
- 5. Six -port Valve
- 6. Pressure Transmitter-Controller
- 7. Electronic Control Valve Actuator
- 8. Split-less injector
- 9. Micropacked column
- 10. TCD Detector
- 11. Flame Ionization Detector

Figure 3.1 Hydrogen Solubility Apparatus



Legend:

- | | |
|---|------------------------------------|
| A. Electronic Valve Actuator Outlet | G. Pressure Transmitter Outlet |
| B. O-ring | H. Vapor Sample Port |
| C. SS Threaded Cap | I. Liquid Sample Port |
| D. Micron Filter | J. Hydrogen Port |
| E. SS Threaded Bushing; 1/2" High, 2 1/8" O.D | K. SS Threaded Bushing; 2 1/8" O.D |
| F. Thermocouple inlet | |

Figure 3.2 Solubility Cell

3.2 Solubility Cell

The modified experimental apparatus consists of a solubility cell contained in a high temperature oven. The cell is made of 316 stainless steel and contains two 2 μ m filters placed at the top and bottom of the cell. Refer to Figure 3.2. This is to prevent the spillage and leakage of the hydrocarbon from the cell into chambers where no contamination needs to occur. At the bottom of the cell, four ports make up the chambers in which hydrogen will enter the cell. The tubing connected to these ports is designed such that the distance traveled by the hydrogen into the ports is equal on all four sides. The gas passes through the filter in the form of small bubbles ensuring intimate contact with the liquid. This will help achieve saturation or equilibrium of the system within a short period of time. Other ports incorporated in the cell design include two ports on the side of the cell used for obtaining liquid and vapor samples, two more ports opposite the cell containing a thermocouple and pressure transmitter respectively, and a port on the top of the cell for the use of an electronic valve actuator linked to the pressure transmitter to control pressure within the cell. Also contained in the oven are a three-port valve and a six-port valve and a heater coil. The coil is used to heat the hydrogen gas before it enters the cell.

3.3 Sampling Valves

The two position valves are used for the sole purpose of obtaining the liquid and vapor samples from the cell after equilibrium has been attained. A diagram showing the three-port valve and six port valve at the two different positions are displayed in Figures

3.3 and 3.4, respectively. The three-port valve is set up to collect the vapor and liquid samples. A switch on the three port valve is used to control the transfer of the liquid or vapor sample to the six port valve where it is trapped in a 5 μ L loop. Figure 3.4 shows the tubing routes and positions A and B of the six port valve. In position A, the sample is shown entering port 3 and traveling through the sample loop and then out to the vent. The vent has a needle valve connected to it to prevent extensive flow of the sample. The carrier gas (argon) enters port #1 travels to the injection port of the gas chromatograph. In position B, the rotor of the valve changes the port connections such that the carrier gas flows through the sample loop, picking up the sample, and transferring it to the injection port of the GC, while the sample line goes straight to the vent. In the first sequence, the hydrocarbons are held up in the column while hydrogen is allowed to pass through and carried away to the thermal conductivity detector for analysis. In the second sequence, the hydrocarbons are released by the column and carried away to the flame ionization detector for analysis.

The sampling technique designed for the system is very unique because it can measure the composition of both hydrogen and hydrocarbon in the vapor liquid phases accurately and continuously. The major advantage of this technique is the six-port valve can be operated remotely in conjunction with the GC. The sample drawn from the vapor phase is rich in hydrogen, while the sample from the liquid phase is rich in hydrocarbon. Therefore, a selective amount of the components present in each phase have to be sent to the column and the detector to avoid overloading the column and obtain accurate results. To avoid this problem, a split/splitless injection system was added to the chromatograph.

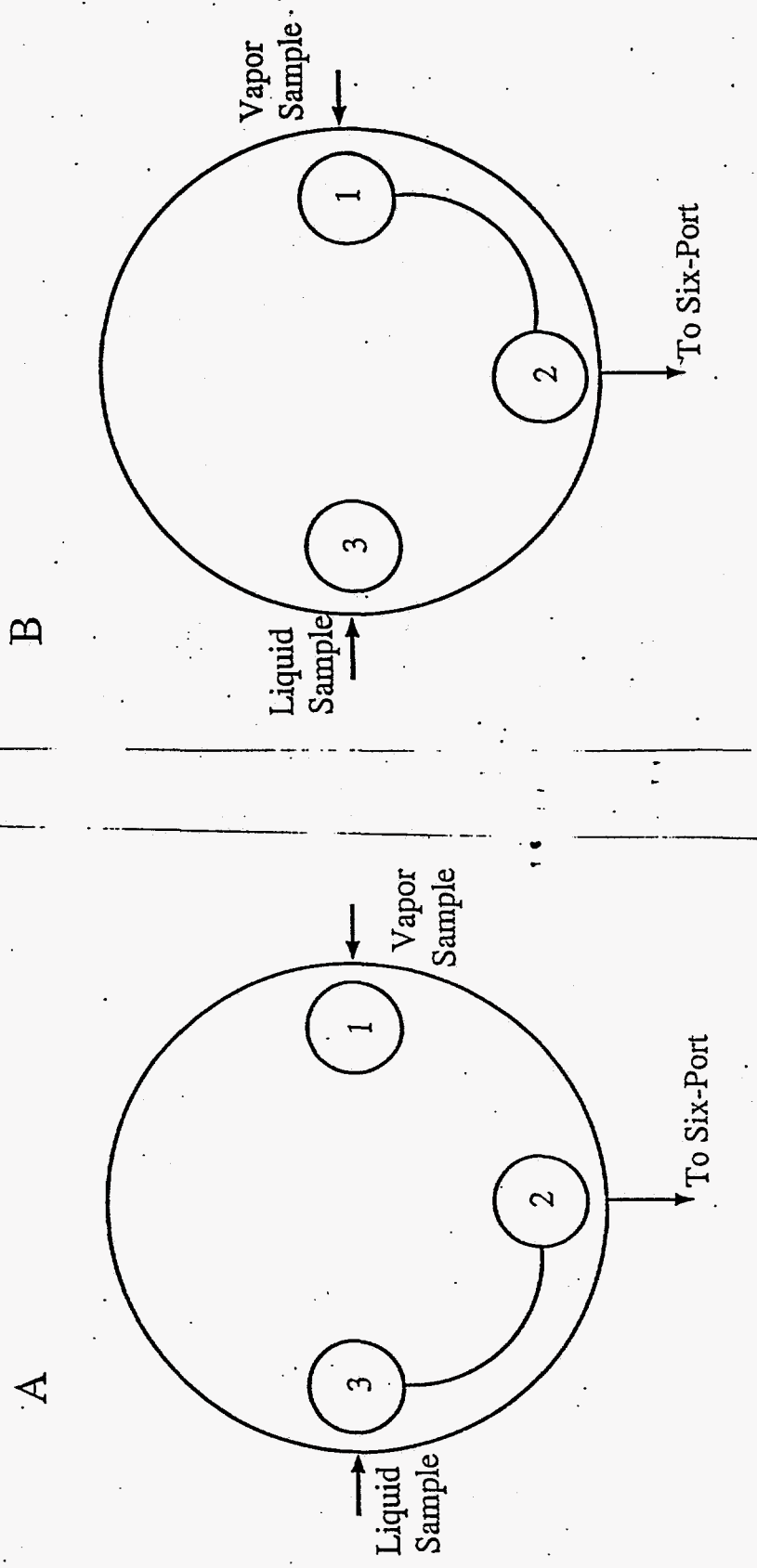


Figure 3.3 Three-Port Valco Valve Setup

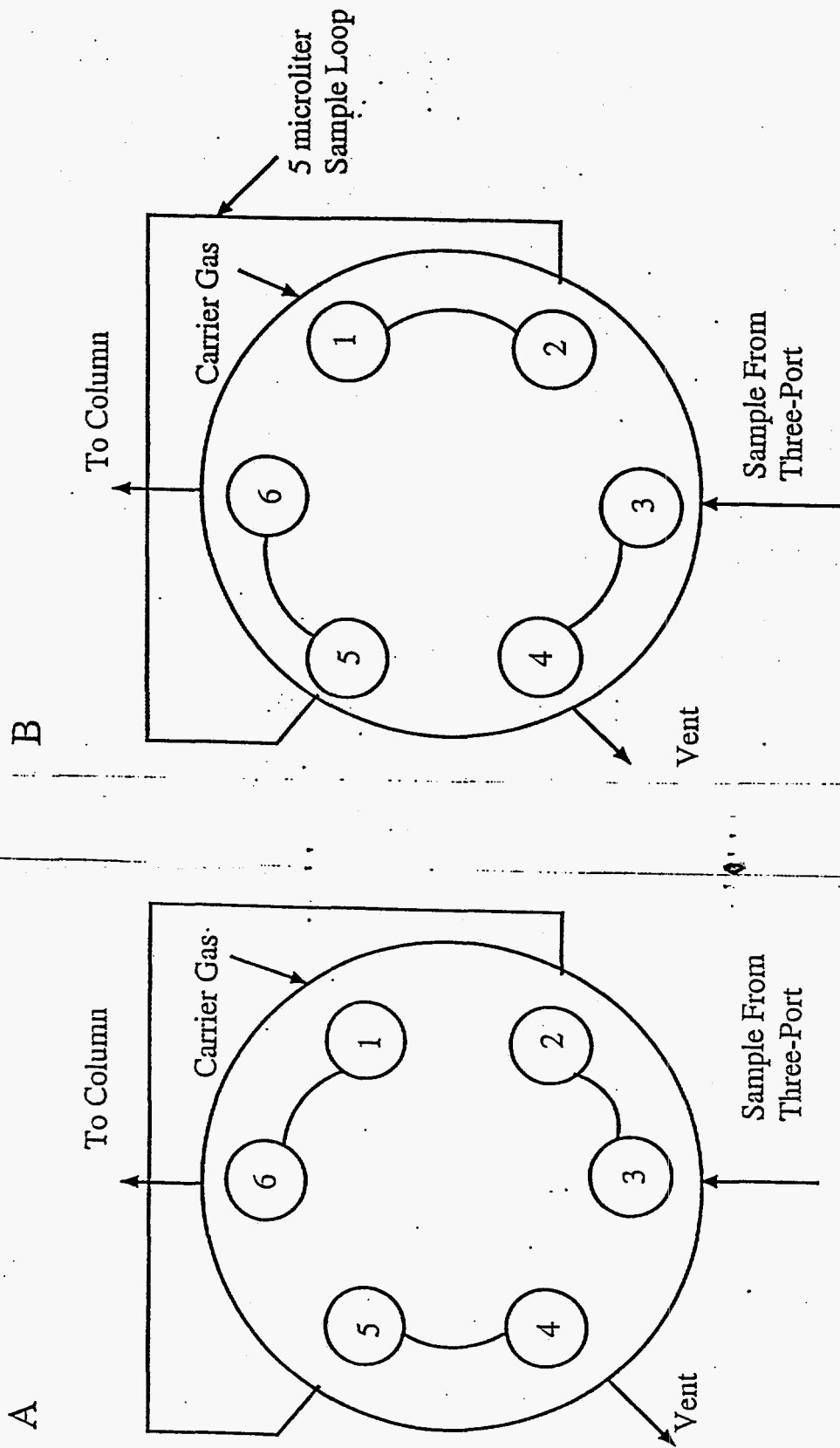


Figure 3.4 Six-Port Valco Valve Setup

3.4 Gas Chromatograph

The type of gas chromatograph that was used for the analysis of this study was a Perkin Elmer Autosystem GC containing a split/splitless injector and flame ionization and thermal conductivity detectors. The system consists of one column; that being a 15 foot micropacked column containing 10% SP-2100 Supelcoport. The micropacked column is used to separate the hydrocarbon as the hydrogen within the sample is allowed to pass through and go to the thermal conductivity detector. The injector is temperature programmed in order to time the analysis of the sample being introduced. The sample enters the split/splitless injector through the carrier gas inlet line of the injector. A liner inside the injector is packed tightly with glass wool. The purpose of the glass wool is to collect any hydrocarbon contained in the sample so that the hydrogen is allowed to pass freely, for a specific time. Initially the temperature of the injector is very low for this collection to occur. The injector is immediately ramped up to the anticipated boiling point of the hydrocarbon in order for vaporization to occur. A timed event is also included in the injector's program. By determining the time taken to analyze a component, the injector can be told to turn the split valve "on" or "off" at the end of the time it takes for the component to be completely analyzed.

To better illustrate this system take for example the analyzation of a liquid sample.

3.5 Method Development

The most critical section of this process is the development of a feasible chromatographic method. This method is needed to ensure an accurate analysis of the sample being measured. Time and temperature, timed events and split ratios are the major parameters involved in developing a precise method. First, the boiling point of the hydrocarbon must be known in order to achieve complete vaporization of the sample. This temperature must be used throughout the program to prevent any condensation from occurring. It is common to use a temperature higher than the boiling point as such a precaution. The run time for the analysis is also needed to give ample time for the sample to travel through the column and to the detectors. Various trial runs should be done to test the time and temperature conditions. In some cases timed events inconcordance with split ratios are incorporated into the method to prevent sample overloading occurring in the detectors.

For this specific process, the boiling point of the hydrocarbon is 300° C. Several trial runs were done setting the injector, oven and detector temperatures above this temperature (350) to determine if a peak of the hydrocarbon can be achieved. The peak is then analyzed and recorded. In order for satisfactory peak analysis to take place, a sharp peak has to be achieved. Because the sample of the hydrocarbon was injected into the GC as a liquid, a broad plateau peak was developed, causing an overload into the detector. Therefore various split ratios were tried with the method until a satisfactory peak was displayed. The gas chromatograph has a split vent needle valve that can be varied to the desired split needed. . The run time considered is based on time taken for the sample to

travel from the six-port valve to the detector. This time is determined at the point which the peak of the sample is first detected. This process is repeated for the hydrogen analysis and both retention times are recorded.

Once the preliminary setup has been done, the method is tested with an injection of a mixture of known amounts of hydrogen and hydrocarbon. Trial runs are continually done until satisfactory results are acquired. The final proposed method is shown below:

Oven temp: 350° C
Split/splitless injector (PSS) temperature 1: 100
Injector Time 1: 2.0 minutes
PSS rate: 200 C/min
PSS Temp 2 : 335 C
PSS Time 2: 7.0 minutes
Carrier Flow: 3.0 ml/min
TCD temp: 340 C
FID temp: 340 C
Total run time: 12 minutes

These parameters are subject to change depending on changing conditions.

3.7 Experimental Procedure

1. Place micron filter in the bottom of cell and tighten bushing.
2. Pour desired amount of hydrocarbon into cell not exceeding top side left port (vapor sample port).
3. Place top bushing with micron filter in cell and tighten.
4. Place clean o-ring in cell groove. Make sure groove is clean.
5. Tighten cell cover using tool prongs.
6. Place cell in oven and connect and tighten all tubing.

7. Leak test all fittings by using commercial air as your gas.
8. Disconnect air from the line and turn on hydrogen and argon gas.
9. Turn on oven and heat cell up to desired temperature (not to exceed 350°C) and pressure.
10. Adjust three-port valve such that liquid will enter into six-port valve.
11. Allow the system to remain at desired temperature for approximately one hour so that system can equilibrate.
12. Allow 5 μ L loop in six-port valve to fill.
13. Switch valve to inject mode to allow sample to be sent to GC.
14. Analyze sample.

(Appendix)

3.5 Micropacked Column

The micropacked column for the gas chromatograph was purchased from SUPELCO. It's specifications are as follows:

Packing: 80/100 Supelcoport, 10% SP-2100
Column: 15' x 1/16' stainless steel
Carrier: Argon, 20 mL/min

Any brand new column must be conditioned when it is first installed. It was conditioned using the following procedure.

1. All heaters must be turned off (oven, injector, and detector).
2. Set carrier gas. Use the optional flow readout and menu template on the GC display panel. Set for 20 mL/min. Then turn the carrier gas valve on the GC counterclockwise until actual flow matched the specified flowrate.
3. Attach one end of the column into the packed injector.
4. Perform a leak test on the system. The GC manual suggests using a 50/50% mixture of isopropyl alcohol and water to avoid contamination.
5. Condition the column using a temperature program. The maximum temperature for the column is 350° C, so conditioning must stay below this temperature. Start the oven at 50° C for 10 minutes then ramp at 5° C/min to a plateau of 345° C and hold for 999 minutes.
6. After conditioning, turn all heater off and allow system to cool. Attach other end of column to split-splitless injector.
7. Perform leak test on other end of column.

3.6 Setting up Flame Ionization Detector

Setting up the FID on the GC is carried out by the following procedures:

1. Attach bubble flowmeter to the FID outlet.

2. Adjust hydrogen flow by the following steps:
 - a. Make sure air flow to GC is turned off. Check by turning air control valve on GC completely clockwise.
 - b. Turn on hydrogen at the tank and adjust the line pressure to 30 psig.
 - c. Turn the hydrogen control valve on GC completely counterclockwise.
 - d. Remove the protective cap from the control valve to bare the needle valve inside.
 - e. Use a small flat screwdriver to turn the needle valve and adjust the hydrogen flow to 65 mL/min. Read the flow from the bubble flowmeter. The carrier gas is flowing continuously at 20 mL/min so the reading that is shown on the flowmeter is the hydrogen flow and carrier gas flow combined.
 - f. Turn the outer ring of the control valve completely clockwise and replace the protective cap.

Note: This procedure must be repeated any time the line pressure is changed from 30 psig.
3. Set air flow to 470 mL/min using the same procedure as in (2).
4. Make sure air is turned off. Heat FID to at least 100° C.
5. Turn hydrogen on and allow the gas to purge the detector for approximately 60 seconds.
6. Press the [Auto Zero] on the GC control panel until the FID Autozero Screen appears. Read the initial signal.
7. Place the ignitor assembly on top of the FID outlet cap until it glows.
8. Hold the ignitor on top and slowly turn on the air until a slight "pop" is heard.
9. Remove the ignitor and read the signal on the display. This signal should be more than the initial signal to let you know that the detector has been ignited. Further check by placing a wrench or smooth metal object over the FID outlet cap and look for condensation to develop.

3.7 Setting Up Thermal Conductivity Detector

1. Turn on the oven and detector heaters. Set detector to desired temperature. In this case, the temperature was set to 300° C. Wait for temperature to stabilize.
2. Open the detector cover to expose the carrier gas outlets and balancing potentiometer.
3. Attach bubble flowmeter to the top of the analytical outlet (port closest to the front of the GC).
4. Measure the column flow rate through the analytical channel.
5. Disconnect the bubble flow meter and connect it to the reference outlet (port closest to the back of the GC).
6. Measure the flow through the reference channel.
7. Repeatedly adjust and measure the flow through the channel until it is within $\pm 20\%$ of the analytical channel flow. This is done by using the TCD reference flow knob.
8. Remove the bubble flowmeter and press [Status Escape] button on GC.
9. Select a bridge current range using Table 3.1 and 3.2
10. Press [Range][Range] and type the appropriate range. Then press [Enter].
11. Balance the bridge by the following steps.
 - a. Press [Autozero] twice.
 - b. Allow the system to stabilize for about 20 minutes.
 - c. Open detector cover and locate the TCD Potentiometer (knob behind detector).
 - d. Adjust the potentiometer until the Autozero display reads between 0.0 and 20.0 mV.
 - e. Wait for drifting to stop as indicated by a constant reading on the display.
12. Close Detector cover.

Table 3.1
Bridge Current Range vs. Max. Detector Operating Temperature

Bridge Current Range	Recommended Maximum Detector Operating Temperature		
	He or H ₂	N ₂	Argon
↓	He or H ₂	N ₂	Argon
↓			
±4	Up to 100° C	DO NOT USE 4	DO NOT USE 4
±3	Up to 300° C	DO NOT USE 3	DO NOT USE 3
±2	Up to 350° C	Up to 110° C	DO NOT USE 2
±1	Up to 350° C	Up to 350° C	Up to 350° C

Table 3.2
Correlation Between Bridge Current and Range

Bridge Current (mA)	Range Entry
Off	± 0
40	± 1
80	± 2
120	± 3
160	± 4

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