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Prediction of Molecular Diffusion Coefficients of Gases in Hydrocarbon Liquids at High Pressure and Temperature

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Abstract

Mass transfer by molecular diffusion is the basic physical mechanism underlying many important areas of chemical engineering and petroleum engineering. In recent years, the problem of mass transfer by the mechanism of molecular diffusion in oil reservoirs, when a non-equilibrium gas is injected into the reservoir, has become increasingly important. In oil recovery projects, gas is injected into oil reservoirs for different reasons such as maintenance of reservoir pressure and enhanced recovery of oil. In these two cases the rate of dissolution of a gas such as methane in a quiescent body of hydrocarbon oil is controlled primarily by the rate of diffusion of the dissolved gas from the gas-oil interface into the body of the liquid phase.

In all the above situations, molecular diffusion of gas into liquid or transfer of dissolved gas between enriched and heavier liquid phase due to differences in compositional gradients between gas and liquid phases is important. The most important property required to determine the rate of mass transfer between the two phases in all these cases is the molecular diffusion coefficient at high pressure and temperature.

The present investigation is aimed at a systematic study of the mechanism of molecular diffusion of gases in liquids by measuring the diffusion coefficients of methane in dodecane and in a typical Iranian crude oil up to a pressure of 35 MPa and at several temperatures. All tests are conducted in an accurate high-pressure diffusion cell with “finite-domain” moving boundary behavior. The data acquired is used to assess the predictions of various available correlations for diffusion coefficients.

Several liquid hydrocarbon swelling tests comprising dodecane and a typical Iranian crude oil as liquids and methane as gas are performed and swelling heights of liquid as a result of gas molecular diffusion are measured at various temperatures (T=25°C to 82°C) and pressures (P=3.2 to 35 MPa), characterized by a sharp increase in volume followed by gradual increase toward the saturation concentration of methane
in the liquid phase. A mathematical model is developed to calculate diffusivities using semi-infinite boundary conditions. In this model, a variable power profile with time is introduced to allow for the moving interface boundary. The current solutions offer significant improvement over those in previous literature that assume a steady-state interface boundary condition with a parabolic concentration profile. The proposed model offers excellent predictions of experimental data for diffusion coefficients of methane-dodecane and crude oil systems.

A computer program using a neural network model is set-up to predict the dimensionless diffusivity for special use with more complex systems such as crude oil reservoir flows in fractures and matrix conditions. The results obtained by this software show about ±2% deviation in comparison with the experimental data from the diffusion cell experiments.
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NOMENCLATURE

a constant in variable power profile (see equation (4.35))

a_0, a_1 coefficients in equation (4.25)

A area of liquid perpendicular to the direction of flow in equation (2.3), \( m^2 \)

b_0, b_1 coefficients in equation (4.29)

C_a instantaneous solute concentration in the liquid phase, \( \text{kg/m}^3 \)

\( \bar{C}_a \) average mass concentration of solute in the liquid phase, \( \text{kg/m}^3 \)

C_{Ai} interfacial mass concentration of solute in the liquid phase, \( \text{kg/m}^3 \)

C_e equilibrium concentration of gas in solution in equation (2.3), \( \text{kg/m}^3 \)

C_k Center vector

C_{ik} Weight factor in network

D diffusion coefficient, \( \text{m}^2/\text{s} \)

D_{AB} diffusion coefficient in dilute solution, \( \text{m}^2/\text{s} \)

f(v) Activation function

f(v) function of the molecular volume

I_k Euclidean summation

J_a rate of diffusion of solute, \( \text{kg/m}^2.\text{s} \)

K_B Boltzman constant, \( \text{J/K} \)

m_A total mass of solute in the liquid phase, kg

M_{WA} molecular weight of solute, \( \text{kg/mol} \)

M_{WB} molecular weight of solvent, \( \text{kg/mol} \)

n variable power profile exponent in equation (4.29)
P  pressure, Pa

P_{CA}  critical pressure of solute, Pa

P_{CB}  critical pressure of solvent, Pa

P_r  reduced pressure

Q  quantity of gas which has passed through interface in equation (2.3), kg

r_A  radius of diffusing molecules, m

r_A  rate of generation by chemical reaction in equation (4.5), kg/m^3.s

S  cross-sectional area of diffusion cell, m^2

t  time, s

T  temperature, K

T_r  reduced temperature

u  velocity of interface, m/s

v_A  solute molar volume at normal boiling point, m^3/kmol

v_B  solvent molar volume at normal boiling point, m^3/kmol

V_0  volume of the liquid phase at time t=0, m^3

V_t  volume of the liquid phase at time t, m^3

w_{ij}  Weight factor for network

X  input vector for network

x  coordinate of direction, m

x_A  composition of solute in liquid phase

y_A  composition of solute in vapour phase
$Z$ liquid height, m
$Z_0$ liquid height at time $t=0$, m
$Z_r$ reduced compressibility factor
$Z_t$ liquid height at time $t$, m
$Y$ output vector for network

**Greek symbols**

$\varphi$ Radial Base Function

$\theta_j$ Internal threshold

$\Phi$ association factor for solvent

$\alpha_1-\alpha_7$ parameters of equation (4.36), given in Table 4.1

$\mu_s$ viscosity of solution, kg/m.s

$\rho$ density, kg/m$^3$

$\rho_0$ density at low pressure, kg/m$^3$

$\rho_r$ reduced density

$v_A$ partial specific volume of solute in the liquid phase, m$^3$/kg

$\omega$ defined by equation (4.30)

$\omega$ acentric factor
1. INTRODUCTION

When a gas and a liquid phase, which are not thermodynamically in equilibrium, are brought into close contact a transfer of one or more components may occur from the gas phase to the liquid or vice versa by the mechanism of molecular diffusion. Mass transfer by molecular diffusion is the basic physical mechanism underlying many important areas of chemical engineering and petroleum engineering. The removal of one or more selected components from a mixture of gases by absorption into a suitable liquid is a major operation of chemical engineering and petroleum industries. Gas absorption is the most widely used method of achieving this task, which is based on inter-phase mass transfer controlled by the rate of molecular diffusion. The chemical reaction between gaseous and liquid reactants catalyzed by a solid is called a multi-phase reaction in the context of heterogeneous catalytic reactions. A multi-phase reactor is usually used when the liquid reactant is too non-volatile to vaporize. For instance reactors of this type are commonly used for hydrogenating and cracking of petroleum feedstock of a wide boiling point range. One of the most common reactors for multi-phase reactions is the slurry reactor in which catalyst particles are suspended in the liquid reactant by agitation and gas flow, and the gas phase reactant is fed to the reactor through a suitable distributor located at the bottom. The catalyst particles are very small (~100 μm) and the heat capacity of the liquid is high so that isothermal conditions usually prevail. The main external resistance in multi-phase reactors lies in the mass transfer across the liquid film surrounding the gas bubbles. The reliable prediction of liquid-side mass transfer coefficients is, therefore, one of the most important parameters for optimum and economical overall design of such equipment.

In recent years, the problem of mass transfer by the mechanism of molecular diffusion in oil reservoirs, when a non-equilibrium gas is injected into the reservoir, has become increasingly important and received significant attention (e.g. Gurger and Mohanty, 1995; LeGallo et al., 1997). In oil recovery projects, gas is injected into oil reservoirs for different reasons such as maintenance of reservoir pressure and enhanced recovery of oil. In the first case, some of the gas, which is injected into the dome above the oil zone, dissolves in the oil, thus lowering its viscosity, surface tension and density.
These favorable changes resulting from re-pressuring of the oil reservoir have created interest in the rate at which the gas may be expected to dissolve under different prevailing conditions. Previous investigators (e.g. Hill and Lacy, 1934; Bertram and Lacey, 1935; Reamer et al., 1956) have shown that the rate of dissolution of a gas such as methane in a quiescent body of hydrocarbon oil is controlled primarily by the rate of diffusion of the dissolved gas from the gas-oil interface into the body of the liquid phase.

In the second case, when gas is injected for the purpose of enhanced oil recovery, understanding and modelling of the diffusion process may be of great importance for the planning and evaluation of gas injection projects in oil reservoirs. Furthermore, the secondary oil recovery by gas or water injections always leaves a substantial amount of residual oil in the flooded zone. To overcome the disadvantages of secondary recovery processes, miscible displacement is used as an alternative. In this process, a chemical slug of a certain size is injected into the reservoir followed by a cheap displacing fluid. If the size of the solvent slug is greater than necessary, the solvent cost will increase without any compensatory increase in oil recovery. If a small size slug is used, some of the oil that could have been produced will be left behind. The required slug size and its degradation depend mainly on the rate of mass transfer between slug and oil and between slug and displacement fluid. As the flooding progresses, the two mass transfer zones at both ends of the slug grow and consequently the slug size decreases.

Most oil reservoirs in the Middle East are highly fractured media. In these reservoirs, the dispersive and segregated flux through fractures tends to accentuate compositional differences between matrix and fracture hydrocarbons, generating molecular diffusion potential. When depleting high relief fractured reservoirs, important changes in fluid saturation pressure may occur due to the segregation of liberated gas in the fractures and dissolution of free gas in contact with the under-saturated matrix oil. Convectional upward flow and diffusion of enriched oil to the secondary gas cap take place in parallel with downward flow of the resulting heavier oil, after release of excess dissolved gas with diffusion of solution gas into under-saturated oils brought in
contact. In Iran, gas injection into the fractured and under-saturated Bangestan and Asmari oil fields in the south of the country has started. The dry gas will be dissolved in the fractured and matrix oil, resulting in increasing saturation pressure and oil swelling, together with decreasing viscosity and interfacial tension. In these conditions, molecular diffusion of gas dispersed through the fractures is the main oil recovery mechanism of matrix oil.

In all the above situations, it is a question of molecular diffusion of gas into liquid or transfer of dissolved gas between enriched and heavier liquid phases due to differences in compositional gradients between gas and liquid phases. The most important property required to determine the rate of mass transfer between the two phases in all these cases is the molecular diffusion coefficient at high pressure and temperature. Molecular diffusion is more complicated than viscous flow and heat conduction because molecular diffusion deals with mixtures. The kinetic theory has been shown to be adequate for estimation of momentum diffusivity, thermal diffusivity and molecular diffusivity in low pressure gases through the Chapman-Enskog theory (1939). For low pressures liquid systems, empirical correlations are used. These correlations are based on the Stokes-Einstein equation, which relates inversely the diffusion coefficient and liquid viscosity. An advanced kinetic theory (Hirschfelder et al., 1954) predicts that in binary mixtures there will be only a small effect of composition. Descriptions of these correlations and conditions for which their application has been recommended are summarized by Reid et al. (1977), and Taylor and Krishna (1993).

For high-pressure systems, most theories based on correlations of molecular diffusivity fail to perform properly, and for this reason empirical correlations have been developed. Unfortunately the available correlations are not suitable for the prediction of diffusion coefficients of hydrocarbon gases in hydrocarbon liquids at high pressure and temperature. One of the main reasons for this is the lack of reliable high-pressure molecular diffusion experimental data. The data at high pressure are still very scarce and fragmentary; at least in part, a consequence of the difficulty of performing these measurements in the laboratory. The ultimate objective of any
fundamental approach to the problem of molecular diffusion of gases in liquids is to be able to predict the diffusion coefficient at high pressure and temperature through the knowledge and understanding of the processes involved.

1.1. Scope of the present work

Enhanced Oil Recovery (EOR) techniques may be conveniently grouped into three major classifications. These are:

(i) Thermal methods:
   - Steam stimulation
   - Steam flooding (including hot water injection)
   - In-situ combustion

(ii) Miscible and immiscible methods
   - Miscible hydrocarbon displacement
   - Carbon dioxide displacement
   - Inert gas displacement
   - Water flooding

(iii) Chemical methods

Thermal methods are most suitable for the recovery of very heavy crude oils, where moderate increases in temperature result in significant reductions in oil viscosity. These methods will be important in the United States, Venezuela and Canada where there are large reserves of heavy crude oil. However, it is unlikely that they will find wide application in the Middle East, where light crudes are the predominant type. The appropriate EOR technologies in the Middle East are, therefore, the miscible and chemical methods. On the basis of the United States National Petroleum Council (NPC) study (U.S Department of Energy, 1984), one may conclude that the relative contributions of these methods to future EOR production in the Middle East will be approximately 70% miscible methods and 30% chemical methods. Miscible flooding is therefore the more important EOR technology for the Middle East, and may be expected to have increasing relevance on the global scene. Successful implementation of these miscible techniques will require a more thorough understanding of the
fundamental processes, which occur when miscible fluids are introduced into oil reservoirs. Displacement efficiency of miscible flooding depends on the development of favorable phase behavior effects, resulting from mixing between gas and oil. Molecular diffusion is responsible for mixing at the pore level and has been shown to be an important rate controlling mechanism in miscible flooding.

The aim of the present investigation is to study systematically the mechanism of molecular diffusion of gases in liquids by measuring the diffusion coefficients of methane in dodecane and in a typical Iranian crude oil up to a pressure of 40 MPa and at several temperatures. All tests will be conducted in an accurate high-pressure diffusion cell with "finite-domain" moving boundary behavior. The data acquired will be used to assess the predictions of various available correlations for diffusion coefficients.

The present understanding of diffusion of gases in liquids in high temperature and pressure is far from satisfactory. Despite many attempts that have been made to relate the transport properties of liquids to the molecular properties through the kinetic theory and the approach of statistical mechanics, exact theoretical equations are still not available. The main difficulty in the development of the theory of diffusion in liquids is the lack of a comprehensive theory of liquid state; therefore a wide variety of empirical and semi empirical correlations subject to many limitations have been proposed to estimate diffusion coefficients of gases in hydrocarbon liquids.

Even though the previous investigations have not been successful in producing a generally applicable correlation for the prediction of molecular diffusion at high pressures, they have nevertheless been successful in identifying the main variables affecting on molecular diffusion. These variables are molecular weight of gases and liquids, molar volume of gases and liquids, temperature and pressure. Previous investigations show that dependency on these diffusion variables is complex and exhibits strong non-linearity. A regression approach may be adopted; however, the selection of an appropriate regression equation would be problematic and purely empirical.
In recent years, there has been an increasing interest in the development of artificial neural network computational models for solving such complex problems. These networks are non-algorithmic, analog, and distributive and massively parallel information-processing methods that have proven to be powerful pattern recognition tools. Since they process data and learn in a parallel and distributed fashion, they are able to discover highly complex relationships between several variables that are presented to the network. As a model-free function estimator, neural networks can map input to output no matter how complex the relationship.

In this thesis, a thorough literature review was primarily carried out to find the importance of molecular diffusion of gases in liquids at high pressure and temperature and the factors and parameters that may affect molecular diffusion in various operations. Chapter 2 provides some general aspects and fundamentals relevant to molecular diffusion of solute gases in liquids and reviews the most well-known correlations for prediction of molecular diffusion at elevated pressures. Chapter 3 is concerned with details of experimental equipment and procedures used for measuring molecular diffusion at high pressure. Experimental results and factors influencing the molecular diffusion are given and discussed in Chapter 4. In this chapter, various methods of determining molecular diffusion data from experimental observations are addressed and advantages and disadvantages of these are discussed critically. A semi-infinite mathematical model is developed for the prediction of diffusion coefficients from experimental data at high pressure. The experimental results are given in Chapter 4 and the effect of operating pressure on molecular diffusion is discussed. Comparisons between experimental results and the predictions of various models are given and discussed. Basic principles of Radial Basis Function neural networks are given in Chapter 5. The philosophy that neural networks technique is used in the industries is:

1-Solving of physical problem in a wide range:

Neural Networks provide a generally applicable method solution for solving problems such as scientific prediction and categorization. Therefore neural network is a famous and appropriate solution among the others.
2- Innovation of relevant answers for complex problems:
Comparing with standard statistics and decision tree techniques, neural networks are more powerful and applicable in a wide range of industries.

3- Ability of working on continuous and discontinuous variables:
Neural networks are able to use continuous and discontinuous variables in input and output data.

4- Availability of neural networks software package:
Because of complete structure of neural networks techniques very good answers were utilized by the help of this method. Therefore, many powerful software have been developed on the basis of neural network techniques.

In this investigation, neural network technique is used for two reasons:
1- Parametric models for prediction of D are very sensitive just on viscosity. But in our experiment which has been performed, it was found that many parameter such as molecular weight, molar volume, ... affect on the accuracy of result. In order to consider all above parameters we have to use an alternative approach such as neural network modeling.

2- When the number of components is large such as in crude oil, the number of tuning parameters will increase and for predicting diffusivity in different crude oil this problem will increase. In these cases, parametric models are not reliable. After using neural network we find that the percentage of error was lower than other models (less than 2%)

In chapter 5 the results of the prediction of this network and the effects of various parameters are discussed. Finally, some topics for future investigations will be proposed.
2. LITERATURE REVIEW

In the context of the present thesis, diffusivity means mass transfer between a gas and a liquid phase. It is the transport of mass due to random molecular motion and is independent of any convective forces in the system. The diffusivity of gas in liquid has been studied for fundamental purposes and for the petrochemical and chemical industries. It is one of the most important properties required for mass transfer calculations, but sadly not much information is available in the literature about the specific systems. Therefore, it will take researchers still many years of experiments and research to obtain the required data.

In petroleum reservoirs, it is necessary to estimate the rate of mass transfer caused by molecular diffusion for determining the amount of gas diffusing into oil in gas injection projects. Riazi et al. (1994), Sigmund (1976), Grogan and Pinczewski (1987), Renner (1988), and Grogan et al. (1988), Zhang and his co-workers (1999) have discussed the importance of molecular diffusion in the study of petroleum recovery techniques. It is very important to understand the effects of molecular diffusion on the total amount and on the rate of gas dissolution in vertical miscible floods. The conditions at which the diffusion process is important in comparison to dispersion in porous media were discussed by Perkins and Johnston (1963). In the calculations of the rate of gas dissolution by diffusion, the diffusion coefficient under reservoir conditions is the most important property. In spite of this, a lack of sufficient experimental data on diffusion coefficients at high pressures for multi-component mixtures and reservoir fluids still exists.

In recent years, the problem of diffusional mass transfer in fractured reservoirs when a non-equilibrium gas is injected into the reservoir has become increasingly important and has received significant attention by the Iranian Oil Company. Understanding and modeling of the diffusion process is of great importance to the planning and evaluation of gas injection projects in naturally fractured reservoirs. Usually for economical reasons, natural gas, nitrogen or carbon dioxide if available are more suitable for onshore reservoirs. Saidi (1987) discusses some aspects of diffusion in naturally fractured reservoirs based on his experience with reservoirs in the Middle
East. Lagalaye and his co-workers (2002) performed some experiments on the process of acid gas diffusion in carbonate fractured reservoirs.

When a soluble gas comes into close contact with a liquid, mass transfer takes place from the interface to the bulk of the liquid phase as a result of the concentration gradient. The mass transfer continues until the liquid phase is saturated and the concentration gradient in the liquid phase is reduced to zero. The one-dimensional molar rates of mass transfer due to molecular motion under steady state and unsteady state are given by Fick's first and second law respectively:

\[ J_A = -D_{AB} \frac{\partial C_A}{\partial x} \]  

(2.1)

\[ \frac{\partial C_A}{\partial t} = D_{AB} \frac{\partial^2 C_A}{\partial x^2} \]  

(2.2)

The proportionality constant between the flux and the concentration gradient, \( D_{AB} \), is the diffusion coefficient or diffusivity of the solute, \( A \), in the liquid phase. The diffusion coefficient of methane in hydrocarbon systems is the fundamental value for designing successful enhanced oil recovery projects, providing the basis for the prediction of mass transfer rates and information on hydrodynamic conditions in the system. Despite the importance of diffusion of methane in hydrocarbon systems comparatively few studies have been published in the literature on the measurement of molecular diffusion coefficients at reservoir conditions. The available data do not cover the entire range of temperature and pressure that is of interest in any particular application. The aim of this chapter is to summarize the work on diffusion coefficients of gases into hydrocarbon liquids. For easier understanding, information is presented under the headings of experimental and theoretical investigations.

2.1. Experimental investigations

Many experimental methods have been developed for measurement of diffusion coefficients in gases and liquids (Reamer and Sage, 1958, Gavalas et al., 1968, Schmidt et al., 1982, Renner, 1988, Nguyen and Farouq-Ali, 1995). There is no
universal method of calculating the diffusion coefficients from known properties of the systems.

Most conventional methods utilised for compositional analysis are time consuming and tedious (Moulu, 1989).

Some literature contains data for diffusion of carbon dioxide in liquid hydrocarbons at atmospheric pressure over a broad range of liquid viscosities (Hayduk and Cheng, 1971; McManamey and Woollen, 1973; Davis et al., 1967; Rajan and Goren, 1967). The corresponding data for methane in liquid hydrocarbons are much more limited (Renner, 1988). Data for carbon dioxide in water at atmospheric pressure are abundant, dating back to the 19th century. However, in this review, only the more recent data are considered. Pomeroy et al. (1933) and Hill and Lacey (1934) have shown experimentally that the rate of solution of a gas such as methane or propane in a quiescent body of hydrocarbon oil is controlled primarily by the rate of diffusion of dissolved gas from the gas-oil interface into the body of the liquid. The rate for such a process is given quantitatively up to half-saturation by the equation:

\[ Q = 2C_e A \sqrt{\frac{Dt}{\pi}} \]  

where

- \( Q \) = quantity of gas which has passed through the interface
- \( C_e \) = final equilibrium concentration of gas in solution
- \( A \) = area of liquid perpendicular to direction of flow
- \( D \) = diffusion coefficient
- \( t \) = time

Methods for the estimation of diffusion coefficients of methane and propane in various hydrocarbon oils have been suggested.

Bertram and Lacey (1936) have studied the rate of solution of gaseous methane in hydrocarbon oils, which entirely filled the interstices of closely packed silica sands. They have shown that this process is substantially the same as for the case of quiescent oils in the absence of sand. In the case with sands present, the overall area at right angles to the path of diffusion must be multiplied by the fraction of the total
volume of the sand body which is occupied by the oil, and by a constant whose value is 0.82. The constancy of this factor has only been experimentally verified with unconsolidated sands and therefore for a relatively narrow range of porosities. Electrical conductance experiments with copper sulfate solutions held in similar sand bodies gave practically the same value of the constant, indicating that the effect of the sand is only geometrical.

Reamer et al. (1956) have measured diffusion coefficients for the transport of methane in the liquid phase of the system methane-decane. Studies were made at temperatures between 40 °C and 280 °C for pressures up to 27 MPa (4000 psi). They interpreted their results on the basis that no interfacial resistance existed. A nomograph for predicting the values of the diffusion coefficient for methane in decane at various temperatures and pressures has also been proposed.

Tang and Himmelblau (1965) measured the diffusion coefficients of carbon dioxide through ethanol-water, benzene, toluene and carbon tetrachloride. The results were interpreted in terms of an effective binary diffusion coefficient. Two semi-empirical correlations were derived with the aid of the absolute reaction rate theory to predict the effective binary diffusion coefficient from the binary diffusion coefficients of the solute in the individual pure solvents.

Brow et al. (1970) measured the diffusivity of methane in crude oil from the Rangely field at 18 MPa (2600 psia) and 70 °C. They reported a diffusion coefficient of 0.334×10^{-8} m^2/s. This value is similar in magnitude to those for methane in normal paraffin solvents measured at atmospheric pressure and temperatures in the range of 0 to 50 °C reported by Hayduk and Buckley (1972). Sigmund (1976) presented measurements of the diffusivity of methane in propane and butane for pressures in the range of 1.5 to 20 MPa (220 to 2900 psi) and temperatures from 35 to 105 °C. The reported diffusion coefficients are in the range of 1.6×10^{-8} to 7.6×10^{-8} m^2/s. These values are considerably higher than the diffusivities for methane in normal paraffins measured at atmospheric pressure (Brow et al., 1970). Solvent viscosity for Sigmund’s (1976) conditions, however, is considerably lower than that for the
atmospheric pressure measurements, which shows diffusivity to increase with decreasing solvent viscosity (Hayduk and Cheng, 1971). Thus the evidence available suggests that diffusivities for methane at high pressures are not greatly different from those measured at atmospheric conditions provided that solvent viscosities are similar. Hayduk and Cheng (1971) measured diffusivities of ethane in normal hexane, heptane, octane, dodecane and hexadecane at 25 °C and atmospheric pressure. Measurements were made by means of the steady state capillary cell technique. The general relation between diffusivities in dilute liquid solutions and solvent viscosities for non-complexing systems was reviewed. It was found that in general diffusivity and solvent viscosity were not inversely related but that the diffusivity depended on the solvent viscosity raised to some power, which was depending on the diffusing substance. Neither temperature nor solvent molecular weight or molar volume was required to describe the observed relationship between diffusivities and solvent compositions.

The concentration of carbon dioxide in oil is the most important effect in the immiscible displacement of oil by carbon dioxide gas since it was found by Rojas (1985) that among other mechanisms, an increase in the carbon dioxide concentration in oil leads to an increase in oil recovery. This is true because the presence of carbon dioxide in oil greatly reduces the viscosity of the liquid and promotes the swelling of the oil. Viscosity reduction and swelling of the oil lower the water-oil mobility ratio, consequently leading to an increased oil recovery.

Denoyelle and Bardon (1984) published carbon dioxide diffusion coefficients for two stock-tank oils at elevated temperature and pressure. The reported diffusion coefficients of carbon dioxide in oil that are some 5 to 10 times higher than those measured at atmospheric conditions. They concluded that measurements of diffusivity at atmospheric conditions can not be used as reasonable estimates of diffusivity at high pressures and temperature. That conclusion is at variance with the work of de Boer et al. (1984) who observed that diffusion rates of carbon dioxide in crude oil at elevated pressures were consistent with calculated rates derived from diffusion coefficients measured at atmospheric pressure, provided that the system was clean and
that there was no precipitation of asphaltenes. Asphaltenes were observed to form a highly resistive layer at the oil/water interface, which greatly reduced the mass transfer rate. Thus uncertainty remains concerning the magnitude of diffusion coefficients at reservoir conditions and the relationship that these coefficients have to the corresponding measurements at atmospheric conditions. Such a relationship is important because diffusion coefficients at high pressure and temperature are difficult to measure, and because, in contrast to the scarcity of experimental data available for high pressure and temperature, a large body of data measured at atmospheric pressure exists for systems of interest to process and reservoir engineers.

In addition, Lansangan and Smith (1991) showed that the presence of a contaminant gas in carbon dioxide affects the diffusion rate of carbon dioxide into a hydrocarbon liquid. They worked on the diffusion of a 10 mole-% nitrogen – 90 mole-% carbon dioxide mixture in oil and showed that the diffusion rate of carbon dioxide drastically decreased with the presence of nitrogen, which formed a stagnant phase through which carbon dioxide had to diffuse before contacting the liquid phase. This lowered the interfacial equilibrium carbon dioxide concentration, decreasing the rate of mass transfer, even at low nitrogen concentration. Studies conducted by Anada (1980) to investigate the use of flue gas (containing mainly nitrogen and carbon dioxide) showed that flue gas may be used in place of pure carbon dioxide for shallow heavy oil reservoirs. Anada (1980) also provided explanations on the phenomena that may occur when flue gas is used in place of pure carbon dioxide. He explained that while the carbon dioxide component of flue gas dissolved in oil to reduce liquid phase viscosity, the nitrogen component provided the energy for driving the mobilized oil.

Spivak and Chima's (1984) simulation studies showed that only a small volume of nitrogen in the 82 mole-% carbon dioxide – 18 mole-% nitrogen mixture dissolved in Wilmington oil at 6.9 MPa and 49° C and that the viscosity reduction was less due to the decreased solubility of carbon dioxide in oil in the presence of nitrogen. They also noted that the gas breakthrough was earlier, the recovery was lower, and the compositional fronts were more dispersed as compared to those for pure carbon
dioxide. They explained that nitrogen was essentially insoluble in oil and contributed to an increased free gas saturation at any point of injection.

Renner (1988) developed a method for measuring molecular diffusion coefficients of carbon dioxide and other gases in consolidated porous media at pressures up to 5.8 MPa (850 psi). Experimental diffusion coefficients are reported for carbon dioxide in decane, carbon dioxide in 0.25N sodium chloride and for ethane in decane. All experiments were conducted in Berea cores saturated with the liquid phase at 37 °C. Cores were oriented both vertically and horizontally to assess the effect of gravity-induced convection on the observed mass transfer. Apparent diffusion coefficients for carbon dioxide in liquid hydrocarbon were essentially independent of pressure and appear to be representative of combined molecular diffusion and gravity-induced convection processes. The experimental diffusion coefficients obtained from this study have also been correlated empirically, together with literature data for methane, ethane and propane as a function of liquid viscosity and thermophysical properties of the diffusion gases.

Grogan et al. (1988) reported the results of measurements of the diffusivity of carbon dioxide in liquid hydrocarbons and water at 25 °C, for pressures up to 6 MPa (870 psi). The measurements were made with techniques based on the direct observation of the motion of an interface caused by the diffusion of carbon dioxide through oil. Diffusion coefficients were determined by fitting the mathematical models to the observed motion of the interfaces. Correlations for diffusion coefficients in liquids at atmospheric pressure were shown to give reasonable estimates of diffusion coefficients for carbon dioxide in fluids at high pressures. The measured diffusion coefficients and mathematical models are used to assess the impact of diffusive mixing on carbon dioxide floods at various length scales to examine the relationship between laboratory-scale corefloods and field scale displacements.

Hafskjold and Helbæk (1993) developed and constructed essential NMR (Nuclear Magnetic Resonance) and high-pressure equipment for diffusion measurements, and to provide accurate self-diffusion data for binary and multi-component mixtures of
selected gaseous and liquid hydrocarbons under high pressure and at elevated temperatures. Self-diffusion coefficients have been measured at various temperatures, pressures and compositions for binary mixtures of methane/hexane, ethane/hexane, methane/octane, ethane/octane, methane/decane, and ethane/decane and in a ternary system of methane/benzene/hexane. The operating pressure varied between 30 MPa and 50 MPa at two temperatures of 30 °C and 60 °C. They reported results ranging from $9.1 \times 10^{-10}$ to $1.05 \times 10^{-7}$ m$^2$/s, and compared their results with the prediction of the correlation of Sigmund (1976). Significant deviations are observed between calculated and experimental data.

Based on a set of experimental data, Riazi et al. (1994) developed a complex mathematical model for estimating the amount of mass transfer in a matrix-fracture system when a non-equilibrium gas is injected into a naturally fractured reservoir. Two cases are considered; first when gas in the fracture is stagnant, and second when there is a high flow of gas in the fracture. A single mass transfer coefficient has been introduced for both liquid and gas phases for a specified system, which theoretically depends on the gas flow rate in the fracture.

Nguyen and Faroug-Ali (1998) conducted an experimental study to investigate the effect of nitrogen on the rate of mass transfer of carbon dioxide into Aberfeldy crude oil by measuring the solubility and diffusivity of impure carbon dioxide gas containing nitrogen as the contaminant gas. They concluded that the presence of nitrogen reduces the solubility and diffusivity of carbon dioxide, which decrease with increasing nitrogen content.

Zhang and his co-workers (1999) developed a simpler experimental technique than Riazi’s method for measuring gas diffusion coefficients in heavy oils. They evaluated the feasibility of the method by monitoring the pressure change in a PVT cell. The PVT cell used by Zhang et al. is quite similar to the one used in the present experiments. It is an air-tight container made of stainless steel which is filled with the crude oil and the gas. As the gas is filled into the cell, a high pressure is created. The equipment is then left to stand for a period of time. As time passed, the pressure in the
container will drop until it has reached equilibrium. Gas diffusivity is thus calculated from the measured pressure drop.

2.2. Prediction of diffusion coefficients of gases in liquids

For high temperature and pressure systems, most theory-based correlations fail to perform properly, and for this reason empirical correlations have been developed. A theory for estimating diffusion coefficients in liquids is not possible at present because a conclusive theory of the liquid state is still unavailable. It is generally best to have a predictive theory of diffusion, which combines theoretical and empirical considerations to yield workable predictions along with fundamental understanding. Investigations done at low temperature and pressure were reviewed and discussed by Taylor and Krishna (1993) and Reid and Sherwood (1987). There is still great uncertainty when predicting diffusion coefficients of gases in liquids even at low pressure and temperature. Normally, two steps are employed to estimate diffusion coefficients of gases in liquids at high temperature and pressure. First the infinite dilution diffusion coefficient, \( D_{AB}^0 \), is calculated from one of the predictive methods. The value of the diffusion coefficient at the desired condition is then estimated with one of the correlations proposed to relate the effect of operating variables on the diffusion coefficient.

2.2.1. Infinite dilution diffusion coefficient

In contrast to the case for gases, where an advanced kinetic theory is available for explaining molecular motion, theories of the structure of liquids and their transport characteristics are still inadequate to permit a rigorous treatment. Inspection of published experimental values for liquid diffusion coefficients at low pressure reveals that they are several orders of magnitude smaller than gas diffusion coefficients and that they depend on concentration due to the changes in viscosity with concentration and changes in the degree of ideality of the solution. Certain molecules diffuse as molecules while others, which are designated as electrolytes, ionize in solutions and diffuse as ions.
Two theories, the Eyring "hole" theory and the hydrodynamic theory, have been postulated as possible explanations for diffusion of non-electrolyte solutes in low-concentration solutions. In the Eyring concept the ideal liquid is treated as a quasi-crystalline lattice model interspersed with holes. The transport phenomenon is then described by a unimolecular rate process involving the jumping of solute molecules into the holes within the lattice model. These jumps are empirically related to Eyring's theory of reaction rate (Glasstone et al., 1941). The hydrodynamic theory states that the liquid diffusion coefficient is related to the solute molecule's mobility; that is, to the net velocity of the molecule while under the influence of a unit driving force. The laws of hydrodynamics provide relations between the force and the velocity. An equation that has been developed from hydrodynamical theory is the Stokes-Einstein equation (Welty et al., 1984).

The empirical correlations developed for low pressure gas-liquid systems are hence based on the Stokes-Einstein (1901) equation in which diffusivity and solvent viscosity are inversely related:

\[ D^0_{AB} = \frac{K_B T}{6 \pi \mu_B r_A} \]  

(2.4)

where \( D^0_{AB} \) is the diffusion coefficient of component \( A \) infinitely diluted in solvent \( B \), \( K_B \) is the Boltzmann constant, \( \mu_B \) is the viscosity of the solvent, and \( r_A \) is the radius of the diffusing molecules. This simple relation is valid only if the molecules of the diffusing species are very large compared to the solvent molecules (Evans et al., 1981). It has been successful in describing the diffusion of colloidal particles or large round molecules through a solvent, which behaves as a continuum relative to the diffusing species. This restriction is one of the assumptions made in the derivation of equation (2.4).

The results of the Eyring "hole" and the hydrodynamic theories can be rearranged into the general form:
in which \( f(\tilde{V}) \) is a function of the molecular volume of the diffusing solute at normal boiling point. Empirical correlations, using the general form of equation (2.5), have been developed which attempt to predict infinite dilution diffusivities of solutes in liquids in terms of the solute and solvent properties. Wilke and Chang (1955) have proposed the following correlation for non-electrolytes in an infinitely dilute solution:

\[
\frac{D_{\text{AB}}^0 \mu_{\text{B}}}{K_n T} = 7.4 \times 10^{-8} \sqrt{(\text{MW}_B \Phi)} \frac{\tilde{V}_{\text{AB}}^{0.6}}{\tilde{V}_{\text{AB}}}
\]

(2.6)

The authors claimed that 155 data points for 123 different solute-solvent systems are expressed by the correlation with an average deviation of 12% between calculated and observed results. Equation (2.6) is perhaps the most frequently used correlation for liquid diffusion coefficients.

Eliminating the association parameter \( \phi \), Scheibel (1954) modified the Wilke-Chang (1955) correlation to give:

\[
\frac{D_{\text{AB}}^0 \mu_{\text{B}}}{T} = \frac{8.2 \times 10^{-8}}{\sqrt[4]{\tilde{V}_{\text{AB}}}} \sqrt[3]{1 + \frac{3 \tilde{V}_{\text{B}}}{\tilde{V}_{\text{A}}}}
\]

(2.7)

Reddy and Dorarswamy (1967) also suggested a set of equations by modifying the Wilke-Chang correlation. They replaced the association parameter \( \phi \) by the square root of the solvent molar volume:

\[
\frac{D_{\text{AB}}^0 \mu_{\text{B}}}{T} = \frac{10 \times 10^{-8} \sqrt{\text{MW}_B}}{\sqrt[4]{\tilde{V}_{\text{A}} \tilde{V}_{\text{B}}}} \quad \text{if} \quad \frac{\tilde{V}_{\text{B}}}{\tilde{V}_{\text{A}}} \leq 1.5
\]

(2.8)
Average errors of 13.5% for equation (2.8) applied to 76 systems and 18% for equation (2.9) with 20 systems were found when comparing values calculated with the proposed correlations with experimental data. Diffusivities in liquids at moderate pressures are about $10^4 - 10^5$ times lower than those in gases. At higher pressures this ratio reduces significantly for near critical systems.

2.2.2. Diffusion coefficients at high concentration (i.e. high pressure)

In reviewing past attempts to obtain a correlation that would meet the requirements for high pressure and temperature, there are some indications that a corresponding states approach may have the best chance for success. The correlations, which are following the corresponding states relation are of the form:

$$\frac{\rho D}{\rho_D^{0D_{AB}}} = F(\rho_r, T_r, Z_r)$$  \hspace{1cm} (2.10)

Reviewing the existing literature shows that relationships of this type are used extensively to correlate both mutual and self-diffusion data for a variety of systems over a wide range of operating conditions. Some of the most important correlations of this type are summarized in the following.

Slattery and Bird (1958) generalized chart

Slattery and Bird (1958) developed a generalized chart for estimation of diffusion coefficients in dense gases. Their chart is based on the Enskog theory and on real gas viscosity and volumetric data. The equation on which they base their chart may be written in the following form:
\[
\frac{\rho D}{\rho^0 D^0_{AB}} = Z \mu \left( \frac{1}{\mu_0 \left( 1 + 0.8y + 0.761y^2 \right)} \right)
\]  

(2.11)

where

\[ y = \rho \beta_0 Y \]

\[ Y = \left[ \frac{\tilde{V}}{\tilde{V}_0} \right] + \frac{1}{2} \left[ \frac{\tilde{V}_0}{\tilde{V} + b} \right] \left[ \frac{a}{b} \right] \left[ 1 + \frac{1}{2} \frac{a}{b} \right] \frac{1}{RT^{\frac{3}{2}}} \]

\[ Z = \text{compressibility factor} \]

\[ \mu/\mu_0 = \text{ratio of dense gas viscosity to dilute gas viscosity} \]

\[ \frac{\rho D}{\rho^0 D^0_{AB}} = \text{ratio of dense gas density-diffusivity product to dilute gas density-diffusivity product, which is equal to:} \]

\[
\frac{\rho D}{\rho^0 D^0_{AB}} = Z \left( \frac{\rho D}{\rho^0 D^0_{AB}} \right)
\]

(2.12)

The generalized compressibility tables of Lydersen et al. (1955) and the charts of \( \mu/\mu_0 \) by Carr et al. (1955) and Comings et al. (1954) were used by Slattery and Bird (1961) to construct the original generalized self-diffusivity chart. The generalized chart constructed in this manner is shown in Figure 1. The chart extends to a reduced pressure of 5 and is based on few experimental data. In a strict sense the original chart was designed only for the estimation of self-diffusion coefficients in single component gases. However, as Bird (1956) has suggested, the chart might also be used to estimate mutual diffusion coefficients in binary mixtures by defining pseudocritical pressures and temperatures. Such an approach has previously been used with reasonable success to estimate both compressibilities and viscosities in multicomponent mixtures. However, as pointed out by Reid and Sherwood (1987), it has up to the present time been difficult to assess the reliability of the original chart with respect to the prediction of diffusivities. This has been especially true for binary dense
gas diffusion coefficients for which few data have been available. Later, this chart was recommended in the APT Technical Data Book (1977) for estimation of binary diffusion coefficients of dense hydrocarbon systems.

Figure 1. Generalized chart for diffusion coefficients at high pressures (Slattery and Bird)

**Dawson et al. (1970) correlation**

Dawson et al. (1970) measured self-diffusion coefficients of methane from 150 to 350 K and from 1.4 to 34 MPa (200 to 5000 psi) with the exclusion of the critical region. They found that the density-diffusivity product, $\rho D$, remains constant at constant temperature below the critical density and drops as the density increases above the critical value. The shape of the $\rho D$ versus $\rho$ curves is nearly independent of temperature. The self-diffusion data below the critical density agree well with results of the Chapman-Enskog theory (1931) provided the experimental value of density is used. The Lennard-Jones parameters calculated from the data agree well with those found by other methods. The following correlation is developed based on their own self-diffusion coefficients of methane and the data of Oosting (1968):
Literature Review

\[
\frac{\rho D}{\rho_0^0D_{AB}} = 1 + 0.329826\rho - 1.15006\rho^2 - 6.99167\rho^3
\]  

(2.13)

where \(\rho_0D_0\) is the low-pressure density diffusion product which is to be calculated from the Chapman-Enskog theory.

Sigmund (1976) correlation

Sigmund (1976) reported some experimental data for binary diffusion coefficients of dense hydrocarbons up to 14 MPa (2000 psi) pressure and 105 °C (220 °F). For the first time, they combined liquid binary diffusivities with those of gases in terms of reduced density in the following form:

\[
\frac{\rho D}{\rho_0^0D_{AB}^0} = 0.99589 + 0.096016\rho - 0.22035\rho^2 + 0.032874\rho^3
\]  

(2.14)

where \(\rho_0D_0\) is the zero pressure limit of the density-diffusivity product. The values of \(\rho_0D_0\) may be obtained from extrapolation of values of \(\rho D\) at each temperature to zero density, from low pressure experiments at each temperature or from the Chapman-Enskog theory. For a binary mixture of \(A\) and \(B\):

\[
\rho_0^0D_{AB}^0 = \frac{2.2648 \times 10^{-6}}{\sigma_{AB}^2\Omega} \sqrt{T\left(\frac{1}{MW_A} + \frac{1}{MW_B}\right)}
\]  

(2.15)

where:

\[
\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}
\]  

(2.16)
\[
\sigma_i = \frac{1.866 \sqrt{\frac{V_c^3}{Z_{Ci}^2}}} (2.17)
\]

\[
\Omega_{AB} = 0.703 \left(1 + 1.05 \frac{\varepsilon_{AB}}{KT} \right) (2.18)
\]

\[
\varepsilon_{AB} = \frac{\varepsilon_A \varepsilon_B}{K} \sqrt{\frac{K}{K}} (2.19)
\]

and

\[
\varepsilon_i = 65.3 T_{Cl} Z_{Cl}^{3.6} (2.20)
\]

The reduced densities used in equation (2.14) were calculated from the expression:

\[
\rho_r = \frac{\rho}{\rho_c} (2.21)
\]

where \(\rho_c\) is the molar critical density and \(\rho\) the molar density of the diffusing mixture at its average mole fraction of methane. The values of \(\rho\) were obtained from the experimental data of Sage et al. (1940) and the value of \(\rho_c\) from the correlation for binary critical volumes of Prausnitz et al. (1968). The correlation is:

\[
\rho_c = \frac{1}{V_{em}} (2.22)
\]

\[
V_{em} = \theta_A \tilde{V}_{CA} + \theta_A \tilde{V}_{CB} + \theta_A \theta_B \left( \tilde{V}_{CA} + \tilde{V}_{CB} \right) \delta_{AB} (2.23)
\]

\(\theta_A\) and \(\theta_B\) are the surface fractions of components \(A\) and \(B\) and are given by:

\[
\theta_A = \frac{y_A \sqrt[3]{\tilde{V}_{CA}^2}}{y_A \sqrt[3]{\tilde{V}_{CA}^2} + y_B \sqrt[3]{\tilde{V}_{CB}^2}} (2.24)
\]
Sigmund (1976) used his correlation to construct a new generalized chart for estimation of diffusion coefficients in dense gases and liquids based on both self and mutual diffusion data, as has been suggested by Bird (1956). The generalized compressibility tables of Lydersen et al. (1955) with \( Z_c = 0.27 \) were then used to calculate the values shown in his chart. To illustrate the differences of the various predictive methods, which have been discussed above, a plot of \((pD)/(\rho_0D_0)\) versus reduced density, \( \rho_r \), for each method is shown in Figure 2. For the purposes of comparison, the curves generated from each equation were for the system methane-normal butane at a temperature of 71 °C and a mole fraction of 0.9 of methane. Examination of the curves in Figure 2 indicates that a consistent trend exists in all these correlation. At reduced densities up to 1 the approximate dense gas molecular theory (ADGMT) and the correlation of Sigmund (1976) are in good agreement with each other, and the parameter \((pD)/(\rho_0D_0)\) is almost independent of the reduced density of the system, while the Thorne-Enskog theory predicts that \((pD)/(\rho_0D_0)\) decreases with reduced density. At reduced densities of about 2 the Thorne-Enskog theory and the Sigmund correlation are in reasonable agreement. In this region the ADGMT predicts results, which are approximately 30% too high. At reduced densities of about 2.5 both the ADGMT and the Thorne-Enskog theory predict results, which are considerably higher than the Sigmund correlation. Figure 2 also shows a drastic reduction in reduced diffusivity, \((pD)/(\rho_0D_0)\), when the reduced density increases from 2 to 3. Therefore, a slight change in density causes a much higher deviation of the predicted diffusivities in liquid systems. This strong dependency of diffusivity on density becomes very important when predicted values of densities are used. Extrapolation of Sigmund’s correlation shows that diffusivity approaches zero at a reduced density of about 3.5, which is not correct for oil reservoirs.
Sigmund’s (1976) correlation found practical applications in mass transfer calculations for reservoir systems because it was claimed by the author that it could be used for both liquids and gaseous systems at high pressures. However, most data used in his correlation for liquid systems were at atmospheric pressure. He reported absolute average deviations of 40% for liquid diffusivities and 10% for gas diffusivities when using his correlation. Although Sigmund’s correlation is the most convenient correlation available in the literature for estimating high-pressure diffusivities for gases, for high-pressure liquid systems it grossly overpredicts the correct values, particularly for systems in which a gas is dissolved in liquid hydrocarbons at high pressures. Riazi et al. (1993) critically examined Sigmund’s correlation and stated that equation (2.14) predicts diffusivities of gases dissolved in liquid hydrocarbons at high pressures which are 80-100% higher than reported experimental values.

![Comparison of density-diffusivity product ratio from various correlations for the CH₄-nC₄H₁₀ system](image)

Figure 2. Comparison of density-diffusivity product ratio from various correlations for the CH₄-nC₄H₁₀ system
Da Silva and Belery (1989) correlation

To avoid physically impossible negative values at high reduced molar densities, Da Silva and Belery (1989) modified the Sigmund (1976) correlation by replacing the Sigmund reduced density functionality with a decreasing exponential function for reduced densities greater than or equal to 3. This value corresponds roughly to the end of the range of experimental data investigated by Sigmund. It follows that diffusion coefficients for $\rho_r > 3$ are given by:

$$\frac{D_{ab}}{\rho_0 D_{ab}} = 0.18839 \exp(3 - \rho_r)$$

(2.26)

Hafskjold and Helbæk (1993) compared the prediction of the Da Silva and Belery (1989) extended Sigmund correlation with experimental data. The results of this comparison are summarized in Figure 3, indicating that neither equation (2.26) nor equation (2.14) predict the diffusion coefficients of methane in decane satisfactorily.

Figure 3. Comparison of the prediction of the Da Silva and Belery (1989) and Sigmund (1976) correlations with experimental data
Riazi et al. (1993) correlation

Riazi et al. (1993) proposed two different correlations to estimate diffusion coefficients for hydrocarbon systems. The authors suggested that these correlations can be used for both gases and liquids up to a pressure of about 40 MPa (6000 psi). Their first correlation is obtained from the modification of the correlation of Sigmund (1976):

\[
\frac{\rho D}{\rho^0 D^0_{AB}} = 1.0644 - 0.1228\rho_r - 0.1118\rho_r^2 + 0.01983\rho_r^3
\]

in which the reduced density is defined as:

\[
\rho_r = \left(\frac{\frac{5}{2}\frac{V_A^3}{V_{CA}} + \frac{\frac{5}{2}V_B^3}{V_{CA}}}{\frac{5}{2}\frac{V_A^3}{V_{CA}} + \frac{\frac{5}{2}V_B^3}{V_{CB}}}\right)\rho
\]

Here, \(V_C\) is the critical molar volume and \(\rho\) is the mixture molar density. Perhaps the most important relationship between diffusivity, viscosity and density of a system is the Schmidt number, \(\mu/(\rho D)\). They represented this relationship at high pressure as:

\[
\frac{\rho D}{\rho^0 D^0_{AB}} = \left(\frac{\mu}{\mu_0}\right)^n
\]

Low pressure density-diffusivity products \(\rho_0 D_0\) can be calculated from the Chapman-Enskog equation (2.15). Riazi et al. (1993) recommended that the collision integral, \(\Omega_{AB}\), be calculated from:
\[ \Omega_{AB} = \frac{1.06036}{(T_{AB})^{0.136}} + 0.193\exp(-0.47635T_{AB}^*) + 1.76474\exp(-3.89411T_{AB}^*) + 1.03587\exp(-1.52996T_{AB}^*) \] (2.30)

where

\[ T_{AB}^* = \frac{T}{\varepsilon_{AB}} \] (2.31)

\( \varepsilon_{AB} \) is also defined by equation (2.19). Based on 283 data points from the literature, Riazi et al. (1993) revised equation (2.29) to apply to both gas and liquid systems:

\[ \frac{\rho D}{\rho_0^0 D_{AB}^0} = 1.07\left(\frac{\mu}{\mu_0}\right)^{b + c\varepsilon_r} \] (2.32)

where

\[ P_r = \frac{P}{P_c}, \quad b = -0.27 - 0.38\omega \quad \text{and} \quad c = -0.05 + 0.1\omega \] (2.33)

For a binary system of components \( A \) and \( B \) with mole fraction \( x_A \) and \( x_B \) pseudo-critical properties are given by:

\[ P_c = x_A P_{CA} + x_B P_{CB} \quad \text{and} \quad \omega = x_A \omega_A + x_B \omega_B \] (2.34)

Although most experimental data which were used in the development of equation (2.29) were for hydrocarbon systems at low pressure, the authors claimed that it can also be used for hydrocarbon and non-hydrocarbon systems over a wide range of pressure.
Hayduk et al. (1973) correlation

Hayduk et al. (1973) measured the diffusivities of propane gas in a variety of organic solvents. They have shown that for each diffusing substance the following relation between diffusivity and solvent viscosity exists:

$$D_{AB} = C_1\mu^{C_2}$$  (2.35)

where constants $C_1$ and $C_2$ vary from one substance to another. For dilute solutions where experimental diffusivities are more accurate, solvent viscosity is almost the same as solute-solvent mixture viscosity. The parameters $C_1$ and $C_2$ were obtained from analysis of their experimental data by Hayduk et al. (1973) as follows:

$$D_{AB} = 0.591 \times 10^{-10} \mu^{-0.545}$$  (2.36)

This equation is expected to apply at any temperature in the range of 0 to 50°C and to any solvent with the exception of solvents in which molecular interactions are extreme such as water.

Swapan and Butler (1996) correlation

There are abundant resources of bitumen and heavy oil in Canada and Venezuela, which may be potential sources of petroleum products in this century. Due to their high viscosities ($10^4 - 10^6$ MPa.s or even higher) these crudes are highly immobile and in the vast majority of these reservoirs they are semisolid at reservoir temperatures. The in situ recovery of these huge resources necessitates the reduction of viscosity. In the newly developed “VAPEX” vapor extraction process, vaporized hydrocarbon solvents e.g. ethane, propane and butane, are used to extract these crudes. Diffusion plays a vital role in the Vapex process. Swapan and Butler (1996) used a Hele-Shaw cell [an instrument which is used for experimental tests] to obtain
empirical correlations for the diffusivities of propane and butane in Peace River bitumen. The following relationship for diffusivity was obtained:

\[ D_{AB} = 4.13 \times 10^{-10} \mu^{-0.46} \] (2.37)

Equation (2.37) similar to the correlation of Hayduk et al. (1973), is a function of the mixture viscosity, which in turn is a function of concentration and temperature of the system.

**Grogan et al. (1986) correlation**

Grogan et al. (1986) reported measurements of the diffusivity of carbon dioxide in hydrocarbons and water at high pressure. The measurements were made by the direct observation of the motion of an interface caused by the diffusion of carbon dioxide through oil or oil shielded by water. Measured diffusion coefficients are reported for carbon dioxide in pentane, decane and hexadecane at 25 °C and pressures up to 6 MPa. They reported that the Stokes-Einstein equation provides reasonable estimates of the diffusivity of carbon dioxide in water at high pressure:

\[ D_{AB} = 5.72 \times 10^{-12} \frac{T}{\mu_w} \] (2.38)

They concluded that in tertiary floods, where there is no precipitation of asphaltene which form a resistive layer at the oil–water interface, the transport of carbon dioxide through the water phase is the rate-controlling step in swelling residual oil. They also reported that the diffusivity of carbon dioxide in pure hydrocarbons at high pressure is dependent primarily on solvent viscosity. From this they also concluded that the empirical correlation of McManamey and Woollen (1973) for the diffusivity of carbon dioxide in hydrocarbon solvents in terms of solvent viscosity, developed from
measurements at atmospheric pressure, provides realistic estimates for the diffusion coefficient at reservoir conditions.

\[ D_{ab} = 1.41 \times 10^{-10} \mu_L^{-0.47} \]  

(2.39)

Good agreement is reported between the experimental data and the prediction of equation (2.39) for diffusion coefficients of carbon dioxide in hydrocarbon solvents.

**Renner (1988) correlation**

An in-situ method for measuring molecular diffusion coefficients of carbon dioxide and other gases in consolidated porous media was developed and described by Renner (1988). Experimental diffusion coefficients are reported for carbon dioxide in decane up to 5.86 MPa (850 psia), for carbon dioxide in 0.2 N brine, up to 5.86 MPa (850 psia), and for ethane in decane up to 4.14 MPa (600 psia). All tests were performed in Berea cores saturated with the liquid phase at 311 K. Renner (1988) correlated the experimental diffusion coefficients obtained from this study together with literature data for methane, ethane and propane as a function of liquid phase viscosity and thermophysical properties of the diffusing gases:

\[ D_{ab} = a \mu_{\beta}^2 \mu_{\alpha}^{\beta} MW_{\alpha}^{\beta} V_{\alpha}^{\beta} P^{\epsilon} T^{\eta} \]  

(2.40)

Statistical analysis of all combinations and permutations of equation (2.40), containing from one to six of the correlating parameters, indicated that liquid hydrocarbon viscosity, molecular weight of gas, molar volume of gas, pressure and temperature all highly correlated with the diffusion coefficient. Gas viscosity was not found to be statistically significant in the correlation. A least squares fit of all the data as a function of \( \mu_B, MW_A, V_A, P \) and \( T \) according to equation (2.40) and \( \beta=0 \) leads to the following relationship:
\[ D_{AB} = 10^{-9} \mu_B^{-0.4362} MW_A^{-0.6896} V_A^{-1.7061} P^{-1.8311} T^{-4.524} \] (2.41)

Note that original units have been retained for the variables in equation (2.41): \( \mu \) in cP; \( MW \) in g/gmole; \( V_A \) in cm\(^3\)/gmole; \( P \) in psia and \( T \) in K.

Most of these methods and correlations for estimating diffusion coefficients of dense fluids are based on experimental data, which sometimes differ for a given system by more than 100% from one source to another. For example Sigmund (1976) reports \( 3 \times 10^{-8} \) m\(^2\)/s for methane – propane at 311 K and 7.4 MPa (1069 psi), while Graue (1965) reports \( 0.7 \times 10^{-8} \) m\(^2\)/s for the same system under the same conditions. This difference is much greater for the case of liquid systems at high pressure. The concentration dependency of binary diffusion coefficients is much greater for liquid systems than it is for gases. Reported experimental diffusivities for liquids may be considered reliable at very low solute concentrations. Lack of sufficient experimental data on diffusion coefficients at high pressures has limited the attempts to develop methods for estimating this important property. The main objective of this work is to improve the understanding of mass transfer at high pressure and temperature by measuring the diffusion coefficients of methane in dodecane over a wide range of operating pressure and temperature. The results can be used to examine the limits of the models suggested by the various investigators and to assist in attempts to develop a model for the prediction of diffusion coefficients of gases in liquids at high pressures.
3. EXPERIMENTAL EQUIPMENT AND PROCEDURE

Over the years, several methods have been developed to measure the diffusivity of gases in liquids. Unfortunately, most of these methods are applicable only for pressures less than 6800 kPa (1000 psia). Less information is available for measuring the diffusivity at high pressure. Some of these methods are summarized here.

Johnson and Babb (1956) provide a comprehensive review of some of the earlier methods for measuring diffusion coefficients, including the widely used diaphragm cell technique and methods based on refractive index. The diaphragm cell consists of two chambers separated by a porous frit or sintered glass diaphragm. The solute is transferred from one chamber to the other and the rate of change of concentration of solute in the chambers is used to calculate solute diffusivity. This requires efficient stirring of the contents in the chambers for accurate determination of diffusivity. Above methods cannot be applied at the high pressure conditions of specific interest in miscible flooding because of the difficulty of directly measuring concentration changes at high pressure. Refractive index or interferometric methods measure the gradients in fluid refractive index, which occur when two liquids with different compositions are contacted across a sharp interface. These gradients are related to concentration gradients and are used to calculate accurate diffusion coefficients (Tyrrell, 1961). Ertl et al. (1974) describe more recent developments in experimental techniques, including the use of Nuclear Magnetic Resonance (NMR) in which the diffusion coefficient is determined by analysis of the motion of molecules in a strong magnetic field. Most of these methods have been developed to measure diffusion coefficients at atmospheric pressure and ambient temperature. The NMR method has been successfully employed to determine diffusivity at high pressure (Ertl et al., 1974), but is limited by the sophistication and expense of the equipment required.

Sun and Chen (1985) used the Taylor dispersion method, which relates the molecular diffusion coefficient to the observed dispersion of a solute in a fluid flowing slowly through a tube in laminar flow, to measure the diffusion coefficient of aromatic hydrocarbons in liquid cyclohexane from 25 °C to 250 °C and pressures up to 3.44
Experimental Equipments and Procedure

MPa (500 psia). This method is suitable only for determining trace diffusion coefficients i.e. the concentration of solute in the flowing liquid must be low.

The diffusivity of carbon dioxide in water between 18.5 ºC and 75 ºC was determined by Thomas and Adams (1964) using a laminar jet technique. The measured diffusion coefficients correlated well with the Wilke-Chang equation i.e. the Stokes-Einstein equation written for water (Bird et al., 1960). Measurements also agreed well with those of Unver and Himmelblau (1964) for carbon dioxide diffusion coefficients in water from 6 ºC to 65 ºC, which were also measured using a laminar jet technique.

Davies et al. (1967) used a short wetted wall column to measure the diffusion coefficient of carbon dioxide in several organic liquids at 25 ºC and atmospheric pressure. McManamey and Woolen (1973) report diffusivities for carbon dioxide in organic liquids at 25 ºC and 50 ºC using the unsteady state capillary cell technique.

Ruiz-Bevia et al. (1985) and Mahers and Dawe (1984) used laser holography techniques to estimate diffusion coefficients in porous media for alcohol-water systems at low pressure. This technique is based on determining the variation in refractive index in liquid mixtures in which diffusion is occurring by resolving optical interference patterns generated by passing a laser through the mixture. The composition of the mixture throughout the diffusion field is determined from the relationship between fluid composition and refractive index. Again, the experimental measurements were carried out at low pressure.

Pomeroy et al. (1933) pioneered a method for the measurement of diffusion coefficients at high pressures. The diffusion coefficient is calculated from the rate at which the solute gas methane dissolves in a column of hydrocarbon liquid. The rate of gas solution into the liquid is determined by measuring the decrease in volume of the gas phase, which is in contact with the liquid column. This method was used by Brow et al. (1970) to determine the diffusivity of methane in crude oil at 70 ºC and 18 MPa (2460 psia), and then by Denoyelle and Bardon (1984) to determine the diffusivity of carbon dioxide in a number of crude oils at 75 ºC and 15 MPa. Unfortunately,
Pomeroy’s theoretical analysis (Pomeroy, 1933) of the diffusion process does not account for the movement of the gas-liquid interface, which occurs as a result of gas dissolution, nor the possibility of the existence of significant convective velocities, which may be induced in the liquid by high mass transfer rates or as a result of gravitational effects. When carbon dioxide dissolves in crude oil the resulting mixture density may be greater than that of the original oil. This may result in convective mixing, which enhances mass transfer rates and results in calculated diffusivities, which are much greater than those due to molecular diffusion alone. The analysis also assumes equal specific volumes for the solute component and the liquid hydrocarbon component.

There is a clear need for a simple and reliable method for measuring diffusion coefficients at high pressure. Grogan et al. (1988) developed a novel technique based on the direct observation of the motion of an interface caused by the diffusion of carbon dioxide into hydrocarbons. The method allows the measurement of diffusion coefficients without the need to determine compositions and it minimises the effects of gravity induced convection. This method is modified in this study for measuring the diffusivity of methane in hydrocarbon liquids at high pressure by “semi-infinite” and “finite domain moving boundary” methods. In the following the experimental equipment and the experimental procedure which is used in this investigation are presented.

3.1. Experimental equipment

The complete diffusion apparatus is shown in Figure 4. Basic components of the test rig are:

1 - Constant temperature air chamber
2 - Diffusion cell
3 - Mercury pump
4 - Gasometer
Experimental Equipments and Procedure

5 - Density meter apparatus
6 - High pressure and temperature viscometer

Figure 4. Schematic diagram illustrating parts of the experimental setup

The description, calibration and operating range of these components are as follows:

1- Constant temperature air bath:

The test system is installed in a constant temperature air chamber, which is designed for use with a high pressure and high temperature diffusion cell. Its temperature range is from ambient to 180 °C and it is equipped with a cathetometer capable of detecting volume changes of 0.01 cm$^3$. The Model 2320 Air Chamber, used with the volatile oil/condensate and expansion cells, is electrically heated and temperature is controlled by a solid-state temperature controller. The chamber consists of a heavy angle iron frame covered with a metal alloy sheet and insulated with two inches of compressed glass wool. The interior is lined with insulated board. The chamber is partitioned to separate a duct from the area reserved for the cell. Louvers are installed at the duct outlet to permit adjustment of air circulation.

The air chamber is equipped with a precision cathetometer which consists of a sliding telescope and illumination system, which allows the operator to safely observe
volumetric changes through a mirror image rather than viewing the pressurized windowed cell directly. The air chamber includes fittings and tubing suitable for eventual H$_2$S service. Figure 5 is a photograph of the air chamber and its auxiliaries.

Figure 5. Photograph of air chamber and its auxiliary components

2- Diffusion cell

The diffusion cell has a volume of 400 cm$^3$ and three glass windows arranged on the face of the cell to allow observation of any liquid level in the cell. If the fluid level is not visible to the operator, the cell can be inverted to permit level sighting. Volumetric reading can be determined as described in Table 3.1

<table>
<thead>
<tr>
<th>Normal position</th>
<th>Inverted position</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 to 100 cm$^3$</td>
<td>Lower window</td>
</tr>
<tr>
<td>160 to 210 cm$^3$</td>
<td>Middle window</td>
</tr>
<tr>
<td>240 to 330 cm$^3$</td>
<td>Upper window</td>
</tr>
<tr>
<td></td>
<td>80 to 170 cm$^3$</td>
</tr>
<tr>
<td></td>
<td>200 to 250 cm$^3$</td>
</tr>
<tr>
<td></td>
<td>310 to 400 cm$^3$</td>
</tr>
</tbody>
</table>
The readings are obtained with a cathetometer. The volumetric relationship between cathetometer readings and fluid level in the cell must be established by calibration in the laboratory.

The cross-sectional area of the cell bore has been precision machined to ensure that 1 mm in fluid level change equals 1 cm\(^3\) of change in volume. The cathetometer permits readings to 1/10 th of a cm\(^3\).

Cell windows are made of optical quality glass, chemically treated for hardness and are approximately 2.54 cm (1 inch) thick. They are recessed into the main body of the cell and each has an opening of 9.52 cm (3\(\frac{3}{8}\) inch) long by 0.47 cm (\(\frac{3}{16}\) inch) wide. The recess is honed to provide a scratch-free seat for the gasket and window. The window is held in place by a heat-treated frame ground for flatness and the removal of tool marks. The frame is bolted to the cell body in a manner which minimizes stress around the edges, which can cause the glass to crack. The frames are designed with clamping and balancing screws to reduce strain on the glass, while insuring positive sealing at high pressures and temperatures. A flatness kit is included when a new cell is purchased which should be used each time the cell is subjected to any significant pressure or temperature change which may affect the flatness of the window frame.

The cell is supported in the 2320 air chamber by a journal. This allows the cell to be revolved from the vertical upright position through the horizontal to the vertical position with the bottom end up. When the cell is in the vertical position, both the top and bottom valves can be operated by extension handles installed through the door of the air chamber.

The inlet and outlet of the cell are connected to the inlet valves of the chamber assembly by two stainless steel tubing spirals. All connections and tubing are suitable for H\(_2\)S service. When the cell is brought to the horizontal position, the rocking mechanism of the chamber can be engaged either manually or with a motor-drive to agitate the sample, causing the mercury in the cell to become the agitator. Three shallow holes are drilled into the cell for thermocouples to determine when temperature equilibrium has been obtained. Rocking the cell will also help to alleviate pressure gradients that may occur.

To remove the cell from the air chamber, the tubing spirals and thermocouples must be disconnected and the bolts which hold the cell to the journal must be loosened. A
Experimental Equipments and Procedure

A lug is provided on the cell to allow the cell to be lifted through the top cover of the chamber. The diffusion cell permits volumetric and phase behavior studies of condensate and volatile oil samples for pressures up to 68 MPa (10000 psi) and temperatures up to 150 °C (302 °F). It must be emphasized that the diffusion cell must never be viewed directly. A photograph of the diffusion cell apparatus is shown in Figure 6 and the detailed specification of the diffusion cell are given in Table 3.2.

Table 3.2. Specification of diffusion cell

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume</td>
<td>400 cm³</td>
</tr>
<tr>
<td>Working Pressure</td>
<td>68 MPa</td>
</tr>
<tr>
<td>Test Pressure</td>
<td>102 MPa</td>
</tr>
<tr>
<td>Net weight</td>
<td>48 kg</td>
</tr>
<tr>
<td>Standard material</td>
<td>416 S.S</td>
</tr>
<tr>
<td>H₂S Service</td>
<td>As required</td>
</tr>
<tr>
<td>Outlets</td>
<td>3/16&quot; RIC Female</td>
</tr>
</tbody>
</table>

Figure 6. Photograph of the diffusion cell
Experimental Equipments and Procedure

3- Mercury Pump

The injection of the gas and liquid phase at the desired pressure was performed using fully automatic mercury pumps. Positive displacement pumps are precision instruments enabling the user to meter, feed, or proportion predetermined quantities of fluids under high pressures with an accuracy unattainable by any other means.

The pump design concept is similar to a precision high-pressure syringe. An accurate mechanical piston is driven through a packing gland into a cylindrical chamber, displacing a fluid. By driving the piston with a precision-machined, threaded spindle, the fluid is displaced in a smooth, pulseless fashion. When the pump is motorized, the displacement takes places at a predetermined rate.

All the components of the pump are made of stainless steel and each pump has a volume scale in cubic centimeters with a dial indicator for enhanced resolution. On some pumps, a vernier that permits resolution as small as 0.001 cm\(^3\) is installed. In some experiments a twin mercury pump has been used. This twin pump consists of two individual cylinder-piston arrangements. The mover of the piston is a helical rod that is connected to a gearbox by chain. The gearbox is equipped with four main and seven auxiliary gears, which provide 28 different positions for the exit shaft. The pump is highly accurate and operates fully electronically. The flow rate in each pump is variable from 1 cm\(^3\)/hr to about 1500 cm\(^3\)/hr. The operating pressure of each pump is up to 70 MPa (10000 psi) and a calibrated ruler is installed between the two pumps, which enables to read the outlet volume with 0.01 cm\(^3\) accuracy. Figure 7 is a photograph of the twin mercury pump.
Experimental Equipments and Procedure

4 - Gasometer

The RUSKA Model 2331 Gasometer accurately measures atmospheric gas in the PVT laboratory. The unique design permits dual chambers to be used separately or in series providing a wide range of volume-resolution combinations.

The Gasometer consists of two pyrex chambers which can be used separately or together. A floating piston in each chamber is connected to a rock and pinion, which can be positioned through panel control knobs. The movement and position of the piston can be monitored by use of dual scales with verniers calibrated in cm$^3$. Materials in contact with the gas will resist the corrosive effects of hydrogen sulfide. Safety shields and relief valves are provided for protection. A null pressure gauge (the name of the gauge indicates that outlet gas pressure of the PVT cell is reduced to atmospheric pressure) is provided for each chamber. A photograph of the gasometer apparatus is shown in Figure 8, and the detailed specifications of the gasometer are given in Table 3.3.
Table 3.3. Specification of gasometer

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Left Chamber</td>
<td>3000 cm$^3$</td>
</tr>
<tr>
<td>Right Chamber</td>
<td>2000 cm$^3$</td>
</tr>
<tr>
<td>Working Temperature</td>
<td>21- 26 °C</td>
</tr>
<tr>
<td></td>
<td>Range</td>
</tr>
<tr>
<td>Net Weight</td>
<td>16 kg</td>
</tr>
<tr>
<td>Materials</td>
<td>suitable for sweet or sour gas</td>
</tr>
<tr>
<td>Size</td>
<td>9.27 x 33.65 x 18.45 cm$^3$</td>
</tr>
</tbody>
</table>

Figure 8. Photograph of gasometer

The gasometer is calibrated according to the following procedure. With the system open to atmosphere, the null gauge is set to zero gauge pressure, and the position is raised to the topmost position (zero on the scale). As gas is admitted to the chamber, the piston is displaced. When equilibrium is reached, the piston is
adjusted until the pressure gauge reads zero. At this time the gas volume is read on the scale and vernier.

Because of the principle of operation, the measured gas remains in its separated condition, non-contaminated to guarantee that further true gas analysis is possible. The techniques described in the operating manual make it a simple matter to time the gas flow, thereby effectively using the gasometer as a flowmeter or flow calibrator.

5 - Density meter apparatus

The density determination is based on measuring the period of oscillation of a vibrating U-shaped sample tube, which is filled with sample liquid or through which the sample liquid flows continuously. The following relationship exists between the period Te and the density:

\[ \rho = A(Te^2 - B) \]

A and B are instrument constants which are determined by calibration with fluids of known density. Since all external measuring cells use the period of oscillation of the sample tube as output signal, the interpretation of this period depends only on the processing unit which digitally indicates the value for period Te. The processing unit is characterized by a definite number of decimal places in the measurement as well as by computing electronics, which determine the resolution of the measurement. The first digit in the model designation signifies to how many decimal places of resolution the instrument is capable of working. Therefore, different steps have been taken to obtain the required stability in the various measuring cells.

DMA 512 that was used in the present experiments is a remote cell specially designed for density measurements under extreme pressure and temperature conditions. The sample tube is made of stainless steel with a wall thickness of about 0.3 mm and an inside diameter of 2.4 mm. The tube is housed in a brass housing which is temperature-controlled by the thermostat liquid. The system is excited by two magnetic dynamic converters in connection with an electronic control and amplifier circuit which guarantees a constant amplitude of the oscillator tube even under extreme measurement conditions. The maximum operating temperature is determined by the sealing materials being used and by the insulating material on the coils of the
Experimental Equipments and Procedure

excitation system. The system can be used for continuous operation between -20 °C and +150 °C and, for short periods, up to 180 °C. Should the temperature exceed 200 °C, the system will be damaged. An important characteristic of this system is that it can be used for pressures up to 400 bar. Exit ports to and from the remote cell are factory equipped with Swagelok fittings for tubes of 3 mm outside diameter, which guarantees a tight connection for the sample transfer. Figure 9 shows a photograph of the DMA.

Figure 9. Photograph of density meter apparatus

6 - High Pressure and High Temperature Viscometer

The Model 1602 Rolling Ball Viscometer is designed for operation at elevated pressures up to 68 MPa (10000 psi) and high temperatures to 150 °C. The RUSKA Viscosimeter has automatic timing and can measure viscosities of most reservoir fluids with a repeatability of better than 0.1%. The viscosimeter can measure viscosities from 0.1 to 3000 cP. Approximately 70 cm³ of liquid are required to fully charge the viscosimeter; however, viscosity measurements can be made if as little as 20 cm³ are available. This feature is particularly advantage when viscosity
determinations are made with liquid volume which shrinks due to degassing of dissolved gases.

The RUSKA High Pressure Viscosimeter may be used to determine the viscosity of petroleum fluids under reservoir conditions or liquid phase viscosities at various pressures and temperatures. It is equipped with an electric heating jacket and a solid-state-temperature controller for precise adjustment of the fluid temperature. A picture of the high pressure and high temperature viscometer is shown in Figure 10 and its specifications are given in Table 3.4.

<table>
<thead>
<tr>
<th>Table 3.4. Specifications of high pressure and temperature viscosimeter</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Working Pressure</strong></td>
</tr>
<tr>
<td><strong>Test Pressure</strong></td>
</tr>
<tr>
<td><strong>Net Weight</strong></td>
</tr>
<tr>
<td><strong>Materials</strong></td>
</tr>
<tr>
<td><strong>H₂S Service</strong></td>
</tr>
<tr>
<td><strong>Inlet and Outlet</strong></td>
</tr>
</tbody>
</table>

The operation of the viscosimeter is simple. After it has been filled with the test liquid and the desired temperature has stabilized (usually after 4 hours), the cell is rocked with the barrel seal open. The ball rolls back and forth in the barrel and mixes the liquid. This ensures thermal equilibrium and eliminates pressure transients. The cell is then held in its inverted position to bring the ball to rest against the barrel seal. A button on the control box marked “HOLD” is pushed and the barrel seal is closed. Pressing the button energizes the selenoid to hold the ball at the upper end of barrel when the cell is rotated to its upright position for measurement. A button designated “ROLL” is then pressed, to simultaneously break the selenoid circuit, release the ball, and start a digital timer. When the ball strikes the contact at the lower end of the barrel, the timer stops and a buzzer sounds.

The rolling time of the ball is proportional to the viscosity of the test fluid. By using fluids of known viscosities and densities, a calibration curve can be established for the instrument. The viscosity of the fluids under investigation is determined from the
available curves in chemical handbooks. For highly viscous fluids, smaller diameter balls may be used. Figure 10 is a photograph of viscosimeter.

Figure 10. Photograph of high pressure high temperature viscosimeter

3.2. Experimental procedure

In preparation for a typical diffusion test, the cell is cleaned, dried and the system connected to a vacuum to remove air or any other gases present in the system. Once the pressure of the system has reached approximately 0.025 kPa (0.2 mmHg), the liquid is introduced by injection from the bottom upward until it fills about 35% of the cell volume. Pure methane is also introduced into the reservoir cylinder of the air chamber at the desired pressure. Then, the mains power of the air chamber heaters is switched on and the temperature of the system allowed to rise very gradually. When the desired temperature is reached, the control heater will begin to cycle as noted by the red and white lights on the controller panel. Various combinations of main heaters may have to be used in order to reach a desired temperature. Five thermocouples, three on the diffusion cell and two in the main body of the chamber, record the temperatures at various parts of the diffusion cell and the air chamber. The system is
degassed and then left at the desired pressure and temperature for about 10 hours to ensure a homogeneous condition throughout the system. Afterwards, while the mercury is withdrawn from the bottom of the diffusion cell, the top three-way valve of the cell is connected to the high pressure gas reservoir cylinder. When the pressure in the cell reaches the desired value, the top valve is closed and the liquid level recorded. The pressure of the diffusion cell kept constant during the course of the experiments by continuous injection of mercury from the bottom of the cell. As time passes, methane diffuses into the liquid phase, therefore, the liquid level raises and its volume increases. Meanwhile, the pressure of the gas phase tends to drop very slowly, which should be restored again by injecting more mercury into the bottom of the diffusion cell to compress methane inside the cell and keep the pressure constant. From the movement of the interface and from the position of the piston rod of the mercury pump, the volume of dissolved methane in the liquid phase may be determined as a function of time. Acquisition of a complete set of volume-time data usually requires two to ten days. The diffusion coefficient may then be determined from the volume-time data. At the end of each experiment, samples of the liquid and gas phases were withdrawn from the bottom and top parts of the cells respectively. The liquid sample was accumulated in the cylinder and the volume of gas liberated from the liquid was collected in a gasometer, and its composition analyzed with a gas chromatograph. The liquid collected was weighed and from the volume of collected gas and the weight of the liquid phase, the composition of gas was calculated for cross-checking. The composition of the gas phase was also analyzed to check the possibility of evaporation of the liquid phase, which proved to be negligible. All experimental runs were performed in random fashion and some runs were repeated later to check the reproducibility of the experiments, which proved to be excellent.
3.3. Accuracy of experimental equipment

The accuracy of the tests is improved by gauge and cell calibration according to the following procedure.

3.3.1. Gauge calibration

The gauge is calibrated periodically. For calibration of the gauge a dead weight tester was used. Before the experiment was started the gauge was calibrated and the calibration curve for this gauge prepared. Then the value read from the gauge was corrected according to this curve. The calibration curve is shown in Figure 11.

![Calibration Curve for Gauge](image1)

**Figure 11. Calibration curve for gauge**

3.3.2. Diffusion cell calibration

By applying pressure to the diffusion cell, the volume of the cell increases. This expansion can be represented as a coefficient called expansion coefficient of the cell. In the experiment, this coefficient was measured and during the experiment the volume of the cell was corrected according to this value. For the present experiments the expansion coefficient is $1.00325 \times 10^{-4}$ cm$^3$/psi
3.3.3. Accuracy analysis of the equipments:

The accuracy and working range of each equipment which is used in these experiments are given in Table 3.5.

Table 3.5. Accuracy and working range of equipments

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Accuracy</th>
<th>Range of T&amp;P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercury Pump</td>
<td>±30 psia</td>
<td>T=Ambient, P=Zero -10000 psia</td>
</tr>
<tr>
<td>Diffusion Cell</td>
<td>±0.01 cm³</td>
<td>T=Ambient -150 °C, P=14.7 - 10000 psia</td>
</tr>
<tr>
<td>Air Chamber</td>
<td>±2 °C</td>
<td>T=Ambient -26 °C, P=14.7 psia</td>
</tr>
<tr>
<td>Density Meter</td>
<td>±1 x 10⁻⁴ g/cm³ in the range of ±0.5 g/cm³, ±1 x 10⁻⁵ g/cm³ in the range of ±0.1 g/cm³</td>
<td>T=(−20) to 150 °C, P=14.7-6000 psia</td>
</tr>
<tr>
<td>Viscometer</td>
<td>±0.02 cP</td>
<td>T=Ambient -150 °C, P=14.7-10000 psia</td>
</tr>
<tr>
<td>Gasometer</td>
<td>±0.01 cm³</td>
<td>T=Ambient -25 °C, P=59 inches water</td>
</tr>
</tbody>
</table>

For the clean methane-dodecane system the solution is clear. Hence, the interfacial area between gas and dodecane can be detected and read very accurately in the diffusion cell. Furthermore the thermodynamic and physical properties of methane and dodecane are well known and there is almost no error in determining these properties. Therefore, the diffusivity of methane in dodecane can be determined with an average error of ±2%.

On the other hand crude oil is dark and as a result there are some errors in detecting the interface between gas and liquid and reading the swelling height in the diffusion cell. As can be seen from tables 3.6 and 3.7, crude oil is a mixture of various components and there are some traces of materials which can not be measured experimentally, even though these materials have a significant effect on the physical and thermodynamic properties of the crude oil. Therefore there are also some errors in the measurement of these properties. The diffusivity of methane in crude oil can therefore only be determined with an average error of ±5%.
3.4. Test fluids

Diffusion experiments were performed using pure methane as gas phase and pure normal dodecane and a typical Iranian crude oil as liquid phases. Accurate knowledge of physical properties and phase behavior of the methane-dodecane and methane-crude oil systems under various operating temperatures and pressures is an essential pre-requisite for determination of diffusion coefficients from volume-time data. A limited number of gas solubility measurements were performed using a standard PVT cell apparatus. The complete PVT apparatus is shown in Figure 12. The system is based on the principle that gas dissolved in the liquid phase evolves when the pressure is released and the temperature of the system is increased. The solubilities of pure methane in dodecane were measured at several pressures and temperatures. In each run, the equilibrium was detected by noting a constant pressure on the pressure gauge of the PVT cell. To make sure that complete phase equilibrium is obtained, the PVT cell was mixed for another week. Then, a sample of liquid was withdrawn from the bottom of the cell. The liquid was accumulated in the cylinder and the volume of gas liberated from the liquid was collected in a gasometer. Its composition is then analyzed by using a gas chromatograph. Knowing the volume of gas and the weight of the liquid phase, the solubility of the gas phase was calculated. These data were used to tune the Peng-Robinson equation of state in the range of operating pressures and temperatures of this investigation. After obtaining a match of the measured data, the fitted equation of state is used to determine gas- and liquid-phase densities, viscosities, molar volumes and saturation concentration of methane in dodecane and crude oil. Figures 13 presents a plot of solubility of methane and molar volume of the solution versus pressure at different temperatures. As is shown, the solubility of methane in dodecane increases as pressure is increased or the temperature of the system decreased. Molar volume of the solution is decreased with pressure and increased with increasing temperature. Composition and properties of crude oil sample are given in Table 3.6 and 3.7.
Figure 12. Schematic diagram illustrating various parts of the P.V.T apparatus

Figure 13. Variation of saturation concentration of methane and molar volume of the liquid phase (dodecane) with operating pressure
Table 3.6. Iranian crude oil composition used in this study

<table>
<thead>
<tr>
<th>No</th>
<th>Component</th>
<th>Weight%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>IC5</td>
<td>2.576573</td>
</tr>
<tr>
<td>2</td>
<td>NC5</td>
<td>3.70447</td>
</tr>
<tr>
<td>3</td>
<td>C6</td>
<td>9.261175</td>
</tr>
<tr>
<td>4</td>
<td>C7</td>
<td>13.20364</td>
</tr>
<tr>
<td>5</td>
<td>C8</td>
<td>15.48013</td>
</tr>
<tr>
<td>6</td>
<td>C9</td>
<td>12.19992</td>
</tr>
<tr>
<td>7</td>
<td>C10</td>
<td>10.83402</td>
</tr>
<tr>
<td>8</td>
<td>C11</td>
<td>6.074089</td>
</tr>
<tr>
<td>9</td>
<td>C12</td>
<td>4.304636</td>
</tr>
<tr>
<td>10</td>
<td>C13</td>
<td>3.652732</td>
</tr>
<tr>
<td>11</td>
<td>C14</td>
<td>3.476821</td>
</tr>
<tr>
<td>12</td>
<td>C15</td>
<td>3.611341</td>
</tr>
<tr>
<td>13</td>
<td>C16</td>
<td>2.535182</td>
</tr>
<tr>
<td>14</td>
<td>C17</td>
<td>2.214404</td>
</tr>
<tr>
<td>15</td>
<td>C18</td>
<td>1.924669</td>
</tr>
<tr>
<td>16</td>
<td>C19</td>
<td>1.800497</td>
</tr>
<tr>
<td>17</td>
<td>C20</td>
<td>1.365894</td>
</tr>
<tr>
<td>18</td>
<td>C21</td>
<td>0.745033</td>
</tr>
<tr>
<td>19</td>
<td>C22</td>
<td>0.558775</td>
</tr>
<tr>
<td>20</td>
<td>C23</td>
<td>0.475993</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 3.7. Properties of crude oil above 3.5 Mpa and at T=50°C

<table>
<thead>
<tr>
<th>Density (g/cm³)</th>
<th>Specific gravity</th>
<th>API</th>
<th>Molecular weight</th>
<th>Viscosity (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.79535</td>
<td>0.7961382</td>
<td>46</td>
<td>118.7</td>
<td>0.28</td>
</tr>
</tbody>
</table>
4. RESULTS AND DISCUSSIONS

For checking the calibration of the test rig, some control runs were performed using the CO$_2$/decane system. In recent years, several investigators (i.e. Renner, 1986; Grogan et al., 1988) have used this system for studying diffusion of gases in liquids up to 10 MPa (1500 psi) pressure. Figure 14 shows a comparison between reported diffusion coefficients and those obtained in this investigation as a function of pressure. The agreement between the present results and the values reported by other investigators is excellent. The results clearly prove the reliability of the equipment used in the present investigation.

![Graph showing diffusion coefficient of CO$_2$ in decane with pressure](image)

Figure 14. Variation of the diffusion coefficient of CO$_2$ in decane with pressure

Figures 15a-15i show the swelling height of dodecane as liquid phase as a function of time for pressures ranging from 3.5 to 35 MPa (500 to 5000 psi) at three different temperatures (45 °C, 65.5 °C, and 81 °C). Figures 15j-15k show the swelling height of crude oil at various pressures at 25 °C and 50 °C as a function of time. The characteristics of this crude oil were given in Tables 3.6 and 3.7. The
general shape of the increase in liquid volume versus time curves is remarkably concordant. It is characterized by a sharp initial increase in volume followed by a gradual increase toward the saturation concentration of methane in the liquid phase. The extent of the variation in the swelling with time is strongly affected by the adjusted pressure. Swelling at high pressures increases faster and to a larger extent than at low pressures. The extent of the swelling decreases as the solubility of methane decreases. The solubility of methane decreases as the temperature of the system increases or the operating pressure of the system decreases. The dissolution of methane in the liquid phase results in lowering its viscosity, surface tension and density. Figure 16 displays the relationship between the viscosity and density of the solution with pressure at different temperature for dodecane. The maximum reduction in viscosity and density of the solution is observed when all of the methane gas in the cell dissolves in the liquid phase. With further increase in the pressure the density and viscosity of the solution are gradually increased.

Figure 15a. Variation of swelling height with time at P=4137 kPa and various temperatures
Results and Discussion

Figure 15b. Variation of swelling height with time at $P=6895$ kPa and various temperatures

Figure 15c. Variation of swelling height with time at $P=9653$ kPa and various temperatures
Results and Discussion

Figure 15d. Variation of swelling height with time at P=13790 kPa and various temperatures

Figure 15e. Variation of swelling height with time at P=16548 kPa and various temperatures
Results and Discussion

Figure 15f. Variation of swelling height with time at $P=20685$ kPa and various temperatures

Figure 15g. Variation of swelling height with time at $P=23443$ kPa and various temperatures
Results and Discussion

Figure 15h. Variation of swelling height with time at $P=26201$ kPa and various temperatures

Figure 15i. Variation of swelling height with time at $P=28959$ kPa and various temperatures
Results and Discussion

Figure 15j. Variation of swelling height with time at $T = 25 \degree C$ and various pressures

Figure 15k. Variation of swelling height with time at $T = 50 \degree C$ and various pressures
Figure 16. Variation of viscosity and density of the methane-saturated liquid phase with operating pressure

It is convenient to express the amount of methane dissolved in the liquid phase in terms of mean solute concentration defined as:

$$\bar{C}_A = \frac{1}{V} \int C_A dV = \frac{1}{Z_0} \int C_A dx$$

(4.1)

The amount of swelling of the liquid phase is equal to the variation of the volume of the system as a result of diffusion of methane across the interface:

$$\frac{dV}{V} = d(v_A \bar{C}_A)$$

(4.2)

Integrating the resulting equation, between the limits $Z_0$ and $Z_i$ gives:

$$\bar{C}_A = \frac{1}{v_A} \ln \frac{V_i}{V_0} = \frac{1}{v_A} \ln \frac{Z_i}{Z_0}$$

(4.3)
In the range of this investigation the dimensionless product of $C^v A << 1$. Hence, applying this condition to equation (4.3), it may simplify to:

$$\overline{C}_A = \frac{Z_t - Z_0}{Z_t v_A} \quad (4.4)$$

Equations (4.3) or (4.4) can be used to calculate the average methane concentration in the liquid phase as a function of time at various operating pressures and temperatures. The results of these calculations are plotted in Figures 17a-17i at 45 °C, 65 °C and 81 °C for various pressures for the methane-dodecane system and in Figures 17j-17k for the methane-crude oil system at temperature of 25 °C and 50 °C and various pressures. The average concentration profiles will be used to determine the diffusion coefficients from diffusion-controlled liquid swelling experiments and to evaluate various published correlations from the literature. Early stages of dissolution are often affected by convective mixing arising from initially high mass transfer rates and surface tension driven instabilities. This initial brief period of curvature is referred to as “incubation period” (Chukwuma, 1983; Renner, 1986), which will be discussed in section (4.6) of this chapter. During the incubation period methane dissolves in dodecane at the gas-liquid interface to establish boundary conditions. The results of this investigation show that the incubation period increases as operating pressure and solubility of methane in the solution increases. However, this period decays with increasing contacting time. Hence middle and late time data are more reliable for estimation of diffusion coefficients from experimental data.
Figure 17a. Variation of methane concentration in the liquid phase with time at $P=6895$ kPa and various temperatures

Figure 17b. Variation of methane concentration in the liquid phase with time at $P=9653$ kPa and various temperatures
Figure 17c. Variation of methane concentration in the liquid phase with time at $P=13790$ kPa and various temperatures

Figure 17d. Variation of methane concentration in the liquid phase with time at $P=16548$ kPa and various temperatures
Figure 17e. Variation of methane concentration in the liquid phase with time at $P=20685$ kPa and various temperatures

Figure 17f. Variation of methane concentration in the liquid phase with time at $P=23443$ kPa and various temperatures
Figure 17g. Variation of methane concentration in the liquid phase with time at $P=26201$ kPa and various temperatures

Figure 17h. Variation of methane concentration in the liquid phase with time at $P=28959$ kPa and various temperatures
Figure 17i. Variation of methane concentration in the liquid phase with time at $P=31717$ kPa and various temperatures.

Figure 17j. Variation of methane concentration in crude oil with time at $T=25^\circ C$ and various pressures.
**4.1. Determination of diffusion coefficients from experimental data**

Figure 18 shows the schematic change of concentration across an interface between gas and liquid phase. According to these concentration profiles, a number of mathematical models have been proposed to determine the diffusion coefficients from volume-time profiles obtained from experiments. All these models are developed from the equation of continuity for the solute:

\[
\frac{\partial C_A}{\partial t} + \nabla \cdot C_A u^V = -\nabla \cdot J_A^V + r_A \tag{4.5}
\]

in which:

- \(C_A\) = solute concentration
- \(u^V\) = volume average reference velocity
- \(J_A^V\) = molar diffusion flux
- \(r_A\) = rate of generation by chemical reaction
Inserting Fick's law into equation (4.5) gives:

$$\frac{\partial C_A}{\partial t} + \nabla \cdot C_A u^V = \nabla \cdot (D \nabla C_A) + r_A$$

(4.6)

In the absence of a chemical reaction and assuming a constant diffusion coefficient $D$, equation (4.6) takes the form:

$$\frac{\partial C_A}{\partial t} + \nabla \cdot C_A u^V = D \nabla^2 C_A$$

(4.7)

Furthermore, if the velocity $u^V$ is zero (Hong Siang 2000), then equation (4.7) becomes:

$$\frac{\partial C_A}{\partial t} = D \nabla^2 C_A$$

(4.8)

For the one-dimensional capillary tube of the diffusion cell, equation (4.8) simplifies to:

$$\frac{\partial C_A}{\partial t} = D \frac{\partial^2 C_A}{\partial x^2}$$

(4.9)
Before the start of the diffusion process, the concentration of solute in the liquid phase is zero. Thus, the initial condition of the test tube is:

\[ C_A = 0 \text{ for } t = 0 \text{ and all values of } x \quad (4.10) \]

According to the film theory of Whiteman (1923), the gas and liquid phases at the interface are thermodynamically in equilibrium, which means that the interfacial concentration of solute, \( C_{Al} \), remains unchanged as long as temperature and pressure of the system are kept constant. Hence:

\[ C_A = C_{Al} \text{ for } t > 0 \text{ at the gas - liquid interface} \quad (4.11) \]

After methane and dodecane are brought into close contact mass transfer commences, and methane diffuses into the liquid phase across the interface. As a result, the liquid phase swells and the interface moves to a new position \( Z_r \). Depending on contact time, height of liquid phase, and rate of mass transfer, the system may be considered as either "semi-infinite" or "finite-domain moving boundary". In the following, the determination of the diffusion coefficients from the experimental data based on these two systems is discussed.

4.2. Modelling of semi-infinite systems

The assumption of a semi-infinite system is valid as long as the solute does not reach to the bottom of the diffusion cell during the course of the experiment. This condition prevails when the test tube is long or the time of contact between gas and liquid phase is short. By locating the liquid-gas interface at \( x = 0 \) and the bottom of the test tube at \( x = \infty \), the boundary conditions of equation (4.9) are as follows:

\[ C_A = C_{Al} \text{ for } x = 0 \quad (4.12) \]
\[ C_A = 0 \text{ for } x = \infty \quad (4.13) \]
The solution of equation (4.9) subject to these boundary conditions is given by Crank (1975):

\[ C_A(x, t) = C_{A0} \text{erfc} \left( \frac{x}{2\sqrt{Dt}} \right) \quad (4.14) \]

The total mass of methane transferred into the liquid phase after time \( t \), \( m_A \), may be calculated from equation (4.14) by integration over the volume of the diffusion cell:

\[ m_A = \int_0^\infty C_A(x, t) \, dV = \int_0^\infty C_A(x, t) \, dx = 2S \cdot C_{A0} \sqrt{\frac{Dt}{\pi}} = K \cdot \sqrt{t} \quad (4.15) \]

Equation (4.15) predicts that a plot of \( m_A \) versus the square root of time should provide a straight line with a slope of constant \( K \). Hence calculating the value of \( K \) from experimental data, the diffusivity of the solute in the liquid phase can be obtained from:

\[ D = \pi \left( \frac{K}{2SC_{A0}} \right)^2 \quad (4.16) \]

Most investigators (i.e. Renner, 1986; Grogan et al. 1988) used this method for determination of diffusion coefficients from volume-time profiles obtained from experiments. The mass-average concentration of solute can also be obtained from the combination of equation (4.15) with equation (4.1):

\[ \bar{C}_A = \frac{m_A}{V} = \frac{m_A}{S \cdot Z_0} = \frac{2C_{A0}}{Z_0 \exp(v \cdot \bar{C}_A)} \sqrt{\frac{Dt}{\pi}} \quad (4.17) \]

The use of the semi-infinite solution limits the number of experimental data, which can be used to determine diffusion coefficients to the very early times of the experiments. This limitation is a serious drawback of this method, as early time experimental data are affected by convective mixing arising from initially high mass...
transfer rates especially at high pressure where the solute has a high solubility in the liquid phase. This initial mixing effect decreases with increasing contacting time, hence middle and late time data are less affected and provide better estimates of diffusion coefficients.

4.3. “Finite-domain moving boundary” model

From the experimental point of view, the finite systems provide conditions for more precise estimates of diffusion coefficients. These systems allow design and construction of small and compact apparatus, which is a great advantage for working at high pressure and temperature. When the liquid in the diffusion cell comes into close contact with the gas phase, diffusion commences. Since the cell is sealed and is of finite length, there can be no mass transfer across the walls of the cell. If the bottom of the test tube is located at $x = 0$ and the liquid-gas interface at $x = Z_t$, the boundary condition of equation (4.9) in a finite system is:

$$\frac{\partial C_A}{\partial x} = 0 \quad \text{for} \quad x = 0$$  \hspace{1cm} (4.18)

$$C_A = C_{Ai} \quad \text{for} \quad x = Z_t$$  \hspace{1cm} (4.19)

The solution of equation (4.9) in conjunction with the finite domain moving boundary condition may be obtained assuming that the diffusion coefficient itself is either independent or dependent on the solute concentration in the liquid phase. Therefore, the diffusivity may remain constant in the course of the diffusion process or alternatively, it may change as diffusion time increases and the solution becomes more concentrated with the solute. Some investigator such as Danckwerts (1950) proposed solutions for diffusion equations for moving boundary problems.
### 4.4. Concentration-independent diffusion coefficient

Integration of equation (4.9) with the assumption of constant diffusivity between $x = 0$ to $x = Z_f$ yields:

\[
\int_0^{Z_f} \frac{\partial C_A}{\partial t} \, dx = D \int_0^{Z_f} \frac{\partial^2 C_A}{\partial x^2} \, dx = D \frac{\partial C_A}{\partial x} \bigg|_{Z_f}
\]  

(4.19)

Applying Leibnitz's integration rule, equation (4.19) simplifies to:

\[
\frac{d}{dt} \int_0^{Z_f} C_A(x, t) \, dx = \frac{d}{dt} \int_0^{Z_f} \frac{dC_A}{dt} \, dx + C_A(Z_f, t) \frac{\partial Z_f}{\partial t}
\]

(4.20)

\[
\frac{d}{dt} \int_0^{Z_f} C_A(x, t) \, dx = D \frac{\partial C_A}{\partial x} \bigg|_{Z_f} + C_A \frac{\partial Z_f}{\partial t}
\]

(4.21)

Differentiating equation (4.1) with respect to time after some mathematics gives:

\[
\frac{d\bar{C}_A}{dt} = \frac{1}{Z_f} \frac{d}{dt} \int_0^{Z_f} \overline{C}_A(x, t) \, dx - \overline{C}_A \frac{dZ_f}{dt}
\]

(4.22)

Combining equations (4.21) and (4.22) results in:

\[
Z_f \frac{d\bar{C}_A}{dt} = (C_A - \overline{C}_A) \frac{dZ_f}{dt} + D \frac{\partial C_A}{\partial Z} \bigg|_{Z_f}
\]

(4.23)

Substituting for $Z_f$ and its derivative from equations (4.2) and (4.3) yields:

\[
\frac{d\bar{C}_A}{dt} = (C_A - \overline{C}_A) \nu_A \frac{d\bar{C}_A}{dt} + \frac{D}{Z_0 \exp(\nu \overline{C}_A)} \frac{\partial C_A}{\partial x} \bigg|_{Z_f}
\]

(4.24)

Equation (4.24) relates the rate of diffusion of solute into the liquid phase to the concentration profile at the interface. The main problem in the solution of this
equation is that the interfacial concentration profile, \( \frac{\partial C_A}{\partial x} \bigg|_{z_i} \) is unknown. Do and Rice (1986) have shown that for fixed boundaries it is satisfactory to assume that the shape of the concentration profiles at any time is parabolic:

\[ C_A = a_0 + a_1 x^2 \quad (4.25) \]

The interfacial and mean solute concentrations at any time can be calculated from equation (4.25), and from its combination with equation (4.1) respectively. The results of these calculations are:

\[ C_{Ai} = a_0 + a_1 Z_i^2 \quad (4.26) \]

\[ \overline{C}_A = a_0 + \frac{a_1}{3} Z_i^2 \quad (4.27) \]

The parameters \( a_0 \) and \( a_1 \) can be obtained in terms of \( C_{Ai} \) and \( \overline{C}_A \) from the simultaneous solution of equations (4.26) and (4.27):

\[ a_0 = 1.5 \overline{C}_A - 0.5 C_{Ai} \quad (4.28) \]

and

\[ a_1 = \frac{3(C_{Ai} - \overline{C}_A)}{2(Z_0 \exp(v_A \overline{C}_A))^2} \quad (4.29) \]

The interfacial concentration gradient can also be obtained by differentiating equation (4.25) with respect to \( x \):

\[ \frac{\partial C_A}{\partial x} \bigg|_{z_i} = 2a_1 Z_i = \frac{3(C_{Ai} - \overline{C}_A)}{Z_0 \exp(v_A \overline{C}_A)} \quad (4.30) \]
Substituting equation (4.30) into equation (4.24) after some algebraic manipulation and rearrangement results in:

\[
\frac{d\bar{C}_A}{dt} = \frac{3D (C_{AI} - \bar{C}_A)}{Z_0 \exp(\nu_A \bar{C}_A)^2 \left(1 + \nu_A \bar{C}_A - \nu_A C_{AI}\right)}
\]  

(4.31)

Equation (4.31) with the initial condition defined by equation (4.10) can be solved numerically using a 6th order Runge-Kutta method in the MatLab environment.

If equation (4.4) and its derivative are used instead of equation (4.3) equation (4.23) reduces to:

\[
\frac{d\bar{C}_A}{dt} = \frac{3D (C_{AI} - \bar{C}_A)(1 - \nu_A \bar{C}_A)^3}{Z_0^2 (1 - \nu_A \bar{C}_A)}
\]

(4.32)

The method of separation of variables can be used to integrate the above equation. The result of the integration after some mathematics is:

\[
\frac{1}{(1 - \nu_A C_{AI})^3} \ln \left[\frac{\nu_A C_{AI}(1 - \nu_A \bar{C}_A)}{\nu_A (C_{AI} - \bar{C}_A)}\right] - \frac{\nu_A \bar{C}_A}{(1 - \nu_A C_{AI})^2 (1 - \nu_A \bar{C}_A)} - \frac{\nu_A \bar{C}_A (2 - \nu_A \bar{C}_A)}{2(1 - \nu_A C_{AI})(1 - \nu_A \bar{C}_A)^2} = \frac{3D t}{Z_0^2 (1 - \nu_A C_{AI})}
\]

(4.33)

At the beginning of the diffusion process, the concentration profile defined by equation (4.17) is not yet affected by its non-flux boundary condition. Hence the prediction of equation (4.33) should coincide with the exact semi-infinite solution of equation (4.17) at the beginning of the diffusion. The validity of the parabolic concentration profile is illustrated in Figure 19 where the prediction of equation (4.33) and the numerical solution of equation (4.31) are compared with the exact solution of equation (4.17). While the results of the numerical solution of equation (4.31) agree well with its approximate analytical solution, the assumption of a parabolic concentration profile
for the solute is a very poor approximation. The results clearly demonstrate that the parabolic concentration profile of the fixed boundary diffusion processes introduces significant errors to the moving boundary diffusion problems.

4.5. Variable powered solute concentration profile

Do and Pinczewski (1991) proposed a more realistic concentration profile for the solute throughout the diffusion process:

\[ C_A = b_0 + b_1 x^n \]  

(4.34)

where the exponent \( n \) is a function of time and given by:

\[ n = a \omega \quad \text{where} \quad \omega = \frac{C_{Ai}}{C_A} \]  

(4.35)

![Figure 19. Comparison of analytical and numerical solution of finite domain parabolic concentration profile with semi-infinite exact solution](image)
Results and Discussion

The parameter $\alpha$ is positive and independent of time and should be determined for each system from experimental data. The mean concentration profile can be obtained in a manner analogous to that for the parabolic concentration profile:

$$\overline{C_A} = b_0 + \frac{b_1}{a\omega + 1} \left( \frac{Z_0}{1 - \nu_A \overline{C_A}} \right)^{a\omega} \tag{4.36}$$

Similarly, the parameters $b_0$ and $b_1$ can be obtained by writing equation (4.34) for the interface and utilizing equation (4.35), which after some mathematics yields:

$$b_0 = \overline{C_A} + \frac{\overline{C_A}}{a} \left( \frac{1 - \omega}{\omega} \right) \tag{4.37}$$

and

$$b_1 = \left( C_{Ai} - \overline{C_A} \right) \left( \frac{a\omega + 1}{a\omega} \right) \left( \frac{1 - \nu_A \overline{C_A}}{Z_0 \overline{C_A}} \right)^{a\omega} \tag{4.38}$$

The concentration gradient at the interface can also be calculated from equations (4.34), (4.37) and (4.38):

$$\frac{\partial C_A}{\partial x} \bigg|_{z_i} = \frac{(C_{Ai} - \overline{C_A}) (a C_{Ai} + \overline{C_A}) (1 - \nu_A \overline{C_A})}{Z_0 \overline{C_A}} \tag{4.39}$$

Substituting equation (4.39) into equation (4.24) gives:

$$\frac{d \overline{C_A}}{dt} = \frac{D (1 - \nu_A \overline{C_A})^3 (C_{Ai} - \overline{C_A}) (a C_{Ai} + \overline{C_A})}{Z_0^2 \overline{C_A} (1 - \nu_A C_{Ai})} \tag{4.40}$$

Integrating equation (4.40) using the separation of variables method as illustrated in Appendix A yields:
\[
\frac{1}{\alpha_7} \ln \frac{(aC_{Ai} + \bar{C}_A)^{\alpha_1}}{(C_{Ai} - \bar{C}_A)^{\alpha_1} (1 - aC_{Ai})^{\alpha_2/a} + 2a \alpha_7 (1 - aC_{Ai})^{2} + \frac{\alpha_4}{a \alpha_7 (1 - aC_{Ai})} + \frac{\alpha_5}{\alpha_7} = D \cdot t \tag{4.41}
\]

The values of the parameters \(\alpha_1\) to \(\alpha_7\) are given in Table 4.1.

**Table 4.1. The coefficients of equation (4.41)**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha_1)</td>
<td>(-aC_{Ai}/C_{Ai}(1 + aC_{Ai})(1 + a))</td>
</tr>
<tr>
<td>(\alpha_2)</td>
<td>(1/(1 + a)(1 + v_A C_{Ai})^3)</td>
</tr>
<tr>
<td>(\alpha_3)</td>
<td>(a(\alpha_1 - \alpha_2))</td>
</tr>
<tr>
<td>(\alpha_4)</td>
<td>(v_A/(v_A C_{Ai} - 1 + \alpha_2 + \alpha_3 + \alpha_4))</td>
</tr>
<tr>
<td>(\alpha_5)</td>
<td>(-[\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4]/a C_{Ai})</td>
</tr>
<tr>
<td>(\alpha_6)</td>
<td>(-\alpha_1 \ln(aC_{Ai}) + \alpha_2 \ln(C_{Ai}) - \frac{\alpha_4}{2a} - \frac{\alpha_5}{a})</td>
</tr>
<tr>
<td>(\alpha_7)</td>
<td>(1/Z_0^2(1 - v_A C_{Ai}))</td>
</tr>
</tbody>
</table>

The applicability of the variable profile concentration of solute is demonstrated in Figure 20. In this figure the amount of methane transferred into the liquid phase predicted from equation (4.41) is compared with the exact semi-infinite solution, equation (4.17), for several different values of adjustable parameter \(a\). Excellent agreement can be seen between equations (4.17) and (4.41) with a value of \(a=0.54\) at short contacting times where the finite solution of equation (4.41) coincides with the solution for semi-infinite boundary conditions according to equation (4.17).

If the left hand side of equation (4.41) is plotted versus time, a straight line should result with a slope of diffusivity of solute gas in the liquid phase at the specified conditions. Eliminating the initial incubation period, plots of LHS of equation (4.41)
Results and Discussion

are shown in Figures 21a-21c as a function of time for the methane -dodecane systems at three different temperatures. The results for the methane-crude oil system are also plotted in Figure 21d at 25 °C. These figures clearly illustrate that the experimental results conform very well to the straight lines predicted by equation (4.41). This means that the finite diffusion mathematical model, equation (4.41), which was developed in this work for the finite diffusion cell can predict the diffusion process in the diffusion cell. Significant deviation in the prediction of equation (4.41) were been observed for the initial incubation period in all experiments especially at high pressures where the rate of mass transfer is high due to high solubility of gas phase in the liquid.

The failure of equation (4.41) in the prediction of the experimental data in the incubation period indicates that mass transfer during this time is not only by the mechanism of molecular diffusion and that convective mass transfer may also exist. However, convective diffusion decays throughout this period with increasing contacting time. Beyond the incubation period, mass transfer is only controlled by the mechanism of molecular diffusion and equation (4.41), which is developed based on diffusion mechanisms, fits the experimental data of this period well.

![Comparison between variable power profile and semi-infinite exact solution](image)

Figure 20. Comparison between variable power profile and semi-infinite exact solution

- $P = 15.85$ MPa
- $T = 293$ K
- $D = 0.67 \times 10^{-9}$ m$^2$/s
- $\nu_A = 0.00125$ m$^3$/kg
- $C_{AI} = 30.48$ kg/m$^3$
Results and Discussion

Figure 21a. Plot of left hand side of equation (4.41) versus time at T = 45 °C

Figure 21b. Plot of left hand side of equation (4.41) versus time at T = 65 °C
Results and Discussion

Figure 21c. Plot of left hand side of equation (4.41) versus time at $T = 81 \, ^\circ C$

Figure 21d. Plot of left hand side of equation (4.41) versus time at $T = 25 \, ^\circ C$
The diffusion coefficients are determined from the slopes of the straight lines in Figures 21a-d by the linear least squares technique.

The results of these calculations are given in Figure 22a as a function of pressure at different temperatures for the methane-dodecane system and in Figure 22b for the methane-crude oil system. The diffusion coefficient of methane into dodecane increases steadily with increasing operating pressure up to about 31 MPa. For operating pressures higher than this value, the molecular diffusion of methane in the liquid phase is gradually decreased. Similar behaviour is also observed for the diffusivity of methane in crude oil as illustrated in Figure 22b.

![Figure 22a. Variation of Methane diffusion coefficient in dodecane as liquid phase with pressure at different temperatures](image)

Both sets of data presented in Figures 22a and 22b with the behaviour predicted by the Stockes – Einstein equation which is proposed for diffusion at infinite dilution of 2 species in a dense gas. It appears that the elevation of the working pressure to values in excess 20 To 30 MPa as required by oil reservoir conditions, renders the liquid phase rheology ( e.g. viscosity effects) of marginal importance. This is contrary to earlier observations discussing in chapter 2 by previous works who reported significantly varying effects of viscosity and diffusivities of liquids and gases; see Figure 26 on page 94.
4.6. Time-dependent diffusion coefficient

Despite many attempts that have been made to clarify the mechanism of mass transfer from the gas phase into the liquid phase after the initial incubation period, no information could be found about the mechanism of mass transfer during the incubation period. There is no explanation yet why the mass transfer rate at the initial period of contact between gas and liquid phase is so high especially at high pressures. To provide some explanations for the high mass transfer rate in the initial incubation period attempts have been made to solve the equation of diffusion under the condition that the diffusion coefficient is not constant and varying with diffusion time. These calculations are performed to elucidate further the mechanisms of mass transfer in the incubation period.

In the literature very few attempts are made to describe the dependency of the diffusion coefficient on the volume-averaged concentration of a solute which is
changing with time. Sano and Yamamoto (1990) assumed the diffusion coefficient to be a function of the concentration, and one or more parameters were fitted to different correlations. Van der Zanden (1998) presented a numerical procedure to obtain the dependency of the diffusion coefficient on the concentration, if the space-averaged concentration is known as a function of time. A number of methods are available to solve equation (4.6) numerically when the diffusion coefficient varies as the contacting time increases and the solution becomes more concentrated. Thus, the equation of continuity is to be rearranged as:

\[
\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C_A}{\partial x} \right)
\]  

(4.42)

An implicit finite-difference method is used to solve equation (4.42) numerically in conjunction with initial and boundary conditions of the diffusion cell defined by equations (4.18) and (4.19). The finite difference approximations are:

\[
\left. \frac{\partial C_A}{\partial t} \right|_{c_i} = \frac{C_{j+1}^i - C_j^i}{\Delta t} \quad \text{and} \quad \left. \frac{\partial^2 C_A}{\partial x^2} \right|_{c_j} = \frac{C_{i+1}^{j+1} - 2C_i^{j+1} + C_{i-1}^{j+1}}{\Delta x^2}
\]

(4.43)

Replacing the derivatives by the mean of its finite-differences, equation (4.42) can be approximated by:

\[
\lambda C_{i+1}^{j+1} - (1 + 2\lambda)C_i^{j+1} + \lambda C_{i-1}^{j+1} = -C_i^j
\]

(4.44)

where the variable \( \lambda \) is defined as:

\[
\lambda = \frac{D \cdot t}{(\Delta x)^2}
\]

(4.45)

Solving equation (4.44) for \( C_i^{j+1} \) results in:
Since all the values of \(C_t^0\) are known, all the values of \(C_t^1\) can be calculated and in this manner the remaining concentrations can be computed in turn. However, there are two unknowns in equation (4.46), namely the concentration profile at time \(t+\Delta t\) and the diffusion coefficients at these concentrations, \(D(C_t^{i+1})\). To overcome this problem the successive substitution method is used. In this technique, the diffusion coefficients at the new concentrations, as a first approximation, are set equal to the previous value, i.e. \(D(C_t^{i+1}) = D(C_t^i)\). With this assumption the new concentration profile can be calculated. Once the new profile is computed, the volume average solute concentration can also be obtained from equation (4.1). Next, the values of \(D(C_t^{i+1})\) can be computed and the same time step must be repeated to calculate the value of \(C_t^{i+1}\) more accurately. The computations have been performed in the MatLab environment and the iterative substitution continued until the resulting volume-average concentrations coincided with the values obtained from the experiment. The listing of the program is provided in Appendix B. In the programming, non-equal time steps have been used. At the beginning where the concentration profiles are steep, small time steps are used; as the diffusion process proceeded, the time steps have been increased. This method requires the volume-average concentration versus time, the boundary conditions and the first estimate for the diffusion coefficient.

Typical results of the numerical calculations are illustrated in Figures 23a-b, where the computed diffusion coefficients are plotted as a function of time for the case of 13.8 and 28.9 MPa at 65 °C. The computed volume-average concentration profile calculated from the predicted diffusion coefficients is also depicted in this figure. As expected, the experimental data and the predicted values are perfectly coinciding. The general shape of the diffusion coefficient versus time curves is characterized by an initial sharp decrease in diffusion coefficient (Region 1), followed by a gradual decrease towards a constant value (Region 2). Comparing these results with those shown in Figure 17h, consistent trends are found. Region 1 corresponds to the incubation period where mass transfer occurs by both molecular diffusion and
Results and Discussion

Convection decays quickly with increasing contacting time, even though this is strongly affected by the adjusted pressure. With increasing pressure, the extent of Region 1 increases and the operating time within this region increases. The convection at high pressures decays slower and to a smaller extent than at low pressures. In Region 2, mass transfer from the gas phase into the liquid phase is controlled by molecular diffusion. In this regime, the dependency of diffusion coefficient on contacting time and solute concentration is weak, which is in agreement with the advanced kinetic theory of Hirschfelder et al. (1954), which predicts only a small effect of composition on diffusion in binary mixtures. Near the end of diffusion operation, when the entire gas phase is dissolved in the liquid phase, the rate of mass transfer decreases towards zero and as a consequence the solute concentration in the liquid phase approaches a constant value. The diffusion coefficients predicted from equation (4.41) are also displayed in Figures 23a-b. Excellent agreement exists between the diffusion coefficients obtained from equation (4.41) and the measured molecular diffusion coefficients in Region 2. With exception of the beginning (Region1), the mass transfer process is entirely controlled by the mechanism of molecular diffusion (Region 2). In the present work, the measurements which have been made in this region are used to determine the molecular diffusion coefficients. As mentioned before the incubation period increases as operating pressure and solubility of methane in the solution increases. This fact is reproduced in figures 23a-b.
Results and Discussion

Figure 23a. Comparison between constant and time dependent diffusivity at 13.8 MPa

Figure 23b. Comparison between constant and time dependent diffusivity at 28.9 MPa
4.7. Effect of liquid viscosity and operating temperature

Figures 24a-b show the variation of the diffusion coefficient with liquid phase viscosity for methane-crude oil and methane-dodecane systems. At each temperature the diffusion coefficient decreases steadily as the liquid phase viscosity increases. Almost all correlations available for the prediction of molecular diffusion of gases in liquids show that at a certain temperature the diffusion coefficient depends primarily on the liquid phase viscosity. For this reason, as been shown in Chapter 2, some investigators tried to model their experimental data with respect to liquid phase viscosity. The dissolution of a gas into a liquid reduces its viscosity, which results in an increase in the molecular diffusivity of the solute gas in the liquid phase. Liquid phase viscosity also decreases with increasing liquid phase temperature. Therefore, as the experimental results show, the diffusion coefficient also increases as liquid phase temperature increases, even though increasing the temperature reduces the solubility of the gas phase in the liquid phase. In this investigation for the methane-dodecane system, the maximum value of the diffusion coefficient appears at a pressure of about 31 MPa and 81 °C. As the pressure is further increased after this point, the viscosity and the density of the solution are also increased and, as a result of this experiment the diffusion coefficient gradually decreased.

Many efforts have been made by several investigators (Riazi et al., 1993; Hayduk, 1973; Swapan and Butler, 1996; McManamey and Woollen, 1973 and Grogan et al., 1986) to correlate the molecular diffusion of gases in liquids in terms of liquid phase viscosity. The general model of these investigators may be expressed as:

$$D(T, P) = a \mu^b$$

where $a$ and $b$ are constants and must be obtained from experimental data. The coefficient $a$ varies from $0.5 \times 10^{-10}$ to $0.4 \times 10^{-11}$. On the other hand, almost all investigators reported that the coefficient $b$ is negative and varies from -0.45 to -0.8. This indicates that the diffusion coefficient has an inverse relationship with liquid
Results and Discussion

Phase viscosity. There is no doubt that the liquid phase viscosity is the main operational parameter affecting the diffusivity, but fitting all the experimental data obtained at various operational conditions to equation (4.47) is impractical. Other parameters such as molar volumes of gas and liquid phases also have an effect on the diffusion coefficient even though this effect is not as pronounced as the liquid phase viscosity.

The experimental data of the present work at each temperature agree quite well with equation (4.47) as being illustrated in Figures 24a-b. For fitting the data the viscosity is used in centipoise (cP) and the diffusivity in m²/s. The methane-dodecane experimental data at each temperature can be correlated with an absolute mean average error of less than 2% by equation (4.47). The coefficients of this correlation at various temperatures are summarized in Table 4.2.

Table 4.2. The coefficients of equation (4.47) for methane-dodecane and methane-crude oil systems at various temperatures.

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>Methane-dodecane system</th>
<th>Crude oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>T = 45 °C</td>
<td>T = 65 °C</td>
<td>T = 81 °C</td>
</tr>
<tr>
<td>a</td>
<td>0.24719×10⁻⁸</td>
<td>0.26309×10⁻⁸</td>
</tr>
<tr>
<td>b</td>
<td>-1.0005994</td>
<td>-1.0001175</td>
</tr>
</tbody>
</table>

It is interesting to see that for methane-dodecane system the coefficient b is almost independent of temperature and remains constant at the value of one for all different temperatures. This finding is in agreement with the equation of Stokes-Einstein which is the basis for almost all mathematical models developed for the prediction of diffusivity of gases in liquids:

\[
D = \frac{K_b T}{3 \pi \mu d}
\]  

(4.48)
Results and Discussion

where $T$ is the liquid temperature in degree Kelvin, $k_B$ is the Boltzmann constant $1.38 \times 10^{23}$ J/K, $\mu$ is the liquid phase viscosity and $d$ is the solute molecule diameter.

While equation (4.48) fits the diffusivity of methane in dodecane liquid very well at any specified temperature, the variation between the experimental data and the prediction for the methane-crude oil system is about 10%, which is considerable. The best fit is obtained with a value for the constant $b$ equal to 0.8 instead of one, which is obtained for the methane-dodecane system at various temperatures. However, it is encouraging that the prediction of equation (4.47) for crude oil also shows the same trend for the experimental data. The reason for this inconsistency arises from the presence of various components in the crude oil and from uncertainties with respect to the physical and thermodynamic properties of such a complex solution.

![Graph showing variation of diffusivity of methane in dodecane with liquid viscosity](image)

Figure 24a. Variation of diffusivity of methane in dodecane with liquid viscosity
Figure 24b. Variation of diffusivity of methane in crude oil with liquid viscosity

Table 4.2 shows that the parameter \( a \), for the methane-dodecane system, increases as the operating temperature increases, which is in accordance with equation (4.48). Writing equation (4.48) in the following general form:

\[
\frac{D\mu}{T} = \frac{K_B}{3\pi\eta} = \text{constant} \quad (4.49)
\]

Equation (4.49) predicts that if its left hand side is plotted as a function of operating pressure all the experimental data should fall onto one line. The results are plotted in Figure 25. It indicates that the experimental data agree well with the predicted trend of equation (4.49) at various temperatures.
Figure 25. Plot of LHS of equation (4.49) with respect to pressure

Figure 25 illustrates that all experimental data cross the Y-axis at a constant value of $7.78 \times 10^{-15}$. Therefore, substituting this constant value in equation (4.49) and solving with respect to diffusion coefficient gives:

$$D = 7.78 \times 10^{-15} \frac{T}{\mu}$$  (4.50)

where $T$ is in Kelvin and the viscosity is in Pa.s.

4.8. Correlation of experimental data

The knowledge of molecular transport behaviour is essential for process and reservoir engineering calculations. Present understanding of diffusion of gases in liquids at high pressures is far from satisfactory. Despite attempts to relate the transport properties of statistical mechanics, exact theoretical equations are not yet available.
According to this investigation the general model for correlating the experimental data can be expressed as:

$$D(x, a) = f(x_1, x_2, \ldots, x_p; a_1, a_2, \ldots, a_m)$$  \hspace{1cm} (4.50)$$

where the $a_j$'s are a set of adjustable parameters and the $x_i$'s are the operating variables. Selecting a model as the estimator of the truth requires the selection of a functional form for $f(x_j, a_j)$, which must be chosen to reflect the true underlying process as closely as possible, followed by the determination of the optimal model parameters by minimizing a suitably defined merit function measuring the agreement with the measured data. Modelling of a process covers a broad spectrum. At one extreme lie theoretical models based on a fundamental knowledge of the process, such models have physically meaningful and measurable parameters. These kinds of models can not be developed yet for the diffusivity of gases in the liquids due to the lack of a comprehensive theory of the liquid state. At the other end lie empirical models. These models do not rely on the fundamental principles governing the diffusion process. Such models involve a set of parameters with no physical meaning related to the actual process. In practice, as a compromise between these two extremes, semi-theoretical models are employed to describe the diffusion of gases in various liquids. These models provide a compromise between the model complexity and the effort needed for the measuring of the parameters.

In this approach, parts of the model are approximated by empirical correlations obtained by curve-fitting available experimental data. Evidently, the parameters based on theoretical concepts may be well-defined but the empirical parameters may have little or no physical meaning. Error analysis of semi-theoretical model proves difficult because the final error in the model predictions may be due to inappropriate theoretical assumptions or inaccurate empirical correlations or both.

A wide variety of empirical and semi-empirical correlations subjected to many limitations have been proposed to estimate diffusion coefficients of gases in liquids. Descriptions of these correlations and the conditions for which their applications have
been recommended are given in Chapter 2. Unfortunately, there is significant confusion and contradiction in the reported literature, countless recommended correlations, but little in the way of unifying theory. To put the accuracy of these correlations into perspective, their predictions are compared with the experimental data in Figure 26. The low-pressure density diffusivity products $\rho_0D_0$, as recommended by most investigators are calculated from the Chapman-Enskog correlation in conjunction with the Stiel-Thodos (1962) equation for estimation of the molecular parameters. The results show that the correlation of Riazi (1993) predicts a gradual reduction in molecular diffusion as the operating pressure increases, which contradicts almost all experimental observations. Contrariwise, the correlations suggested by Bhat (1961) and by Reddy and Doraiswamy (1967) predict a sharp increase in diffusivity with increasing operating pressure. According to Grogan (1988), Hayduk (1973) and Renner (1988) the diffusivity is almost constant over the whole range of pressure investigated in the present work. Not only the predicted trends, but also the absolute values predicted by the different correlations deviated significantly. At low pressure, the best agreement between measured and predicted values is obtained with the correlations of Hayduk (1973) and Renner (1988). The reason for this deficiency lies in the complex nature of the diffusion process of solute gases in liquids, especially at high pressure and the dependence of diffusion coefficients on a number of inter-dependent parameters. i.e., liquid phase viscosity, density of gas and liquid phase, molar volume of gas and liquid, molecular weight of gas and liquid, solubility of solute gas in the liquid, etc. Each parameter affects diffusion in a different way and to varying degrees, making a common empirical or semi-empirical correlation based on all possible parameters most difficult. In the case of crude oil, the situation is even worse, because crude oil is a mixture of various organic and inorganic materials accompanied by traces of several impurities, which may have a significant effect on physical properties, solubility and as a consequence on the diffusion coefficient of solute gas in the crude oil. Developing a parametric mathematical model for such a complex system requires sufficient knowledge about the underlying processes, which determine the system’s overall performance. Furthermore, a large number of experimental parameters need to be estimated, and sophisticated computing techniques must be employed to obtain the required precision.
of the model. As an alternative approach to the parametric modelling, especially when the number of tuning parameters is large and the interaction between these parameters is not clear, artificial neural networks are recommended. Being a model-free function estimator, neural networks can map input to output no matter how complex the relationship may be. The application of neural networks for the prediction of diffusion coefficients of methane in dodecane and crude oil is discussed in the following chapter.

![Investigated correlation](image)

Figure 26. Comparison of measured and predicted diffusion coefficient
5. Prediction of diffusivity using an Artificial Neural Network (ANN)

5.1. Introduction

Conventional engineering systems behave remarkably rigidly when compared to biological ones. They lack the ability to learn from their environment or adapt gracefully to new situations compared to even the simplest biological organisms (Chester, 1993; Baughman and Liu, 1995). This low level of achievement is due to the fundamental differences between the design of biological nervous systems and present day computers (Lerner, 1984, Omohundro, 1987). To bridge this gap researchers in the fields of neurophysiology, psychology and computer science are seeking to understand and implement the mechanisms of intelligence.

Artificial neural networks may be regarded as initial attempts at developing artificial intelligence. Similar to their biological counterparts, these networks are composed of many simple interconnecting elements, or neurons, working in parallel to solve a problem. The most versatile feature of them is the fact that once the network has been set up, it can learn in a self-organized way that seems to mimic simple biological nervous systems.

Numerous companies and research laboratories are investing heavily in projects related in some way to neural networks (Omohundro, 1987). Despite the increase in applications of neural networks in many fields such as electrical, electronics, civil, and control engineering, they were practically unknown to many chemical engineers until the 1990’s. Serious efforts to apply neural network for the simulation and optimization of chemical, biochemical and mineral processes have only begun since the late 1980’s. A concise review of the reported applications of neural networks to chemical and bio-chemical engineering problems is given elsewhere (Baughman and Liu, 1995). In this chapter a brief introduction of the structure of neural networks is given and then their application to the prediction of diffusivity of gases in liquids is discussed.
5.2. Biological neuron

A very simple schematic diagram of an individual biological nerve cell or neuron is shown in Figure 27. It has three major regions:

1. The cell body or soma
2. The dendrites
3. The axon

![Biological model of a neuron](image)

Figure 27. Biological model of a neuron

5.2.1. Cell body or soma

The cell body or soma provides the support functions and the structure of the cell. It contains the nucleus which is the carrier of genetic material. Soma or cell bodies act as information processors, as they receive input from other neurons via synaptic connections.
5.2.2. Dendrites
Dendrites are designed to receive information from other nerve axons via synapses. Dendrites can be densely branched, and can grow from one or more different location of a cell body.

5.2.3. Axon

The axon is a branching fiber that carries signals away from the neuron. The axon, as output mechanism for the neuron, conducts signals away from the cell to other cells via interconnection point called synapses. Although there is only one axon for each cell, it can branch tremendously and thereby send separate branches to different locations. The neuron receives multiple inputs from other neurons via input dendrites. The gap between an output axon of one neuron and the input dendrites of another is the location of the synapses. When the input reaches the synapse's terminal, certain chemicals called "neurotransmitters" are released. The neurotransmitters diffuse across the synaptic gap, to enhance or inhibit dependent on the type of the synapse. The synapse's effectiveness can be adjusted by the signals passing through it so that the synapses can learn from the activities in which they participate. As for the site of "intelligence" within the brain, the increasing belief of people involved in this field is that intelligence resides not within the interiors of the neurons, but diffusely throughout the rich network of interconnections.

5.3. Model of a neuron

Figure 28 shows the model suggested for a neuron. Four basic elements of a neuron can be identified as described in the following subsections.

5.3.1. Synapses or connecting links

Each of the synapses is characterized by a weight or strength of its own. When the $i^{th}$ neuron sends a signal to the $j^{th}$ neuron that signal is multiplied by the weighting on
the \( i,j \) synapse, \( w_{ij} \). When the weight \( w_{ij} \) is positive, it will excite the neuron, increasing

![Figure 28. Mathematical model of a neuron](image)

its activation and hence represents a stimulus synapse (tending to turn the \( j^{th} \) neuron on). If it is negative, the synapse is inhibitory.

### 5.3.2. An adder (or linear combiner)

Each neuron has an adder for summing the input signals, weighted by the respective synapses of the neuron:

\[
u_j = \sum_{i=1}^{n} w_{ij} x_i\]  

(5.1)

### 5.3.3. Internal Thresholds

The next important factor governing the output from a neuron is the internal threshold of the neuron, \( \theta_j \). The internal threshold controls activation of that neuron. When the neuron finished the calculation of all its \( (w_{ij}x_j) \)'s and the sum of them, \( u_j \), the neuron calculates its total activation, \( v_j \), by subtracting the internal threshold value:
If the internal threshold, \( \theta \), is positive, the node has high internal threshold hence inhibit node firing. Conversely, if \( \theta \) is zero or negative (bias), the node has low internal threshold, which excites node firing.

### 5.3.4 Activation function

The activation function is for limiting the amplitude of the output of a neuron. Typically, the normalized amplitude range of the output signal of a neuron is written as the closed unit interval \([0,1]\) or alternatively \([-1,1]\). Therefore, the output signal of the neuron, \( y_j \), becomes:

\[
y_j = f(v_j) = f\left[ \sum_{i=1}^{n} w_{ij} x_i - \theta_j \right]
\]  

(5.3)

Theoretically, any activation function (such as square root, logarithmic, exponential and so on) can be used. However, according to the researches which have been done by mathematicians and computer scientists it is recommended to use one of the following three activation functions: (1) threshold function, (2) sigmoid function and (3) hyperbolic tangent function.

The sigmoid function is by far the most common form of global activation function with the limiting values between \([0,1]\) which is used in chemical engineering problems.

\[
y_j = f(v_j) = \frac{1}{1 + e^{-\beta v_j}}
\]

(5.4)

where \( \beta \) is the slope parameter of the sigmoid function. By varying the parameter \( \beta \), sigmoid functions of different slope can be obtained.
5.4. Network architectures

The manner in which the neurons of a neural network are structured is intimately linked the learning algorithm used to train the network. In general the neurons can be interconnected in two main architectures, feed forward networks and feed backward networks. In feed forward networks there is no loop, therefore, they are static. On the other hand in feed backward networks, loops occur because of feedback connections, therefore, feedback networks are dynamic and generally used in control systems.

5.4.1. Fully connected feed forward networks
These networks which are commonly used in chemical engineering (Baughman and Liu, 1996), networks depending on the type of neurons which is used are classified into two categories:

1. Multi-layer feed forward network
2. Radial basis function network

5.4.1.1. Multi-layer feed forward network
The neural network of Figure 29 is the general architecture of multi-layer feed forward network. The network is fully connected in the sense that every node (neuron) in each layer of the network is connected to every other node in the adjacent forward layer. In other words, this network is strictly of a feed forward type. The network contains one input layer of source nodes. But it may have one or more hidden layers, whose computation nodes are correspondingly called hidden neurons or hidden units. The function of the hidden neurons is to intervene between the external input and the network output. By adding one or more hidden layers, the network is enabled to extract more information by virtue of the extra set of synaptic connections and increased neural interactions. The ability of the hidden neurons to extract more information is crucial for large input dimensions. Almost all networks which are being used in chemical engineering have just one hidden layer because improvement
Prediction of diffusivity using an Artificial Neural Network (ANN) which is observed with more than one hidden layer was negligible in comparison to the extra mathematical efforts needed to train the network.

Figure 29. A simplified architecture of the three layer feed forward neural network

The development of a multi-layer feed forward network takes places in three consecutive phases:

1. Training or learning phase
2. Recall phase
3. Generalization phase

The training or learning phase

Training a network means that to develop a hyper surface between the input and output spaces. In neural network development this phase is the longest and most time consuming and it is critical to the success of the network. The training algorithm deals with the adjustment of the weight factors between neurons until the specified input
pattern yields the desired output pattern. Through these adjustments the neural network learns the correct input-output response behavior. Many engineering applications are concerned with the estimation of an underlying trend or function from a limited number of input-output data points with little or no knowledge of the form of the true function. This problem is sometimes referred to as non-parametric regression function approximation. In neural network parlance, it is usually called supervised learning. The underlying function is learned from the exemplars which a teacher supplies. The set of examples (the training set) contains elements that consist of paired values of the independent input and the dependent output variables. A supervised learning algorithm adjusts the network parameters according to the differences between the measured response and the network outputs corresponding to a given input. In practical applications the measurements are by definition subject to error. The learning algorithm should therefore be equipped with proper provisions to effectively filter out the noise. The most popular algorithm available to train multilayer feed forward network is the error back propagation algorithm (Baughman and Liu, 1995). This algorithm is a trial and error optimization method and is based on the error correction learning rule. A major drawback of this method is that there is no guarantee that it always converges or converges at global optimum point, especially when the number of neurons in each layer is large. Another difficulty with the back propagation algorithm is the extensive time required to train the network. Depending on the size of the neural network, training can take hours or even days.

**The recall phase**

One of the most important aspects in developing neural networks is determining how well the network performs once training is completed. First of all it should be determined responses (output vector) from data set used to train the network. Thus the input data which is used to train the network must be introduced to the network and the output error assess from the desired input-output response. A well trained network should be able to produce an output that deviates very little from the desired value.
The generalization phase

In the generalization phase, the unseen feed inputs are fed to the trained network. If it sensibly interpolated the data, it is considered that the network generalized well. A well trained network should provide input-output mapping with good generalization capacity. To effectively visualize how well a network performs recall and generalization, a learning curve is often generated. The learning curve is a plot of average error for both recall of training data sets and generalization of data set not used in network training as a function of the number of examples in the training data set. Figure 30 shows a typical learning curve divided into multiple training segments. Two main uses of the learning curve are:

(a) to find the number of training examples required to achieve a fixed average error. In Figure 30, the network reaches a fixed average error the approximately 5 time intervals.

(b) to estimate the minimum average error attainable through adding data sets. In Figure 30, the minimum average error for generalization is about 5%.

Figure 30. Typical learning curve for a well trained neural network
5.4.1.2. Disadvantages of multi-layer feed forward network

Multi-layer feed forward neural networks are the most popular ones. They have already been used as a tool to model and simulate various chemical processes (i.e. Shaw et al., 1997). Ungar et al. (1990) point out that the limitation of these networks are as follow:

1. Large number of iterations before convergence i.e. slow learning

2. Rapid forgetting due to seldom seen exemplars and the lack of first principle knowledge.

5.4.2. Radial Basis Function network

The Radial Basis Function (RBF) which is a special class of multi-layer feed forward networks. Figure 31 shows a frequently used architecture for a radial basis function network. These networks have just three layers, input layer, hidden layer and output layer. Powell (1985) surveyed the early work on RBF neural networks.

![Figure 31. The architecture of a radial basis function networks](image-url)
Input layer

As input pattern enters the input layer and is subjected to a direct transfer function, i.e., the output of the node equals the input. Thus for an input vector \( x \) with elements \( x_i \) (\( i = 1 \) to \( N \)), the output from the input layer is also vector \( x \).

Hidden layer

The hidden layer is the most important processing step in a radial basis function network. Its nodes satisfy the unique property of being radially symmetric, it must have the following:

(a) a center vector \( c_k \) in the input space, made of cluster centers, with elements \( c_{ik} \) (\( i = 1 \) to \( N \)). The vector is typically stored as the weight factors from the input layer to the hidden layer as being demonstrated in Figure 31.

(b) a distance measure to determine how far an input vector \( x \), with the elements \( x_i \) (\( i = 1 \) to \( N \)), is from the center vector \( c_k \). Typically, the standard Euclidean distance measure between \( x \) and \( c_k \) to define a Euclidean summation, \( I_k \) (\( k = 1 \) to \( L \)) is used, where \( L \) is the number of nodes in the hidden layer:

\[
I_k = \| x - c_k \| = \sqrt{\sum_{i=1}^{n} (x_i - c_{ik})^2} \tag{5.5}
\]

(c) a transfer function which transforms the Euclidean summation \( I_k \) (\( k = 1 \) to \( L \)) to give an output for each node. This Gaussian function also has a width of \( \sigma_k \) (\( k = 1 \) to \( L \)). The resulting output from the \( k^{th} \) node, \( v_k \) (\( k = 1 \) to \( L \)) is:

\[
v_k = \exp \left( -\frac{I_k^2}{\sigma_k^2} \right) \tag{5.6}
\]
To summarize, the hidden layer processes the output from the input layer in two steps, namely, a distance calculation, equation (5.5), and a transfer function, equation (5.6).

**Output layer**

As Figure 31 shows, there are weight factors $w_{kj}$ ($k = 1$ to $L$; $j = 1$ to $M$) between the $k^{th}$ node in the hidden layer and the $j^{th}$ node in the output layer. The output vector $y_j$ ($j = 1$ to $M$) would be found from the output layer through a standard procedure as in the back propagation network.

With respect to this network, learning is equivalent to finding a surface in a multidimensional space that provides a best fit to the learning data. Correspondingly, generalization is equivalent to the use of this multidimensional surface to interpolate the test data. The construction of a RBF network in its most basic form involves three entirely different layers. The input layer is made up of inputs nodes. The second layer is a hidden layer of high enough dimensions, which serves a different purpose from that in the multilayer feed forward network. The output layer supplies the response of the network to the activation patterns applied to the input layer. In contrast to the multilayer feed forward network, the transformation from the input space to the hidden layer space is non-linear, whereas the transformation from the hidden layer space to the output space is linear. When the output vector has just one element, like in the case of diffusion, the biggest advantages of RBF networks is that the training phase, unlike the multilayer feed forward network, has an exact solution, which is discussed in detail in the section on the modeling of the experimental data.

**5.5. Modeling of experimental data using RBF neural network**

Although the previous investigations have not been successful in producing a generally applicable correlation for the prediction of molecular diffusion of gases in liquids at high pressures, they have nevertheless been successful in identifying the
main variables affecting molecular diffusion of a gas in a liquid. The results of this work and previous findings can be expressed by the following functional relationship:

\[ D = F(\mu_G, \mu_L, \text{MW}_G, \text{MW}_L, \nu_G, \nu_L, P, T) \] (5.7)

Equation (5.7) can be expressed in terms of dimensionless groups:

\[ \frac{\rho D}{\rho D_0} = F\left(\frac{\mu_G}{\mu_{G0}}, \frac{\mu_L}{\mu_{L0}}, \frac{\text{MW}_G}{\text{MW}_{G0}}, \frac{\text{MW}_L}{\text{MW}_{L0}}, \frac{\nu_G}{\nu_{G0}}, \frac{\nu_L}{\nu_{L0}}, \frac{P}{P_0}, \frac{T}{T_0}\right) \] (5.8)

The subscript zero in equation (5.8) refers to the diffusivity and physical properties of the solution at standard conditions. This functionality is complex and may exhibit strong non-linearity with respect to some variables. A regression approach may be adopted; however, the selection of an appropriate regression equation would be problematic and empirical. Furthermore, when new experimental data are available retuning the model is difficult and time consuming. Therefore, in the following it is attempted to investigate the applicability of a neural network to the above functionality. As aforementioned, in the cases similar to this problem, where the output vector has just one element, the RBF is more suitable than multilayer feed forward neural networks.

The input vector may be defined by vector \( X \) and it contains eight variables:

\[ X = [x_1, x_2, \ldots, x_8] \] (5.9)

where the elements \( x_1 \) to \( x_8 \) are viscosity ratio, molecular weight ratio, molar volume ratio and finally pressure and temperature ratios corresponding to the elements on the right hand side of equation (5.8). The output vector has one element, which is diffusivity, \( D \). The RBF training phase has an exact solution and does not need a trial and error optimization approach. The problem can be stated as follows:
For a set of $N$ different input conditions obtained from the experiment at various operating conditions defined as:

$$\{ x_i \in \mathbb{R}^8 \mid i = 1, 2, \ldots, N \}$$  \hspace{1cm} (5.10)

and a corresponding set of $N$ diffusion coefficients:

$$\{ D_i \in \mathbb{R}^1 \mid i = 1, 2, \ldots, N \}$$  \hspace{1cm} (5.11)

the objective is to find a function defined as:

$$F: \mathbb{R}^8 \rightarrow \mathbb{R}^1$$  \hspace{1cm} (5.12)

This function must satisfy the interpolation condition of:

$$F(x_i) = D_i , \quad i = 1, 2, \ldots, N$$  \hspace{1cm} (5.13)

Note that for strict interpolation as specified here, the interpolating surface (i.e. function $F$) is constrained to pass through all the training data points.

The RBF networks consist of choosing a function $F$ that has the following form (Powell, 1988):

$$F(x) = \sum_{i=1}^{N} w_i \phi(||x - x_i||)$$  \hspace{1cm} (5.14)

where

$$\{ \phi(||x - x_i||) \mid i = 1, 2, \ldots, N \}$$  \hspace{1cm} (5.15)

is a set of $N$ nonlinear functions known as radial basis functions and $\| \cdot \|$ denotes a norm that is taken to be Euclidean. The known data points $\{ x_i \in \mathbb{R}^8, i = 1, 2, \ldots, N \}$ are
taken to be the centers of the radial basis functions. Substituting the interpolation
conditions of equation (5.13) in (5.14) the following set of simultaneous linear
equations for the unknown coefficients (weights) of the expansion can be obtained:

\[
\begin{bmatrix}
\varphi_{11} & \varphi_{12} & \cdots & \varphi_{1N} \\
\varphi_{21} & \varphi_{22} & \cdots & \varphi_{2N} \\
\vdots & \vdots & \ddots & \vdots \\
\varphi_{N1} & \varphi_{N2} & \cdots & \varphi_{NN}
\end{bmatrix}
\begin{bmatrix}
w_1 \\
w_2 \\
\vdots \\
w_N
\end{bmatrix} =
\begin{bmatrix}
D_1 \\
D_2 \\
\vdots \\
D_N
\end{bmatrix}
\]  
(5.16)

where

\[
\varphi_{ji} = \varphi \left( \| x_j - x_i \| \right), \quad j, i = 1, 2, \ldots, N
\]  
(5.17)

\( \varphi(\cdot) \) is an arbitrary nonlinear function known as radial basis function. In this work, the
best results are obtained using a multivariate spine basis function:

\[
\varphi(r) = r^2 \cdot \ln(r)
\]  
(5.18)

Let

\[D = [D_1, D_2, \ldots, D_N]^T\]
\[w = [w_1, w_2, \ldots, w_N]^T\]
(5.19)

The N by 1 vectors \( D \) and \( w \) represent the desired response vector and linear weight
vector, respectively. Let \( \Phi \) denote an N by N matrix with elements \( \varphi_{ji} \) :

\[
\Phi = \{ \varphi_{ji} \mid j, i = 1, 2, \ldots, N \}
\]  
(5.20)

Hence equation (5.16) may then be rewritten in compact form:

\[
\Phi w = D
\]  
(5.21)
Providing that the data points are all distinct, the matrix $\Phi$ is definite. Therefore, equation (5.21) can be solved for the weight vector $w$:

$$w = \Phi^{-1} D$$

(5.22)

In practice, some of the experimental data points may be very close to each other or identical. Therefore, the interpolation matrix $\Phi$ would be singular or very close to singular and, as a consequence, equation (5.22) cannot be solved. For these conditions, regularization theory can be used to stabilize the solution of equation (5.22) by perturbing matrix $\Phi$ to $\Phi + \lambda I$. The principle of the regularization theory is finding the function $F(x)$ which minimizes the cost function $\xi(F)$ defined by (Powell, 1988):

$$\xi(F) = \xi_s(F) + \lambda \xi_c(F)$$

(5.23)

where $\lambda$ is a regularization parameter, $\xi_s(F)$ and $\xi_c(F)$ are the standard error and regularization terms, defined as (Poggio and Girosi; 1990a):

$$\xi_s(F) = \frac{1}{2} \sum_{i=1}^{N} [D_i - F(x_i)]^2$$

$$\xi_c(F) = \frac{1}{2} \lambda \|PF\|^2$$

(5.24)

where $P$ is a linear differential operator. Operator $P$ is generally referred as a stabilizer in the sense that it stabilizes the solution $F$, making it smooth and therefore continuous. Substituting equation (5.24) into equation (5.23) gives:

$$\xi(F) = \frac{1}{2} \sum_{i=1}^{N} [D_i - F(x_i)]^2 + \frac{1}{2} \lambda \|PF\|^2$$

(5.25)

$\lambda$ is a positive real number called regularization parameter. In particular, the limiting case $\lambda$ approaching zero implies that the problem is unconstrained, with the solution
F(x) being completely determined from the training data. On the other hand, the other limiting case, \( \lambda \) approaching infinity, implies that the data are unreliable. Using the Green's Function Theorem (Poggio and Girosi; 1990a) the minimization solution of equation (5.23) yields:

\[
F(x) = \sum_{i=1}^{N} w_i G(x_i, x)
\]  

(5.26)

where

\[
w = - \frac{1}{\lambda} \left[ D_i - F(x_i) \right]
\]  

(5.27)

In matrix notation equations (5.26) and (5.27) become:

\[
F = GW
\]  

(5.28)

and

\[
W = \frac{1}{\lambda} (D - F)
\]  

(5.29)

\( G(x; x_i) \) are Green's functions centered at \( x_i, i = 1 \) to \( N \). These functions depend only on the Euclidean form of the difference vector \( (x - x_i) \) as defined by:

\[
G(x; X_i) = G(||X - X_i||)
\]  

(5.30)

Eliminating matrix \( F \) between equations (5.28) and (5.29) and rearranging the terms, yields:

\[
(G + \lambda I)W = D
\]  

(5.31)

The solution of linear system equation (5.31) for the unknown weight vector, \( W \), and the appropriate value of regularization parameter \( \lambda \) yields:
\[ W = (G + \lambda I)^{-1} D \]  

(5.32)

In such a case, the regularization solution of equation (5.26) reduces to:

\[ F(x) = \sum_{i=1}^{N} W_i G(\|x - x_i\|) \]  

(5.33)

5.6. Network architecture

Figure 32 depicts the architecture of the network for a single output used in this work. This network is obtained from the expansion of equation (5.33) in terms of the Green's function \( G(x; x_i) \) centered at \( x_i \). It consists of three layers. The first layer is the input layer and the number of its nodes is equal to the dimension of the input vector \( x \); in this work it is equal to eight. The second layer is the hidden layer, composed of nonlinear units that are connected directly to all of the nodes in the input layer. There is one hidden unit for each data point \( x_i, i=1 \) to \( N \), where \( N \) is the number of training data. The activation functions of the individual units in the hidden layer are defined by the Green's functions. The output layer consists of a single linear unit and its output is diffusivity. The only parameters that need to be trained in this network are the linear weights in the output layer. Equation (5.32) may be used to obtain weight vector \( W \), for a specified output vector \( D \). First about 40 sets of the available experimental data are randomly partitioned into two sets. About eight data are set aside for testing the network integrity and robustness after training. The remaining data are used to train the network by solving equation (5.32) for the unknown weight vector. The program has been written in Matlab environment using its neural network tool box. List of the program is given in Appendix B.

Once the weight vector is calculated, the most important remaining task is to determine how well the network performs at the completion of the training. Checking the performance of a trained network involves the following two main criteria:
Figure 32. Regularized radial basis function network architecture

(1) how well the neural network recalls the output vector from the data set used to train the network; and
(2) how well the network predicts responses for test data sets that were not used in training (i.e. generalization of the network)

As discussed before, network performance is easily tested through the generation of the learning curve. The learning curve is a plot of absolute mean average error for both recall of learning data and generalization of data sets not used in network training as a function of the number of examples in the training data sets. Figure 33 shows learning curves obtained for the data which are used in learning and recall phases. The network reaches fixed average errors of 2.5% approximately after about 10 data sets.

The neural network prediction of diffusion coefficients of methane in the liquid dodecane is plotted in Figure 34 as a function of liquid phase viscosity and operating pressure at different temperatures.
Figure 33. Learning curve for the trained network.

Figure 34. Variation of diffusion coefficient of methane in dodecane with pressure and liquid phase viscosity.
The predicted results are also compared with the experimental data. The results illustrate that excellent agreement exist between the prediction of the network and the experimental data. It also clearly illustrates that as operating pressure increases more gas dissolves in the liquid phase, hence viscosity of the solution decreases and as a result diffusivity of gas in the liquid phase increases. The applicability of the neural network for the prediction of diffusion coefficient is further demonstrated in Figures 35 and 36 where all the experimental data over a wide range of pressures and temperatures are compared with values predicted from the neural network. The absolute mean average error between the prediction and the experimental data is less than 3% which shows the applicability of the neural network.

Figure 35. Comparison of measured diffusion coefficient with values predicted from the neural network in different temperatures
Figure 36. Comparison of measured diffusion coefficient with values predicted from the neural network in different pressures.
6. CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

The diffusion coefficients of methane in dodecane and in a typical Iranian crude oil have been measured over a wide range of pressure and temperature using a precision high-pressure diffusion apparatus. Initially, a mathematical model is developed to describe the diffusion process in the diffusion cell using semi-infinite boundary conditions. In this model, a variable power profile assumption has been made which allows simple approximate analytical solutions to be written for diffusion controlled moving-boundary condition. The solutions offer a significant improvement over previously reported solutions for fixed boundary conditions which assume a parabolic profile and provide estimates of mass transfer rates which are valid for all diffusion times. Measurements of diffusion coefficients at high pressure are made conveniently by measuring the motion of the interface between gas and liquid phases. Composition measurement at high pressure is not required though solubility data and molar volume must be available. From these measurements the following specific conclusions can be drawn:

1. The results show that as the operating pressure is increased the solubility of methane in the solvent is increased. Therefore, the viscosity of the solutions is decreased; as a result the molecular diffusion of methane in the dodecane and the crude oil is also increased. In this investigation the maximum value of diffusion coefficient is observed at pressure corresponding to the point at which the gas phase is disappeared and all dissolved in the liquid phase. As the pressure is further increased and density of the solution increased and, as a result the diffusion coefficient is decreased.

2. When the operating temperature is increased, the viscosity of the solvent is decreased; as a result the molecular diffusion of methane in dodecane and crude oil is increased.
3. The diffusivity of methane in both dodecane and crude oil at high pressures is dependent primarily on solvent viscosity as determined from measurements of diffusivities at various pressures. While this correlation can predict the diffusivity of methane in dodecane, it is purely empirical and its application is limited to the range of the experimental conditions which is used in this investigation.

4. The predictions of various correlations from the literature are compared with the experimental data. The agreement between experimental data and predicted values can be recommended to be used for the prediction of the diffusivity of hydrocarbon gases in liquids at high pressures.

5. The suitability of artificial neural networks for identification of the process variables is evaluated. The radial basis function neural network architecture was used successfully to predict the diffusion coefficients of solute gases in hydrocarbon liquids and crude oil. The experimental data of the present investigation and some data reported in the literature by other investigators have been used to train this network. The trained network can predict the diffusivity of hydrocarbon gases in liquids solvents which were been used in this investigation. The advantage of this approach is not only that all variable are implemented in the network but that it can also easily be retrained when new experimental data are available.

6.2. Future work

1. All present experiments are performed with pure gas which means that there is no resistance against mass transfer in the gas phase. In reality there are always some impurities in the gas phase which may have significant effects on the rate of mass transfer of methane into the liquid phase. It is recommended to perform some experiments in the presence of ethane and propane in the gas phase as impurities to clarify the effect of gas phase resistance against diffusion of methane into the liquid phase.
Conclusions and Future work

2. In the last test, the liquid selected was a typical Iranian crude oil which caused some difficulties and problems in measuring the change of liquid level during the test. Hence, different method for measuring diffusivity of gases into crude oil should be investigated.

3. In this work the experimental data for crude oil are limited only to one temperature. The reason, as discussed before, was that recording the interface with crude oil is difficult, time consuming and subject to error. It is recommended to perform experiments with crude oil under constant volume and variable pressure where detecting the swelling height is not needed and only the pressure need to be recorded.
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Appendix A- Derivation of equation (4.41)

\[
\int \frac{y dy}{(1-ay)(b-y)(c+y)} = \int \left[ \frac{A_1}{1-ay} + \frac{A_2}{(1-ay)^2} + \frac{A_3}{(1-ay)^3} + \frac{A_4}{b-y} + \frac{A_5}{c+y} \right] dy \tag{A.1}
\]

\[
\int (ax+b)^n dx = \frac{(ax+b)^{n+1}}{a(n+1)} + c \quad n \neq -1 \tag{A.2}
\]

\[
\int (ax+b)^{-1} dx = \ln|ax+b| + c \tag{A.3}
\]

\[
\int \frac{A_1 dy}{1-ay} = -\frac{A_1}{a} \ln|1-ay| + c_1 \tag{A.4}
\]

\[
\int \frac{A_2 dy}{(1-ay)^2} = \frac{A_2}{a(-2+1)} + c_2 = \frac{A_2}{a(1-ay)} + c_2 \tag{A.5}
\]

\[
\int \frac{A_3 dy}{(1-ay)^3} = \frac{A_3}{a(-3+1)} + c_3 = \frac{A_3}{2a(1-ay)^2} + c_3 \tag{A.6}
\]

\[
\int \frac{A_4 dy}{(b-y)} = -A_4 \ln|b-y| + c_4 \tag{A.7}
\]

\[
\int \frac{A_5 dy}{(c+y)} = -A_5 \ln|c+y| + c_5 \tag{A.8}
\]

\[
C' = c_1 + c_2 + c_3 + c_4 + c_5 \tag{A.9}
\]

\[
\int \frac{y dy}{(1-ay)(b-y)(c+y)} = -\frac{A_1}{a} \ln|1-ay| + \frac{A_2}{a(1-ay)} + \frac{A_3}{2a(1-ay)^2} - A_4 \ln|b-y| + A_5 \ln|c+y| + C' \tag{A.10}
\]

\[
A_1(1-ay)^3(b-y)(c+y) + A_2(1-ay)(b-y)(c+y) + A_3(b-y)(c+y) + A_4(1-ay)^3(c+y) + A_5(1-ay)^3(b-y) = y \tag{A.11}
\]

1) Assume \( y = b \)

\[
A_4(1-ay)^3(c+y) = y \rightarrow A_4(1-ab)^3(c+b) = b
\]

\[
A_4 = \frac{b}{(b+c)(1-ab)^3} \tag{A.12}
\]
II) assume \( y = -c \)

\[
A_3(1 - a( - c)) \gamma (b - ( - c)) = -c \quad \rightarrow \quad A_3(1 + ac) \gamma (b + c) = -c
\]

\[
A_3 = \frac{-c}{(b + c)(1 + ac) \gamma ^3}
\]

(A.13)

III) assume \( y = \frac{1}{a} \)

\[
A_3 \left( \frac{b - 1}{a} \left( \frac{c + 1}{a} \right) \right) = \frac{1}{a}
\]

\[
A_3 \left( \frac{ab - 1}{a} \left( \frac{ac + 1}{a} \right) \right) = \frac{1}{a} \quad \rightarrow \quad A_3(ab - 1)(ac + 1) = a
\]

\[
A_3 = \frac{a}{(ab - 1)(1 + ac)}
\]

(A.14)

\[
(1 - ay)^3 = 1 + a^2y^2 - 2ay, \quad (1 - ay)^3 = 1 - 3ay + 3a^2y^2 - a^3y^3
\]

(A.15)

\[
A_4(1 - ay)^3(b - y)(c + y) = A_4(1 + a^2y^2 - 2ay)(bc + by - cy - y^2) = A_4(-a^2)y^4 + A_4(2a - a^2c + a^2b)y^2 + A_4(2ac - 2ab + a^2bc - 1)y + A_4abc
\]

(A.16)

\[
A_4(1 - ay)(b - y)(c + y) = A_4(1 - ay)(bc + by - cy - y^2) = A_4(a)y^3 + A_4(ac - ab - 1)y^2
\]

(A.17)

\[
A_5(b - y)(c + y) = A_5(-1)y^3 + A_5(b - c)y + A_5bc
\]

(A.18)

\[
A_4(1 - ay)^3(c + y) = A_4(1 - 3ay + 3a^2y^2 - a^3y^3)(c + y) = A_4(-a^3)y^4 + A_4(3a^2 - a^3c)y^3 + A_4(-3a + 3a^2c)y^2 + A_4(1 - 3ac)y + A_4c
\]

(A.19)
Appendix A

\[ A_2 (1-ay)^3 (b-y) = A_2 (1-3ay+3a^2y^2-a^3y^3)(b-y) = A_2 (a^3) y^4 + A_2 (-3a^2-a^3 b) y^3 + A_2 (3a+3a^2 b) y^2 + A_2 (-1-3ab) y + A_2 b \]

\[ (-a^2 A_1-a^3 A_4+a^3 A_2) y^4 = 0 \rightarrow A_1 + a A_4 - a A_2 = 0 \]

\[ A_1 = a (A_5 - A_4) = a \frac{\frac{-c}{(1+ac)^3 (b+c)} - \frac{b}{(1-ab)^3 (b+c)}}{\frac{1}{(1+ac)^3 (b+c)} - \frac{1}{(1-ab)^3 (b+c)}} = \frac{-c (1-3ab+3a^2 b^2-a^3 b^3)}{(1+ac)^3 (1-ab)^3 (b+c)} \]

\[ A_1 = \frac{\frac{a^3 b^3 c - 3a^3 b^2 c - a^2 b c^2 - 3a^3 b c^3 - b-c}{(1+ac)^3 (1-ab)^3 (b+c)}}{\frac{1}{(1+ac)^3 (b+c)} - \frac{1}{(1-ab)^3 (b+c)}} \]  

(A.20)

\[ A_2 bc + A_1 bc + A_2 bc + A_4 c + A_2 b = 0 \rightarrow A_2 = \left( \frac{A_4}{b} + \frac{A_1}{c} + A_3 + A_1 \right) \]

\[ A_2 = -\left( \frac{1}{(1-ab)^3 (b+c)} - \frac{1}{(1+ac)^3 (b+c)} + \frac{a}{(ab-1)(ac+1)} + A_1 \right) \]

\[ A_2 = \left[ a^3 b^3 c - 3a^3 b^2 c - a^2 b c^2 - b-c + 3a x + 3ab + 3a^2 b^2 - 3a b^2 + a^2 c + a b^2 \right] \]

\[ \frac{a}{(ab-1)(ac+1)} \]  

(A.21)
Appendix B

Appendix B. List of program for solving finite difference equation of continuity with
time dependent diffusion coefficient.

function fig = Diffusion()

setDiffpath;

load DiffMat

Main_Hndl = figure('Units','points', ...
    'windowstyle','normal',...
    'CloseRequestFcn','DIFF_closereq', ...
    'Color',[0.75 0.75 0.75], ...
    'Colormap',mat0, ...
    'FileName','D:\MATLAB3\work\DIFF\GUI\HSim.m', ...
    'MenuBar','none', ...
    'Name','Diff Simulator V1.0', ...
    'NumberTitle','off', ...
    'PaperPosition',[18 180 576 432], ...
    'PaperUnits','points', ...
    'Position',[174.75 188.25 221.25 158.25], ...
    'Resize','off', ...
    'ResizeFcn',figure(gcf);redraw', ...
    'Tag','DIFFMain', ...
    'ToolBar','none');

%Initialize Menu
%1-File Menu and its children
File_Hndl = uimenu('Parent',Main_Hndl, ...
    'Label','&File', ...
    'Tag','File');

h2 = uimenu('Parent',File_Hndl, ...
    'Callback','DIFFmenu("New Project",gcf)', ...
    'Label','&New Project', ...
    'Tag','NewProject');

Open_Hndl = uimenu('Parent',File_Hndl, ...
    'Label','&Open', ...
    'Tag','Open');

OpenData_Hndl = uimenu('Parent',Open_Hndl, ...
    'Callback','DIFFmenu("OpenDataFile",gcf)', ...
    'Label','Open &Data File', ...
    'Tag','OpenDataFile');

OpenOutput_Hndl = uimenu('Parent',Open_Hndl, ...
    'Callback','DIFFmenu("OpenOutput",gcf)', ...
    'Label','Open &Results File', ...
%2-Feed Menu and its children
h1 = uimenu('Parent',Main_Hndl, ...
'Callback','DIFFmenu("Feed",gcf)', ...
'Enable','off',...
'Label','&Feed', ...
'Tag','Feed');

%3-Run Menu and its children
h1 = uimenu('Parent',Main_Hndl, ...
'Label','&Run', ...
'Tag','Run');

h2 = uimenu('Parent',h1, ...
'Callback','DIFFmenu("Run Project",gcf)', ...
'Label','&Run Project', ...
'Enable','off',...
'Tag','RunProject');

h2 = uimenu('Parent',h1, ...
'Callback','DIFFmenu("Show Result",gcf)', ...
'Separator','on',...
'Label','&Show Result', ...
'Enable','off',...
'Tag','ShowResult');

%4-Help Menu and its children
h1 = uimenu('Parent',Main_Hndl, ...
'Label','&Help', ...
'Tag','Help');

h2 = uimenu('Parent',h1, ...
'Callback','DIFFmenu("Content",gcf)', ...
'Label','&Content...', ...
function [ds,ts]=time1()

%This function is used for generating
time and date as a strings

c=fix(clock);
% c = [year month day hour minute seconds]

year=c(1);
month=c(2);
day=c(3);
%---------
hour=c(4);
minute=c(5);
seconds=c(6);

%This function is used for setting Diff simulator paths
%it must run any time Diff simulator used
%the path variables must set at the installation step

if nargin<1
    flag=1;
end;
Appendix B

% Please set this path after installation
% the software

DiffPath = ['d:\diffusion\Diff\'];

% Please do not change the following section
MainPath = [DiffPath, 'Main\'];
GUIPath = [DiffPath, 'GUI\'];
MATHPath = [DiffPath, 'MATH\'];
DataPath = [DiffPath, 'Data\'];

%- Save OuPutPath in Config.mat

d = dir(MainPath);
if ~isempty(findstr([d.name], 'Config.mat'))
    delete([MainPath, 'Config.mat']);
end;

function RunDiff()

% PROGRAM FOR SOLVING IMPLICIT EQUATIONS
% DIFFUSION SIMULATION BY VARIED LENGTH
% D((d^2)c)/(d(x^2))=dc/dt
% FINITE DIFFERENCE EQUATIONS :
% D(c(i+1,n+1)-2.u(i,n+1)+c(i-1,n+1))/(dx^2)=(c(i,n+1)-c(i,n))/(dt)
% D(dt)/(dx^2)=lambda
% lambda.c(i-1,n+1)-(1+2.lambda).c(i,n+1)+lambda.c(i+1,n)=-c(i,n)
% tl : initial time
% t2 : final time
% dt : time interval
% xl : first boundary
% x2 : second boundary
% dx : distance interval

% 1-Load data

clear all
load('swap','DIFFInput');
load(DIFFInput, '-mat'); %this load the Concent_PVA

dt=TStep;
t2=FTime;
D=DiffCoef; % diffusivity

% tl=8000;
nu=0.004424;
L0=121.2e-3;%m
Ci=56.54;

x1=0;
dx=0.01*L0; %m
x2=L0;
x(:,1)=[x1:dx:x2]';
t=[t1:dt:t2];
tol=0.1;

n=fix((t2-t1)./(dt)+1);
m=round((x2-xl)./(dx)+1);
c=ones(m,n);
D1(1)=D;
for i=1:m
    c(i,1)=0;
end;

plot(x(:,1),c(:,1),'-r');
hold on;
pause(2);
title('IMPLICIT EQUATION');
xlabel('Distance');
ylabel('Function');
A=zeros(m);
B=zeros(m,1);
dx(1)=dx;
L(1)=L0;
Cavexp=fun3(t,L0,nu);
for k=2:n
    l=0;
    while 1
        lambda=D.*(dt)./(dx(k-1).^2);
        i=1;
        A(1,1)=-(1+2.*lambda);
        A(1,2)=2.*lambda;
        B(1)=-c(1,k-1);
        for i=2:(m-l)
            A(i,i-l)=lambda;
            A(i,i)=-(1+2.*lambda);
            A(i,i+l)=lambda;
            B(i)=-c(i,k-1);
        end;
        i=m;
        A(m,m)=1;
        B(m)=Ci;
        C=A\B;
        c(:,k)=C;
cav=sum(C);
cav=cav./m;
Differ=abs(cav-Cavexp(k));
if (Differ<tol)
   Cav(k)=cav;
   L(k)=L0.*exp(nu.*cav);
   dx(k)=L(k)./(m-1);
   x(:,k)=[x1:dx(k):L(k)]';
   D1(k)=D;
   break
else
   if cav < Cavexp(k)
      D=D+.005e-8;
   else
      D=D-.005e-8;
   end;
   end;
l=l+1;
end;
k
end;

%------------------------------------------------------------------

%------------------------------------------------------------------
load config DataPath MainPath;
FileName='DIFFOut$$$.mat';
d=dir(DataPath);
if ~isempty( findstr([d.name],FileName) )
   delete([DataPath,FileName]);
end;
tl=t(:)./3600; %sec
L=L(:);
Cav=Cav(:);
Cavexp=Cavexp(:);
D1=D1(:);
save a.mat t L Cav D1
save([DataPath,FileName],'t1','L','Cav','Cavexp','D1');
%save the name and path of outputs
DIFFOutput=[DataPath,FileName];
save([MainPath,'swap.mat'],DIFFOutput,'-append');
clear t1 L Cav Cavexp D1
clear DataPath;
%------------------------------------------------------------------

function Cavexp=fun3(t,L0,nu)
aa=123.644986;
Appendix B

bb=2.19859e-5;
ce=3.7827e-9;

dd=1.171e-11;
ff=-31.7415101;
L=aa+bb.*t+cc.*t.^2+dd.*t.^2.5+(ff./t.^0.5);
L=L./1000;
Cavexp=(l./nu).*log(L./L0);