THE MOLECULAR DESIGN OF A NEW SOLVENT FOR THE ABSORPTION OF CARBON DIOXIDE

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SUMMARY

Gas absorption, the removal of one or more constituents from a gas mixture, is widely used in chemical processes. In many gas absorption processes, the gas mixture is already at high pressure and in recent years organic solvents have been developed for the process of physical absorption at high pressure followed by low pressure regeneration of the solvent and recovery of the absorbed gases. Until now the discovery of new solvents has usually been by expensive and time consuming trial and error laboratory tests.

This work describes a new approach, whereby a solvent is selected from consideration of its molecular structure by applying recently published methods of predicting gas solubility from the molecular groups which make up the solvent molecule. The removal of carbon dioxide from methane or hydrogen was used as a commercially important example. After a preliminary assessment to identify promising molecular groups, more than eighty new solvent molecules were designed and evaluated by predicting gas solubilities. The other important physical properties were also predicted by appropriate theoretical procedures, and a commercially promising new solvent was chosen to have a high solubility for acid gases, a low solubility for methane and hydrogen, a low vapour pressure, and a low viscosity.

The solvent chosen, of molecular structure CH_3-$COCH_2$-CH_2-CO-CH_3, was tested in the laboratory and shown to have physical properties, except for vapour pressure, close to those predicted, gas solubilities were within 10% but lower than predicted, viscosity within 10% but higher than predicted and a vapour pressure significantly lower than predicted.

A computer program was written to predict gas solubility in the new solvent at the high pressures (25 bar) used in practice. This is based on the group contribution method of Skold Jorgensen (1984). Before using this with the new solvent, acetonylacetone, the method was shown to be sufficiently accurate by comparing predicted values of gas solubility with experimental solubilities from the literature for 14 systems upto 50 bar.

A test of the commercial potential of the new solvent was made by means of two design studies which compared the size of plant and approximate relative costs of absorbing acid gases by means of the new solvent with other commonly used solvents. These were refrigerated methanol (Rectisol process) and the dimethyl ether of polyethylene glycol (Selexol process). Both studies showed in terms of capital and operating cost some significant advantages for plant designed for the new solvent process.

KEYWORDS : Gas absorption, Carbon Dioxide, Molecular Design of Solvent, UNIFAC, Process Plant Design.

Dedicated to my wife and my daughter

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INTRODUCTION

The removal of acid gases such as carbon dioxide and hydrogen sulphide from industrial gas mixtures is an essential step in many of the processes used in the natural gas, petroleum and chemical industries. In several applications the gas mixture is already at high pressure and this has led to the development of several acid gas removal processes based on physical absorption into a solvent, followed by low pressure regeneration of the solvent and recovery of the acid gases. In recent years several new physical solvent absorption systems have been used for gas purification. The essential difference between these processes is the solvent which is used to absorb the acid gases. For example, the Rectisol process is based on refrigerated methanol, the Purisol process on n-methyl-2-pyrrolidone, the Fluor process on propylene carbonate and the Selexol process uses the dimethyl ether of polyethylene glycol. Clearly there are marked differences between these solvents in terms of molecular structure and physical properties. It is unlikely that any of them represents the optimal solvent choice, and it is known that work has been carried out in industrial laboratories for finding better solvents for acid gas removal processes.

In this present work we focus mainly on the development of methods for designing a new physical solvent for the acid gas removal process, particularly for removing carbon dioxide. The solvent must have a high acid gas solubility, low hydrocarbon solubility, low vapour pressure, low viscosity, absence of side reactions, minimum corrosion of carbon steel and other common materials of construction, and ready availability at low cost. The solubilities of gases in the absorbing liquid are perhaps the most important criterion for selecting a suitable solvent; it is, therefore, necessary to have information on the solubility of a gas or gas mixtures in the absorbing liquid. If such information is not available from collections of published data, it has usually been necessary to determine it in the laboratory.

Thus for the past several years, it has been a very difficult task to develop commercial solvents for gas absorption processes. Generally, it has been done by selecting several potential solvents or solvent mixtures, measuring the solubilities of gases in the solvents in the laboratory followed by experiments with a selected solvent in a pilot scale plant. This solvent selection procedure is expensive both in time and money to find a suitable solvent and it may not be succesful, if none of the candidate solvents are found by experiment to be suitable.

This work describes a new approach to solvent selection, that of designing the molecular structure of the solvent so that it has the required properties. The approach based on recently published methods for predicting gas solubility in solvents from the contributions of the molecular groups of the solvent molecule. The approach used is to first identify those molecular groups which produce a high solubility for acid gases, and then to rearrange them to form a new molecular structure for a new gas absorption solvent. The solubility and other physical properties of the new solvent are then predicted and used in a process design study which evaluates the commercial promise of the new process.

In 1977, Fredenslund et al. [54] developed a group-contribution method called UNIFAC (Universal quasichemical Functional group Activity Coefficients) for predicting liquid phase activity coefficients, and the method has been very successful for predicting the vapour-liquid equilibrium of many systems. Later a method, based on UNIFAC, for predicting gas solubility at low to moderate pressures was developed by Sander et al. [142]. Because the UNIFAC method relies on interaction parameters between substituent groups in molecules, rather than on interactions between the molecules, it can then in principle be used to precalculate the solubility of a gas in any solvent on condition that the interaction parameters of the substituent groups of that solvent are available. As a means of designing a new physical solvent, this work has used the UNIFAC method to predict the solubility of carbon dioxide, hydrogen and methane in a number of molecules obtained from various combinations of the available UNIFAC functional groups. A new physical solvent was selected by considering the solubility results and physical properties of the solvent.

During the course of this work, the second part of the method for predicting gas solubility was presented by Steen Skjold-Jorgensen [146]. This method is called GCEOS and is based on group contributions and an equation of state. The GCEOS method can predict gas solubility over a wide range of pressures and has the same functional groups as the method of Sander et al. This provided an opportunity for the prediction of gas solubilities at high pressures which it is necessary to know for designing commercial absorption systems.

A gas solubility apparatus has been built to measure the solubility of carbon dioxide, hydrogen and methane in the selected solvents at atmospheric conditions. In order to check the capability of the apparatus, the experimental results are compared with those estimated by the UNIFAC method and with published data. The solubility of carbon dioxide, hydrogen, methane and propane in the new solvent are also determined, and compared with values predicted by the UNIFAC method.

After the new physical solvent had been discovered, an attempt was made to evaluate the new solvent for acid gas purification processes. There are a variety of such acid gas removal processes, e.g. treating natural gas containing carbon dioxide and sulphurous compounds, treating synthesis gas from shift conversion in the ammonia synthesis process, etc. There are many existing solvents which have been used in these acid gas removal processes, for instance Rectisol is generally used in carbon dioxide removal in ammonia synthesis plant, and, for bulk removal of carbon dioxide and hydrogen sulphide in natural gas, Selexol seems to be very popular.

Preliminary design calculations for gas absorption in natural gas processing and ammonia synthesis with the new solvent were made and compared with those for Rectisol and Selexol. In the gas absorption designs, emphasis was placed on the bulk removal of carbon dioxide rather than on the selectivity between carbon dioxide and hydrogen sulphide in both the natural gas and ammonia systhesis processes.

Three main computer programs were written: for the design of a new solvent; for calculating the solubility of gases at high pressure; and for the preliminary process design calculations using Selexol, Rectisol and the new solvent. These computer programs are designed to be used on any IBM or compatible microcomputer.

The use of molecular groups theory for designing new solvents for gas absorption processes, by methods such as those described in this work, may well lead to a new dimension in separation process design.

CHAPTER 1

LITERATURE REVIEW

1.1 Introduction

Physical solvents are growing in use for the removal of acid gases from natural gas and coal gasification products, and for the purification of synthesis gas. Physical solvents lend themselves to the more economical bulk removal of acid gases from streams of high pressure and high acid gas content. This has encouraged the development and application of a number of physical solvent processes which reduce plant investment and operating cost. Usually solubility characteristics are the most important for these applications, a high acid gas solubility greatly reduces the solution circulation rate and is mainly responsible for the reduction in equipment size and cost and in operating utility cost. Other physical properties such as density, viscosity and vapour pressure also effect the operating cost of the plant.

There is a vast amount of literature on gases absorbed in both chemical and physical solvents. Since the main objective of this work is to find a new physical solvent for gas absorption, the gas solubilities of materials used in chemical absorption processes will be ignored. The necessary published theories and applications concerned with physical solubility and solvents will be reviewed in the following sections, followed by a review of work concerned with the other important physical properties.

Table 1.0 Undesirable gases encountered in gas absorption process.

Type of impurity	Acid gas removal
Acid gases	CO_2, H_2S, SO_2
Organic sulphur compounds	COS, CS_2, Thiophene Mercaptans(RSH) Organic sulphides (RSSR, RSR)
Other impurities	H_2O, HCN, NH_3, O_2 HCl, HBr, SO_x, NO_x Hydrocarbons etc.

1.2 Acid gas removal processes

Gas absorption is the process by which an undesirable gas is removed from a mixture of gases. The absorption may be by a purely physical absorption or it may involve reaction of the gases in the liquid solution. The undesirable gases which may be encountered in gas absorption processes are listed in table 1.0. In general, carbon dioxide and hydrogen sulphide are two of the most common impurities in acid gas removal processes. Carbon dioxide and hydrogen sulphide often occur in very large concentrations in the chemical industries. They have to be removed to reach a target specification which varies from process to process. There are many varieties of raw gas stream to be treated, such as synthesis gas from reformed natural gas, gases from shift conversion, etc. Table 1.1 shows some major industrial processes, the acid gases for treating, and the cleanup targets.

To treat these acid gases requires a solvent or solvent mixture. Water and basic materials such as lime, alkali hydroxides and carbonates are the solvents which have been used for removing carbon dioxide and hydrogen sulphide since the start of the industrial revolution. In the 1920's, modern industrial gas treating began with the discovery of solvents such as aqueous solutions of aminoalcohols and these solvents dominated gas treating for several years. In 1959 Benson and Field [16] developed the Benfield process which uses high pressure hot potassium carbonate to absorb carbon dioxide and hydrogen sulphide. The Benfield process has been improved to such an extent that investment has been reduced by about 10% and the heat requirement for regeneration of the solution has been lowered.

For several years, chemical solvents were regularly used in industrial processes until the discovery of natural gas at high pressure containing very high concentrations of carbon dioxide and hydrogen sulphide, which resulted in a shift in interest from chemical solvents, of which MEA (monoethanolamine) and DEA (diethanolamine) are the most common, to the physical solvents. The advantages of the use of physical solvents over chemical solvents when the acid gas loading is at a high pressure has been explained in more detail by Strelzoff [154, 155] and Astarita et al. [6]. A comparison of capital cost and operating cost between the chemical solvents (MEA and hot potassium carbonate) with a physical solvent (Selexol) was illustrated by Sweny and Valentine [157]. Physical solvents may be more economical than aqueous chemical solvents when the feed gas for the absorption process has a high acid gas partial pressure, usually above 50 psi. However, a disadvantage of physical solvents over chemical solvents is their tendency to co-absorb hydrocarbons heavier than methane from the gas stream, this means a loss in fuel value of the gas since heavy hydrocarbons are rejected with the acid gas.

The physical solvent absorption processes have all been developed since 1960. The following sections will review some of the commonly used commercial physical solvents.

The Fluor solvent (propylene carbonate) [20] was one of the first physical solvents to be applied commercially. It was originally aimed at bulk removal of large concentrations of carbon dioxide (up to 50% and above) from high pressure natural gas and consequently leaves about 1 to 2% carbon dioxide in the treated gas.

The Selexol process [90, 115, 130, 79] utilises the dimethyl ether of polyethelene glycol as the solvent. It is aimed at bulk removal of carbon dioxide and hydrogen sulphide and is not intended for low pressures or low acid gas concentrations. Commercial applications have been primarily in natural gas treating. The solubility of hydrogen sulphide in the solvent is about 10 times that of carbon dioxide at a given temperature and pressure. This makes it possible to design a plant to remove substantially all of the hydrogen sulphide in a concentrated form, while leaving a certain amount of carbon dioxide in the residual gas. The disadvantages of the Selexol solvent are typical of physical solvent processes. It absorbs heavy hydrocarbons (C^{+5}), this means a loss in fuel value since some hydrocarbons are rejected with the acid gases. In addition, the recovered acid gas is unsuitable for feed to a Claus sulfur recovery plant.

The Purisol process [87], based on N-methyl-2-

pyrrolidone, has also been utilised largely for the bulk removal of acid gases. It is claimed that hydrogen sulphide can be reduced to a pipeline specification of 0.25 gr of gas per 100 scf. Because of the much greater solubility of hydrogen sulphide than carbon dioxide in the solvent, the process can be used to selectively remove hydrogen sulphide even at relatively low ratios of hydrogen sulphide to carbon dioxide. If only bulk removal of the acid gases is required, regeneration can be accomplished by simple pressure reduction with no heat applied to the lean solvent. If pipeline specification hydrogen sulphide is required, hot regeneration must be used to reduce the acid gas in the lean solution. The solvent will dehydrate gases if a steam heated solvent drying column is provided. Acidic components do not degrade the solvent. No corrosion problems have been encountered in all carbon steel construction.

The Rectisol process [154, 155], based on cold methanol (-40°C), has been applied mainly for synthesis gas cleanup before a nitrogen wash in ammonia or methanol plants and before LNG cryogenic plants. The solvent can reduce carbon dioxide from high concentrations, e.g. 35 mole%, down to a few parts per million. Methanol is relatively cheap compared to the other physical solvents. However, the solvent has a very high vapour pressure, therefore refrigeration is required to lower the feed gas to the required operating temperature so as to prevent excessive losses of the solvent in the purified gas.

Finally, BASF has developed the Sepasolv MPE (oligoethylene glycol methyl isopropyl ethers) solvent [176]. This solvent is claimed to have very high selectivities for hydrogen sulphide relative to carbon dioxide and methane. As a result of the high selectivity, it is possible to remove gases with relative inexpensive equipment. However, the solvent has a very high molecular weight of 316, and a high viscosity of 7.2 Pascal sec which is likely to result in a very large absorption column.

Table 1.1 Major industrial processes that need gas treating.

Process	Acid gases for treating	Cleanup targets
Hydrogen manufacture	CO_2	<0.1% CO_2
Petroleum desulphurisation	CO_2+H_2S+COS	10 ppm H_2S
Ammonia manufacture	CO_2	<16 ppm CO_2+CO
(H_2/N_2 mixture)	CO_2+H_2S+COS	0.01 ppm H_2S
Natural gas purification		
Pipeline gas	H_2S,CO_2,COS,	<4 ppm H_2S;<1%CO_2
LNG feedstock	RSH etc.	1-2 ppm H_2S;
		<50 ppm CO_2
Coal gasification		
SNG(high Btu gas)	CO_2,H_2S,COS	500 ppm CO_2;
		0.01 ppm H_2S
Low Btu gas		100 ppm H_2S
Oil desulphurisation	H_2S	100 ppm H_2S
Refinary flue gas treating	H_2S,CO_2,COS	100 ppm H_2S

All the above information obtained from Astarita et al. [6]

1.3 The calculation of gas solubility

In recent years there has been increased interest in both the experimental determination and theoretical prediction of the solubility of gases in liquids. For chemical process design it is often necessary to estimate the physical properties of mixtures, but there is no adequate theory for mixtures wherein one component (the gas) is a supercritical component, and reliable experimental data for gas solubilities are not plentiful.

Many of the published experimental data are scattered, there are only a few compilations of data, Seidell [146], Stephen et al. [152] and Wilhelm and Battino [173], and these are far from complete. It frequently happens that for a given gas-liquid system at a fixed temperature and pressure, two experimentalists have published significantly different results. There are a few books (by Hildebrand and Scott [81, 82], Hildebrand and Prausnitz [83] and Gerrald [60]) which deal with gas solubility, and many references to individual papers. The recent literature is summarized in reviews on the solubility of gases in liquids by Battino and Clever [9], Scott [144] and Wilhelm and Battino [173], The latter is a supplement of the earlier review article by Battino and Clever [9].

A satisfactory theory of the solution of gases in liquids still needs to be developed. However, various attempts have been made [81, 82, 83, 59, 78, 90, 33, 34, 171] to correlate the solubilities of gases in liquids as a function of temperature and also of the nature of the solvent.

The first well known equation for a gas in equilibrium with a liquid was established, and extensively tested by W. Henry [80] in 1803 in a series of measurements of the dependence on pressure of the solubility of gases in liquids at moderate pressure. The equation can be written as

$$P_i = H_i x_i \tag{1.1}$$

where P_i is the partial pressure of gas i absorbed by the liquid, x_i is the mole fraction of the gas i in the liquid, and H_i is Henry's constant which is a function of temperature and the nature of the gas and the absorbing liquid.

Some 50 years after Henry's law was established, Bunsen [21] proposed that gaseous bodies are absorbed by liquids, in which no chemical reaction occurs, in quantities depending upon the essential nature of the gas and of the liquid, the temperature, and the pressure to which the gas is subjected. Bunsen expressed the gas solubility as the Bunsen Coefficient, α , defined as the volume of gas, reduced to 0°C and 760 mmHg, which is absorbed by unit volume of a solvent (at the temperature of the measurement) under a gas pressure of 760 mmHg. By way of example, an equation which can be used to calculate the Bunsen coefficient is

$$\alpha = (V_G/V_L)(273.15/T) \qquad (1.2)$$

where V_G is the volume of gas absorbed and V_L is the volume of the absorbing solvent.

Many correlations based on Henry's Law have been developed for many years. Of interest to this work is the concept of fugacity which arises from a consideration of the change in Gibbs energy that results from changes in pressure and temperature. For a non-ideal system at a given temperature T and pressure P, the condition of thermodynamic equilibrium is expressed in terms of fugacities as follows

$$f_i^V = f_i^L \qquad (1.3)$$

where f_i^V and f_i^L are the fugacity of component i in the vapour and liquid phase respectively. Equation 1.3 may be rewritten into two different forms,

$$y_i \phi_i^V (T,P,y) = x_i \phi_i^L (T,P,x) \qquad (1.4)$$

and

$$y_i \phi_i^V (T,P,y) P = x_i \gamma_i (T,P,x) f_i^\circ \qquad (1.5)$$

Whereas equation 1.4 employs fugacity coefficients (ϕ_i^V,

ϕ_i^L) for both vapour and liquid phase, in equation 1.5 fugacity coefficient (ϕ_i^V) is used for the gas phase only, with liquid phase nonidealities being described by activity coefficients (γ_i). The equation 1.5 is usually used for the computation of vapour-liquid equilibrium at high pressures, and the fugacity coefficients are related to temperature, pressure and composition using established thermodynamic relationships. The expressions needed to calculate the fugacity coefficients can be derived from the equations of state. One equation of state which can be used was derived by van der Waals. This van der Waals equation always consists of two terms, one representing the repulsive and one the attractive forces between the molecules.

$$P = P_{rep} + P_{att} \tag{1.6}$$

$$P = (RT/v-b) - (a/v^2) \tag{1.7}$$

The parameters a and b are given by

$$a = \Omega_a \ R \ T_c/P_c$$

$$b = \Omega_b \ RT_c/P_c$$

where Ω_a and Ω_b are numerical coefficients, and vary slightly from substance to substance, but of course with a loss of generality.

There are a large number of equations of state which are modifications of the van der Waals equation, these modified equations of state are conveniently summarised in Walas [170]. The first improvement of the original van der Waals equation was the equation of state derived by Redlich and Kwong [133]. A futher modification was made by Soave [150] who, apart from the critical data, also used the acentric factor for an improved description of vapour pressures. More recent modifications have been introduced, for example, by Peng and Robinson [121] and Schmidt and Wenzel [143]. These modified equations of state have in common that they have all varied only the attractive term of the van der Waals equation and use the simple cubic form for the volume dependence.

Knowledge of the behavior of liquids is less quantitative than that of gases, although much work, both theoretical and correlative, is being done in the area. A correlation of saturated liquid densities by Hankinson and Thomson [75] is typical of recent work. Many equations of state, notably the complex Benedict, Webb and Rubin [13], the simpler Peng-Robinson [121] and Harmens-Knapp [77], also have been designed for good representation of liquid densities. The BWR equation has the advantage of being able to fit a larger number of pure component properties than the other cubic equations of state because it has more parameters. At the same time this produces a problem because the calculation of these parameters require multiproperty data regression and the parameters obtained may not be unique (Lin and Hopke [105]). Application to mixtures of equation of the BWR type relies on empirically based mixing rules, and in spite of their increased complexity, they sometimes provide poorer results than the simpler cubic equations of state (Leland [103]). Similar calculations, based on corresponding states correlations rather than on any explicit equation of state, have also been developed by Edmister [39] and Lee and Kesler [102].

Most modifications of these equations have been empirical and arbitrary, with parameters that are adjustable to fit certain kinds of experimental data such as solubilities, vapour pressures, densities. Adams [2] used most of these correlations in process simulation to calculate thermophysical properties and found that different equations of state show significant differences in predictions of phase equilibria and their functional behaviour. Therefore, it is not practical to use these equations of state for the design of a solvent, because it is going to be difficult to obtain the neccessary parameters for unknown solvents.

In recent years attention on calculating phase equilibria based on equation 1.5 has been increasing. Generally the correlation based on this equation uses ideal vapour, virial equations or a cubic equation of state for the vapour calculation, and activity coefficient models for the liquid. These methods are generally used for nonideal mixtures at low to moderate pressures. Determination of the standard state fugacity f_i° is a problem, since the conventional standard state (pure liquid at system temperature and pressure) does not exist for supercritical compounds. However, at low to moderate pressures, f_i° is often equal to the pure component vapour pressure at the system temperature. In addition, ϕ_i^V, is under these conditions, often equal to unity.

There are many models to correlate activity coefficients. Early models, those of Van Laar and Margules [167, 168], were developed by an expansion of the excess Gibbs energy in terms of the compositions. Later models such as Wilson [174, 175], Renon [138], ASOG [97] and UNIQUAC (Abrams and Prausnitz [1]) use the local composition concept to develop an expression for the excess Gibbs free energy. All of these models involve the concept of binary interaction parameters. A summary of the relevant expressions for each of these can be found in Walas [170] and Reid et al. [135].

UNIFAC (Fredenslund et al. [54]) is one of the most popular models for calculating activity coefficients, it is a predictive technique based on group contribution techniques. It relies on interaction parameters between constituent groups in molecules rather than interactions between the molecules. It may be used directly or indirectly by correlating the UNIFAC activity coefficients with any of the

Wilson, Renon or UNIQUAC model. More details of the UNIFAC method are briefly described later in this chapter. Complications arise in the application of this activity coefficient model when gases or noncondensables are present. In this case the pure component reference functions, such as the reference fugacity coefficient, no longer have any meaning. If the temperature is not too high it is possible to extrapolate the reference functions, as long as the extrapolations are reasonable. This complexity also creates a need for a binary interaction parameter between gas and constituent functional groups in the solvent (for UNIFAC).

In 1983, Sander et al. [142] developed a group contribution method based on UNIFAC to calculate gas solubility at low to moderate pressures. This model provides an excellent tool in this work for searching for a new solvent for a gas absorption process. The details of this method will be also explained later in this chapter. At present the limitations of this method are that it can not be used at high pressures, and also there is a lack of some group parameters. However, despite these limitations it is shown in the present work that the method provided a basis for developing the new solvent for carbon dioxide absorption.

For high pressure vapour-liquid equilibrium, calculations are usually carried out with various forms of the equations of state. However, as mentioned above, it is going to be difficult to obtain parameters for the calculation of gas solubility. In 1985, Tochigi et al. [165] developed a method for predicting high-pressure vapour-liquid equilibrium by applying an equation of state, mixing rules and the ASOG group contribution method. They succeeded in predicting the vapour-liquid equilibrium for binary and ternary systems of n-paraffins, nitrogen, hydrogen and carbon dioxide. Only six molecular groups can be used by this model which thus seems to be inconsistent with the method of Sander et al. With the ideal of combining a van der Waals type equation of state with the group contribution concept, a new group contribution equation of state (GCEOS) has been developed by Skjold-Jorgensen [148]. The GCEOS is in effect a second part of the Sander et al. model. It can predict the solubility of gases over a wide range of temperature and pressure, beyond that of Sander et al. [142]. Twenty three groups are included in the parameter tables (see Chapter 3 and Appendix 2 for more details) which cover solvents like ketones, alcohols, water, aliphatics, aromatic hydrocarbons and nine gases.

Another type of theory which has been often applied to gas solubilities is Regular Solution Theory. This theory is one involving no entropy change when a small amount of one of its components is transfered from an ideal solution of the same composition, the total volume remaining unchanged. There are two books by Hildebrand and Scott [81, 82] which contain excellent explanations of this theory. There are two equations based on regular solution theory frequently used to calculate gas solubilities. The first is the Scatchard-Hildebrand equation [81]

$$-\ln x_2 = -\ln x_2^i + V_2(\delta_1 - \delta_2)^2 /RT \qquad (1.8)$$

where x_2 is the mole fraction gas solubility, x_2^i is the ideal gas solubility (calculable from Raoult's law), V_2 is the partial molar volume of the gas in the solution, and the δ's are solubility parameters where the subscript 1 refers to the solvent and 2 refers to the gas. The solubility parameter, δ, is sometimes referred to as the cohesive energy density, and can be calculated from the molar energy of vaporization, ΔE_v. For solutions where the molecules differ in size, it was found better [61, 64] to use the Flory-Huggins equation which is based on the ratio of molar volumes.

$$-\ln x_2 = -\ln x_2^i+[V_2(\delta_1-\delta_2)^2/RT]+\ln(V_2/V_1)+(1-V_2/V_1) \qquad (1.9)$$

There are many works based on using this regular solution theory. Among these are those by Gjaldbaek-Hildebrand [63], Prausnitz [128, 129], Clever et al. [30], Gjaldbaek and Anderson [63] and King et al. [93]. Three papers by Thomsen and Gjaldbaek [161, 162, 163] have compared calculated with experimental solubilities for a variety of gases in a variety of solvents, and one of their works shows an interesting correlation between the solubility parameter and the heat of vaporization.

$$\delta = [(\Delta H_v - RT)/V]^{1/2} = (E_v/V)^{1/2} \qquad (1.10)$$

Useful papers by O'Connell [180] and Brandani and Prausnitz [38] reviewed the regular solution literature for gas solubilities. Barton [8] presents an excellent summary of the solubility parameters for a large number of solvents.

A recent paper by England (1986) [43] has illustrated the use of solution theory, together with basic pure component properties, to calculate gas solubilities and distribution coefficients. In his paper he used a group contribution method by Fedors [49, 50], which was developed for estimating the energy of vaporization and the molar volume of organic liquids, to calculate the solubility parameter for N-methyl-2-pyrrolidine (the solvent used in the Purisol process). He concluded that the estimation of solubility parameters based on Fedors group contribution is within 10% of the experimental values for common organic substances. Table 1.2 shows some of the group contributions for several organic functional groups as presented by Fedors [49, 50].

Table 1.2 Group additivity data for organic compounds

Group	Δe_i (cal/gm-mol)	Δv_i (cc/gm-mol)
CH_3-	1125	33.5
-CH_2-	1180	16.1
-CH-	820	-1.0
C	350	-19.2
CH_2=	1030	28.5
CH=	1030	13.5
C=	1030	-5.5
-O-(ether)	800	3.8
C=O(ketone)	4150	10.8
OH	7120	10.0
OH(disubstituted or on adjacent C atoms)	5220	13.0
NH_2	3000	19.2
NH	2000	4.5
N	1000	-9.0
-N=	2800	5.0
Ring closure(5 or 6)	250	16.0
N ring closure	2500	16.0

Δe_i and Δv_i are the atomic or group contributions to the energy of vaporization and molar volume at 25°C. For stimating both the energy of vaporization, ΔE_v, and the molar volume, V, of organic liquids, Fedors assumed that

$$\Delta E_v = \Sigma \Delta e_i$$

$$V = \Sigma \Delta v_i$$

1.4 UNIFAC and gas solubility at low to moderate pressures

The UNIFAC method for the calculation of activity coefficients is based on the group-contribution concept. The basic idea is that molecules are made up of smaller functional groups. Therefore, if we assume that a physical property of a fluid is the sum of contributions made by the molecules´ functional groups, we obtain a possible technique for correlating the properties of a very large number of fluids in terms of a much smaller number of parameters which characterize the contributions of the individual groups. The UNIFAC model was developed by Fredenslund et al. [55], and like the UNIQUAC and the ASOG model the activity coefficient may be expressed as the sum of two parts namely:

(i) the combinatorial part, and

(ii) the residual part

For any component i, the activity coefficient is expressed as

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{1.11}$$

The combinatorial contribution γ_i^C is given by

$$\ln \gamma_i^C = [\ln \frac{\Phi_i}{x_i} + 1 - \frac{\Phi_i}{x_i}] - \frac{1}{2} z\, q_i \ln \frac{\Phi_i}{\theta_i} + 1 - \frac{\Phi_i}{\theta_i} \tag{1.12}$$

Where z is a coordination number normally equal to 10 and the segment fraction, Φ_i, and surface area fraction, θ_i, for component i are given by

$$\theta_i = \frac{q_i\ x_i}{\sum_j q_j\ x_j} \tag{1.13}$$

$$\Phi_i = \frac{r_i\ x_i}{\sum_j r_j\ x_j} \tag{1.14}$$

$$q_i = \sum_k \nu_k^{(i)}\ Q_k \tag{1.15}$$

$$r_i = \sum_k \nu_k^{(i)}\ R_k \tag{1.16}$$

R_k and Q_k are the group volumes and surface area parameters for group k, given by Bondi. The residual contribution to the activity coefficient is given by

$$\ln \gamma_i^R = \sum_k \nu_k^{(i)} [\ \ln \Gamma_k - \ln \Gamma_k^{(i)}\ ] \tag{1.17}$$

The activity coefficient Γ_k for group k is given by

$$\ln\Gamma_k = Q_k(1 - \ln(\sum_m \theta_m \varphi_{mk}) - \sum_m \frac{\theta_m \varphi_{mk}}{\sum_n \theta_n \varphi_{nm}}) \tag{1.18}$$

The group fraction X_m for group m is expressed as

$$X_m = \frac{\sum_j v_m^{(j)} x_j}{\sum_j \sum_n v_n^{(j)} x_j} \tag{1.19}$$

The group surface area fraction θ_m is expressed as

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \tag{1.20}$$

where $\varphi_{nm} = \exp(-\frac{a_{nm}}{T})$

To use the UNIFAC method, no experimental data are required for the particular mixture of interest. In addition to the temperature and composition of the system, it is necessary only to know the molecular structure of every component in the mixture and the necessary group interaction parameters.

The UNIFAC model requires two group interaction parameters (a_{ij} and a_{ji}) for each pair of groups, and the volume and surface areas of each individual group for calculation of the activity coefficient γ_i. a_{ij} is a group interaction parameter which measures the difference in the energy of interaction between a group i and a group j. It must be noted that $a_{ij} \neq a_{ji}$ and that the group interaction parameters are assumed to be independent of temperature, having units of reciprocal temperature.

In 1980 Kikic et al. [92] proposed an empirical modification (equation 1.11) of the UNIFAC combinatorial part, this modified expression is to correct for the overly large combinatorial contribution. In the term in square brackets in equation 1.12, Φ_i was replaced by Φ_i.

where

$$\Phi_i = \frac{r_i^{2/3} \; x_i}{\sum_j r_j^{2/3} \; x_j} \qquad (1.21)$$

The UNIFAC group-contribution method has for a number of years been very successful in terms of accuracy and applicability for the phase equilibrium prediction of nonelectrolytic liquid mixtures. In view of the fact that the fundamental equations for the calculation of gas-liquid equilibrium are the same as for vapor-liquid equilibrium, it should also be possible to predict the solubility of a gas in a solvent or solvent mixture by means of the UNIFAC method. That is, from the usual fundamental equation for calculation of gas-liquid equilibrium.

$$f_i^V = f_i^L \qquad (1.22)$$

$$\text{or} \quad f_1^V = f_1^L = x_1 \gamma_1 f_1^o \tag{1.23}$$

For the solvent f_1^o may be estimated from experimental data. The problem in equation 1.23 is the determination of a pure-component reference fugacity f_1^o in the liquid state for the gas. Such a state is hypothetical for supercritical components, and the calculation of this quantity must therefore be based on some kind of extrapolation of information concerning the gas's pure-component fugacity (or vapour pressure) as a function of temperature into the supercritical region. If the difference between system temperature and critical temperature is great, such an extrapolation will be most uncertain. By following Mathias and O'Connell [109]'s approach, Sander et al. [142] proposed that the problem may be changed into one of estimating a Henry's constant for a reference solvent.

In general, for a gas (subscript 2) dissolved in a solvent mixture.

$$f_1^o = \frac{H_{2,s}}{\gamma_{2,s}^{\infty}} \tag{1.24}$$

For gas dissolved in a reference solvent, similarly

$$f_2^o = \frac{H_{2,r}}{\gamma_{2,r}^{\infty}} \tag{1.25}$$

Introduction of equation 1.25 into equation 1.23 leads to

$$f_2 = \frac{x_2 H_{2,r} \gamma_2}{\gamma^{\infty}_{2,r}} \qquad (1.26)$$

For given values of f and T, x can be found from equation 1.26 by iteration. The activity coefficient γ_2 and $\gamma^{\infty}_{2,r}$ are calculated from UNIFAC. The reference Henry's constant $H_{2,r}$ is calculated as a function of temperature from the following relationship.

$$\ln H_{2,r} = A + \frac{B}{T} + C \ln T \qquad (1.27)$$

A, B and C are estimated from experimental solubility data for gas component 2 in the reference solvent which are given in Table 1.3. This method is applicable at moderate pressures (up to 10 bar) and for low solubilities, i.e. for situations where Henry's law holds, and to both nonpolar and polar nonelectrolytic solvents.

This model is still limited for the estimation of the solubility of some gases because of the lack of group interaction parameters. Tables 1.4 and 1.5 show the parameters used for solubility calculations in Sander et al.'s model.

Table 1.3 Constants for calculation of reference Henry's constant.

GAS	A	B	C	REFERENCE SOLVENT
N_2	15.26240	-297.172	-1.15544	Butanol
O_2	26.15770	-924.307	-2.73771	Ethanol
H_2	6.97497	416.123	0.0	Propanol
CO	7.53116	-6.36893	0.0	Propanol
CO_2	27.51460	-1846.89	-2.99332	Hexadecane
H_2S	35.21680	-2669.59	-4.07018	Decane
CH_4	6.97328	-503.214	0.0	Octane
C_2H_6	22.31260	-1977.03	-2.18725	Eicosane
C_2H_4	43.23700	-2890.33	-5.21410	Dodecane
C_2H_2	71.79180	-4284.15	-9.34015	Butanol

TABLE 1.4 UNIFAC group interaction-energy parameters U_{ij} for solvent main groups.

GROUP	CH_2	ACH	$ACCH_2$	OH	H_2O	CH_2CO
CH_2	0.0	-56.6	99.7	-39.6	4.3	-73.2
ACH	-56.6	-139.4	48.5	-245.5	na	-231.5
$ACCH_2$	99.7	48.5	213.7	-25.8	na	0.6
OH	-39.6	-245.5	-25.8	-1312.0	-1440.0	-630.3
H_2O	4.3	na	na	-1440.0	-1576.0	-647.1
CH_2CO	-73.2	-231.5	0.6	-630.3	-647.1	-392.7

(na. means the parameter is not available)

This work has used this model to estimate the solubility of gases in various solvents. As already noted, for the calculation of gas solubilities, modifications to UNIFAC itself have been introduced by Sander et al. They gave group volume (R_k) and surface-area (Q_k) parameters values twice the values used by Gmehling et al. [66]. They did this because Skjold-Jorgensen et al. [149] have shown that the normalization factors used for R_k and Q_k in the original UNIFAC method give rise to some numerical problems and that it is in general better to use double values of R_k and Q_k. Table 1.5 shows the R_k and Q_k values applied.

Table 1.5 UNIFAC group volume and surface area parameters for gas solubility calculations

MAIN GROUP	GROUP	NUMBER	R_k	Q_k
CH_2	CH_3	1	1.8022	1.696
	CH_3'	2	1.8022	1.480
	CH_3''	3	1.8022	1.440
	CH_2	4	1.3488	1.080
	$cyCH_2$	5	1.3488	1.080
	CH	6	0.8938	0.456
	cyCH	7	0.8938	0.456
	C	8	0.4390	0.000
ACH	ACH	9	1.0626	0.800
	AC	10	0.7304	0.240
$ACCH_2$	$ACCH_3$	11	2.5326	1.936
	$ACCH_2$	12	2.0792	1.320
	ACCH	13	1.6242	0.696
OH	OH	14	1.0600	1.168
H_2O	H_2O	15	1.5060	1.732
CH_2CO	CH_3CO	16	3.3448	2.976
	CH_2CO	17	2.8914	2.360
GAS	N_2	18	1.8680	1.970
	O_2	19	1.7640	1.910
	H_2	20	0.8320	1.141
	CO	21	2.0940	2.120

Table 1.3 (Continued)

CO_2	22	2.5920	2.522
H_2S	23	2.3330	2.326
CH_4	24	2.2440	2.312
C_2H_6	25	3.6044	3.392
C_2H_4	26	3.1482	2.970
C_2H_2	27	3.0454	2.784

The Sander et al. method for calculating gas solubility is essentially an empirical method. The solubility calculation relies on the group-interaction parameters between gas and molecules and solvent groups. These group-interaction parameters are usually estimated from experimental vapour-liquid equilibrium data so that it is normally possible to rely on a large data base. A typical vapour-liquid equilibrium data set for a binary mixture will thus contain 10-15 data points with pressure, temperature, liquid phase mole fraction and vapour phase mole fraction values. Nevertheless it has not been possible to estimate gas interaction-energy parameters for some of the solvent groups because of the lack of experimental data.

In Appendix 2 the interaction-energy parameters available between gases and solvent subgroups are presented. As mentioned above, it is evident that many such parameters are missing. At the present, 17 molecular groups and 10 gases are available from the listed group interaction parameters in Sander et al.

1.5 The experimental determination of gas solubility

There are many approaches which have been used to determine the solubility of gases in liquids. These approaches differ greatly in complexity, cost, rapidity of operation and precision. They can be classified as follows:

1). Absorption methods.

2). Desorption and analytical methods.

3). Gas chromatographic methods.

Many methods and apparati have been used to determine the solubility of gases in liquids; these methods can be separated into two major classes, physical and chemical. Primarily physical methods will be considered in this work, and they can be divided into two broad classifications:

1). Saturation or absorption methods in which a previously degassed solvent is saturated with a gas under conditions where appropriate volumes, pressures and temperatures may be determined.

2). Extraction or desorption methods where the dissolved gas in a previously saturated solution is removed under conditions where appropriate volumes, pressures and temperatures may be evaluated.

Before determining the quantity of gas in the liquid, equilibrium between the gas and the liquid involved must be achieved. This equilibrium can be obtained by shaking a mixture of the two, by flowing a film or stream of liquid through the gas, by bubbling the gas through the liquid, or by flowing the gas over the liquid held stationary on some supporting medium (as in gas-liquid chromatography). Clever [28], Hayduk and Cheng [78], Morrison and Billett [115] and King and Al-Najjar [93] achieved equilibrium by allowing the liquid solvent to flow slowly as a thin film through the gas while Ashton et al. [5] and Ben-Naim and Baer [14] achieved the equilibrium by continuous stirring of solvent which is contained in a gas-filled solution vessel. Dymond and Hildebrand [37] obtained the equilibrium in a similar way by continuously circulating the liquid through the gas exposing fresh areas to the gas. Equilibrium also may be attained by magnetic stirring, Lindroos and Dodge [104], or by continuously bubbling the gas through the liquid, Hipkin [86] and Cheng and Lu [24].

In gas solubility determinations contributing factors like purity of materials, and the physical properties of pressure, volume and temperature are usually adequately attained. Cook and Hanson [31], who used a shaking mechanism to achieve the equilibrium, also analysed the following causes of failures which may cause errors in the determination of the solubility of gases;

1) failure to attain equilibrium,
2) failure to completely degas the solvent,
3) failure to ascertain the true amount of gas dissolved, and
4) failure to make certain that the transfer of gas from a primary container to the apparatus does not involve contamination.

The attainment of equilibrium is of primary importance for gas solubility determinations. For flow systems Clever [29], Hayduk and Cheng [78], and Morrison and Billett [115] checked the attainment of equilibrium by determining the solubility at several rates of flow. In nonflow systems it can be attained by vigorous stirring (or shaking). Ashton et al. [5] and Dymond and Hildebrand [37] used various types of magnetic devices for stirring the systems. For each type of apparatus it is important to provide these checks.

The complete removal of gas from a liquid is also important for some types of gas solubility determination, where the solvent must be initially gas free. The most frequently used method of degassing a liquid is to boil away a portion of it under vacuum. Baldwin and Daniel [181] degassed the oils they were studying by permitting the oil to drip into an evacuated chamber. They found that this removed 97-98% of the dissolved gas. A similar method was employed by

Clever et al. [27], they vacuum pumped the boiling solvent until 10-20% of the liquid was evaporated. The liquid was then transfered to another vessel and sprayed through a fine nozzle into an evacuated flask. King and Al-Najjar [93] also degassed the solvent before use by spraying into a continuously evacuated chamber.

1.6 The Prediction of Physical properties

When calculations are in the preliminary stage, estimates of chemical and physical properties must be made because reliable data may not be available or may not be in the pressure and temperature ranges needed. This work is especially concerned with the design of a new molecule for gas absorption, thus the physical properties may not be available, and need to be estimated. It is obvious that most of the estimation methods have different degrees of accuracy. The designer must decide what accuracy is required. The criterion used for selecting a particular method for the estimation of physical properties in this work is to choose the simplest method that has sufficient accuracy for the purpose required.

After the determination of gas solubility, the physical properties required in evaluating solvents for gas absorption are as follows:

1. Vapour pressure, this determines the amount of solvent lost in the gas streams leaving the plant.

2. Liquid viscosity, this determines the liquid phase mass transfer coefficients, which are important in sizing the absorption and stripping columns, and the heat transfer coefficients, which determine the size of any heat exchangers.

3. Liquid density which (together with gas solubility) determines the liquid circulation rate.

A good solvent will have a low vapour pressure (i.e. low solvent loss) and a low viscosity (i.e. smaller capital investment).

There are many calculation procedures available for the prediction of most physical properties which are considered to have sufficient accuracy for use in process design. The following sections review some of the methods which have been recommended elsewhere [135, 122, 124, 32], and one of these methods will be selected to use in this work for each physical property required. A detailed example of the use of each method is illustrated in Appendix 1.

1.6.1 Although boiling point is not used directly in the process design calculations for processes based on regeneration of solvents by pressure reduction only, it would however be important in a process design based on regeneration by solvent boiling. The main importance of boiling point determination in the present work is that it is used in the prediction of other physical properties such as vapour pressure. Boiling point is one of the physical properties for which most of the estimation methods are generally poor. This is important because vapour pressure is the physical property which determines the loss of solvent into the gas stream. Methods for predicting the boiling point are summarized by Reid et al. [136]. Most of these methods involve group-contribution techniques which are used for homologous series with no more than one functional group attached to a hydrocarbon. Meissner´s method (reviewed in Perry and Chilton [122]) is more general than the other methods, in that this method calculates the boiling point in terms of molar refraction, parachor and a chemical-type parameter. It is claimed to give average and maximum errors of 2 and 7 % respectively.

1.6.2 Critical Properties. The critical temperature, pressure and volume are the most widely used quantities in methods of predicting pure-component constants for the prediction of physical properties. Nokay [118], Spencer and Daubert [151], Rao et al. [132], Mathur et al. [111] and Lydersen [108] have proposed estimation methods for calculating the critical temperature. Gold and Ogle [68] have made an extensive comparison between experimental critical temperatures and those estimated by several methods. They concluded that Lydersen´s method is the most accurate. For critical pressure estimations, though many techniques have been suggested, the Lydersen method has again been found to be the most accurate and to be easy to use both for hydrocarbons [151] and organic compounds in general [68]. The Lydersen method, which is based on structural contributions, was also tested and found, by Gold and Ogle [68], to be the most reliable for estimating critical volumes.

1.6.3 Density. Liquid densities at the normal boiling point may be estimated within ±3% by using Benson's method [15]. For other temperatures, the liquid density can be calculated from the equations of Goldhammer [67], Bhirud [17], Gunn and Yamada [74], Yen and Woods [178], Guggenheim [71] and by the modified Rackett equation [147]. Following Goldhammer, Fishtine [71] modified an exponent used in the Goldhammer equation according to compound type. The estimated results gave an average and maximum error of 1 and 6% respectively. The method of Grain [70] is also a modification of that of Goldhammer which has the advantage of ease of use, minimum of input data, and accuracy.

Most of the above methods require at least one liquid density (often this is the critical density) as a reference density at a specified temperature and pressure. This may cause a problem for some molecules. However, there are two other methods by Goyal et al. [69] and Guggenheim [71], which are useful for the direct estimation of liquid densities. These methods require knowledge of the critical properties. Goyal et al.'s method is more accurate than the method of Guggenheim, achieving average and maximum errors of 2% and 4% respectively.

1.6.4 Viscosity. A very large number of methods have been developed to estimate liquid viscosity when no experimental data are available. Of all the estimation methods proposed, four of the best and most general, those of Orrick and Erbar [135], Thomas [160], Morris [135] and Van Velzen et al. [169], are recommended by Reid et al. [135]. None is particularly reliable, and all are empirical. All of these recommended methods employ a group-contribution technique to estimate the liquid viscosity. Reid et al. compared the estimated viscosity from these methods with the experimental values, the errors varied widely, but they reported an average deviation of 17 percent. Reid et al. recommended that, wherever possible, the method of van Velzen et al. should be used to estimate liquid viscosities. If the method of van Velzen can not be applied, the methods of Morris or Orrick and Erbar [135] are recommended. They are not, however, significantly more accurate than the Thomas´ method.

1.6.5 Vapour pressure. The most wellknown of the simpler vapour-pressure correlation equations is probably that of Antoine, if the Antoine´s constants are available. For pressures between 10 mmHg and the critical pressure, Reid et al. recommended that the method of Harlacher-Braun [76] is the most reliable method for estimating the vapour pressure if the Harlacher-Braun constants are available. For non-polar fluids, the methods of Lee-Kesler [102], Riedel

[139], Frost-Kalkwarf-Thodos [57], Riedel-Plank-Miller [135] and Thek-Stiel [158] are sufficiently accurate. All of these methods require only critical pressure and temperature, and the normal boiling point, except for the Thek-Stiel method, which requires a value of the enthalpy of vaporization of the pure fluid at the normal boiling point as well as those three constants. For polar liquids, especially hydrogen-bonded substances, the Thek-Stiel method is probably the most accurate for estimating the vapour pressure.

As well as the above physical properties, there are also other properties such as surface tension, and diffusivities in gases and liquids, which need to be estimated. Most of the methods for predicting these properties can be found elsewhere [135, 182], and will not be reviewed in this work. However, the selected estimation methods by this work are reported in Appendix 1.

The literature leads to the choice of a group contribution method for the design of a new solvent. The group contribution method suggests that many molecules can be created from the combination of appropriate molecular groups and the gas solubility in the designed molecules can then be estimated. This is very useful for investigating the solubility of gases in the molecule for which the experimental data is not available.

The group-additivity method for estimating solubility parameters and the UNIFAC type method by Sander et al. are the two types of group contribution method available for estimating gas solubilities. The group-additivity method was reviewed by England [43], this method uses functional groups to predict the energy of vaporization (ΔE_v) and the molar volume (V) of organic liquids at 25°C, and then uses these two predicted values to calculate the solubility parameters by using equation 1.10. This method seems to have more functional groups available than the method of Sander et al. However, when the temperature and pressure of the system are not the ambient conditions, a problem arises in using this method, since the value of the heat of vaporization changes slowly with the temperature, as well as the partial molar volumes changing with both temperature and pressure. This means additional calculation of the values of heat of vaporization and the partial molar volumes are required. Solubility calculations (Equation 1.9) also need the ideal gas solubility (x_2^i) given by

$$\ln x_2^i = (\Delta H_v / R)(1/T - 1/T_b) \qquad (1.28)$$

Equation 1.28 requires the boiling point of the solvent before the ideal gas solubility can be obtained. Therefore, this type of group contribution method may not be suitable to use at the first stage of designing any new solvent because of the problems as outlined above.

Table 1.6 The molecular groups and the type of organic molecules for which the Sander et al. method can not be used for the prediction of gas solubility.

Group	The type of organic molecules
Molecular Groups:	
RC=CR	Alkenes
RCOH	Aldehydes
ROR	Ethers
RCOOR	Esters
RCOOH	Organic Acids
RCOOCOR	Organic Acid Anhydrides
F, Cl Br, I	Halogens
R_nNH_n	Amines
Gases:	
SO_n, COS, CS_2, RSH, RSSR, RSR, NO_n, NH_3, HCl, HBr, HCN Hydrocarbon gases (C_3H_8, C_4H_{10} etc.)	

NOTE. R = CH_3 or CH_2 or CH or H, n = 1,2,3

The UNIFAC type group contribution method of Sander et al. does not require any physical property data in the calculation except for the group parameters. But even this method can not be used to calculate gas solubilities at pressures above 10 atm, but the group contribution equation of state (GCEOS), which is in effect an extension of the Sander et al. method, can be applied to fill this gap. However, the molecular groups in the Sander et al. method do not yet include all the functional groups that occur in oraganic molecules. The missing molecular groups and gases, and the type of organic molecule which these molecular groups would produce, are listed in Table 1.6.

To extend the range of applicability of this UNIFAC method, the group interaction parameters of these missing molecular groups need to be developed. This can be made by obtaining vapour-liquid equilibrium data for specific systems, for example the estimation of interaction parameters between the groups CO_2 and CH_2O or CH_3O, the vapour-liquid equilibrium data sets for the systems CO_2- alkanes, CO_2-ether and alkanes-ethers are needed at various temperatures, pressures and mole fractions. It should be noted that the greater the number of vapour-liquid equilibrium data sets employed, the greater the improvement in the interaction parameter values.

However, this work will not be concerned with the development of new group-interaction parameters. The aim of this work is to apply the UNIFAC type group-contribution method of Sander et al. to find a new physical solvent for absorption process.

CHAPTER 2

APPROACH TO THE PROBLEM

Until now the development of a new physical absorption solvent requires extensive comparisons of different solvents by trial and error laboratory work. The work described below presents a new approach whereby a solvent is selected on the basis of its molecular structure, and predictions of gas solubility, liquid viscosity and vapour pressure. The experimental work is also required to check the predictions.

2.1 Choosing and testing the method for predicting gas solubility.

First step is to decide how the solubility of the gas in the unknown solvent is going to be predicted, if published data are not available. At this time, it seems that the UNIFAC group contribution method by Sander et al. is best suited for this problem. This group contribution method can be more generally used than any other method because it assumes that the solubility of the gas in the solvent is effected only by interaction between the gas and the functional groups of the solvent molecule. Thus, in general, any molecule can be created from various combinations of the UNIFAC's functional groups and the solubility can be predicted directly, as long as the group-interaction parameters are available.

Thus the required complex computer program will be written to predict gas solubilities by the Sander et al.'s method. The method will be first evaluated by making predictions of the solubility of carbon dioxide, methane, hydrogen, carbon monoxide, nitrogen and oxygen in various solvents and then comparing these with experimental values quoted in the literature.

2.2 Designing a new physical solvent

Before molecules are designed, the effect of functional groups, and the influence of molecular size and shape on the solubility of carbon dioxide has to investigated.

Several candidate molecules were created from the available UNIFAC functional groups, and the solubility of carbon dioxide in the resulting solvents was then calculated, as were other physical properties of these solvents such as the boiling point, and liquid density, viscosity and vapour pressure. The methods selected for predicting the physical properties are given in Appendix 1. Selection of the new solvent was be made mainly from considering the solubility, but also from consideration of the other physical properties.

2.3 Experimental determination of gas solubility in the new solvent.

The validity of the new theoretical procedures were then investigated by measuring the solubility of various gases in the chosen solvent. A gas solubility apparatus identical to that described by King and Al-Najjar [93] was built for this work. The solubility of a gas in the solvent was determined by measuring the volume of the gas absorbed in a measured volume of the liquid used for absorption. The calculation procedures are presented in Appendix 5.

2.4 Determination of other physical properties

The methods used to predict the physical properties are listed below.

Physical Property	**Method**
Density	Grain [69]
Boiling point	Meissner [113]
Critical properties	Lydersen [108]
Viscosity	Morris [135]
Vapour pressure	Thek-Stiel [139]
Surface tension	Sugden [156]

The above physical properties estimation methods were chosen for the preliminary design of the new solvent. After choosing the solvent, the viscosity and boiling point of the new solvent will be measured to check the accuracy of the estimation methods.

2.5 Application of the new solvent in acid gases removal processes

The final part of this work is to compare the approximate size and cost of an acid gas removal plant using the new solvent with those which use commercially available solvents. This will be based on process design calculations. These require predictions of gas solubilities at high pressure and for this the recently published group contribution method GCEOS was used. The method was first be evaluated by comparing predictions with literature data.

CHAPTER 3

PREDICTION OF GAS SOLUBILITY AT LOW TO MODERATE PRESSURES BY THE UNIFAC GROUP CONTRIBUTION METHOD (SANDER ET AL.)

3.1 Introduction

This work has evaluated the use of the modified UNIFAC group contribution method of Sander et al. [142], in a search for a new physical solvent for a gas absorption process. In this chapter we repeat the testing of the method by comparing its predictions of gas solubilities with those available from collections of published data [10, 173].

We should bear in mind that this method can be only used to calculate solubilities at low to moderate pressures (1 to 10 atm). For high pressures, the group contribution equation of state (GCEOS) developed by Skjold-Jorgensen [148] was used, which will be discussed later.

3.2 The calculation of gas solubilities from the UNIFAC group contribution method of Sander et al.

A computer program has been written to calculate gas solubilities at pressures between 1 to 10 atm using the group contribution method of Sander et al. The program is written in the Fortran language, and runs on the IBM PC microcomputer, or IBM compatible alternatives. The program is supplied on diskette number 1, enclosed in the back cover of this thesis, under filenames GASLOW.FOR for the source file, and GASLOW.EXE for the execute file. A schematic diagram and the details of the variables for calculating gas solubilities by using the Sander et al. model are presented in Appendix 2.

3.2.1 Brief calculation background.

The calculation is based on the fundamental equation for gas-liquid equilibrium (Equation 1.5). The vapour phase fugacity coefficient is assumed equal to unity, thus the vapour phase fugacity of each component can be expressed as:

$$f_i^V = y_i P \qquad (3.1)$$

Introduction of equation 3.1 into equation 1.26 leads to

$$y_i P = x_i H_{i,r} \gamma_i / \gamma_{i,r}^{\infty} \qquad (3.2)$$

For given values of P, T and y, x can be obtained from equation 3.2 by iteration until the following criterion is satisfied.

$$\Sigma x_i = 1.0$$

The activity coefficients γ_i and $\gamma_{i,r}^{\infty}$ are calculated by the UNIFAC method, equations 1.11 to 1.20 in Chapter 1. The UNIFAC group volume and surface area parameters are listed in Table 1.5, and the UNIFAC interaction-energy parameters are presented in Appendix 2. The reference Henry's constant $H_{1,r}$ is calculated from equation 1.27 by using appropriate A, B and C constants from Table 1.3.

3.2.2 Computer program

To run the program "GASLOW" is entered and then the instructions on the displays have to be follow. For this step, it is assumed that the user understands the basic concepts of the UNIFAC group contribution method and of the Sander et al. model. The user should check the available UNIFAC parameters before the input of any information. The unit of solubility is the mole fraction of the gas in the liquid. If the user requires the unit of volume of gas per volume of solvent, the user should know the density of the solvent used in the calculation, or the user can choose the options displayed on the screen to use a prediction method for liquid density.

3.3 Results and Discussion

Tables 3.1 to 3.6 show comparisons between experimental [10, 93] and calculated solubilities of six gases, carbon dioxide, methane, hydrogen, carbon monoxide, nitrogen and oxygen, in various solvents. It can be seen that most of the predicted results from UNIFAC compare favourably with the available experimental results for solvent molecules containing seven or less carbon atoms. For a greater number of carbon atoms the error in the predicted gas solubilities starts increasing. This suggests that using the UNIFAC method to estimate the solubility of gases in big solvent molecules may cause unexpected errors. However, this may not effect the design of solvents in this work, because the bigger molecules are associated with a higher liquid viscosity and a low volumetric solubility and are thus not the ideal choice for the design of a solvent for a gas absorption processes. So the UNIFAC model is still a reasonable choice for the application proposed.

At the present time, the UNIFAC group-contribution for calculating gas solubilities at low to moderate pressures (1-10 bar) represents a very promising method for predicting gas solubility by using molecular groups. On using this method to predict the solubilities of carbon dioxide, methane, hydrogen, carbon monoxide, nitrogen and oxygen in various solvents, the error of the predictions was not greater than 10% when they were compared with the experimental solubilities.

The UNIFAC group-contribution method is still limited by the number of molecular groups covered. There are only 17 molecular groups and 10 gases available for this method. They are listed in Table 1.5. These molecular groups do not yet cover all of the functional groups of organic molecules. Nevertheless, even when restricted to the 17 available molecular groups, it is apparent that many molecules may be designed and the solubilities of various gases in the resulting solvents may be estimated with an acceptable accuracy (acceptable that is for solvent screening).

TABLE 3.1 Solubility of CO_2 in various solvents at 298.15 K and gas partial pressure of 1 atm, comparison of UNIFAC predictions and experiments [10, 93].

SOLVENT	MOLE FRACTION		DIFFERENCE
	EXPERIMENT	PREDICTION	
Methanol	0.0056	0.0056	0.0000
Ethanol	0.0064	0.0063	0.0001
Acetone	0.0185	0.0210	-0.0024
Isobutanol	0.0071	0.0070	-0.0001
Pentanol	0.0081	0.0079	0.0002
Octanol	0.0115	0.0092	0.0023
Decanol	0.0123	0.0100	0.0023
n-Hexane	0.0119	0.0118	0.0001
n-Heptane	0.0119	0.0119	0.0000
n-Octane	0.0144	0.0120	0.0024
n-Decane	0.0144	0.0124	0.0020
Cyclohexane	0.0076	0.0075	0.0001
Cyclohexanol	0.0044	0.0058	-0.0014
Benzene	0.0097	0.0097	0.0000
Methylcyclohexane	0.0092	0.0083	0.0009
2,2,4-Trimethylpentane	0.0139	0.0118	0.0020
Toluene	0.0101	0.0099	0.0002

TABLE 3.2 Solubility of CH_4 in various solvents at 298.15 K and gas partial pressure of 1 atm, comparison of UNIFAC predictions and experiments [10, 93].

SOLVENT	MOLE FRACTION		DIFFERENCE
	EXPERIMENT	PREDICTION	
Methanol	0.0009	0.0009	0.0000
Ethanol	0.0013	0.0013	0.0000
Acetone	0.0018	0.0019	-0.0001
n-Hexane	0.0050	0.0050	0.0000
n-Heptane	0.0035	0.0050	-0.0016
n-Octane	0.0030	0.0051	-0.0021
Cyclohexane	0.0033	0.0031	0.0001
Cyclohexanol	0.0013	0.0017	-0.0004
Benzene	0.0021	0.0020	0.0000
Methylcyclohexane	0.0040	0.0037	0.0003
2,2,4-Trimethylpentane	0.0030	0.0052	-0.0022
Toluene	0.0024	0.0023	0.0001

TABLE 3.3 Solubility of H_2 in various solvents at 298.15 K and gas partial pressure of 1 atm, comparison of UNIFAC predictions and experiments [10, 93].

SOLVENT	MOLE FRACTION		DIFFERENCE
	EXPERIMENT	PREDICTION	
Ethanol	0.0002	0.0002	0.0000
Acetone	0.0003	0.0003	0.0000
n-Hexane	0.0006	0.0006	0.0000
n-Heptane	0.0007	0.0006	0.0001
n-Octane	0.0007	0.0006	0.0000
Cyclohexane	0.0004	0.0004	0.0000
Cyclohexanol	0.0002	0.0002	0.0000
Benzene	0.0003	0.0003	0.0000
2,2,4-Trimethylpentane	0.0008	0.0008	0.0000
Toluene	0.0003	0.0003	0.0000

TABLE 3.4 Solubility of CO in various solvents at 298.15 K and gas partial pressure of 1 atm, comparison of UNIFAC predictions and experiments [10, 93].

SOLVENT	MOLE FRACTION		DIFFERENCE
	EXPERIMENT	PREDICTION	
Methanol	0.00038	0.00038	0.00000
Ethanol	0.00048	0.00047	0.00001
Acetone	0.00077	0.00077	0.00000
n-Heptane	0.00172	0.00175	-0.00003
Cyclohexane	0.00099	0.00099	0.00000
Benzene	0.00067	0.00067	0.00000
Toluene	0.00081	0.00081	0.00001

TABLE 3.5 Solubility of N_2 in various solvents at 298.15 K and gas partial pressure of 1 atm, comparison of UNIFAC predictions and experiments [10, 93].

SOLVENT	MOLE FRACTION		DIFFERENCE
	EXPERIMENT	PREDICTION	
Methanol	0.0003	0.0003	0.0000
Ethanol	0.0004	0.0003	0.0001
Acetone	0.0005	0.0005	0.0000
n-Hexane	0.0014	0.0013	0.0001
n-Heptane	0.0014	0.0013	0.0001
n-Octane	0.0013	0.0012	0.0001
Cyclohexane	0.0008	0.0007	0.0001
Cyclohexanol	0.0003	0.0003	-0.0001
Benzene	0.0004	0.0005	-0.0001
Methylcyclohexane	0.0009	0.0008	0.0001
2,2,4-Trimethylpentane	0.0015	0.0017	-0.0002
Toluene	0.0006	0.0005	0.0001

TABLE 3.6 Solubility of O_2 in various solvents at 298.15 K and gas partial pressure of 1 atm, comparison of UNIFAC predictions and experiments [10, 93].

SOLVENT	MOLE FRACTION		DIFFERENCE
	EXPERIMENT	PREDICTION	
Methanol	0.0004	0.0004	0.0000
Ethanol	0.0006	0.0006	0.0000
Acetone	0.0008	0.0008	0.0000
n-Hexane	0.0019	0.0022	-0.0003
n-Heptane	0.0022	0.0021	0.0001
n-Octane	0.0021	0.0021	0.0000
Cyclohexane	0.0012	0.0007	0.0005
Benzene	0.0008	0.0008	0.0000
Methylcyclohexane	0.0016	0.0010	0.0006
2,2,4-Trimethylpentane	0.0028	0.0027	0.0001
Toluene	0.0009	0.0009	0.0000

3.5 Conclusion

The modified UNIFAC group contribution method of Sander et al. has been used to estimate the solubility of gases in various solvents. Comparisons between calculated and experimental gas solubilities showed that the modified UNIFAC group contribution method can be applied to predict the solubilities of gases in both nonpolar and polar nonelectrolyte solvents. The average error from the prediction is less than 10%. A computer program has been written for calculating the gas solubility by using the model of Sander et al.

The following sections describe the use of the available UNIFAC group contribution parameters to find a new physical solvent for the carbon dioxide gas absorption process. It is recognised that at present this approach is limited by the functional groups available. Nevertheless, if successful, the result of using the UNIFAC group contribution method for finding a suitable solvent for gas absorption may well lead to a new approach for the design of solvents for separation processes. In principle more molecular groups may be added to this procedure. However, all that required is more experimental measurements of gas solubilities and computerised calculations.

CHAPTER 4

THE MOLECULAR DESIGN OF A NEW PHYSICAL SOLVENT FOR A GAS ABSORPTION PROCESS

4.1 Introduction

The new solvent is to be suitable for removing carbon dioxide from other gases, thus in designing it we look for an appropriate combination of molecular groups such that the resulting solvent will have:

a. a high carbon dioxide solubility on the basis of moles carbon dioxide per unit volume of solvent,
b. a low solubility for hydrocarbon gases,
c. a low vapour pressure, and
d. a low viscosity.

The solvent will be chosen mainly on the basis of gas solubilities a and b. The vapour pressure (c) is expected to be strongly dependent on molecular weight, and provides initial guidance on the expected size of the ideal solvent molecule. That is, the vapour pressure decreases as molecular weight increases.

However increasing the molecular weight of the solvent may increase its viscosity, thus a range of solvents of different molecular weight will be investigated.

By reference to other commercially succesful solvent processes, it is expected that the molecular weight of the new solvent will be between 50 and 250.

4.2 Molecular design for a high carbon dioxide solubility by the Sander et al. method

Stage 1 Preliminary Analysis.

The following characteristics of the solvent molecule are considered in this section.

1. The identification of which molecular groups are associated with a high carbon dioxide solubility.
2. The effect of molecular weight on carbon dioxide volumetric solubility.
3. The effect of molecular structure on carbon dioxide solubility.

The predictions by UNIFAC are supplemented (and supported) by reference to experimental determinations of carbon dioxide solubility in alcohols [11]. This provides a base case against which the predictions by the Sander et al. method may be compared.

Stage 2 Design of the solvent molecule.

Promising new molecular structures are designed as homologous series, (i.e. groups of molecules of similar structure but of different molecular weight). These are compared, one with another, in terms of the predicted solubility of carbon dioxide in the solvents.

Stage 3 **Choice of a new solvent.**

Promising candidate solvents are evaluated taking into account solubility, vapour pressure and viscosity, leading to the choice of a new solvent.

4.3 Preliminary analysis

The work of Sander et al. [142] provided characteristic interaction parameters for 27 groups, 17 of these are molecular groups and 10 are gases. These 17 molecular groups will be used to investigate the effect on carbon dioxide solubility.

4.3.1 The identification of which molecular groups are associated with a high carbon dioxide solubility

The method used is to define a straight chain alkane, $CH_3-CH_2-CH_2-CH_2-CH_2-FG$, which is used as a reference molecule, and then to predict the effect on carbon dioxide solubility of replacing the FG group by, in turn, one molecular group of each species.

Table 4.1 and Figure 4.1 shows the results for the seventeen molecular groups which were evaluated. The results show quite significant differences between the molecular groups. This is shown even more clearly by putting the groups in rank order of carbon dioxide solubility as shown in Table 4.2.

The carbon dioxide solubility predicted for the alkane plus the ketone group (placed first in the rank order of Table 4.2) is more than twice that for the alkane plus water group which is placed last.

Table 4.1 The effect of UNIFAC functional groups to the solubility of carbon dioxide (at 25°C and 1 atm gas pressure).

Reference alkane molecule (XO) = $CH_3-CH_2-CH_2-CH_2-CH_2-FG$

Group	Adding Functional Group(FG)	Solubility(Mole Fraction)
0	-	0.0096
1	CH_3	0.0118
2	CH_3	0.0111
3	CH_3	0.0110
4	CH_2	0.0097
5	CH_2(cy)	0.0097
6	CH	0.0085
7	CH(cy)	0.0088
8	C	0.0086
9	AcH	0.0102
10	Ac	0.0076
11	$AcCH_3$	0.0104
12	$AcCH_2$	0.0095
13	AcCH	0.0083
14	OH	0.0078
15	H_2O	0.0049
16	CH_3CO	0.0175
17	CH_2CO	0.0157

Table 4.2 The rank order of carbon dioxide solubility in the reference alkane+functional group (at 25°C and 1 atm gas pressure).

Adding Functional Group(FG)	Solubility (Mole Fraction)	CO_2-Functional group Interaction parameters
CH_3CO	0.0175	74.3
CH_2CO	0.0157	74.3
CH_3	0.0118	209.1
CH_3	0.0111	209.1
CH_3	0.0110	209.1
$AcCH_3$	0.0104	297.8
AcH	0.0102	177.8
CH_2	0.0097	256.0
CH_2(cy)	0.0097	257.5
AcCH	0.0095	297.8
CH(cy)	0.0088	239.3
C	0.0086	0.0
CH	0.0085	330.6
$AcCH_2$	0.0083	297.8
OH	0.0078	330.3
Ac	0.0076	1080.7
H_2O	0.0049	980.1

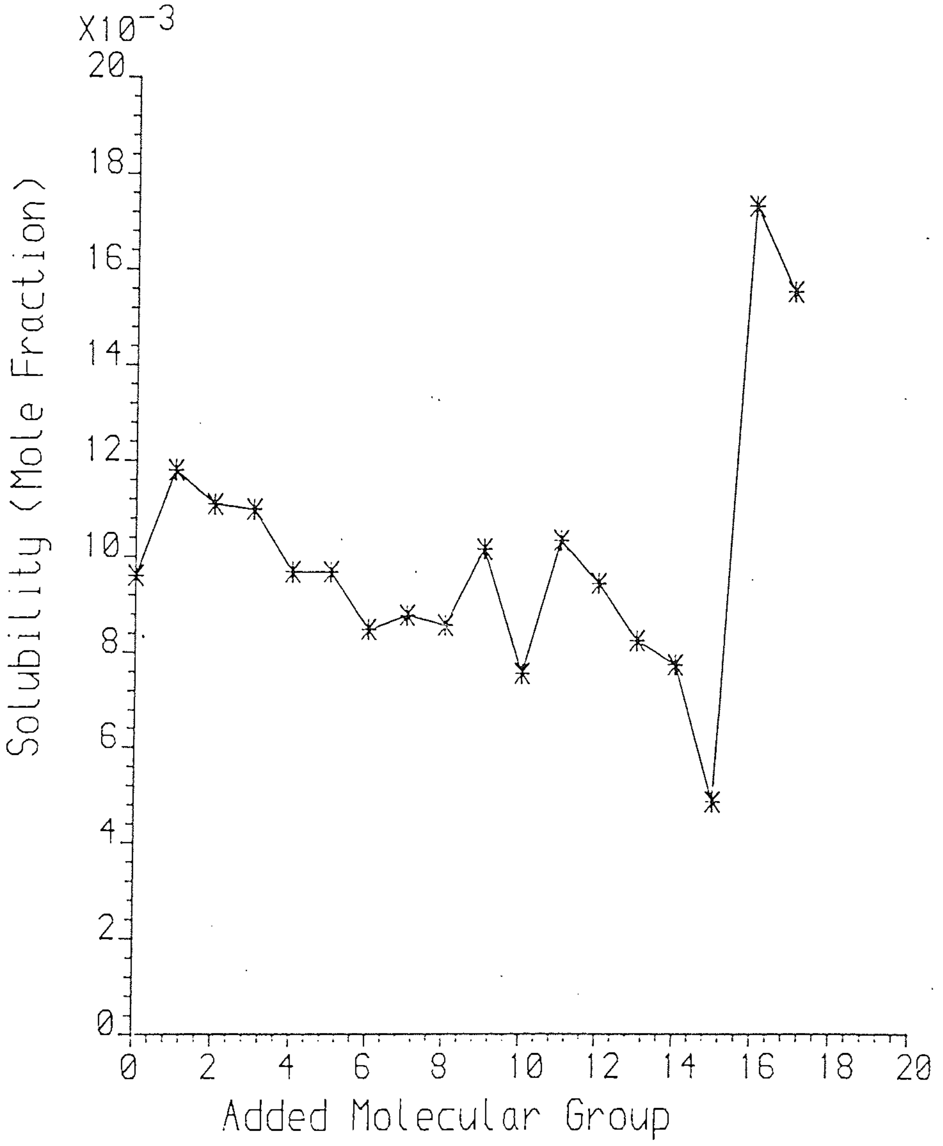


Figure 4.1 The effect of UNIFAC functional groups on the solubility of carbon dioxide at 25°C and 1 atm gas pressure (reference to Table 4.1).

4.3.2 The effect of molecular weight on gas solubility

The solubilities shown in Tables 4.1 and 4.2 are on a mole fraction basis. Volumetric solubilities (i.e. volume of gas absorbed per unit volume of solvent) depend also on the molar density of the solvent and this will go down as the molecular weight of the solvent molecule increases. The effect of molecular weight on carbon dioxide solubility in the alcohols has been determined in a series of experiments and reported by Begley et al. [11]. Their solubility results and comparisons with those predicted by the Sander et al. method are shown in Table 4.3.

TABLE 4.3 The solubilities of CO_2 in alcohols at 25°C, 1 atm gas pressure determined by Begley et al. [11] compared with those predicted from Sander et al.'s model.

SOLVENT	MW	EXPERIMENT		PREDICTION	
		Mole Fraction	$\frac{\text{cc.of Gas}}{\text{cc.of Solv}}$	Mole Fraction	$\frac{\text{cc.of Gas}}{\text{cc.of Solv}}$
Methanol	32	0.0064	3.89	0.0056	3.39
Ethanol	46	0.0065	2.78	0.0063	2.69
Propanol	60	0.0077	2.54	0.0071	2.34
Isobutanol	74	0.0070	1.87	0.0070	1.87
Pentanol	88	0.0081	1.84	0.0079	1.80
Cyclohexanol	100	0.0044	1.02	0.0058	1.35

Table 4.3 shows that for straight chain alcohols carbon dioxide solubility expressed as mole fraction tends to increase with molecular weight. However, the mass density of the alcohols increases with molecular weight and the molar density decreases and the net effect is a reduction of carbon dioxide volumetric solubility as molecular weight increases.

Table 4.3 also shows solubilities predicted by the Sander et al. method which show the same variation of solubility with molecular weight as that of the experimental work.

The Sander et al. method was then used to predict the mole fraction solubility of carbon dioxide in several solvents of different molecular weight forming a homologous series for each of the molecular groups under investigation. The following homologous series were investigated, aromatics and ketones (the K1-series).

For each solvent, the mass density was predicted by the method of Goyal et al. [69] and used to calculate the molar density and volumetric solubility of carbon dioxide. The results are shown in Tables 4.4-4.5 and Figures 4.2-4.3. For all homologous series, as the molecular weight increases the volumetric solubility decreases. The mole fraction solubility for the aromatic homologous series is increased as the molecular weight increases, but for the ketones homologous series (the K1-series) it is reduced as the molecular weight increases.

Considering the molecules of the aromatic homologous series, six functional groups of type 6 constitute molecule number 1, and molecules numbers 2 to 5 were created by replacing each one of the functional groups of type 6 with functional group 11. It can be seen that as the functional group 6 (which was placed seventh in the rank order of Table 4.2) is being replaced by functional group 11 (which was placed sixth in the rank order of Table 4.2), the molecular weight is increasing, and the mole fraction solubility is increasing.

For the ketone homologous series (the K1-series), the molecule number 1 is acetone which is constituted of functional groups 1 and 16 which were placed third and first respectively in the rank order of Table 4.2. As the functional group 4, which was placed eighth in the rank order of Table 4.2, is added to the acetone to make up molecule number 2 and so on, the mole fraction solubility is reduced.

The above results suggest that adding a lower rank order functional group to a higher rank order functional group is likely to reduce the mole fraction solubility.

Table 4.4 The effect of molecular weight on carbon dioxide solubilities in an ketone series (the K1-series). The solubilities are predicted by the Sander et al. method.

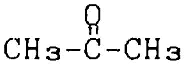
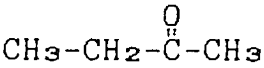
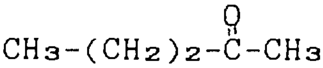
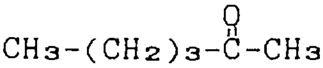
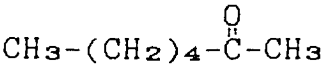
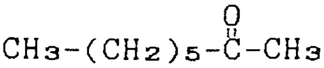
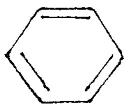
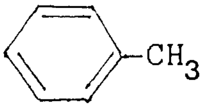
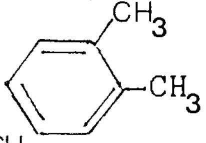
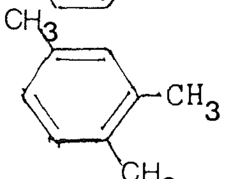
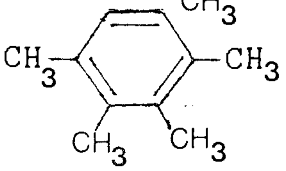
Ketone Molecule	Molecular Weight	Density	Solubility	
			Mole Fraction	cc.of Gas / cc.of Solv
 $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$	58.0	0.7877	0.0210	7.12
 $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$	72.0	0.7815	0.0194	5.25
 $CH_3-(CH_2)_2-\overset{\overset{O}{\|}}{C}-CH_3$	86.0	0.7817	0.0184	4.18
 $CH_3-(CH_2)_3-\overset{\overset{O}{\|}}{C}-CH_3$	100.0	0.7843	0.0179	3.49
 $CH_3-(CH_2)_4-\overset{\overset{O}{\|}}{C}-CH_3$	114.0	0.7877	0.0175	3.01
 $CH_3-(CH_2)_5-\overset{\overset{O}{\|}}{C}-CH_3$	128.0	0.7913	0.0173	2.67

Table 4.5 The effect of molecular weight on carbon dioxide solubilities in an aromatic series. The solubilities are predicted by the Sander et al. method.

Aromatic Molecule	Molecular Weight	Density	Solubility	
			Mole Fraction	$\frac{\text{cc.of Gas}}{\text{cc.of Solv}}$
	78.0	0.8822	0.0098	2.73
	92.0	0.8746	0.0100	2.34
	106.0	0.8697	0.0105	2.14
	120.0	0.8663	0.0113	2.02
	134.0	0.9639	0.0123	1.97

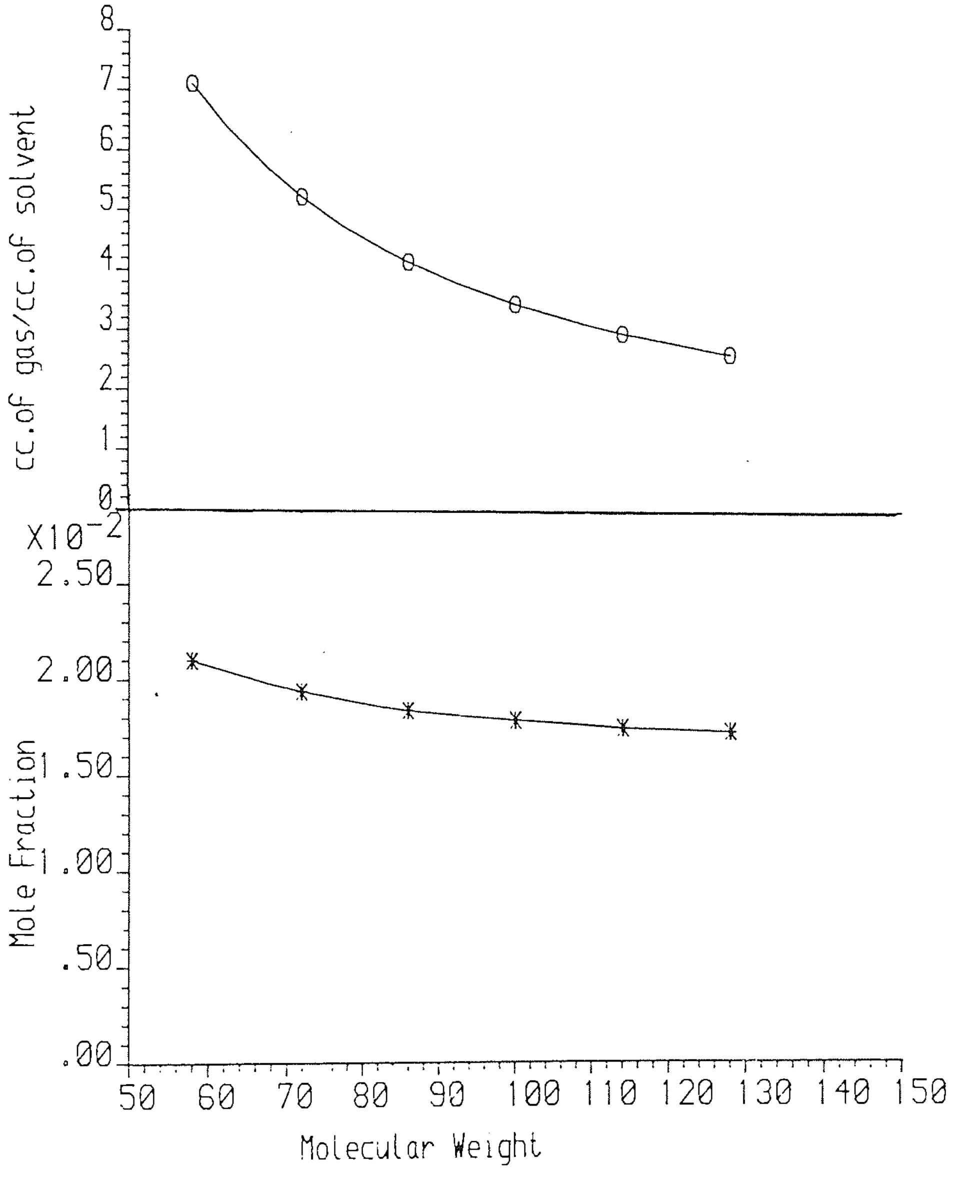


Figure 4.2 The effect of molecular weight on the estimated solubilities of carbon dioxide in K-1-series at 25° C and 1 atm gas pressure.

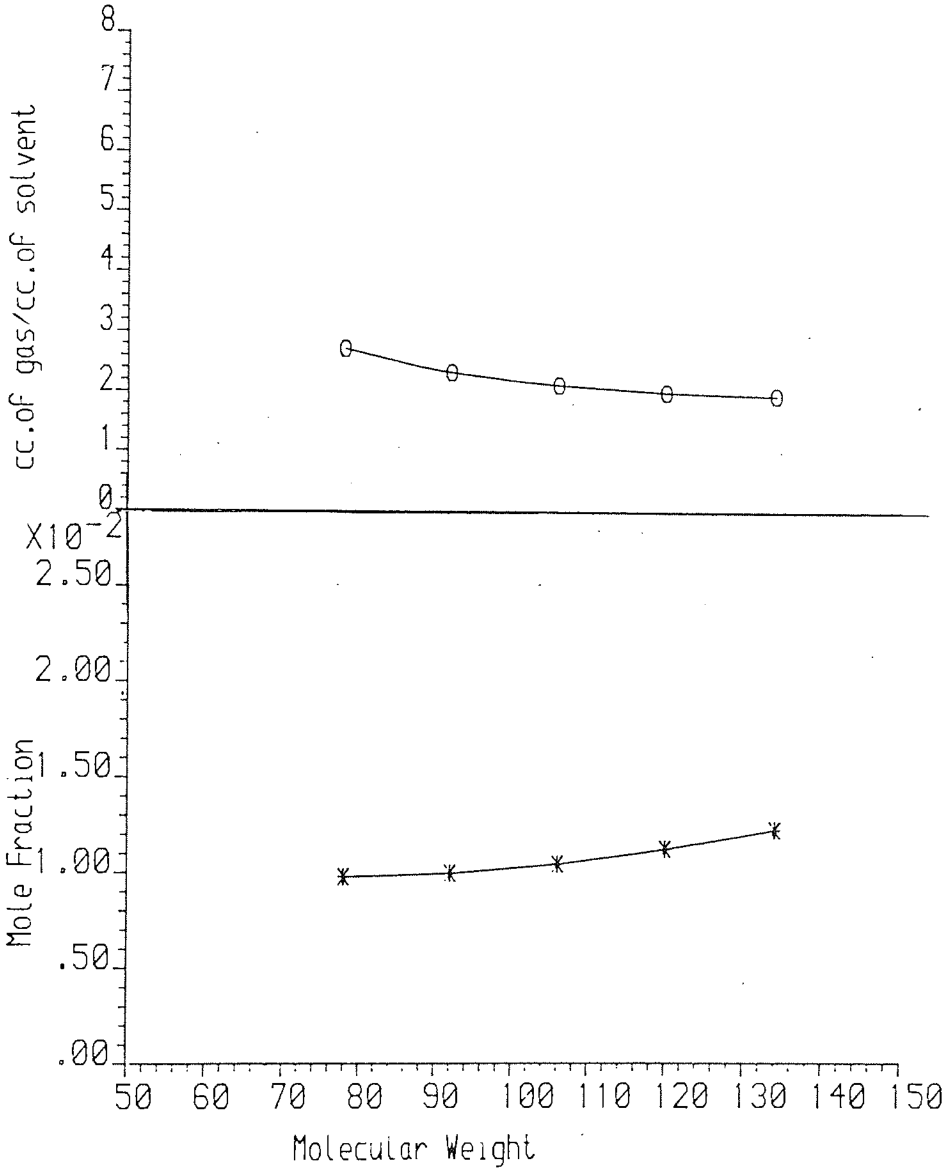


Figure 4.3 The effect of molecular weight on the estimated carbon dioxide solubility in aromatic-series at 25° C and 1 atm gas pressure.

4.3.3 The effect of molecular structure on solubility

The experimental work on alcohols by Begley et al. [11] also included an investigation of the effect of molecular structure on carbon dioxide solubility. They observed that the solubility of carbon dioxide in the straight chain alcohols appeared to be a smooth function of molar volume, except for the values for isobutanol and cyclohexanol which fall above the values for the linear molecules. Their results are presented in Table 4.3. This shows that in comparing the molecular structures, the solubilities of carbon dioxide in the straight chain alcohols seems to be higher than those in the branched chain alcohols.

The UNIFAC method of Sander et al. permits some similar comparisons to be made for alkyl groups. It distinguishes between the alkyl groups CH_3 (neighbouring a CH_2 group), CH_3' (neighbouring a CH group) and CH_3'' (neighbouring a C group). It thus implies that detectable differences in gas solubility resulting from molecular structure have been detected in the empirical correlation of the gas solubility data base which forms the basis for the Sander et al. UNIFAC method.

The effect of straight chain and branch chain variations in molecular structure for several different molecular groups was investigated by the Sander et al. UNIFAC method. The comparison was made keeping molecular weight constant for each comparison. For all the molecules compared, a basis of 6 to 7 carbon atoms was used such that the molecular weights of the molecules compared varied very little, within the range 100-102.

The results of the predictions are shown in Tables 4.6 to 4.8, and also in Figure 4.4. These results confirm the conclusions drawn from consideration of the experimental solubilities in alcohols discussed above. That is, the effect of changing from straight to branched chain molecules produces a change in carbon dioxide solubility but the changes are small, particularly in comparison with the difference between molecular groups. The results also confirm the rank order of molecular groups shown in Table 4.2. That is the carbon dioxide solubilities of the homologous series was in the same order irrespective of molecular weight.

Table 4.6 The effect of molecular structure in the alkane series on the solubilities of carbon dioxide at 25°C and 1 atm gas pressure.

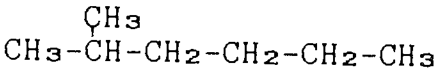
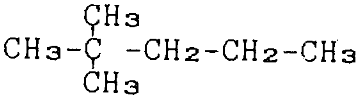
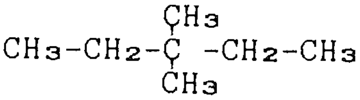
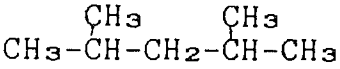
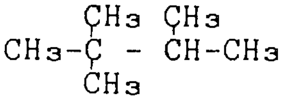
Molecule	Structure	Molecular weight	Solubility
1	$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$	100	0.0119
2	 $CH_3-\overset{CH_3}{CH}-CH_2-CH_2-CH_2-CH_3$	100	0.0114
3	 $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_2-CH_3$	100	0.0125
4	 $CH_3-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_3$	100	0.0135
5	 $CH_3-\overset{CH_3}{CH}-CH_2-\overset{CH_3}{CH}-CH_3$	100	0.0107
6	 $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{CH_3}{CH}-CH_3$	100	0.0117

Table 4.7 The effect of molecular structure in the alcohol series on the solubilities of carbon dioxide at 25°C and 1 atm gas pressure.

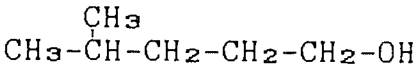
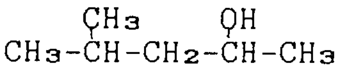
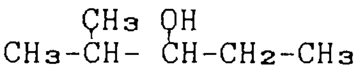
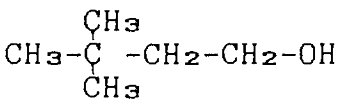
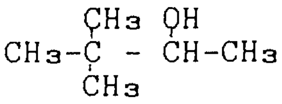
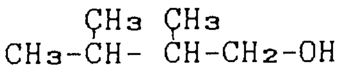
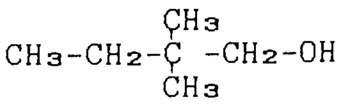
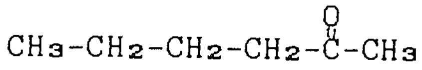
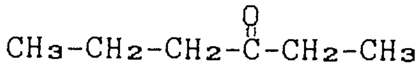
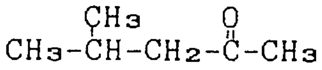
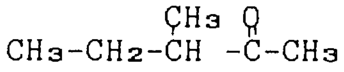
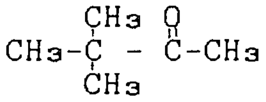
Molecule	Structure	Molecular weight	Solubility
1	$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH$	102	0.0083
2	 $CH_3\text{-}\overset{CH_3}{CH}\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH$	102	0.0079
3	 $CH_3\text{-}\overset{CH_3}{CH}\text{-}CH_2\text{-}\overset{OH}{CH}\text{-}CH_3$	102	0.0079
4	 $CH_3\text{-}\overset{CH_3}{CH}\text{-}\ \overset{OH}{CH}\text{-}CH_2\text{-}CH_3$	102	0.0086
5	 $CH_3\text{-}\underset{CH_3}{\overset{CH_3}{C}}\ \text{-}CH_2\text{-}CH_2\text{-}OH$	102	0.0088
6	 $CH_3\text{-}\underset{CH_3}{\overset{CH_3}{C}}\ \text{-}\ \overset{OH}{CH}\text{-}CH_3$	102	0.0087
7	 $CH_3\text{-}\overset{CH_3}{CH}\text{-}\ \overset{CH_3}{CH}\text{-}CH_2\text{-}OH$	102	0.0079
8	 $CH_3\text{-}CH_2\text{-}\underset{CH_3}{\overset{CH_3}{C}}\ \text{-}CH_2\text{-}OH$	102	0.0095

Table 4.8 The effect of molecular structure in ketone series on the solubilities of carbon dioxide at 25°C and 1 atm gas pressure.

Molecule	Structure	Molecular weight	Solubility
1	 $CH_3-CH_2-CH_2-CH_2-\overset{O}{\overset{\Vert}{C}}-CH_3$	100	0.0179
2	 $CH_3-CH_2-CH_2-\overset{O}{\overset{\Vert}{C}}-CH_2-CH_3$	100	0.0184
3	 $CH_3-\overset{CH_3}{\overset{\vert}{C}H}-CH_2-\overset{O}{\overset{\Vert}{C}}-CH_3$	100	0.0173
4	 $CH_3-CH_2-\overset{CH_3}{\overset{\vert}{C}H}-\overset{O}{\overset{\Vert}{C}}-CH_3$	100	0.0183
5	 $CH_3-\underset{CH_3}{\underset{\vert}{\overset{CH_3}{\overset{\vert}{C}}}}-\overset{O}{\overset{\Vert}{C}}-CH_3$	100	0.0189

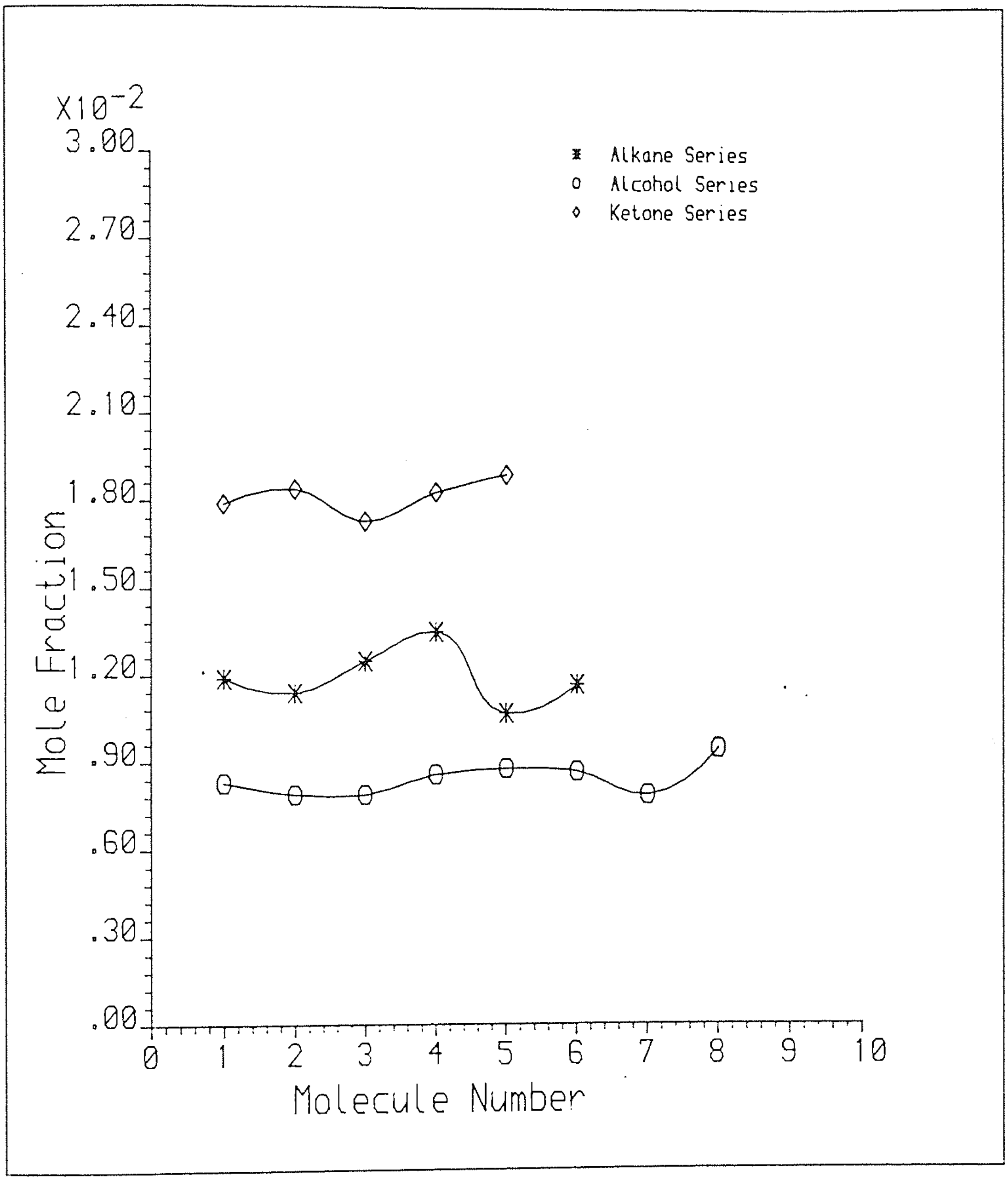
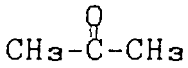
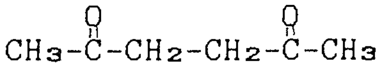
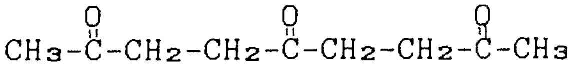
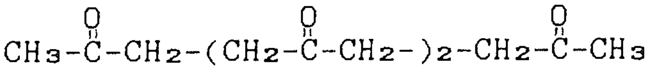
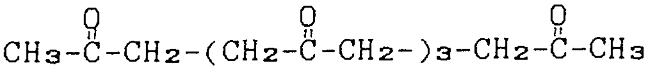
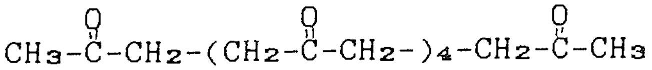


Figure 4.4 The effect of molecular structure on the estimated solubility of carbon dioxide at 25° C and 1 atm gas pressure.

4.4 Design of new solvent molecules

The preliminary analysis described above showed significant differences in solubilities resulting from the molecular groups, and much smaller differences resulting from molecular structure. The ketone group (CH_3CO) was identified as that which produced the highest carbon dioxide solubility. In all of the above investigations, each molecular group studied was attached to an alkane, i.e. a series of CH_2 groups.

In designing new solvents, the approach used was to design molecules consisting of as many promising groups as possible. These were designed as homologous series in which, as molecular weight increased, the number of "promising" groups increased in proportion. This is illustrated below for the B-series which was identified as having the best carbon dioxide solubility.

		Molecular Weight
B1.	 $CH_3-\overset{\overset{O}{\parallel}}{C}-CH_3$	58.0
B2.	 $CH_3-\overset{\overset{O}{\parallel}}{C}-CH_2-CH_2-\overset{\overset{O}{\parallel}}{C}-CH_3$	114.0
B3.	 $CH_3-\overset{\overset{O}{\parallel}}{C}-CH_2-CH_2-\overset{\overset{O}{\parallel}}{C}-CH_2-CH_2-\overset{\overset{O}{\parallel}}{C}-CH_3$	170.0
B4.	 $CH_3-\overset{\overset{O}{\parallel}}{C}-CH_2-(CH_2-\overset{\overset{O}{\parallel}}{C}-CH_2-)_2-CH_2-\overset{\overset{O}{\parallel}}{C}-CH_3$	226.0
B5.	 $CH_3-\overset{\overset{O}{\parallel}}{C}-CH_2-(CH_2-\overset{\overset{O}{\parallel}}{C}-CH_2-)_3-CH_2-\overset{\overset{O}{\parallel}}{C}-CH_3$	282.0
B6.	 $CH_3-\overset{\overset{O}{\parallel}}{C}-CH_2-(CH_2-\overset{\overset{O}{\parallel}}{C}-CH_2-)_4-CH_2-\overset{\overset{O}{\parallel}}{C}-CH_3$	338.0

In all 90 molecules were designed as 12 classes of homologous series plus the alcohol A-series. These 90 molecules were designed by means of combinations of UNIFAC functional groups. The structures of these molecules are shown in Appendix 3. The new molecules were then checked to see if

a) they existed, i.e. that they had been previously synthesised, and

b) if they were available in commercial quantities.

This was done by refering to the Catalogue Handbook of Fine Chemicals by Aldrich Chemical Co. Ltd. More than 50% of these molecules were found to have been synthesised (made in the laboratory) and for many of them the important physical properties of boiling point, viscosity, etc. are reported in the above catalogue.

All of these solvents were compared in terms of carbon dioxide solubility predicted by the method of Sander et al. The results are presented in Figures 4.5 to 4.6 and in Appendix 3.

In Figure 4.7 the carbon dioxide solubility for each homologous series is plotted against molecular weight. As expected, the B homologous series, based on ketone groups, as shown in Table 4.9, is predicted to have significantly higher carbon dioxide solubilities (on a mole fraction basis) than the other homologous series.

Then, for each member of the homologous series, predictions of the boiling point and then solvent density were made by the methods of Meissner [113] and Goyal et al. [69] and predictions of carbon dioxide volumetric solubility were made. These are compared in Figure 4.8.

This confirms the B series as the most promising form of new molecule. In all cases increasing the number of promising groups increases the gas solubility. There is a significant gain in higher carbon dioxide solubility caused by increasing the number of promising molecular groups (ketone group) in proportion to molecular weight than that in molecules containing the combination of ketone group and the other functional groups.

Table 4.9 The estimated solubilities of carbon dioxide in B-series at 25°C and 1 atm gas pressure.

Molecule	Molecular weight	Solubility	
		Mole Fraction	cc.of Gas / cc.of Solvent
B1	58.0	0.0210	7.12
B2	114.0	0.0216	4.07
B3	170.0	0.0241	3.22
B4	226.0	0.0265	2.78
B5	282.0	0.0289	2.51
B6	338.0	0.0312	2.32

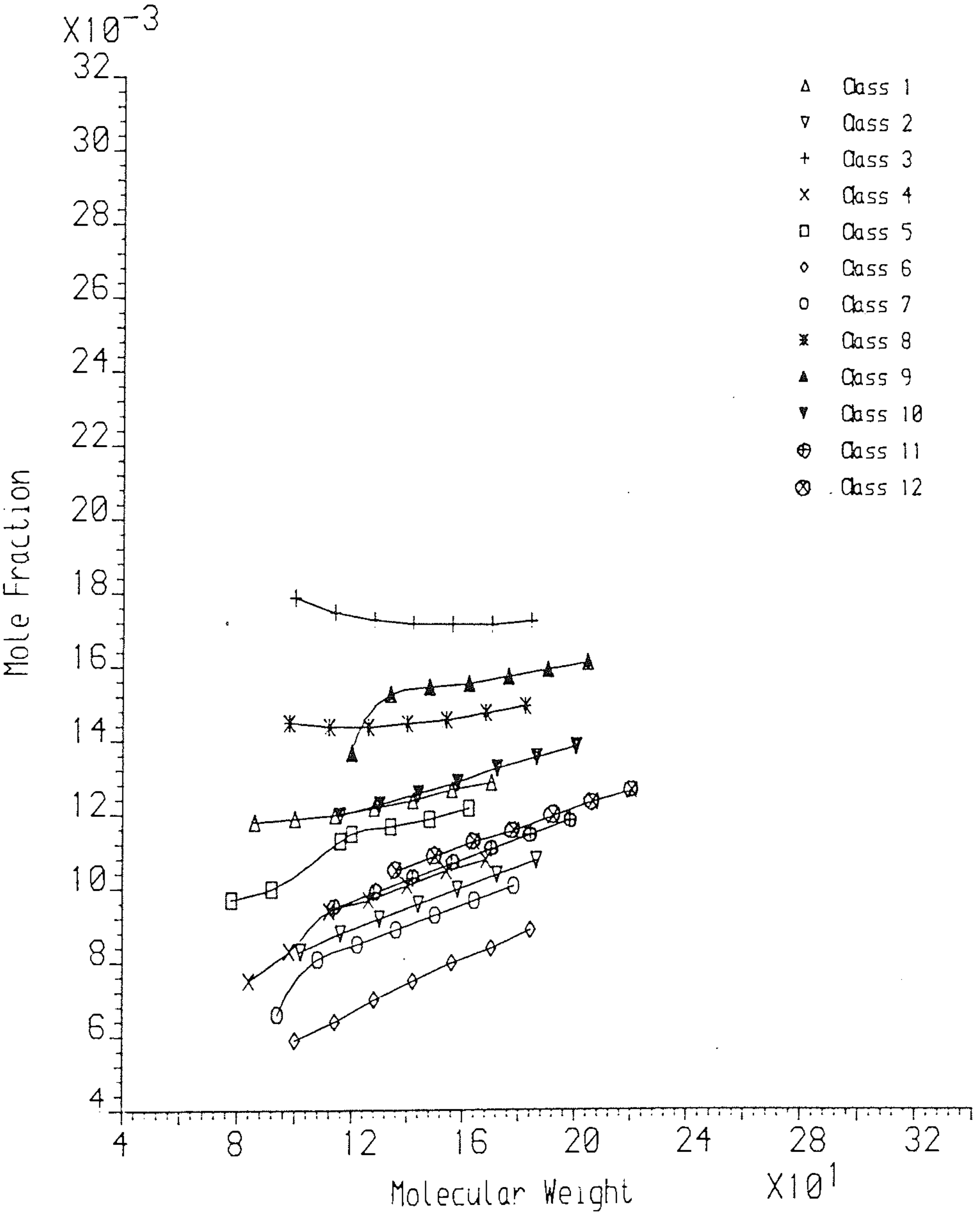


Figure 4.5 The mole fraction solubility of carbon dioxide in the 12 classes of molecules at 25° C and 1 atm gas pressure.

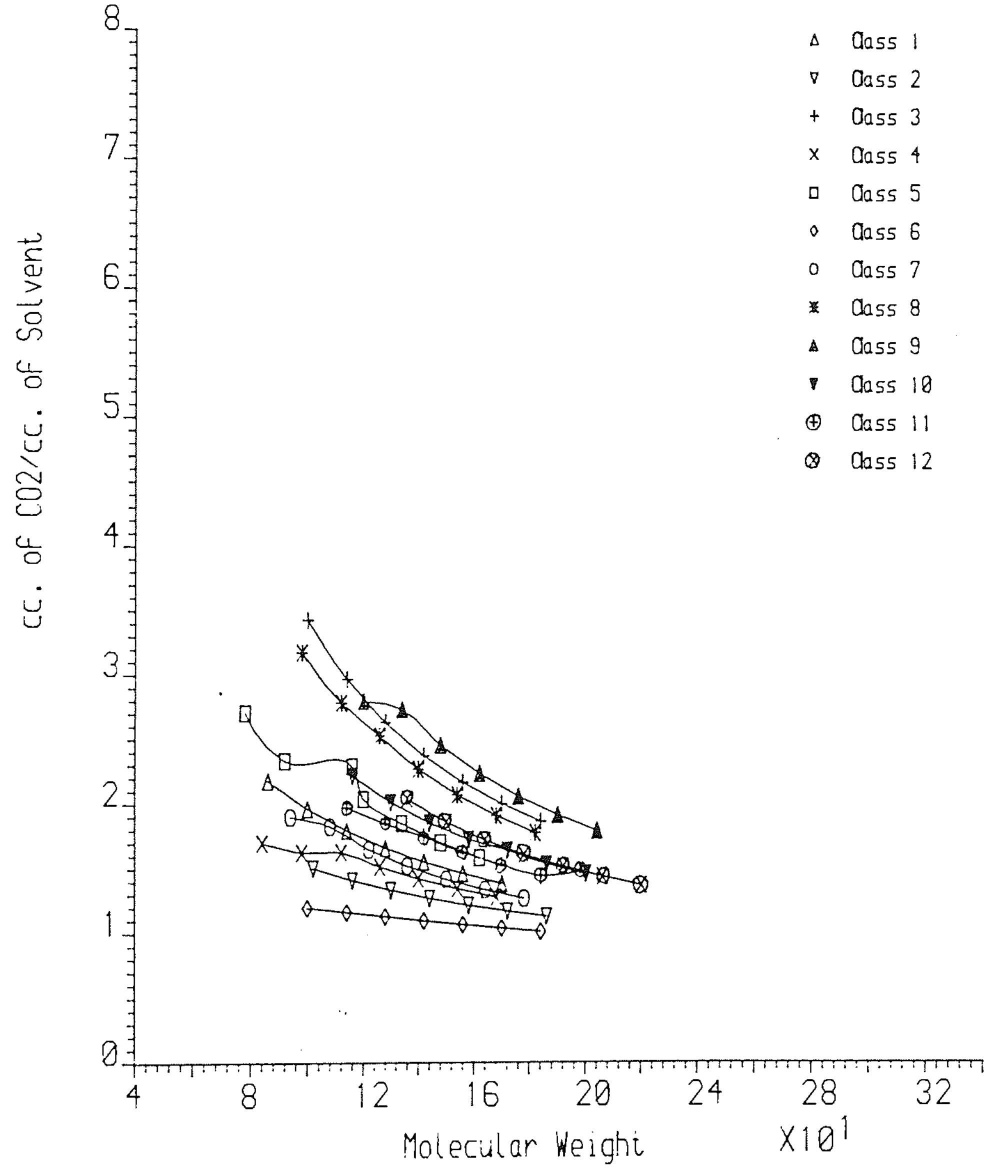


Figure 4.6 The volume of gas per volume of solvent solubility of carbon dioxide in the 12 classes of molecules at 25° C and 1 atm gas pressure.

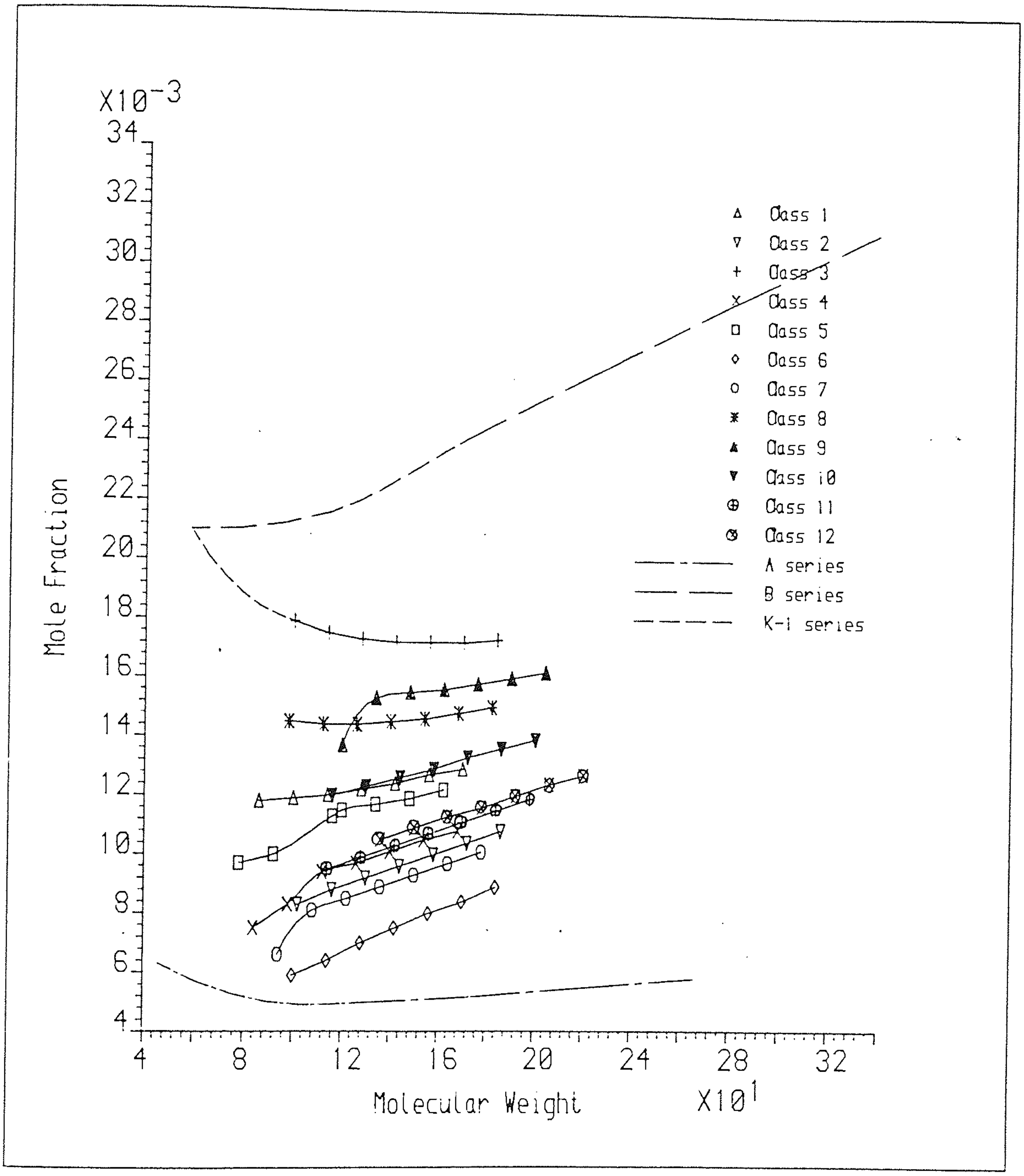


Figure 4.7, The comparison of mole fraction solubility of carbon dioxide in A-series, K-1 series B-series and 12 classes of molecules at 25° C and 1 atm gas pressure.

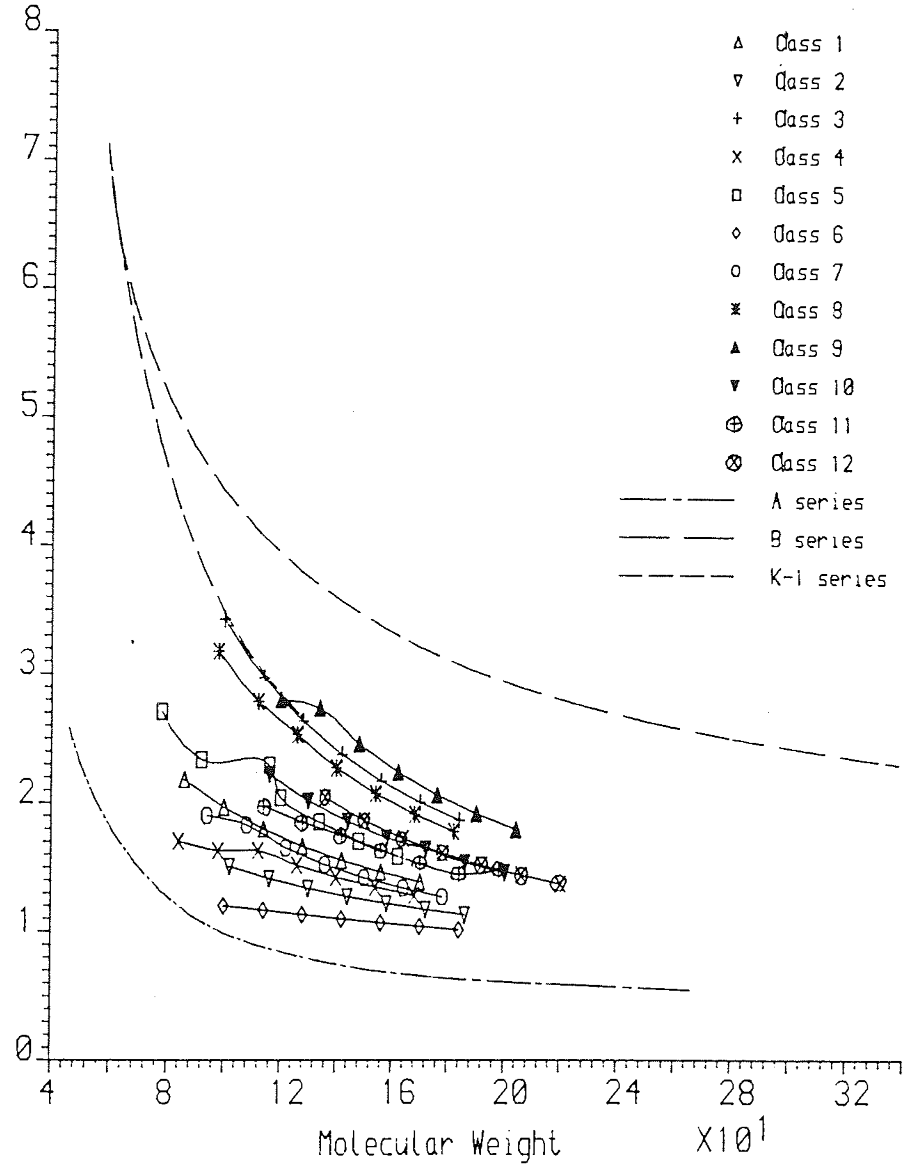


Figure 4.8 The comparison of the volume of gas per volume of solvent solubility of carbon dioxide in A-series, K-1 series, B-series and 12 classes of molecules at 25°C and 1 atm gas pressure.

4.5 Choice of a new solvent

In the B series, solvent B1 is acetone which has a low boiling point (56°C) and thus too high a vapour pressure to make a promising new gas absorption solvent. The volumetric solubility of carbon dioxide in acetone is the highest of the B series and decreases as the molecular weight increases, and the vapour pressure decreases.

The boiling point and vapour pressure at 25°C of all the B solvents were predicted by the methods of Meissner [113] and Riedel [139] respectively. The viscosities were predicted by the method of Morris [135] and the values are shown in Table 4.10.

It was defined that the chosen solvent should have as low as possible vapour pressure at 25°C (a further investigation of the effect of vapour pressure on process cost is given in Chapter 7). Thus from the predicted values of vapour pressure, the solvent to be selected could be B3. The availability of the B3 solvent was checked; and it was found that it is not available commercially, and only one German paper by Stetter et al. [186] presented a study of the syntheses of 1,4,7-triketones.

The boiling point of solvent B2 was checked by reference to data supplied by the manufacture. This is summarised in Table 4.11. This shows that the boiling point of B2 is 191°C which is significantly higher than the predicted value of 107°C. On recalculating the vapour pressure at 25°C using the experimental boiling point, this now becomes 0.00047 atm.

Thus it was concluded that B2 is the best choice of new solvent from the B series. A quantity of B2 was then purchased and its properties (including gas solubilities) were determined in the work described in the next chapter.

Table 4.10 Estimated physical properties of the molecules in B homologous series.

Molecule	MW	T_b (K)	T_c (K)	P_c (atm)	Density (gm/cc)	Vapour Pressure (atm)	Viscosity (cP)
B1	58.0	331.7	517.8	49.4	0.7877	0.26463	0.3356
B2	114.0	380.2	542.1	34.1	0.8597	0.02759	0.6501
B3	170.0	432.9	577.7	25.7	0.9069	0.00129	1.3718
B4	226.0	481.9	614.2	20.6	0.9429	0.00004	3.0412
B5	282.0	526.9	653.0	17.1	0.9722	0.00000	7.2534
B6	338.0	568.6	696.3	14.7	0.9969	0.00000	19.3416

Table 4.11 A comparison of the physical properties of the new physical solvent B2 between the specification from Aldrich Chemical Co Ltd. and those predicted in this work.

General name	B2
Chemical name	Acetonylacetone or 2,5-hexanedione
Chemical formula	CH_3-$COCH_2$-CH_2-CO-CH_3
Molecular Weight	114.15

Physical property	Manufacturer	Predicted
Density, gm/ml, 25°C	0.9730	0.8597
Freezing Point, °C	-6	-
Boiling Point, °C	191.0	107.2
Flash Point, °C	78.0	-
Viscosity, cP	1.75	0.6501
Surface Tension, dynes/cm, 25°C	-	7.4
Vapour Pressure, atm, 25°C	-	0.00047
Critical properties:		
Temperature, K	-	661.7
Pressure, atm	-	34.12
Volume, m^3/kmol	-	0.380

CHAPTER 5

EXPERIMENTAL DETERMINATION OF GAS SOLUBILITY (1 atm), BOILING POINT AND VISCOSITY OF THE NEW SOLVENT

5.1 Introduction

In this work, the absorption method, based on the technique of King and Al-Najjar [93], has been selected. A solubility apparatus has been designed and built using glass as the material of construction. The gas solubility can be measured in two stages.

1). Degassing stage; gases are removed from the liquid solvent before it comes into contact with the gas.

2). Solubility step or attainment of equilibrium; the degassed liquid solvent flows slowly as a thin film through the gas.

The solubility of four gases (i.e. CO_2, CH_4, C_3H_8, and H_2) in different solvents, including the new solvent, were determined at measured temperatures and pressures. These gases were used because they are the common gases to be separated in processes such as hydrogen manufacture, ammonia production, and natural gas purification.

Since this work used the modified UNIFAC method of Sander et al. [142] for finding a new physical solvent for carbon dioxide absorption, it is of interest to compare the solubility measurements with the predictions by UNIFAC.

The boiling point and viscosity of the new solvent were also measured, and comparisons will be made with the results from the estimation methods.

5.2 Gas solubility experiment

5.2.1 Experimental apparatus

The apparatus used for the solubility measurements is operated at atmospheric pressure. As show in Figure 5.1, the experimental apparatus consists of four sections: vacuum pump, gas cylinder tank, degassing section, and solubility section.

The vacuum pump (SPEEDIVAC, Edwards High Vacuum Ltd., England) is used to evacuate the gas out of the liquid solvent in the degassing section. All the experimental gases came from BOC (British Oxygen Corporation Ltd.), and are special gases which are more than 99.99% pure. The experimental gas is charged from the gas cylinder tank to the solubility section, the flowrate of the gas being controlled by a regulator (BOC, Model 50B-GL-BS4). Both the degassing and the solubility sections are constructed of glass.

The degassing section, Figure 5.2, was connected to a vacuum pump to evacuate the gases out of the liquid solvent. The liquid solvent is then boiled and flashes from boiler 1 (B1) to boiler 2 (B2) and flashes again to R1 which condenses the liquid solvent which flows down to collect at resevoir R2.

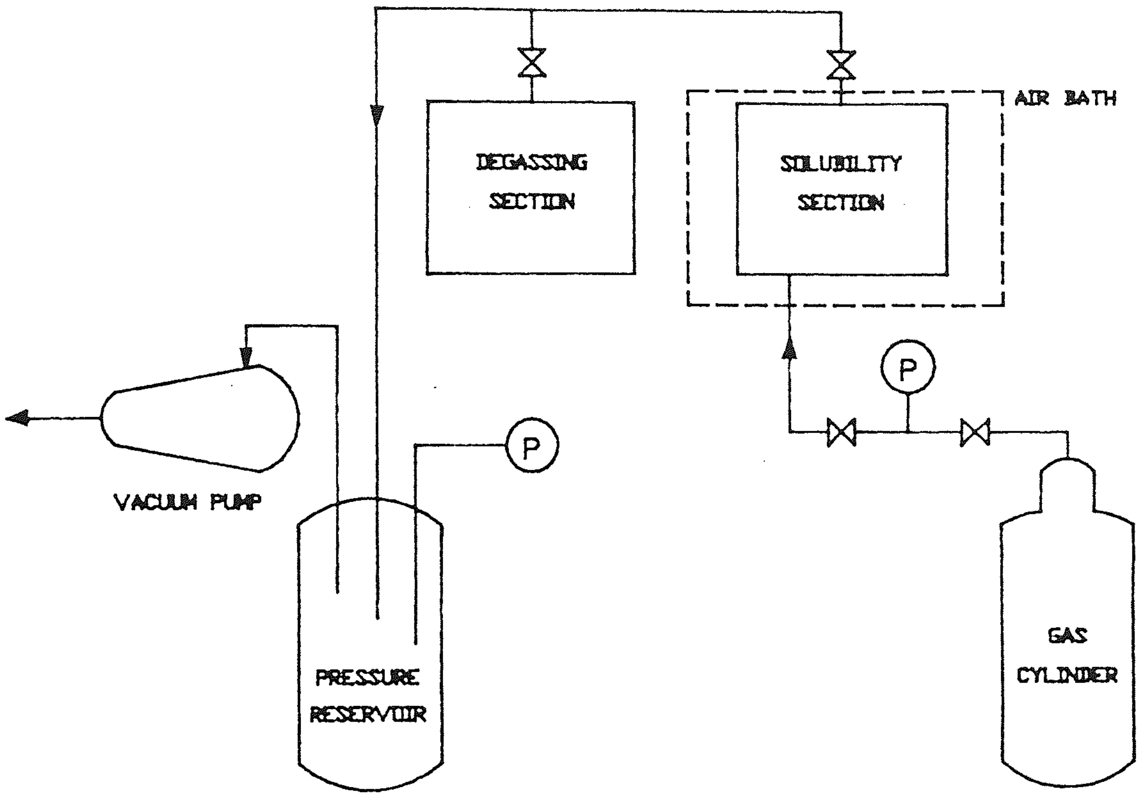


Figure 5.1 General diagram of gas solubility apparatus

The solubility measurement section, Figure 5.3, was placed inside an air bath which was maintained at a constant temperature to within ±1.0°C. The main components in this section were two burettes, one of 50 ml capacity for the gas and one of 50 ml for the solvent. Equilibrium was obtained by passing the solvent down a 1 cm diameter glass tubing spiral of 7 turns each 10 cm in diameter, and a smaller glass spiral of 3 turns each 5 cm in diameter. The small spiral and the tubing connecting the two burettes were of 2 mm inside diameter glass tubing. Their function was to prevent the diffusion of solvent vapour from the solvent burette to the gas burette.

5.2.2 Experimental procedure

Solubility is determined by the following procedures.

Degassing the solvent:

1. Valves 2, 3, 5, 6, 7 and 8 were opened and valves 1, 4 and 9 was closed, the vacuum pump was started.

2. About 60 cc of solvent was introduced to boiler B1 through valve V1. Closing valve V1, the solvent was pretreated by refluxing under vacuum about 10-15 minutes to remove any gases which may be present in the liquid solvent.

3. Valve 3 was closed, the predegassed solvent was transfered to the boiler B2 by letting it flash through valve V7.

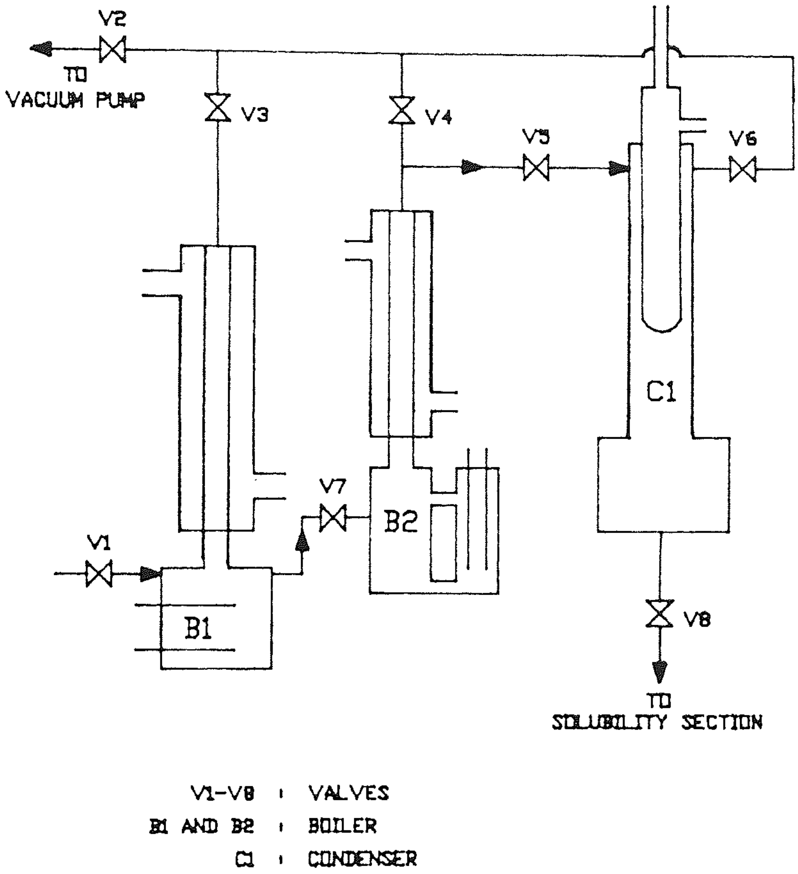


Figure 5.2 Degassing section.

4. Repeats step 2 to 3 until the level of solvent in boiler B2 is approximately 3/4 of the immersed heating element. Valve V7 was closed, the solvent was heated and flashed again to C1 which condenses liquid solvent down to collect at reservoir R1 (see solubility section).

5. Valves 2 and 8 are closed, and the vacuum pump is stopped.

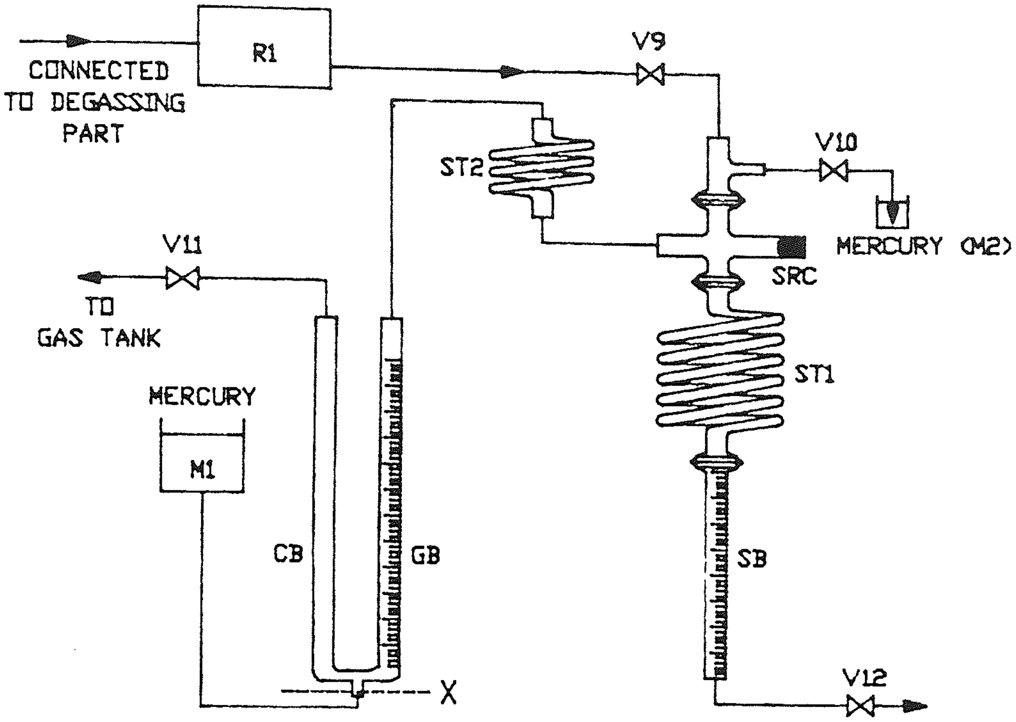
Determination of gas solubility;

6. The degassed solvent from the degassing section is stored in reservoir R1 for about 10-15 minutes to let the temperature of the solvent settle down.

7. With valve 9 still closed, the mercury level in burettes CB and GB was brought down to below level X by adjusting the mercury reservoir M1.

8. Valve 12 was opened and valve 10 was closed, a selected gas from the gas cylinder was introduced into the solubility section through valve V11, burettes CB and GB, a small glass spiral ST2, a large glass spiral ST1, burette SB and out from the solubility section at valve 12.

9. The solubility section was purged with the selected gas for about 15-20 minutes to get rid of the gases inside. Then the flow of the selected gas was stopped, the mercury level was brought up into the burettes CB and GB by adjusting mercury reservoir M1, valve V12 was closed. The whole solubility section was then a closed system.



V9–V12 : VALVES
CB : COMPARISON BURETTE
GB : GAS BURETTE
SB : SOLVENT BURETTE
M1 and M2 : MERCURY RESERVOIR

ST1 : 1 cm DIA, 10 TURNS SPIRAL TUBE
ST2 : 2 mm DIA, 3 TURNS SPIRAL TUBE
SRC : SERUM CAP
R1 : SOLVENT RESERVOIR

Figure 5.3 Solubility section.

10. The level of mercury in the gas burette (GB), the comparison burette (CB) and the mercury reservoir (M1) was made equal by carefully opening valve V10. Then the degassed solvent from reservoir R1 was allowed to flow as drops through the absorption spiral at about 4-10 drops a minute. As soon as the first few drops of solvent fall down into the absorption spiral ST1, the pressure in the solubility section may start to build up due to the vapour pressure of the solvent. The pressure inside the solubility section could then be adjusted to atmospheric pressure by opening valve V11 to let some of the contents of the gas phase flow through this valve and bubble out through the mercury bubbler M2.

11. The levels of mercury in the gas burette (GB), the comparison burette (CB) and the mercury reservoir (R1) are continuously equated while absorption of the gas by the solvent inside the spiral tube (ST1) was taking place.

12. The saturated solvent solution, after leaving the absorption coil, collects at the bottom of the solution burette (SB). Time was allowed for the solution to collect at the bottom of the solution burette SB. After about 10 to 15 ml of solution had collected, the flow of solvent was stopped and left for one hour for the saturated solvent to collect at the bottom.

13. The final levels of the mercury in gas burette GB and solution burette SB were read. Both pressures and temperatures were read at the beginning and the end of every

solubility determination. At the end of every experiment a sample of gas from inside the solubility section was taken by means of serum cap SRC to measure the concentration of air by using a mass spectrometer. This was always less than 1% and is allowed for in making the solubility calculations (Appendix 5).

5.2.3 Safety precuation taken for H_2, CH_4, and C_3H_8

The hydrogen, methane and propane used are flammable gases, therefore, safety precautions are taken during the experimental runs. As mentioned previously, any selected gas used in the experiment was purged for a period of 10 to 15 minutes through the solubility measurement section from valve V10 and out of the equipment at valve V12. For safety reasons the following steps were taken.

1. A gas detector equipment was used to detect any gas leak while running the experiments.

2. No electricity was used in these experiments.

3. The outlet gas from valve V12 was carried through a copper pipe to the outside of the building. The end of the copper pipe was immersed in a large water container, which works like a flame trap to prevent any flame travelling back into the apparatus. This precaution protected against any chance of the gas catching fire, before it was discharged to the atmosphere.

5.2.4 Experimental readings and calculations

Two volumes are measured, the volume of gas in the gas burette and the volume of solution in the solution burette. The gas burette volume was measured after bringing the mercury in the burette to the same level as that in the comparison burette. The solution burette was measured after the time allowed for the solution to collect at the bottom of the solution burette. The temperature was measured by a thermometer placed as close as possible to the gas and solution burettes. The pressure was measured by a barometer placed next to the solubility apparatus. All the experimental readings are reported for each runs and an example is shown as follows.

System = CO_2 + 1-pentanol

Pressure = 743.3 mmHg.

Temperature = 298.15 K

Air content = 0.1 %

	Gas Burette Readings (ml)	Solvent Burette Readings (ml)
Start	43.0	50.0
Final	37.6	43.0

Volume of CO_2 from the gas burette = 5.4 ml

Volume of solution from the solution burette = 7.0 ml

The solubility calculation is based on a mass balance on the solute in the gas phase in the absorption section of the apparatus, i.e. the number of moles of gas absorbed is equal to the different between the number of moles of gas in the gas phase before and after absorption taking place. The number of moles of gas in the gas burette and the solvent burette are taken to be given by $(PV_G/RT+B_1P)$ and $(PV_L/RT+B_mP)$ respectively where P is the total pressure, T is the temperature, R is gas constant, V_G and V_L are the molar volumes of the gas in the gas and solvent burette, and B_m and B_1 are the second virial coefficients of the gas mixture and the pure gas.

The details of the procedure for calculating gas solubility from the experimental readings is given in Appendix 5. A computer program was written for the calculation. Both source (GASEXP.FOR) and executable (GASEXP.EXE) programs are recorded on the diskette which is supplied within the back cover of this thesis.

5.3 Measurement of Boiling point

Figure 5.4 shows the apparatus used for measuring the boiling point of the new solvent. The essential sections are the 50 ml round bottom flask A containing the liquid, the thermometer for recording the temperature, and the condenser C for condensing the liquid. The flask A is filled with liquid and is then connected with the thermometer and the condenser by means of a three ways joint D. The flask A is heated by gas-heating, and the solvent is brought to the boil. While the liquid is being boiled the temperature reading from the thermometer is gradually increasing. The boiling point of the liquid is obtained when the thermometer reading remains unchanged.

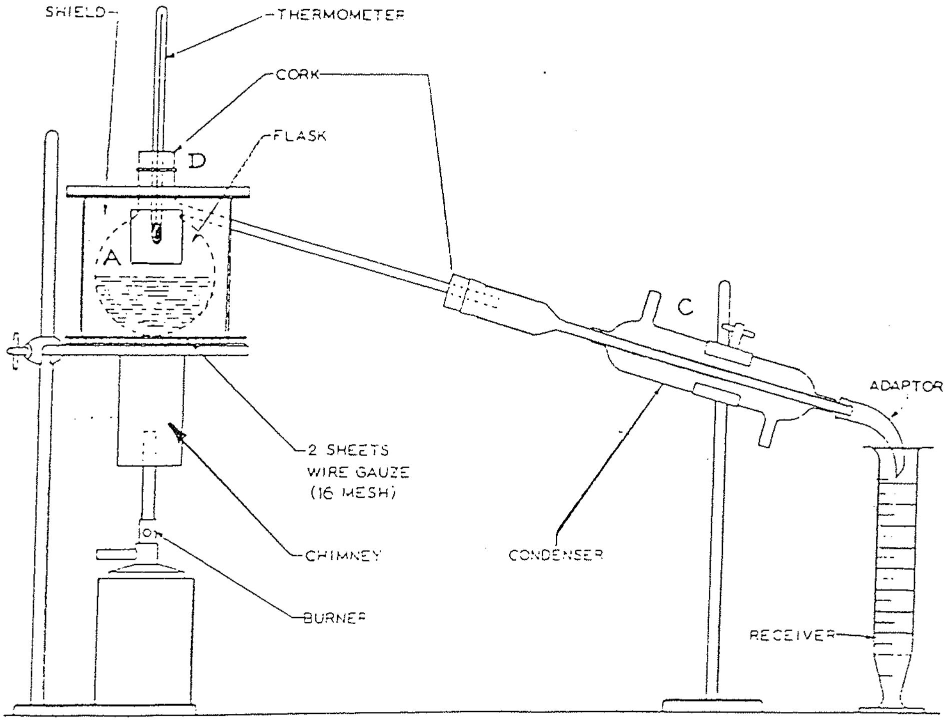


Figure 5.4 Boiling point apparatus

5.4 Measurement of Viscosity

The viscosity can be measured by various measuring techniques with a variety of instruments (viscometers). A viscometer must provide a means of measuring the rate of flow in the liquid and the force exerted or work done in producing the flow. This work has used an automatic viscometer (ROTOVISCO, Model RV 12, from HAAKE Viscometers) to measure the viscosity of the new solvent. This viscometer is a rotaing cylinder viscometer in which a thin film of the liquid is sheared between inner and outer concentric cylinders. Figure 5.5 shows the viscometer ROTOVISCO RV 12. Details of the operating procedure will not be given in this work, they can be found from the operating manual.

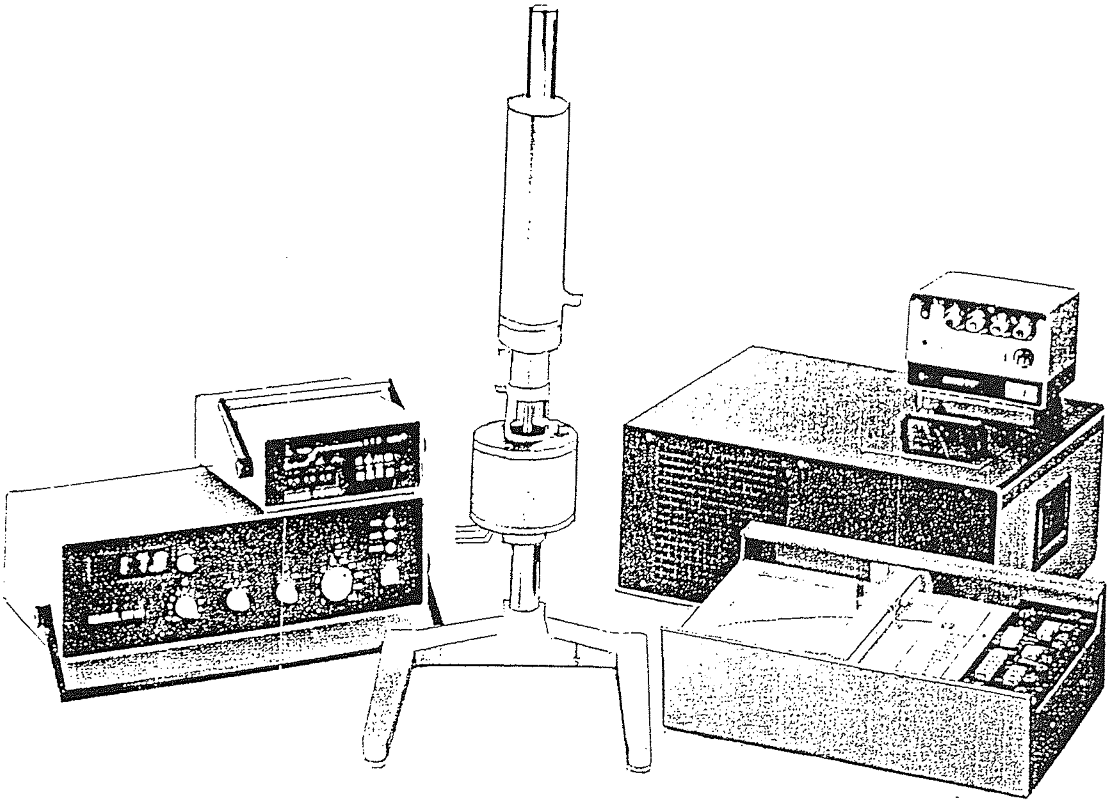


Figure 5.5 Viscosity apparatus

5.5 Experimental results and discussion

5.5.1 Gas solubility results

The solubilities of carbon dioxide, hydrogen, methane and propane were measured in this work. The solubility is expressed in mole fraction of the gas in the solvent at 1 atm partial gas pressure and at the temperature specified. Table 5.1 shows solubilities of carbon dioxide in various solvents at different temperatures along with comparisons with those estimated by UNIFAC, and it also shows the comparisons between the published experimental solubilities [10] and those predicted from UNIFAC. The experimental gas solubility results are slightly higher than those predicted. Average and maximum errors of 5.7 and 9.7% between UNIFAC and experimental solubilities are found for carbon dioxide.

Table 5.2 to 5.3 shows the experimental solubilities of methane and hydrogen at temperatures between 17-23.5°C in various solvents determined in this work and those previously obtained at 25°C taken from the literature [10]. The gas solubility results in this work were expected to be higher than those in the literature because the operating temperatures of 17.0-23.5°C in this work are lower than the 25°C of the literature. The solubility comparisons between the results of this work and those predicted by UNIFAC show quite large differences of 35% and 75% maximum in methane and hydrogen solubilities respectively compare with 0% for work in the literature.

The solubilities of methane and hydrogen could not be measured at 25°C because these two gases are flammable gases and may easily catch fire. Therefore, the measurements have had to be done at atmospheric conditions because the electrical temperature controlling system in the air bath could not be used.

Table 5.4 shows the solubilities of propane in various solvents. It is not possible to calculate the solubility of propane by UNIFAC. The only experimental data found in literature were those of King et al.´s [93]. These results appear to be similar.

TABLE 5.1 Experimental and estimated solubilities of CO_2 in various solvents at 1 atm gas pressure.

SOLVENT	This Work				Literature			
	T(°C)	X (Exp)	X (Calc)	%diff	T(°C)	X (Exp)	X (Calc)	%diff
Methanol	25.0	0.0062	0.0056	9.7	25.0	0.0056	0.0056	-
Ethanol	24.0	0.0069	0.0064	7.2	25.0	0.0066	0.0063	4.5
n-Propanol	23.5	0.0076	0.0072	5.3	25.0	0.0077	0.0071	7.8
n-Butanol	25.0	0.0076	0.0074	2.7	-	-	-	-
n-Pentanol	25.0	0.0081	0.0079	2.5	25.0	0.0081	0.0079	2.5
n-Hexanol	24.5	0.0090	0.0084	6.7	-	-	-	-

TABLE 5.2 Experimental and estimated solubilities of CH_4 in various solvents at 1 atm gas pressure.

SOLVENT	This Work				Literature			
	T(°C)	X (Exp)	X (Calc)	%diff	T(C)	X (Exp)	X (Calc)	%diff
Methanol	17.0	0.0014	0.0009	35.7	25.0	0.0009	0.0009	-
Ethanol	17.5	0.0018	0.0013	27.7	25.0	0.0013	0.0013	-
n-Butanol	17.5	0.0023	0.0020	13.0	-	-	-	-
n-Pentanol	17.5	0.0025	0.0022	12.0	-	-	-	-
n-Hexanol	18.0	0.0028	0.0025	10.7	-	-	-	-
n-Hexane	17.3	0.0058	0.0052	10.3	25.0	0.0050	0.0050	-

TABLE 5.3 Experimental and estimated solubilities of H_2 in various solvents at 1 atm gas pressure.

SOLVENT	This Work				Literature			
	T(°C)	X (Exp)	X (Calc)	%diff	T(°C)	X (Exp)	X (Calc)	%diff
Methanol	23.5	0.0006	0.0002	66.7	-	-	-	-
Ethanol	23.5	0.0008	0.0002	75.0	25.0	0.0002	0.0002	-
n-Butanol	22.0	0.0012	0.0003	75.0	-	-	-	-
n-Hexane	20.5	0.0011	0.0006	45.5	25.0	0.0006	0.0006	-

TABLE 5.4 Experimental solubilities of C_3H_8 in various solvents at 1 atm gas pressure.

SOLVENT	This Work		Literature	
	Temp(°C)	X	Temp(°C)	X
Methanol	19.8	0.0112	-	-
Ethanol	19.5	0.0177	-	-
n-Butanol	19.5	0.0456	-	-
n-Pentanol	17.0	0.0577	-	-
n-Hexanol	18.3	0.0693	-	-
n-Hexane	21.5	0.1100	25.0	0.1150

5.5.2 Error analysis

This section is a discussion of the accuracies of experimental measurements and results. As seen in Tables 5.1 to 5.3, some of the experimental solubility results in this work gave very large errors when these were compared with the literature results, and those predicted from the Sander et al. method, especially the solubility results of methane and hydrogen. These large errors can be explained as follows:

1. For carbon dioxide solubilities (Table 5.1), the results of this work were, as already noted, within 10% of those from the liturature and those predicted by UNIFAC. For these experiments the temperature was controlled at close to 25°C.

2. For methane solubilities (Table 5.2), the temperature in the air bath could not be controlled to 25°C because of the safety problem. The solubility determinations were made at room temperatures between 17.0 and 18.0°C. Therefore, the solubility results are expected to be higher than those reported in the literature for which the solubilities are usually reported at 25°C. The predicted solubilities by UNIFAC agreed with those in the literature at 25°C, but the predicted values gave an average difference of 18% when compared with the solubilities determined in this work. If we consider the solubilities of methane in methanol, ethanol and hexane, the UNIFAC method predicted the mole fraction solubility values of 0.0009, 0.0013 and 0.0050 at 25°C, the

same mole fraction solubility values of 0.0009, 0.0013 and 0.0052 at about 17°C. This may mean that the UNIFAC method (Sander et al.) is not sensitive to temperature.

3. For the solubility of hydrogen (Table 5.3); it was again not possible to control the temperature in the air bath. The solubility determinations were made at room temperatures between 20.5 and 23.5°C. The solubility results obtained in this work show a very large percent difference (an average of 65%) from both those reported in the literature and those predicted from UNIFAC. For example, the solubility of hydrogen in ethanol in this work is shown to be 75% different from both predicted and literature values. Based on the literature value this means that the experimental technique used in this work may not be suitable for determining the low solubility of hydrogen.

In conclusion, the solubility apparatus can be used to determine the solubility of carbon dioxide, and it should not produce an error higher than 10%.

For the solubility of methane, the comparison of experimental results between this work and those reported in the literature could not be conclusive because of the difference of temperatures. However, the methane solubility in this work showed reasonable results with those temperature range.

The solubility of hydrogen is very small, and the experimental results in this work are on average 65% higher than those in the literature. The apparatus may not suitable for measuring such low solubilities.

5.5.3 Gas solubility in the new solvent

As discussed above, in the apparatus used, the accuracy with which gas solubility is measured increases as the solubility increases. The results showed that the solubility of carbon dioxide in various solvents could be measured with sufficient accuracy. The apparatus was then used to measure the solubility of carbon dioxide in B2. Table 5.5 shows a comparison of the solubilities of those four gases in the new solvent B2 from the experiments with those estimated from the UNIFAC group contribution method.

Table 5.5 Experimental solubilities of various gases in the new solvent B2 at 1 atm. partial pressure of gas.

Gas	Temperature °C	Solubility(mole fraction)		%diff
		Experiment	UNIFAC	
Carbon dioxide	8.8	0.0291	0.0281	3.44
	18.0	0.0246	0.0244	0.81
	21.0	0.0214	0.0233	8.88
	25.0	0.0200	0.0216	8.00
Hydrogen	23.5	0.0003	0.0004	33.30
Methane	18.0	0.0012	0.0015	25.00
Propane	19.5	0.0354	-	-

The predicted solubilities of carbon dioxide in the new solvent by the Sander et al. method are within 10% of the experimental results. The predicted solubilities of hydrogen and methane in the new solvent are 33% and 25% different from the experimental results, but, as noted above, this is probably due to the large errors expected for experiments with these slightly soluble gases.

5.5.4 Physical properties of the new solvent

The boiling point and viscosities of the new solvent have been measured in this work. The boiling point is found to be 190.0°C at 753.35 mmHg which agrees with the value published in the Chemical Handbook [124]. The viscosities were measured at various temperatures. A graph of viscosity against 1/T is shown in Figure 5.6.

In Chapter 4 the physical properties of the new solvent (acetonylacetone) were obtained from preliminary estimation by means of equations based on its molecular structure. The estimated boiling point and viscosity have been checked against the values obtained from the measurements in this work. Table 5.6 shows a comparison between the estimated and experimental physical properties.

It can be seen from Table 5.6 that as the estimation methods were changed to the use of the true boiling point in the calculation, the viscosity errors were reduced from 62% to 5% and the density errors were reduced from 11% to 5%.

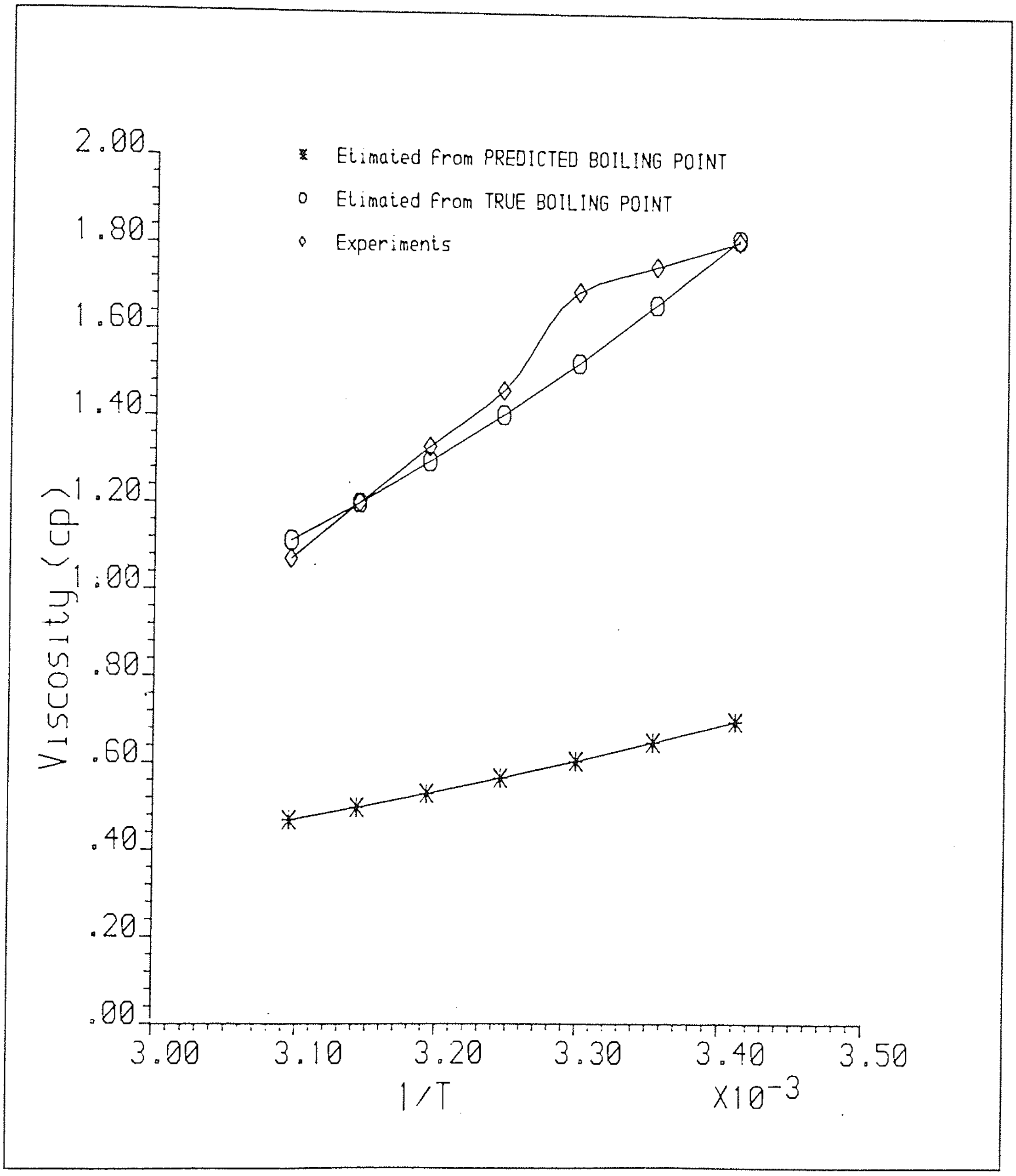


Figure 5.6 The estimated and experimental viscosity of the new solvent B2.

A sixtyfold reduction in the predicted vapour pressure is obtained on using the true boiling point instead of the predicted boiling point.

Thus the increase in boiling point above the predicted (which by definition is unexpected) represented a potentially valuable (in commercial terms) result. However the increase in viscosity (three times) is a disadvantage (higher packed heights).

Table 5.6 The comparison of boiling point, density and vicosity between estimation and experiment.

Physical property	Experiment	Estimation	
		A	B
Boiling point (°C),1 atm	190.000	107.0500	-
Viscosity (cP),25°C	1.750	0.6501	1.661
Density (gm/ml),20°C	0.973	0.8660	0.926
Vapour pressure (atm),25°C	-	0.0270	0.00047

Note.

- Experimental density obtained from the Chemical Handbook [124]
- Viscosity, density, and vapour pressure in estimations A are obtained using the predicted boiling point, and estimations B are obtained using the true boiling point.

5.6 Conclusions

The carbon dioxide solubility results from the experiments compared reasonably well with published results. For low solubility gases such as hydrogen very large errors (65%) were observed. Our solubility apparatus has no complexity, it has simplicity of construction, ease of operation, and a relatively short time is required to obtain a solubility measurement. We estimated that, for the determination of carbon dioxide solubility, the maximum error of the measurements from the apparatus was no greater than 10%. The apparatus was considered completely satisfactory for checking the predicted solubility of carbon dioxide in the new solvent.

The solubility of carbon dioxide, hydrogen, methane and propane in solvent B2 have been measured at atmospheric conditions. A comparison of carbon dioxide solubilities between experiments and estimates from UNIFAC shows a very good agreement within 10%.

The method for estimating boiling points needs to be improved, because the boiling point is usually one of the major variables in most of the methods for predicting physical properties. This is confirmed by using the true value of the boiling point instead of the predicted value, when the errors in vapour pressure and viscosity were dramatically reduced. In this case, the actual boiling point was higher than that predicted and the vapour pressure was thus significantly lower than predicted. This resulted in an unexpected advantage for the solvent B2.

However, had the true boiling point error been in the opposite direction (i.e. lower than predicted) then B2 would most likely have been unsuitable.

CHAPTER 6

PREDICTION OF SOLUBILITY AT HIGH PRESSURE WITH THE GROUP CONTRIBUTION EQUATION OF STATE (GCEOS) METHOD

6.1 Introduction

Many absorption processes in the chemical industry involve mixtures containing supercritical gases and nonpolar or polar liquids at high pressure. For the design of such processes, information about phase equilibria between gas and liquid is essential. From chapter 4, the new solvent B2 has been selected for use as a new physical solvent for carbon dioxide absorption processes. It is then necessary to have information on high pressure gas solubilities for the system consisting of gas components (e.g. hydrogen, nitrogen, methane and carbon dioxide) of the mixture to be separated and B2. Such information obviously is not available in the technical literature. It is possible to determine these solubilities by experiment. This requires a more elaborate and expensive apparatus than that used for the determination of solubilities at atmospheric pressure as described in chapter 5 and the constructing of such a device will inevitably be very time consuming. As the main purpose of this work is to design and evaluate a new solvent by means of calculation (rather than by experiment) a method of predicting gas solubility at high pressures is required.

There are numerous correlations in literature for estimating high pressure solubilities but each has certain limitation as described below.

An equation of state is generally used in high pressure phase equilibrium calculations. Such calculations require only the critical pressure, the critical temperature, the acentric factor of each pure component, and for mixtures, it requires binary interaction parameters. The predictions from equations of state are very sensitive to such input parameters. The mixture parameters are usually determined by reducing experimental phase equilibrium data for binary systems. Furthermore, the parameter determinations must cover a large range of temperature and pressure. From a practical point of view, these methods may not overcome the lack of information existing for the new systems such as the new solvent B2. Therefore, the attention of this work was directed towards group contribution models and in particular to the new group contribution equation of state (GCEOS) developed by Skjold-Jorgensen [148] and succesfully applied so far for predicting gas-solubility at high pressure. The GCEOS model is able to represent data for many components over a wide range of temperature and pressure. The capability of the GCEOS method for predicting gas solubility will be tested against published experimental gas-liquid equilibria of selected systems containing hydrogen, nitrogen, methane and carbon dioxide and various solvents.

6.2 Calculation of phase equilibrium at high pressure

For predicting the vapour-liquid equilibrium of an N component system, the variables of interest are the temperature, total pressure, liquid-phase mole fractions and vapour-phase mole fractions. For two phases which are at the same temperature, the equation of equilibrium for each component i is generally expressed in terms of fugacity f_i.

$$f_i^V = f_i^L \qquad (6.1)$$

The superscript V stands for vapour and L for liquid. We have chosen the GCEOS method (Appendix 6), which combines the group contribution concept with the basic ideas of an equation of state, to determine phases behaviour, therefore, the equation 6.1 can be rewritten as:

$$y_i \ \phi_i^V (T,P,y) = x_i \ \phi_i^L (T,P,x) \qquad (6.2)$$

$$x_i = y_i \frac{\phi_i^V}{\phi_i^L} \qquad (6.3)$$

where ϕ_i^V is the fugacity coefficient of component i in vapour phase and ϕ_i^L is that in the liquid phase. For N components there are N equations of the form (6.2). The fugacity coefficient ϕ_i^V is a function of T, P, $y_1 \ldots\ldots y_i$, and the fugacity coefficient ϕ_i^L is a function of T, P,

$x_1 \ldots\ldots x_i$. Once these functions are established, the problem is, in principle, solved. The solution of these N simultaneous equations requires trial-and-error calculations which can be effectively carried out only by a computer. The solution of the N equations of equilibrium must satisfy the three stoichiometric relations

$$F(x_i) = y_i \, \phi_i^V - x_i \, \phi_i^L \quad <= 0.0001 \tag{6.4}$$

$$SUMX = \Sigma x_i = 1.0 \tag{6.5}$$

and

$$SUMY = \Sigma y_i = 1.0 \tag{6.6}$$

A computer program has been written in the FORTRAN language to perform this calculation of phase equilibria. The program is to be used on a micro computer and it is supplied on the diskette under the filename GASHIGH.FOR for the source program, and GASHIGH.EXE for the executable program. As the program is running, it will read three data files into the program. Two of these data files, STEEND2 and STEEND3, contain the GCEOS parameters. The third one STEEND1 contains the data for the particular system used which can be modified to suit the system need (see more details in Appendix 6).

The computer program calculates liquid-phase mole fractions assuming the gas-phase mole fractions, temperature and pressure as the known variables. The necessary data, such as temperature, pressure, gas-phase mole fractions and GCEOS's parameters, are read in from the data files. The vapour-phase fugacity coefficient (ϕ_i^V) of each components is calculated, and the initializing steps of a rough guess is made of liquid-phase mole fractions (x_i's) in the condition of summation of x_i equal to unity. Then the liquid-phase fugacity coefficient of each component in the mixture is calculated at the initial liquid-phase mole fractions. The first iteration is begun by calculating the new values of x_i's and a new SUMX from the calculated liquid-phase fugacity coefficients (ϕ_i^L) by using equation 6.3. Then the new values of x_i's are used to recalculate the liquid-phase fugacity coefficients. This procedure is followed until successive iterations yields essentially SUMX equal to unity and $F(x_i)$ in equation 6.4 is less than or equal to the tolerance value (0.0001).

6.3 Comparison of predicted solubility from GCEOS with published experimental data at high pressures

Before using the GCEOS method (Appendix 6) to determine the solubility of gases in the new physical solvent, B2, it was first evaluated by using it to predict the solubility of four sets of gas-solvent binary mixtures for which experimental data is available in the literature. These were at pressures up to 50 bar.

6.3.1 Estimating solubility for Carbon dioxide systems

Experimental data for the four systems, carbon dioxide-hexane [119], carbon dioxide-methanol [119], carbon dioxide-benzene [119] and carbon dioxide-cyclohexane [100], are considered in this analysis. Figures 6.2 to 6.5 show the P-x diagram of predicted vapour-liquid equilibria for these four binary systems at the specified temperatures compared with experimental data.

The comparisons of predicted solubilities of carbon dioxide in n-hexane at 298.15 K and 313.15 K (Figure 6.2), carbon dioxide-benzene at 298.15 K and 313.15 K (Figure 6.3), and carbon dioxide-cyclohexane at 473.15 K (Figure 6.4) are in good agreement with the experimental results. However, the comparisons of predicted solubilities of carbon dioxide-methanol (Figure 6.5) system at two temperatures (298.15 and 313.15 K) are shown to be higher than the experimental values. This may be because the prediction requires accurate prediction of the alcohol fugacity coefficient in both gas and liquid phases.

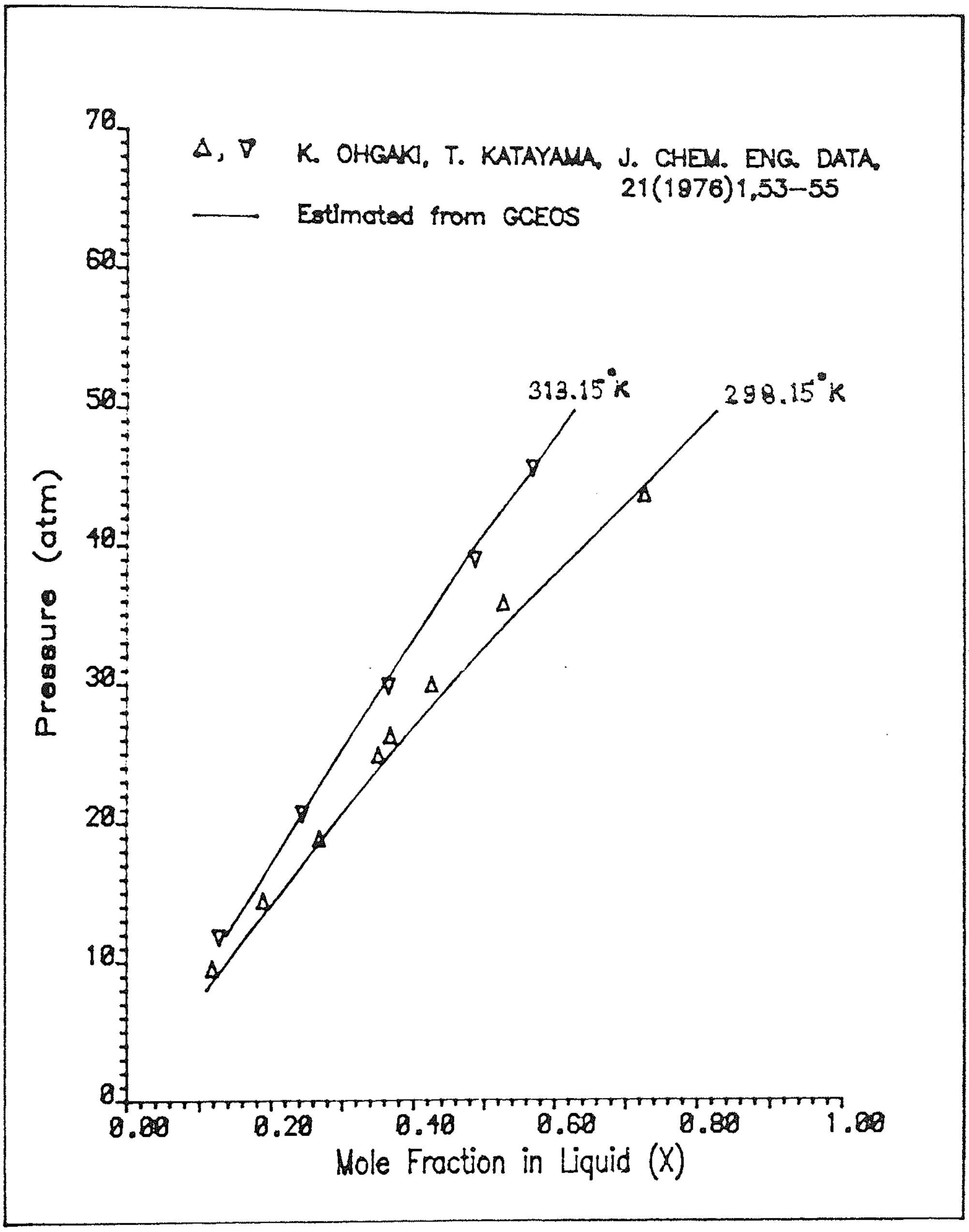


Figure 6.1 Comparison of the VLE of CO_2-Hexane obtained from experiments with estimated from GCEOS method.

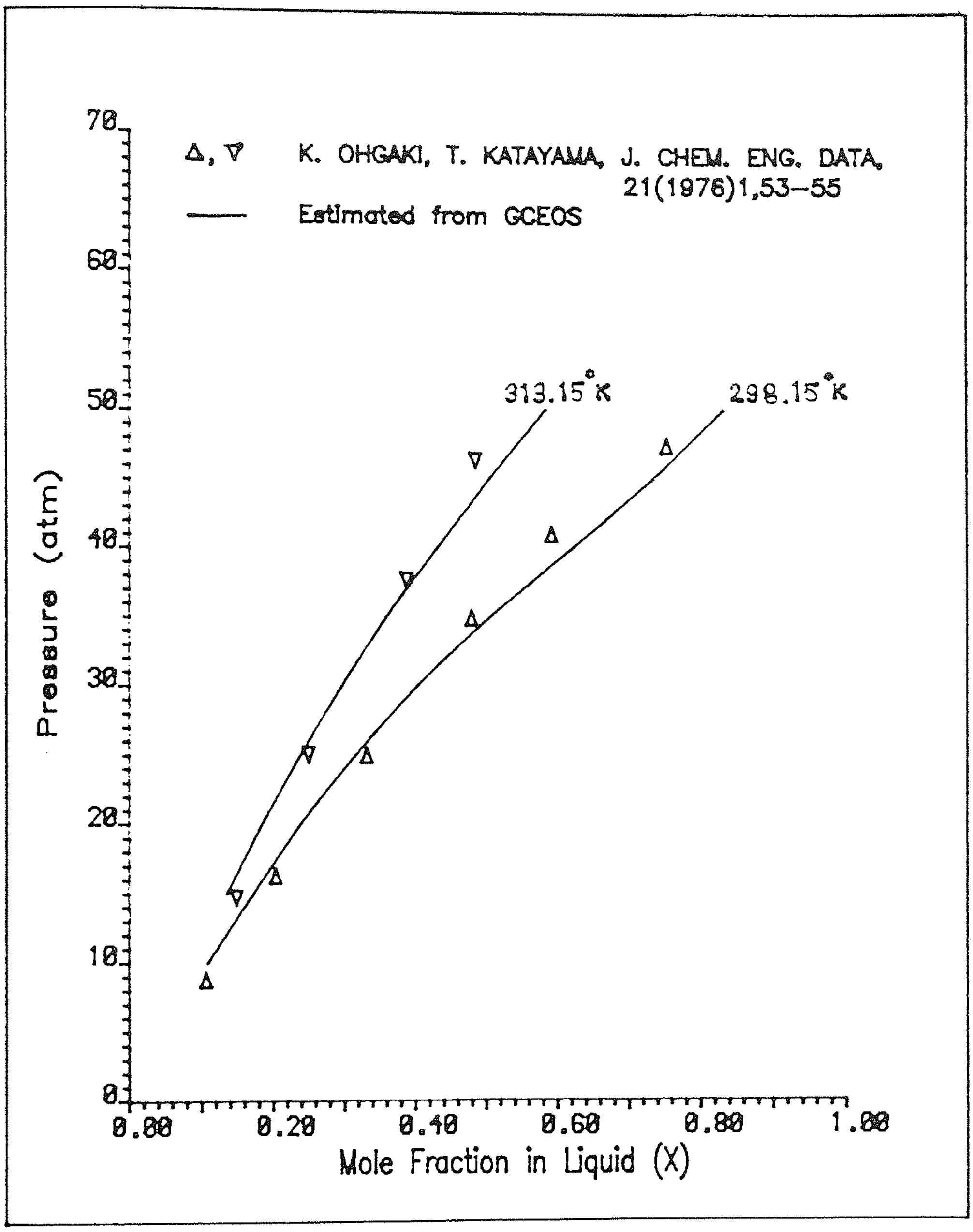


Figure 6.2 Comparison of the VLE of CO_2 -Benzene obtained from experiments with estimated from GCEOS method.

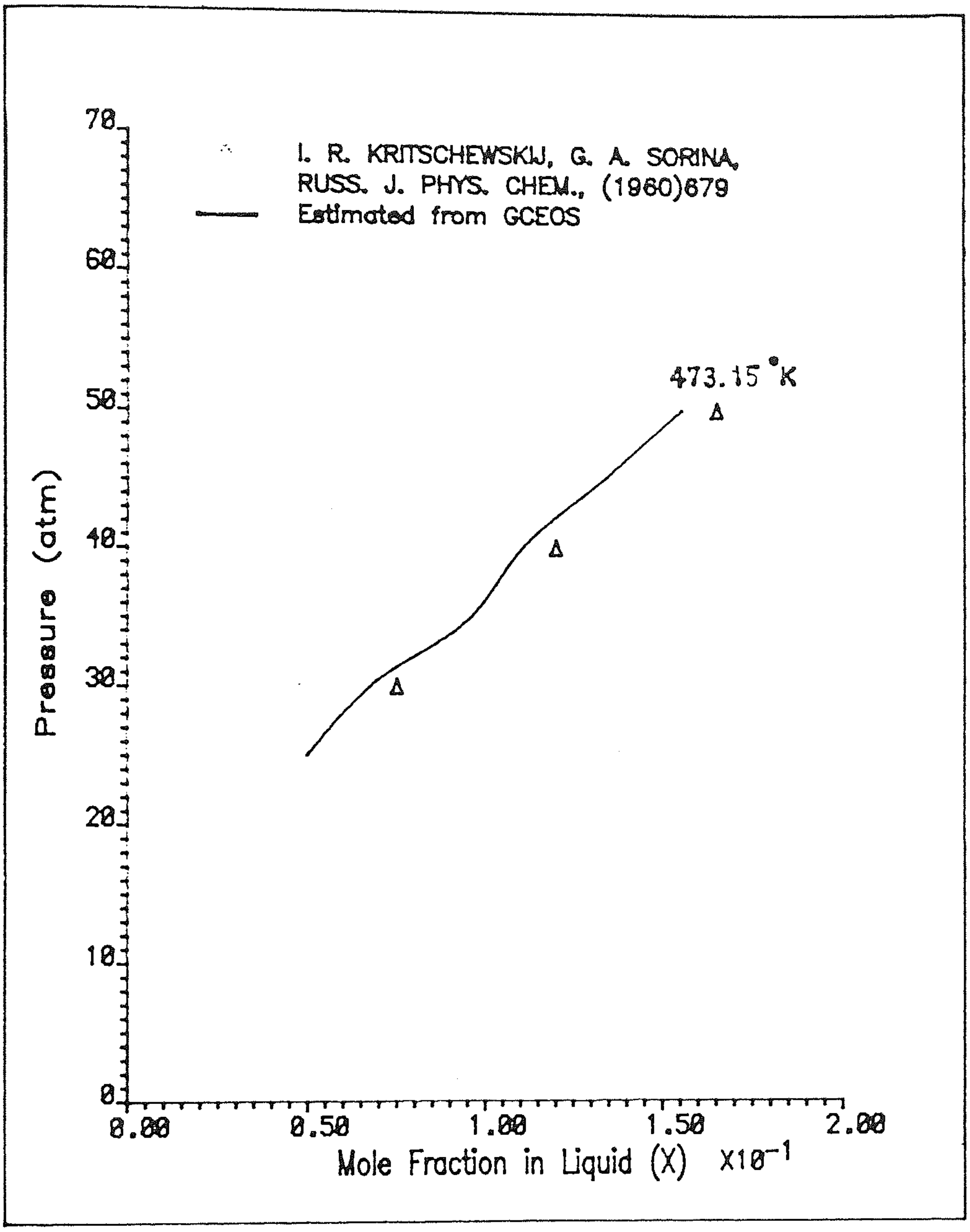


Figure 6.3 Comparison of the VLE of CO_2-Cyclohexane obtained from experiments with estimated from GCEOS method.

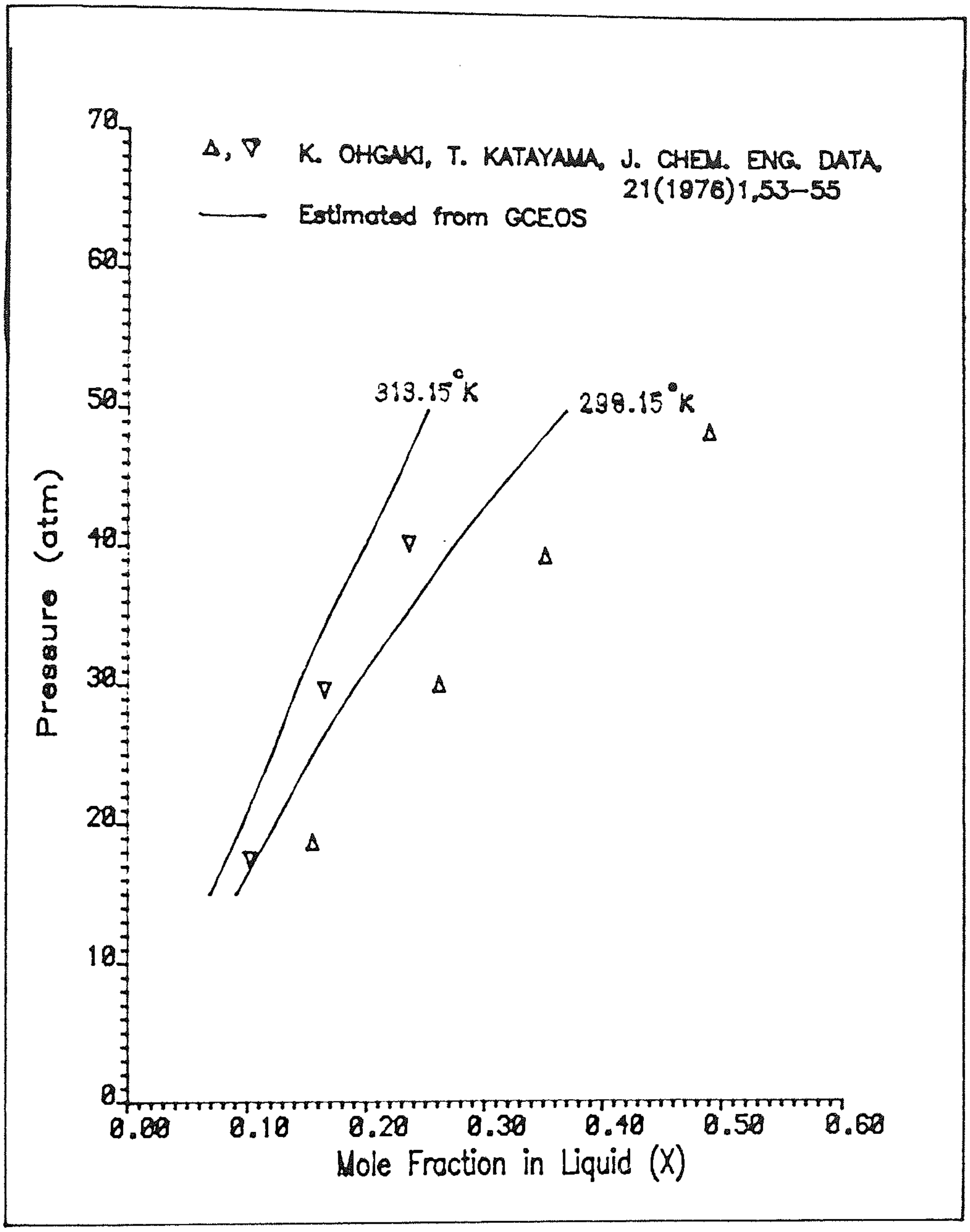


Figure 6.4 Comparison of the VLE of CO_2-Methanol obtained from experiments with estimated from GCEOS method.

6.3.2 Estimating solubility for Nitrogen systems

Nitrogen-hexane experimental phase equilibrium data from R. S. Poston and J. J. McKetta [127] at 310.93 K and 344.26 K are compared with GCEOS predictions in Figure 6.6. The calculated solubilities of nitrogen in n-hexane at low pressure give a good agreement with experiment, however at high pressure the calculated solubility is approximately 2% higher than the experimental values.

6.3.3 Estimating solubility for Methane systems

For methane system, the experimental gas solubility of methane in hexane is obtained from Gunn et al. [72]. The experiments was made at temperatures of 310.93, 344.26 and 377.55 K and in the pressure range of 5 to 45 bar. Figure 6.7 shows that the results of predicted methane solubility in hexane by using GCEOS give the best fit to the experimental solubilities.

6.3.4 Estimating solubility for Hydrogen systems

The GCEOS method is also used to predict a solubility of hydrogen in hexane at temperatures of 277.59 and 310.93 K, and pressure range of 5 to 45 bar. The prediced solubilities are higher than the experimental results of Nichols et al. [117] as shown in Figure 6.8.

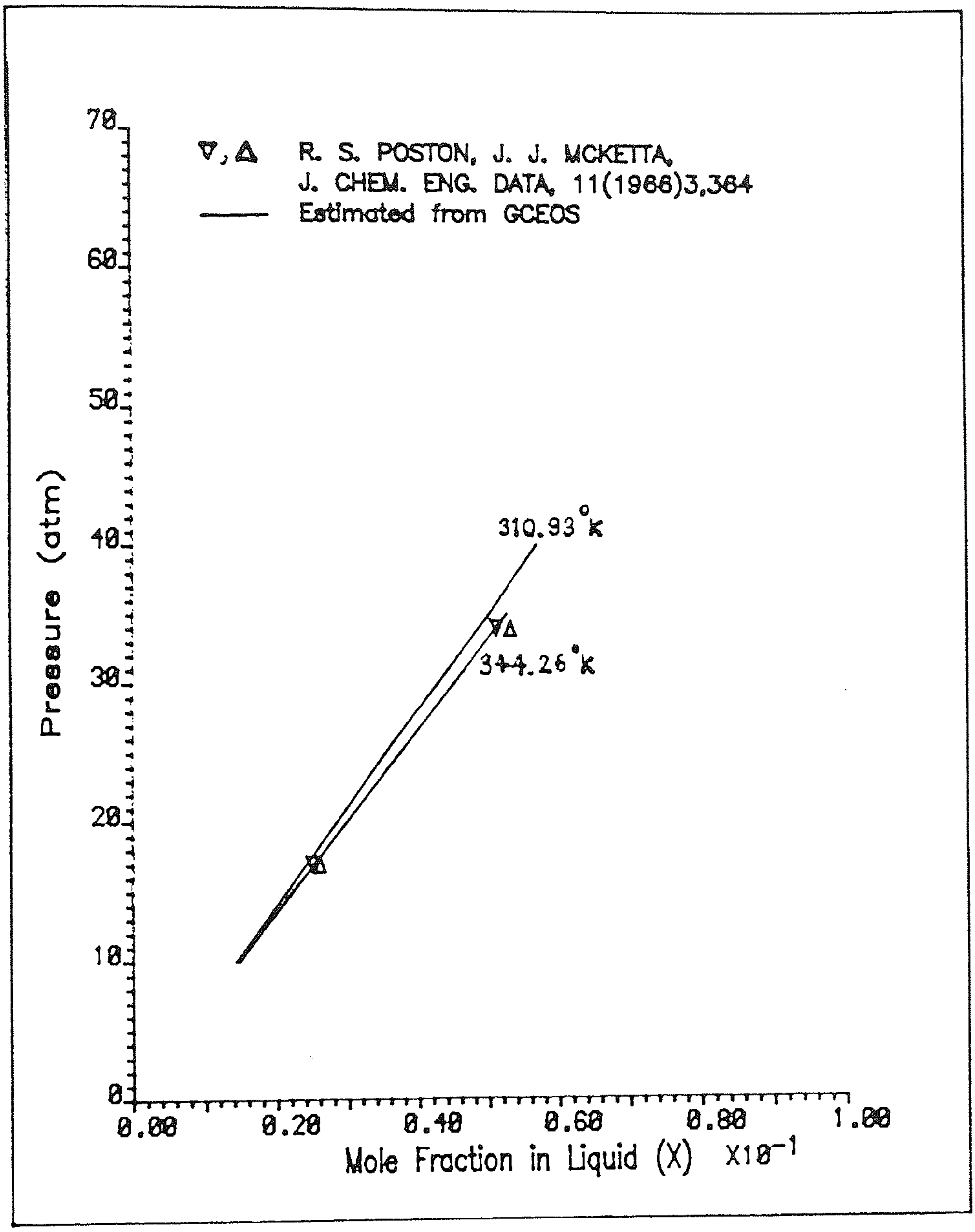


Figure 6.5 Comparison of the VLE of N_2-Hexane obtained from experiments with estimated from GCEOS method.

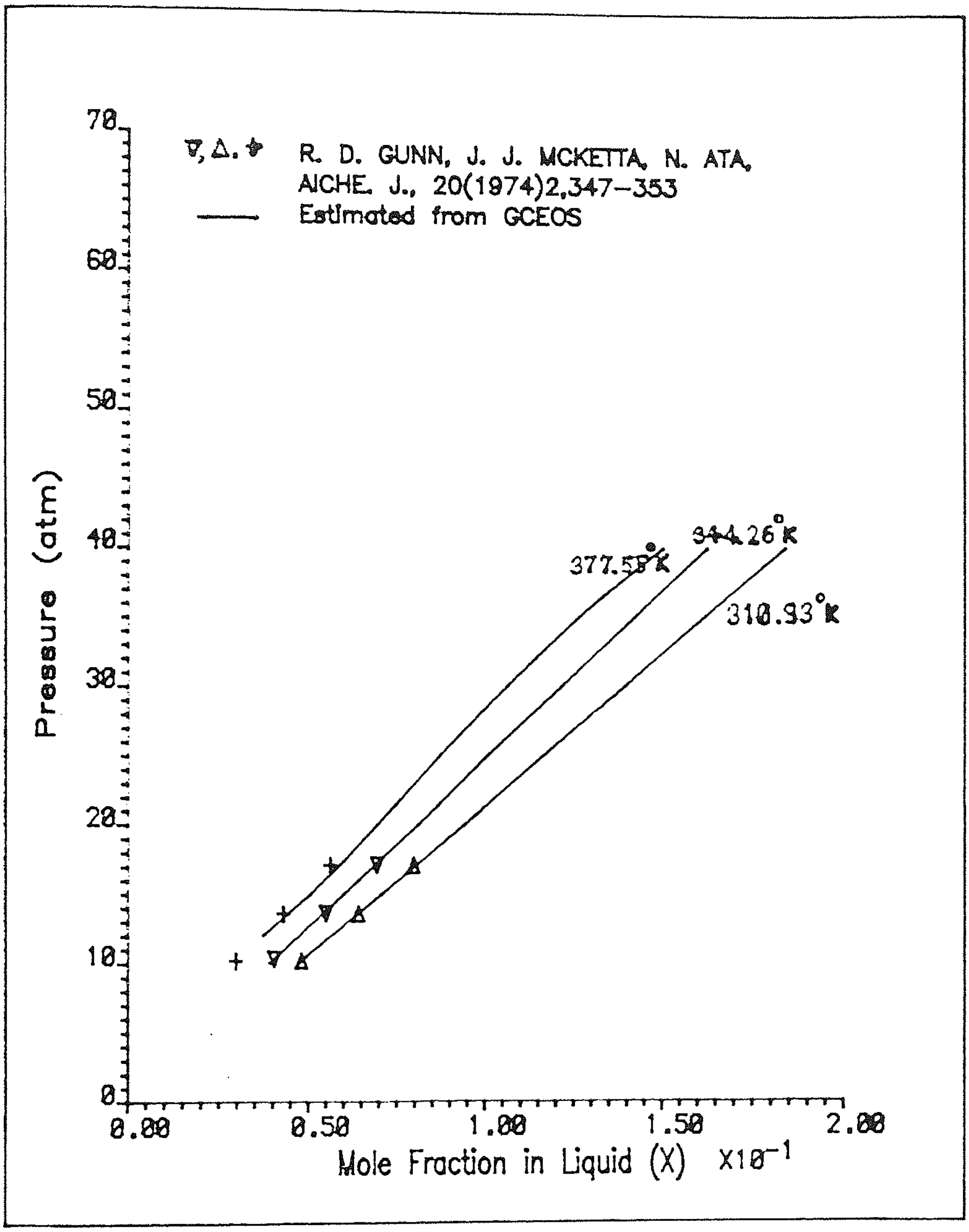


Figure 6.6 Comparison of the VLE of CH_4-Hexane obtained from experiments with estimated from GCEOS method.

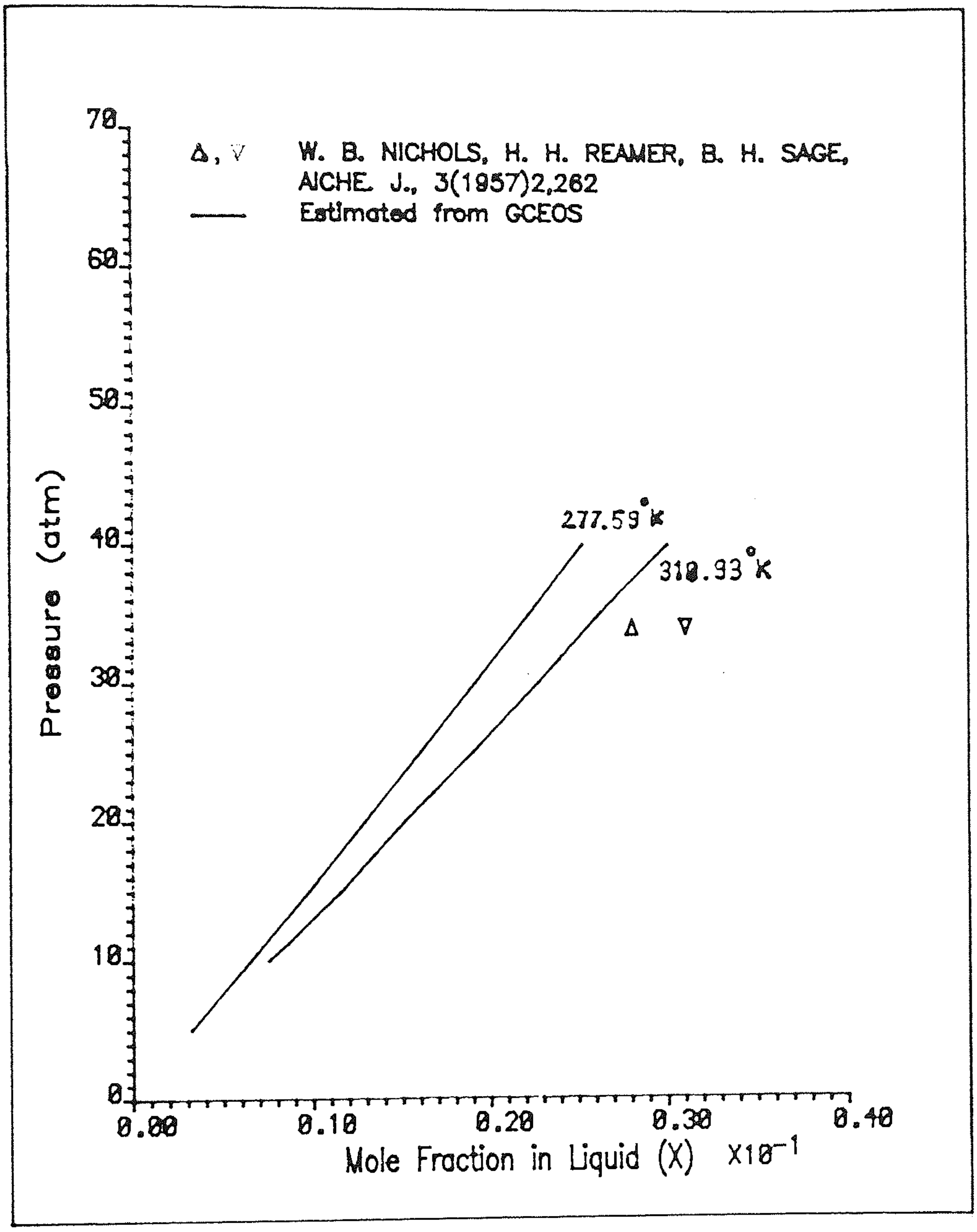


Figure 6.7 Comparison of the VLE of H_2-Hexane obtained from experiments with estimated from GCEOS method.

6.4 The solubility of gases in the new solvent (Acetonylacetone) at high pressure

Figures 6.9, 6.10 and 6.11 show the estimated solubility of carbon dioxide, nitrogen, hydrogen, methane and carbon monoxide in the new solvent B2 at temperatures of 283.15, 293.15 and 298.15 K, and the pressure range of 5 to 45 atm.

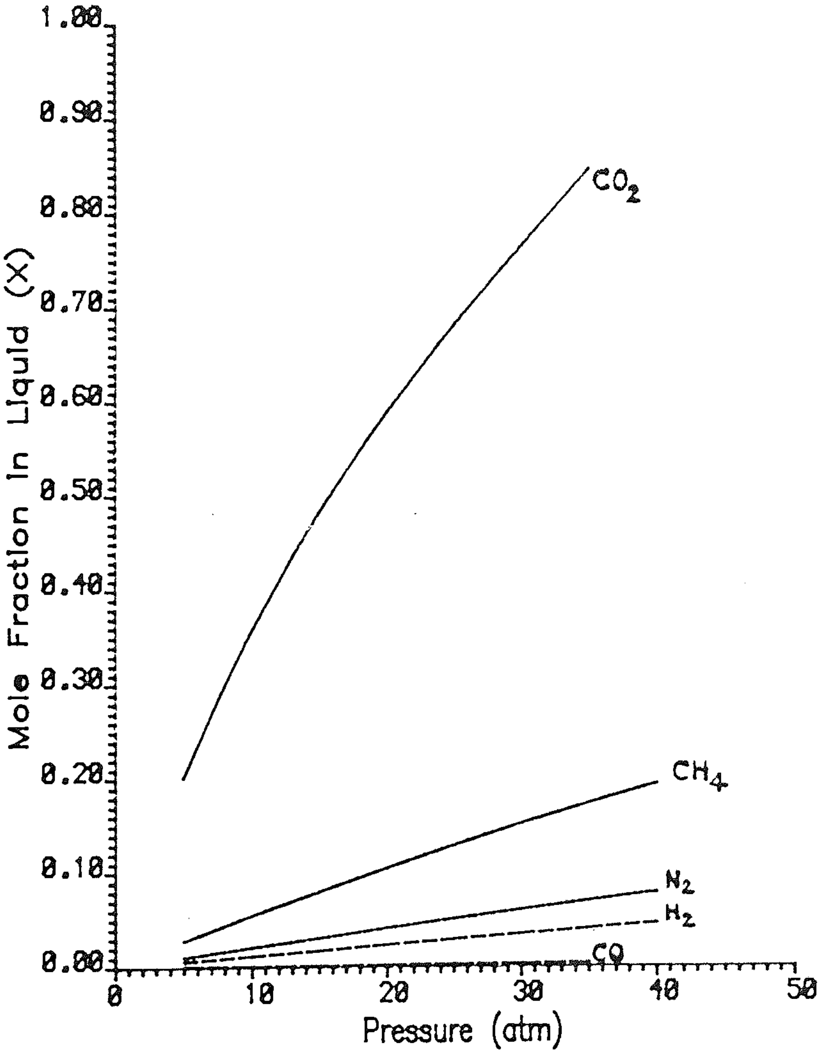


Figure 6.8 Estimated solubility of various gases in the new solvent B2 at 283.15 K.

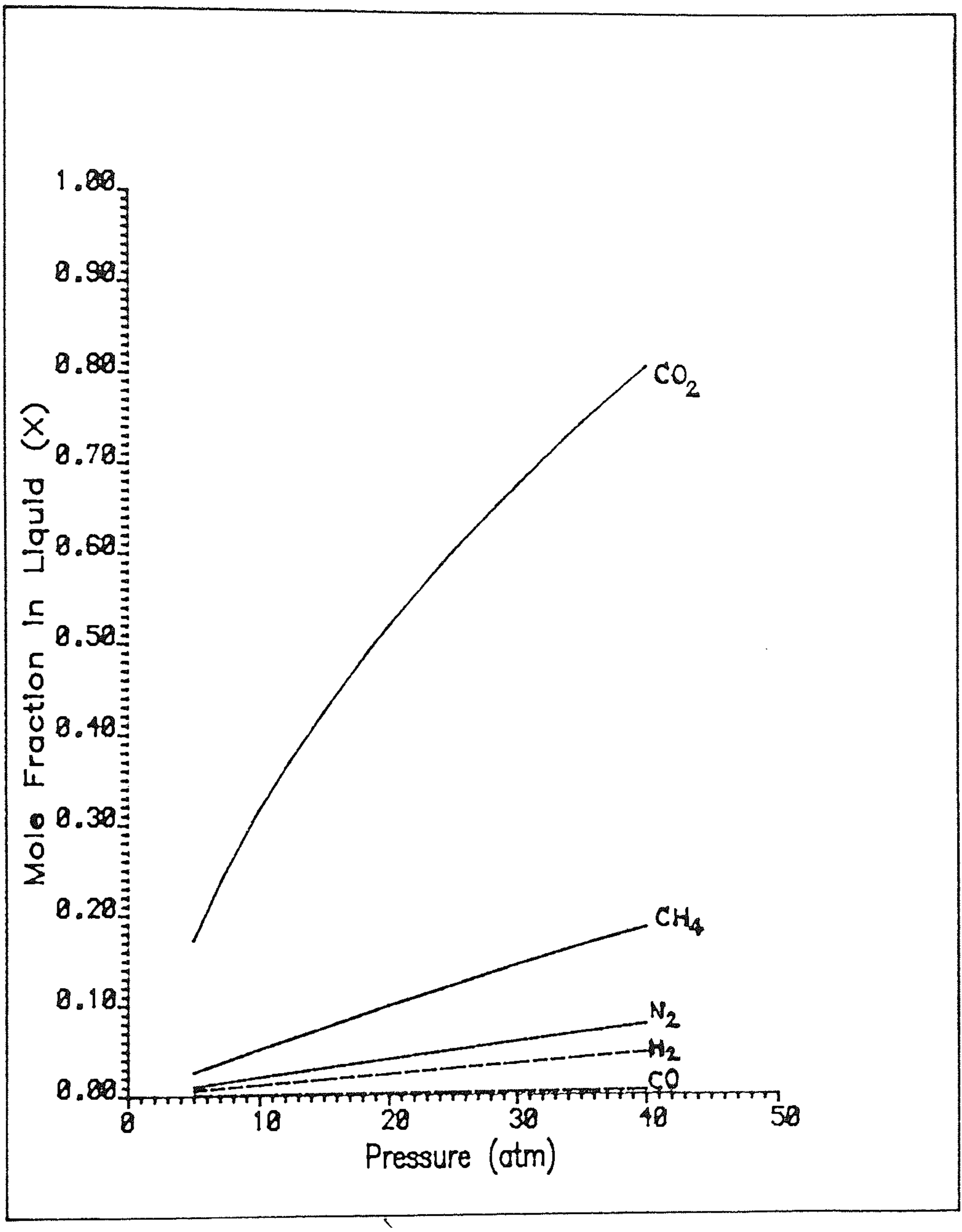


Figure 6.9 Estimated solubility of various gases in the new solvent B2 at 293.15° K.

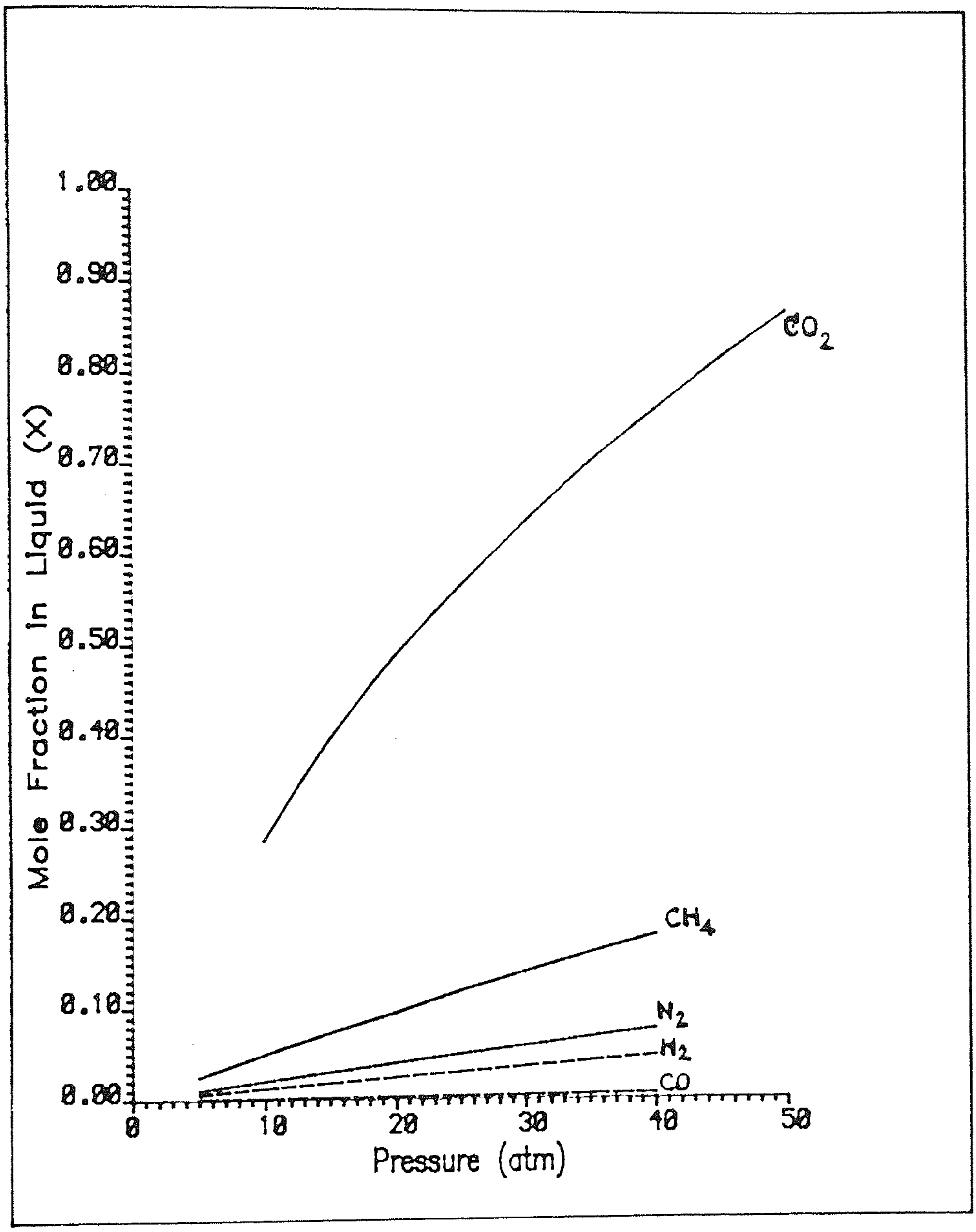


Figure 6.10 Estimated solubility of various gases in the new solvent B2 at 298.15 K.

6.5 Conclusions

A computer program has been written to calculate gas-liquid equilibrium at high pressure by using the GCEOS model. In order to test the capability of the GCEOS model, it was used to predict gas-liquid equilibrium at high pressure of carbon dioxide/liquid, hydrogen/liquid, methane/liquid and nitrogen/liquid systems. The predicted gas-liquid equilibrium was shown to agree with the published experimental results.

The GCEOS model is also a type of group-contribution method, and it has the same molecular groups as in the low pressure Sander et al. model. Thus the GCEOS model is also limited in that it cannot predict gas-liquid equilibrium in some systems, because of the lack of group parameters (see Appendix 7). However, this limitation does not apply in this work. The GCEOS model will be used to calculate gas-liquid equilibrium for the design of carbon dioxide bulk removal processes by using the new solvent B2 in comparison with cold methanol (Rectisol process).

CHAPTER 7

PROCESS DESIGN OF GAS ABSORPTION PLANT USING THE NEW SOLVENT (ACETONYLACETONE OR B2)

7.1 Introduction

As mentioned before, one of the goals of this work is to develop a physical solvent for carbon dioxide absorption from gas mixtures containing low molecular weight components such as hydrogen, nitrogen, carbon monoxide and methane. In previous chapters, many molecules were evaluated in terms of their potential to become this new physical solvent and acetonyl acetone (B2) was selected as the most promising.

In this chapter, the evaluation of B2 is taken a stage further by means of design studies to compare the equipment and services required to remove carbon dioxide using B2 with those required using two other solvents now widely used in commercial gas absorption plant. The first process is industrial gas treating to remove carbon dioxide in ammonia manufacture. The second one is a bulk removal of carbon dioxide and hydrogen sulphide from light hydrocarbon gases such as methane from the natural gas industries. There are many existing chemical and physical solvents used in these two processes such as amines (e.g. MEA, DEA), Hot potassium carbonate, Fluor (propylene carbonate), Sulfolane (tetrahydrothiophene-1,1-dioxide + 3% water), Purisol (n-methyl-2-pyrrolidone), and Selexol (dimethylether of polyethylene glycol) and Rectisol (cold methanol), etc. Table 7.1 shows the solubilities of carbon dioxide, hydrogen sulphide and propane and some physical properties of these physical solvents. However, most of the solvents face potential technical and economic problems for instance, problems in solvent recovery and regeneration, e.g., solvent loss with treated or vent gases (methanol), and problem in using refrigeration unit when the absorption at low temperature is required. It is proposed to evaluate that B2 will be an alternative solvent to overcome these problems in absorption process.

7.2 Principles Design for the Absorption Processes

Impurity gas removal processes based on physical solvent absorption all use variations on a basic process flowsheet which is shown in idealized form in Figure 7.1. The raw gas is contacted countercurrently with regenerated (lean) solvent in an absorber tower which usually operates at low temperature and high pressure. The purified gas leaves overhead from the absorber (sometimes after a water wash to prevent carryover of solvent). The loaded (rich) solvent leaving from the bottom of the absorber is reduced in pressure, sometimes in stages, to flash off dissolved target gas and a portion of the impurity gases in flash drum. The regenerator (stripper) is usually a low-pressure countercurrent tower in which the remaining dissolved impurity gases are stripped out with stripping gas (usually air or nitrogen) or steam generated by reboiling the lean solution. In practice, the rich solution is usually allowed to flash into the top of the regenerator tower (i.e. no separate flash drum is provided). If the regenerator is run hot then the rich solvent may also be heated against the returning hot regenerated lean solvent in a rich/lean heat exchanger.

Table 7.1 CO_2, H_2S, and C_3H_8 solubilities and some physical properties of physical solvents.

Solvents	Solubility			B.P. (°C)	Viscosity (cps)
	CO_2	H_2S	C_3H_8		
Water	0.8	2.5	0.05	100.0	1.00
Fluor	3.5	13.2	1.80	240.0	2.40
Selexol	3.6	26.0	4.70	276.0	5.80
Methanol (-10°C)	8.0	41.0	-	-	-
(-30°C)	15.0	-	-	-	-
Purisol	3.9	49.0	3.80	201.0	1.70
Sulfolane	2.9	15.9	1.10	285.0	11.50
B2	4.3	18.8	7.54	191.0	1.75

Note.
- All the above data are obtained from Ref. 100 except B2
- The gas solubility unit is expressed in term of cc of Gas/cc of Solvent/atm gas pressure and pure gases at 20-25°C.

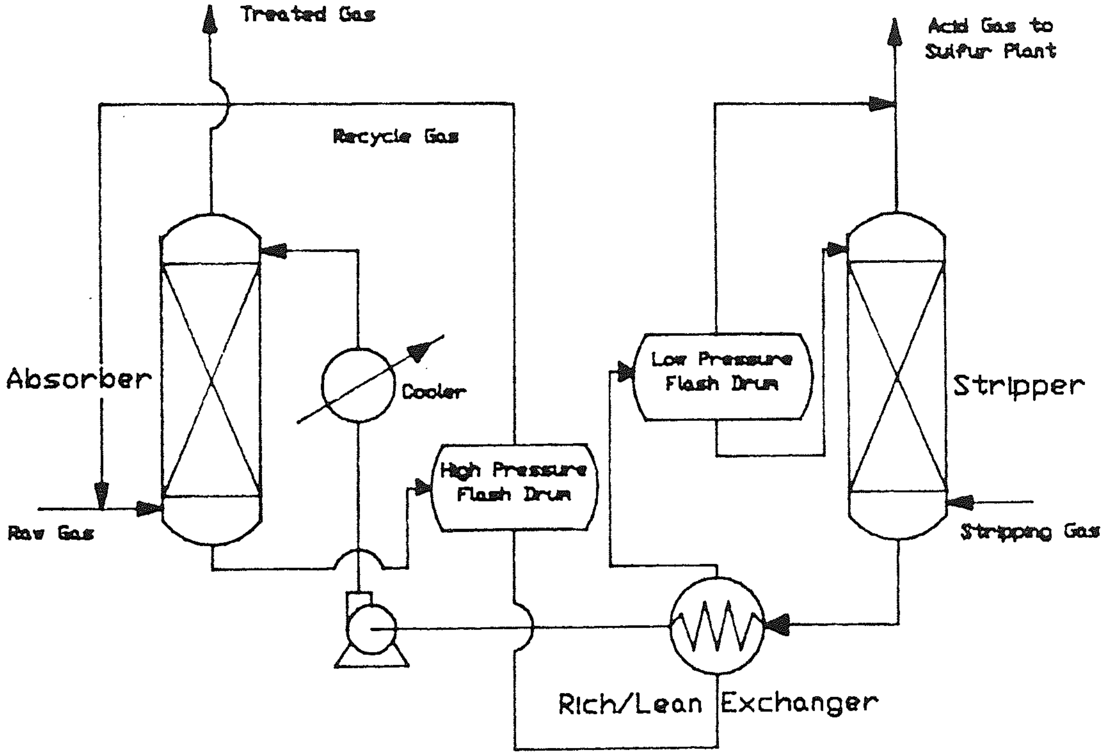


Figure 7.1 Idealized solvent absorption impurity gas removal process.

7.3 Process designs based on the new solvent B2

In order to investigate the capability of B2 when compared with existing solvents in gas absorption processes, the two examples used are the removal of carbon dioxide in ammonia synthesis and in the natural gas industries.

For the ammonia synthesis plant, a comparison will be made with the Rectisol process, and for the natural gas plant a comparison with the Selexol process will be made.

However it is necessary to keep in mind that the calculation results for the design of any particular plant given in this work is only a preliminary design, before next steps of the design which are concerned with optimization to decide which is the best combination of parameters to use in designing a particular plant.

7.3.1 Carbon dioxide absorption in ammonia synthesis

Carbon dioxide is a major undesirable constituent gas in ammonia systhesis. The raw inlet gas to the carbon dioxide absorption section results from the conversion of carbon monoxide by the shift conversion process, generating additional hydrogen and carbon dioxide. The content of carbon dioxide leaving with the purified gas stream, therefore, must be reduced to as small an amount as possible before proceeding to the methanation process, preferably less than 0.1 % by volume of purified gas stream. Various carbon dioxide removal processes are used in practice such as mono-ethanolamine (MEA) absorption, the Benfield process (activated hot potassium carbonate) and the Rectisol process (cold methanol). Rectisol seems to be the most attractive in treating feed gas available at a high pressure, because it is a cheap solvent which can remove carbon dioxide in the purified gas down to less than 60 ppm. Table 7.2 shows the typical composition of sulphur-free raw feed gas to a Rectisol plant.

Table 7.2 The composition of the raw gas from a shift conversion process.

Gas	Kmole	Kmole/hr
Hydrogen	0.584	3966.43
Nitrogen	0.189	1283.66
Carbon monoxide	0.003	20.38
Argon	0.003	20.38
Methane	0.002	13.58
Carbon dioxide	0.219	1487.41
Total	1.000	6791.84

For the carbon dioxide absorption process, assume that solvent B2 and Rectisol (cold methanol) are used. The flowsheets are illustrated in Figures 7.2 and 7.3 respectively, both based on the flowsheet in Figure 7.1. Both absorption towers of each process are packed with 2.0 inch metal Pall rings. The sulphur-free raw gas pressure of 25.0 bar from the shift conversion process enters at the bottom of the absorber column and solvent enters at the top of the column.

Both absorption column are operated at approximately 25.0 bars, and 293.15 K and 233.15 K for solvent B2 and rectisol respectively. For the B2 plant the rich solvent leaving from the bottom of the absorber is assumed to be fed directly to stripping column. For the Rectisol plant with the absorber working at -40°C, the rich solvent is passed through lean/rich heat exchanger to exchange heat with the lean solvent from stripper.

The stripping column for both processes is operated at 1.0 bar and 298.15 K. The dissolved gases from rich solvent are stripped out to leave at the top of the stripper by stripping gas (nitrogen). Lean solvent leaving at the bottom of the stripping column is pumped back to the top of the absorber.

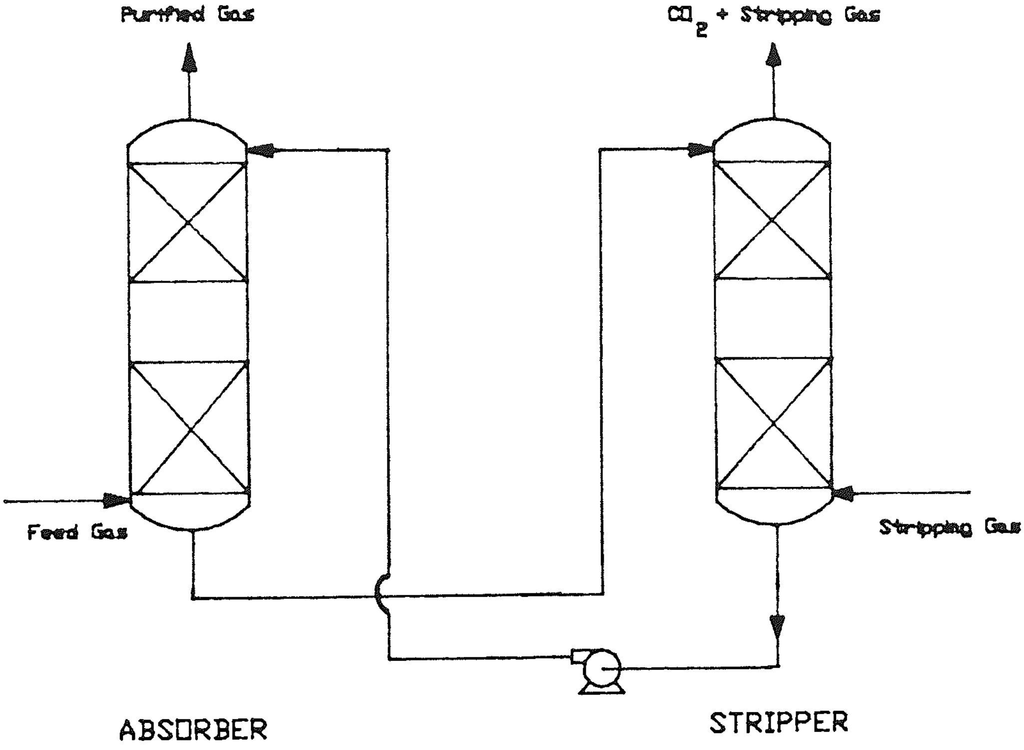


Figure 7.2 Process flowsheet of CO_2 absorption in ammonia synthesis using B2.

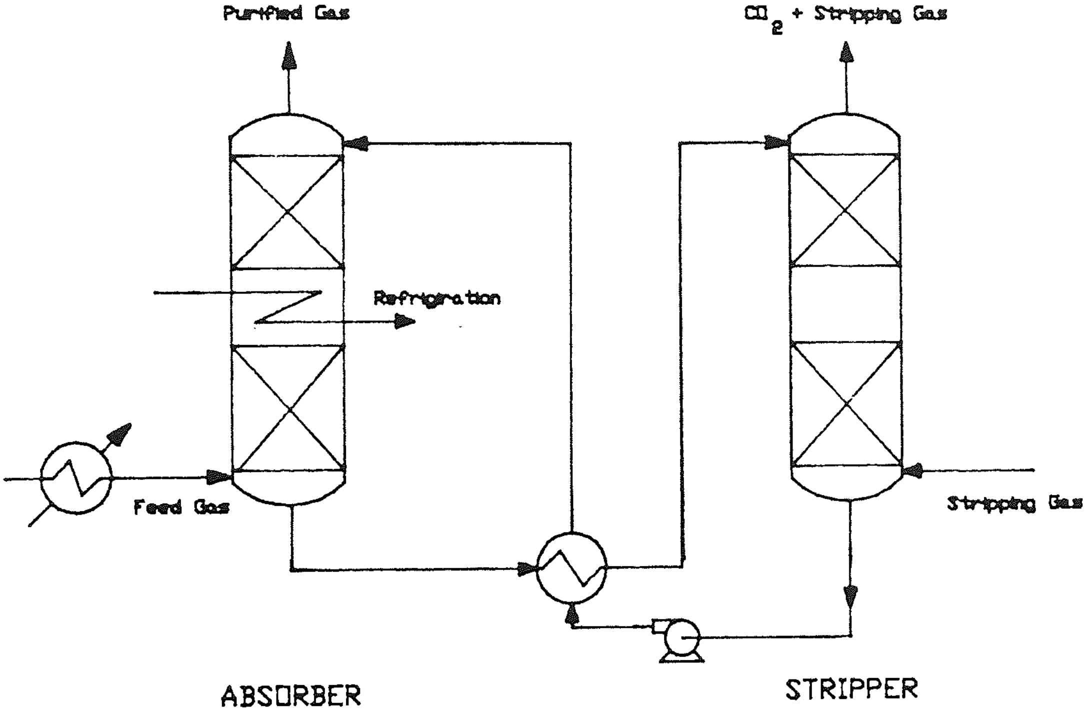


Figure 7.3 Process flowsheet of CO_2 absorption in ammonia synthesis using Rectisol.

7.3.2 Carbon Dioxide and Hydrogen sulphide Removal in Sour Natural Gas processing

Since sour natural gas frequently contains appreciable quantities of carbon dioxide and hydrogen sulphide, it is necessary to remove these acidic components. Absorption with chemical and physical solvents is commonly used. Selexol is a physical solvent which has often been applied successfully for the bulk removal of carbon dioxide and hydrogen sulphide from a variety of feed gases, including natural gas. Table 7.3 shows a typical requirements for pipeline gas composition from the sour natural gas absorption process.

Table 7.3 Natural gas process that need gas treating

Process	Acid gases to treating	Cleanup Target
Natural gas Purification		
Pipline gas	H_2S, CO_2, COS, RSH	<4 ppm H_2S;<1% CO_2
LNG feedstock		1-2 ppm H_2S; <50 ppm CO_2

Sour natural gas composition can vary over a wide range depending on the source. An example from the Wyoming gas fields is given in Table 7.4. It can be seen that carbon dioxide and methane are major constituents. For simplicity of the design calculations, it can be assumed that the sour natural gas feed only consisted of carbon dioxide, methane and hydrogen sulphide. Table 7.5 shows the assumed compositions of feed gas for both Selexol and B2 process calculations. Figure 7.4 illustrates the process flowsheet used.

Table 7.4 Example of Sour Natural Gas Compositions [100]

Component	Wyoming (mole%)
H_2	0.28
N_2	4.20
C_1	71.15
C_2	2.01
C_3	0.49
i-C_4	0.07
n-C_4	0.23
C_5^+	0.25
CO_2	17.56
H_2S	3.76
COS	trace

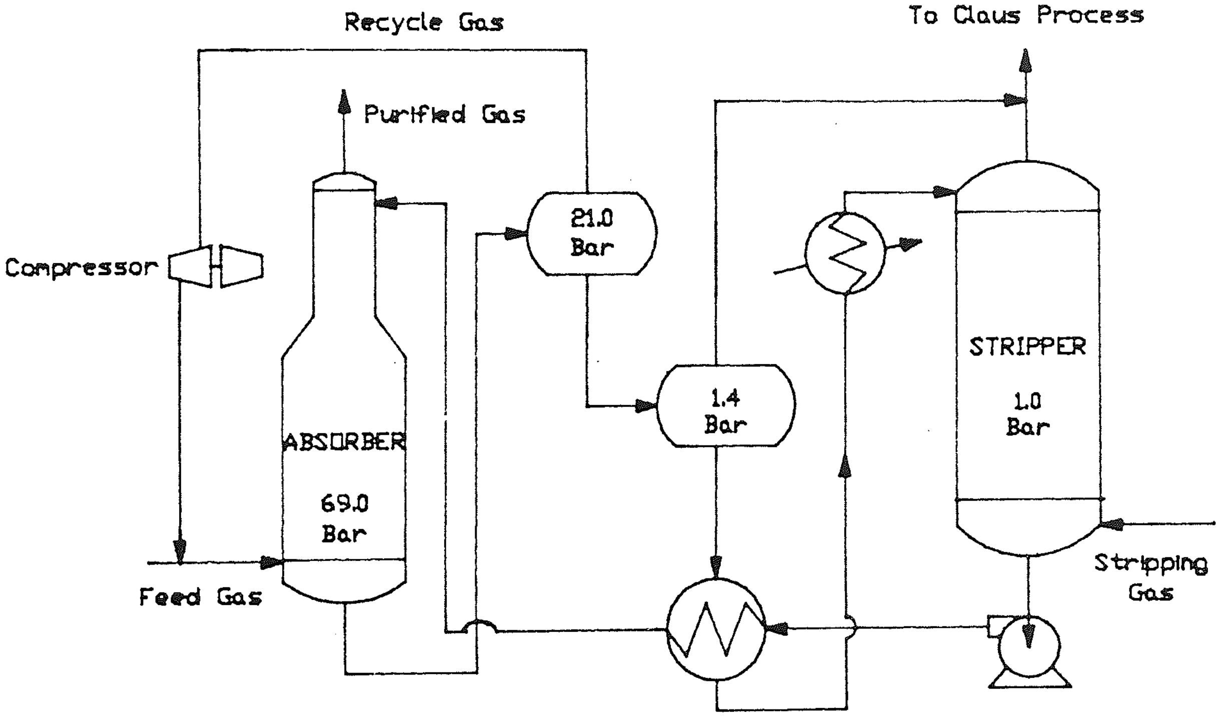


Figure 7.4 Process flowsheet of CO_2 and H_2S in natural gas absorption.

The feed sour gas stream at 298.15 K and 69 bars enters at the bottom of the absorber which is packed with 2.0 inches metal Pall rings. The gas flows through the absorber counter-current to the solvent fed at the top of the column at a temperature of 294.15 K. Rich solvent from the absorber is fed directly to a flash vessel which operates at 298.15 K and 20 bars. Here, some of methane and carbon dioxide are released from the liquid to recover absorbed methane. This gas is recompressed into the feed gas stream. From the first flash vessel, the solvent passes into a second flash tank, which operates at 297.15 K and 1.4 bars, in order to reduce the load on the regenerator. The solvent from second flash drum is charged to the top of the stripping column. This is also packed with 2.0 inches metal Pall rings and operates at a pressure of about 1 bar and temperature of 298.15 K. The lean solvent from the stripper is fed back to the absorber.

Table 7.5 Compositions of feed gas for Selexol and B2 process.

Component	kmole/h
CO_2	1100.0
H_2S	110.0
CH_4	9790.0
Solvent	-
Total	11000.0

7.4 Equilibrium data

The most important physical property data required for the design of absorbers and strippers are gas-liquid equlibria. The equilibrium data define the purity of the gas product, the amount of solvent used and the mass transfer driving force in the system. In this work, the gas-liquid equilibrium data for the solvent B2 and Rectisol processes are determined by using the GCEOS model, but for the Selexol process it was obtained from private communication.

Usually, equilibrium data are presented in the form of the equilibrium constant (K):

$$K = y/x \tag{7.1}$$

The equilibrium constant varies with system pressure, temperature, and composition. In order to simplify the process design calculations, the equilibrium constants of each gas in the solvent B2, and in methanol, are expressed in term of temperature at specified pressure (25 bar). For equilibrium constants at the other pressures this work will use an equation which will be described later.

Table 7.6 gives expressions for the estimation of equilibrium constants of hydrogen, methane, nitrigen, carbon monoxide, hydrogen sulphide and carbon dioxide in the solvent B2 and methanol.

Table 7.6 Equilibrium constants of gases in the solvent B2 and methanol at 25 Bar.

Solvent	Gas	Temperature (K)	K´s values
B2	H_2	283.15-298.15	92.67609 - 0.1861716T
	N_2	283.15-298.15	30.54378 - 2.514256E-2T
	CO	283.15-298.15	1733.891 - 4.919907T
	CH_4	283.15-298.15	7.597545 + 8.282303E-3T
	CO_2	283.15-298.15	-3.233278 + 1.530302E-2T
Methanol			
	H_2	233.15-298.15	8843.540 + 0.000000T
	N_2	233.15-298.15	5120.040 + 0.000000T
	CO	233.15-298.15	4760.000 + 0.000000T
	CH_4	233.15-298.15	-249.7497 + 1.161186T
	CO_2	233.15-298.15	-35.26358 + 0.153401T

The estimation equations for the effect of temperature on the gas-liquid equilibrium of gases in liquid are obtained by considering the thermodynamic behavior of a multicomponent system.

If we look at Table 7.2, argon (Ar) is one of the compositions in the gas stream. The GCEOS model can not be used to estimate the gas-liquid equilibrium for this gas, because it contains no parameters for the argon gas. In this work will be assumed that the equilibrium constant of the argon gas is similar to that of the carbon monoxide. This assumption will not effect the results of the process design calculations because the composition of the argon gas in gas the stream is very small when compared with that of the other gases.

The gas-liquid equilibrium of hydrogen sulphide/solvent B2 also cannot be predicted by the GCEOS model. However, this work will use the method described in England´s paper [43] to estimate the gas-liquid equilibrium of hydrogen sulphide/ solvent B2 system. Although the errors associated with this estimation are not known, nevertheless the predicted results of the solubility of hydrogen sulphide in the solvent B2 (which give the value of 0.0885 mole fraction of hydrogen sulphide in the solvent B2 at 25°C and 1 atm) seems to be reasonable for using in the preliminary process design calculations.

For the simplicity of calculation, appropriate generalized equations of K-value (K_i^*) of each gas in B2 at the given pressure (P^*) are determined as a function of temperature, and using the following equation for system pressure other than P^*;

$$K_i = K_i^* \; (P^*/P\ ) \qquad (7.2)$$

where K = K-value at system pressure

P = system pressure, bar

Use of this formula will provide data which is normally sufficient for all preliminary design work. By using the K-value and the mole fraction in gas phase (y_i) of each component, the equilibrium value of liquid phase mole fraction (x_i) is found from the following equation.

$$x_i = y_i / K_i \tag{7.3}$$

7.5 Absorber and Stripper Calculation

The calculations of absorber and stripper are carried out by using the Kremser-Brown method (Appendix 8). In order to determine the flow rate of B2 and dimensions of equipments, the following procedures will be used.

(a). Assuming that the absorber and stripper are operated adiabatically.

(b). The purified gas leaving the absorber should have a concentration of carbon dioxide of less than 0.1% by volume.

(c). Assuming that the solvent B2 will be completely recovered from the stripper (this assumption is rather incorrect because some of B2 may come out from the stripper with stripping gas. But in the final flowsheet, water wash and a small distillation may be added for recovering the solvent B2 back to the system).

(d). Calculate a material balance and heat balance on both the absorber and the stripper.

(e). Select type and size of packing in both absorber and stripper.

(f). Determine the column diameter, to handle the liquid and gas flow rates. This is based on flooding conditions.

(g). Determine the column height from the number of transfer units and the height of an equivalent theoretical plate. This can be obtained from a knowledge of equilibrium data, physical properties and mass transfer theory.

(h). Select and design the column internals.

Other data used in the calculation, such as the heat capacity of B2 and gas and liquid diffusion coefficients were estimated. The estimation methods involved in the column design are shown in Appendices 1 and 8.

7.6 Flash tanks calculation

Some gas absorption proceses need flash vessels to recover some valuable gases for recycling to the absorber, or desorption of acid gases to reduce the load on the stripper. Several flash tanks may be used in the process, and each of them usually operate at different pressures chosen on economic grounds.

Temperature and pressure can be varied and appear as input parameters to the computer program. For a liquid feed stream contains N components, the material balances and equilibrium of each components are:

$$Fz_i = Lx_i + Vy_i \qquad (7.4)$$

$$y_i = K_i\ x_i \qquad (7.5)$$

where K_i is the equilibrium constant of each components, F is a liquid feed stream rate, V and L are vapour and liquid rate leaving the flash tank, and z_i, x_i, and y_i are the mole fraction of each components in feed stream, liquid and vapour respectively. On combining equations 7.4 and 7.5, and introducing B=V/F, the fraction vaporized, the flash condition becomes

$$f(B) = -1 + K_i x_i = -1 + \frac{z_i}{1 + B(K_i - 1)} = 0 \qquad (7.6)$$

and the corresponding Newton-Raphson algorithm is

$$B = B + [(-1+ \frac{z_i}{1 + B(K_i-1)}) / (\frac{(K_i - 1)z_i}{[1 + B(K_i-1)]})] \qquad (7.7)$$

After B or V/F has been found by successive iteration, the phase compositions are obtained with

$$x_i = \frac{z_i}{1 + B(K_i - 1)} \tag{7.8}$$

and the vapour phase compositions can be found from equation 7.5.

A recalculation option is provided in the process design calculation program for the user to select different operating conditions for the flash tank. This calculation can be repeated until optimum flash conditions are obtained.

7.7 Estimating the Costs of Process Equipment

Because B2 is used as a new solvent for a gas absorption process, therefore a technical and economic study should be put into perspective quantitatively for a new manufacturing plant. The evaluation of a new manufacturing plant must begin by defining the types and sizes of the required equipment, its costs, its efficiencies, its energy consumption, and the work force needed for its operation.

After the flow sheet and sizes of equipment have been calculated, the next step is to determine the price of the individual equipment and then the cost of the plant. Generally, the approximate purchased price of the particular equipment item can be obtained from a supplier, from a reference, or from past experience. For the plants under study, only the cost of absorbers and strippers are estimated by the method which is shown in Appendix 8.

7.8 Results and Discussion

A computer program was written for the preliminary process design calculations. The program was written in Basic language. The programs are not listed in this thesis, but are recorded on a diskette which is supplied in the back cover of this thesis. The calculation procedures for the design of the packed column presented here will not be described in detail, such a description can be found eleswhere [41, 42, 183]. It included heat and mass balances on equilibrium stage calculation. The height equivalent to a theoretical plate (HETP) of the packing is then calculate from mass transfer theory. The comparisons between B2 and Rectisol and Selexol are made as follows.

7.8.1 Comparison of B2 with Rectisol

Table 7.7 shows some results of the preliminary design calculations and outlet gas contents for carbon dioxide absorption in ammonia synthesis by using Rectisol (Process 1) and B2 at two different processes, 25 bar (Process 2) and 35 bar (Process 3). These results show that the solvent B2 can remove the carbon dioxide from the raw gas stream down to less than 0.1% by volume in the purified gas stream. Especially at pressure of 35 bars (Process 3) carbon dioxide was removed down to below 60 ppm. The solvent flow rate in both B2 processes (process 2 and process 3) are larger by a factor of about 1.3 than that in the Rectisol process (Process 1). However, the loss of solvent in the Rectisol process is about 334 times (kg/h) higher than those in B2 processes in this design study.

However the loss of hydrogen and nitrogen in the Rectisol process is very small when compared with the B2 processes which lose 3.8% of the hydrogen and 6.3% of the nitrogen in process 2, and 5.4% of the hydrogen and 9.8% of the nitrogen in process 3.

Table 7.7 Design and operating results for CO_2 absorption in ammonia synthesis plants.

Process variable	Process 1	Process 2	Process 3
Gas feed (kmole/h)	6791.84	6791.84	6791.84
Major feed gas contents:(kmole/h)			
Hydrogen	3966.43	3966.43	3966.43
Nitrogen	1283.66	1283.66	1283.66
Carbon dioxide	1487.41	1487.41	1487.41
Outlet gas contents:(kmole/h)			
Hydrogen	3965.93	3815.11	3750.57
Nitrogen	1283.38	1202.87	1168.30
Carbon dioxide	0.33	6.54	0.18
Solvent flowrate: (kmole/h)	6000.00	8000.00	8000.00

Table 7.7 (Continued)

Absorber:			
No.of stages	15	20	15
Column diameter (m)	3	4	4
HETP (m)	1.76	0.87	0.89
Temperature (K)	233.15	293.15	293.15
Pressure (bar)	25.0	25.0	35.0
Cost ($)	108814.0	132155.0	157395.0
Stripper:			
No.of stages	5	10	10
Column diameter (m)	3	3	3
HETP (m)	0.63	1.32	1.28
Temperature (K)	298.15	298.15	298.15
Pressure (bar)	1.0	1.0	1.0
Cost ($)	19460.0	35818.0	35144.0
Stripping gas:			
flowrate (kmole/h)	38.56	394.65	398.98
Solvent lost (kmole/h)	59.44	0.05	0.05

For the size of absorber, from a comparison of HETP of about 0.87 in process 2 and of 0.89 in process 3 with 1.77

for rectisol, it seems to be that using B2 will produce smaller column than using Rectisol. However, because the diameter of the absorber in the Rectisol process is 1 meter smaller than that in both processes 2 and 3, and the number of plates is 15 in the Rectisol process and 20 and 15 in Processes 2 and 3 respectively, the size of the absorber in the Rectisol process is smaller than those in the B2 processes. This is confirmed by the estimation of the cost of the absorbers, based on June 1981, which shows that the absorber costs $108814 for Rctisol process, and $132155 and $157395 for B2 processes 2 and 3 respectively.

The stripper, is also smaller when using Rectisol than B2 in both processes, and the cost calculations show that the stripper costs $19460 for the Rectisol process, and $35818 and $35144 for both B2 processes. The stripping gas flow rate using Rectisol is also smaller than that for B2. But if we consider the need for a refrigerator (to produce low temperature absorption), and the rich/lean exchanger, the gas exchangers and the loss of solvent in the Rectisol process, these may well cause the Rectisol process to cost more than B2. In brief B2 could replace Rectisol without the need for cold operation. A complete cost comparison would include not only changes in services required but changes in the size of the upstream plant to compensate for 10% nitrogen loss in B2 plant.

7.8.2 Comparision of B2 with Selexol

This section will discuss the results of the design calculations of carbon dioxide and hydrogen sulphide absorption in sour natural gas industry using B2 and Selexol solvents. The design calculations presented here was not optimized, since the operating variables were set somewhat arbitrarily. Solvent flow rate and stripping gas requirements were calculated such that the number of stages in the absorption and stripping columns is the same for the two processes. Both solvents used the same design flowsheet and the process design requirements of feed gas and the contents of purified gas stream.

Feed Gas		
Flow rate	11000.0	kmole/h
Pressure	69.0	bar
Temperature	299.15	K
Composition		
CO_2	10.0	Vol%
H_2S	1.0	Vol%
CH_4	89.0	Vol%
Requirements for product gas		
CO_2	< 3.0	Vol%
H_2S	< 4.0	ppm
CH_4	as balance	

Table 7.8 shows the comparison results from the preliminary design calculations of bulk removal of carbon dioxide in natural process using B2 and Selexol solvents. Both solvents are capable of removing the impurities down to the required target of the purified gas stream. The amount of carbon dioxide in the purified gas stream is larger by a factor of 1.3 when using B2 than Selexol, this may be due to the amount of recycle gas using B2 which is larger by a factor of about 6.0 than that for Selexol. The amount of methane loss in the B2 process is 2.2% compared with 0.85% in the Selexol process.

Considering the size of absorber, the HETP of 3.97 m. in Selexol process is higher than that of 0.98 in B2 process. This means that the column used in the B2 process is smaller than that in the Selexol process for the same number of stages and the same calculated diameter for both solvents. This is shown by the absorber cost calculations which is $172,573 and $93,766 for Selexol and B2 processes respectively.

The stripper cost is also cheaper for B2 than Selexol. It is $42,397 for Selexol process and $13,406 for B2 process. The stripping gas flow rate in Selexol process is approximately a factor of 2.6 higher than B2 process.

Table 7.8 Design results for CO_2 and H_2S absorption for sour natural gas plants.

Process variable	**Solvent B2**	**Selexol**
Gas feed (kmole/h)	11000.0	11000.0
Gas contents:(kmole/h)		
Hydrogen sulphide	(110.0)	110.0
Methane	9790.0	9790.0
Carbon dioxide	1100.0	1100.0
Outlet gas contents:(kmole/h)		
Hydrogen sulphide	(<4 ppm)	<4 ppm
Methane	9574.8	9707.2
Carbon dioxide	238.1	185.5
Recycle gas contents:(kmole/h)		
Hydrogen sulphide	(28.4)	2.4
Methane	1214.2	152.6
Carbon dioxide	649.1	135.2
Solvent flowrate:		
(kmole/h)	3000.0	3000.0
Absorber:		
Diameter (m)	2.0	2.0
No.of stages	8	8
HETP (m)	0.98	3.97
Temperature (K)	296.65	296.65
Pressure (bar)	69.0	69.0
Cost ($)	93766.0	172573.0

Table 7.8 (Continued)

Stripper:		
Diameter (m)	2.0	2.0
No.of stages	8	8
HETP (m)	0.86	2.63
Temperature (K)	297.65	297.65
Pressure (bar)	1.0	1.0
Cost ($)	13406.0	42397.0
Stripping gas:		
flowrate (kmole/h)	381.0	980.9

N.B. The calculation of hydrogen sulphide solubility in B2 is based on a predicted value of the solubility parameter, therefore likely to be less accurate.

7.9 Conclusions

The preliminary design calculations for both gas absorption in ammonia synthesis and sour natural gas industries indicate that solvent B2 has sufficient advantages to warrant further study for gas absorption. This result has demonstrated the potential value of using the group contribution methods for designing physical solvents.

For carbon dioxide absorption in ammonia systhesis process, the B2 plant is operated at ambient temperature, while the Rectisol plant has to operate at the very low temperature -40°C for the absorber. This adds considerably to the cost and complexity of the plant. Practically, the B2 plant need only two major units, i.e. absorber and stripper, while the Rectisol plant needs a lean/rich solvent exchanger, a gas/gas exchanger, besides absorber, stripper and refrigerator. At pressure of 35 bar B2 can remove carbon dioxide down to less than 60 ppm in the purified gas stream. However, the B2 processes suffers from a lack of selectivity and this results in an increased lose of gas products.

For the bulk removal of carbon dioxide in sour natural gas absorption process, the use solvent B2 resulted in a lower cost of plant than Selexol. For the same process flowsheet the B2 plant needed a smaller absorber, stripper and less stripping gas than the Selexol plant. However, the loss of product gas was again increased due to the reduced selectivity.

The above results are only preliminary design calculations. A more accurate cost comparison requires evaluating the cost of services of B2 versus Rectisol and of capital cost of B2 versus Selexol against the increased loss of product gases due to the reduced selectivity of B2. Also this comparison should be made between optimum designs particularly with respect to flash and recycle.

Nevertheless, the first attempt at the molecular design of a new solvent has produced a process which is at least worth further study in comparison with the existing processes.

CHAPTER 8

DISCUSSION

This work has described a new approach for the design of a new solvent for the acid gas removal process based on the UNIFAC type group contribution by Sander et al. This new approach has shown advantages in terms of reducing time and cost of the solvent selection procedure.

Carbon dioxide solubility is the most important property for the absorption process, which has been emphasised in this work. This resulted in the B2 homologous series and it is significant that the measured solubility of carbon dioxide in B2 come within 10% of that predicted by UNIFAC. The solubility of carbon dioxide in B2 is greater than that in other commercial solvents of the same molecular weight. However the selectivity of B2, that is the ratio of solubilities of the gases to be removed to those of the product gases, is less than that of the other solvents thus the reduced cost expected for removing carbon dioxide by B2 is accompanied by an increased loss of product gas. In future work attention should be paid to selectivity.

Physical properties of a solvent are important in determining the cost of gas absorption. These are molecular weight, vapour pressure, liquid density and liquid viscosity. This was shown in detail in Chapter 7 where comparison was made in terms of the costs of absorber and stripper between the new solvent B2 and refrigerated methanol as used in the Rectisol process and between B2 and Selexol. The physical properties of these solvents are shown in Table 7.1 of Chapter 7.

A low molecular weight of solvent results in high value of volume of gas per volume of solvent and this means that the volumetric solubility is higher and the solvent recirculation rate is reduced. However, low molecular weight solvents have a higher vapour pressure and a higher solvent loss unless the temperature is reduced by refrigeration which is both costly and which causes an increase in viscosity. An increased viscosity increases the resistance to mass transfer in the liquid phase and the calculation presented in Chapter 7 show that the HETP in Selexol process, which has a high viscosity of 5.8 cps, was higher than those in B2 which has a viscosity of 1.8 cps. This results in a significant increase in packed height and column cost.

The discussion above suggests that the optimum solvent will depend on the optimum combination of these physical properties. Therefore, at the beginning of designing a solvent, care should be taken for selecting the methods of predicting physical properties. Boiling point is generally an important property in the design, because it is often one of the variables in most of the physical property estimation methods. The limited accuracy of methods of predicting the boiling point was shown in this work where the boiling point of B2 was predicted by Meissner´s method [113] which gave the value of 380.2 K at the beginning of the solvent design. It was found later by reference to the literature and by experiment in this work, that the true boiling point was 464.15 K. This has shown that more work is required to improve methods of boiling point estimation. The effect this error had on the prediction of the other physical properties is discussed in Chapter 5. In this case, the difference in boiling point improved the commercial potential of the solvent as it resulted in a vapour pressure lower than that predicted.

The simple cost evaluation of Chapter 7 have shown that the new solvent B2 proves to be as good as or a better solvent than Rectisol and Selexol i.e. it is seemed to be nearer the optimum than those two solvents, except the selectivity which was less than that of the other solvents. Thus the work as a whole may be claimed as a succesful for attempt at the molecular design of a gas absorption solvent.

However, in this final section of this work it is appropriate to put this achievement into perspective by reviewing the strengths and limitation of the methods used and thereby identifying the need for future work.

Ideally the design of gas absorption solvent would be done to a target specification of physical properties, or at least on the basis of a method which estimated the cost implications of changes in any of the physical properties discussed above. Thus an attempt should be made to reorganise the design methods used in Chapter 7 to design a plant for any specified gas absorption duty, so as to produce methods to evaluate the changes in cost which result from changes in physical properties.

In this work gas solubility was predicted by the UNIFAC group contribution method which is the most advanced method available. One of the methods used, GCEOS, was published during the course of this work. It was a valuable method for predicting gas solubility at high pressure. Nevertheless UNIFAC and GCEOS have certain limitations, for instance the lack of parameters for some important groups which is difficult for any other researcher to improve upon because it needs all the UNIFAC data bank to recalculate the new group parameters and needs a lot of experimental data of the new group in conjunction with the existing groups. The interaction parameters of functional groups 2, 4, 5, 6, 7, 8, 10 and 11 in Table 4.6 of Chapter 4 are not at present available for improving the design of solvents. However, the functional groups 7, 8 and 10 can be ignored because they are likely to result in solvents which may cause corrosion of construction materials.

Nevertheless, despite the limitation in the methods used which have been described above, the solvent designed in this work has been shown to be technically and economically promising in relation to the Rectisol and Selexol solvents which are widely used.

Another published paper by England [43] also came out during the course of this work (1986). It reviewed the method of using molecular groups to predict solubility parameters for the solvent used in the Purisol process. This is another indication that molecular design is likely to be the way of the future development of solvent for separation processes.

Three major computer programs were written during this work, i.e. a program for calculating gas solubility at low pressure (also used for designing a new solvent), a program for estimating gas solubility at high pressure, and a program for calculating gas absorption design. These programs can be put together to permit a first estimation of a plant design from the molecular structure of new solvent. This will reduce the time and effort of the engineer in developing a new solvent for gas absorption process.

CHAPTER 9

CONCLUSION

1. The recently published low (1983) and high (1984) pressure UNIFAC type group contribution methods have been programmed and used to estimate the solubility of gases in the present work.

2. An apparatus has been constructed to determine gas solubility in solvents at ambient conditions, and used to test the results of the new UNIFAC method of predicting gas solubility based on molecular groups. It is shown by the experimental results of gas solubility using 10 solvents and 3 gases that the UNIFAC method can predict the solubility of gases within 10%. However, the UNIFAC methods are still limited by the absence of some group-interaction parameters.

3. An investigation of the influence of molecular weight and functional groups for chosen alcohol and ketone homologeous series has shown that as the molecular weight or the number of functional groups is increased, the solubility of gases (in term of cc.of gas/cc.of solvent at 1 atm gas pressure) is reduced. Also, the investigation of effect of molecular structure from chosen alkane, alcohol and ketone series has shown insignificant changes in the gas solubility when compared with the effect of functional groups.

4. 90 molecules were constructed from different combinations of the available functional groups used in the UNIFAC method and the carbon dioxide solubility in these solvents has been evaluated by UNIFAC. Considering the available functional groups, the ketone group has a higher relative solubility for carbon dioxide than any other group. This means that if the solvent used for gas absorption consists solely of ketone groups, the quantity of gas absorbed is expected to be greater than for a solvent made up of any other groups. This was proved by examining the solubility of carbon dioxide and the physical properties of the molecules in the alcohol series, ketone series and those in the twelve homologous series (84 molecules). The ketone homologous series was shown to have a relatively higher carbon dioxide solubility than other series on the same range of number of carbon atom.

5. From further considerations of the other physical properties which are important in solvent design for gas absorption, such as vapour pressure, density, viscosity etc., B2 (acetonyl acetone) has been selected for a new physical solvent process in gas absorption. The solubility of carbon dioxide in B2 at atmospheric pressure was determined by experiment, and the results was shown to be within 10% with that predicted by UNIFAC. The solubility of propane in B2 was measured experimentally. Propane can not be predicted by the

UNIFAC method because no such propane (gas) UNIFAC interaction parameter is available.

6. For predicting gas solubilities at high pressure, the new UNIFAC group contribution method by Steen Skjold-Jorgensen has been programed and shown to be satisfactory by comparison of predictions with experimental measurements in the literature for the solubility of hydrogen, nitrogen and carbon dioxide in various solvents. This UNIFAC method has been incorporated in the preliminary process design calculations for a gas absorption plant.

7. A design and simple cost estimation of a carbon dioxide absorption plant using solvent B2 for removing carbon dioxide in the ammonia synthesis industry showed some potential advantages compared to the widely used Rectisol process based on refrigerated methanol. Carbon dioxide was removed by solvent B2 down to below 0.1% by volume at 35 bar. The B2 plant operates at ambient temperature, which makes it possible to achieve an advantageous energy consumption, compared to Rectisol plant, which operates at a very low temperature.

8. In addition to removing carbon dioxide in ammonia plant, B2 can also be used to remove carbon dioxide from natural gas. Comparative process design calculations show that a B2

plant is very competitive to the wellknown comercially used solvent, Selexol, for removing acid gases from natural gas. The size of equipment used, particularly absorber and stripper, were shown to be very much smaller in the B2 plant than in the Selexol plant. This is a result of the much lower liquid viscosity of B2 relative to that of Selexol.

9. The selectivity of B2 is less than those of the Rectisol and Selexol solvents and this resulted in a predicted increased loss of product gas. This is the major disadvantage of the new solvent.

SUGGESTION FOR FUTURE WORK

As far as this work concerns it has been the first time in which the group contribution method incorporated with the physical properties was used to design the solvent for a gas absorption process. This work has shown important limitation in the methods now available to predict the physical properties from molecular structure and work is required as follows.

1. The new solvent has a high carbon dioxide solubility but needs better selectivity. Further solvent design is requried taking into account selectivity.

2. Improving the UNIFAC (Sander et al.) functional groups by means of estimating the missing groups, or developing a new method for estimating gas solubility on the basis of molecular groups. This will be better if this new method is not an empirical one. The new method should be capable of application to any operating temperatures and pressures.

3. Improving the accuracy of prediction of all necessary physical properties such as density, vapour pressure, viscosity, and especially boiling point which is often one of the variables needed in most of the physical property estimation methods.

4. The experimental determination of gas solubility in the new solvent at various conditions, especially at high

pressure.

5. Optimization of the plant in terms of process conditions such as temperature and pressure etc., and process flowsheet.

6. Using plant design and costing procedures attempt to derive a cost estimating procedure based only on the physical properties of the solvent.

7. Perform experiments on the pilot plant scale for gas absorption using the new solvent.

APPENDIX 1

THE ESTIMATION OF PHYSICAL PROPERTIES

Estimation of Boiling Point

When the experimental normal boiling point is not available, it can be estimated by the method of Meissner [113]

$$T_b = \frac{637.0\ [R_D] \quad + B}{P} \tag{A1.1}$$

where T_b is the normal boiling point in K, R_D is molar refraction, and P is the parachor. Both molar refraction and parachor are calculated by summation of the additive contributions given in the above reference.

Estimation of Vapour Pressure

Vapor pressures of substances may be estimated from Antoine's equation

$$\log P_v = A - \frac{B}{T - C} \tag{A1.2}$$

where

$$A = B/(T_b - C) \tag{A1.3}$$

$$B = \frac{1}{Z_{vb}} (T_b - C) \frac{\Delta H_{vb}}{2.303\ R\ T} \tag{A1.4}$$

$$C = -18 + 0.19\ T_b$$

The units employed are atmospheres and Kelvins for pressure and temperature respectively, and for most substances at low pressures $1/Z_{vb}$ is assumed equal to 1.05.

T_b is the normal boiling point, ΔH_{vb} is the molal heat of vaporization at the boiling point in cal/mol. This molal heat of vaporization can be estimated from Chen´s equation [135]. But this method loses accuracy for $T_b < 250$ K or for highly polar compounds at $T_r < 0.65$.

This work uses Riedel´s analytical correlation, which is within a maximum error of ±5 per cent for most compounds.

$$\log\left(\frac{P_c}{P_v}\right) = 0.118B - 7\log T_r + (\alpha_c - 7)(0.0364B - \log T_r)$$

where

$$B = \frac{36}{T_r} - 35 - (T_r) + 42 \ln T_r$$

$$\alpha_c = 0.9076\left(1 + \frac{T_{br} \ln P_c}{1 - T_{br}}\right)$$

T_b is boiling point, $T_{br} = T_b/T_c$, T_c is critical temperature, P_c is critical pressure, and P_v is vapour pressure.

Estimation of Critical Properties

The critical properties, such as temperature, pressure and volume, are normally needed for many calculations when the calculations require reduced conditions. If reliable experimental values cannot be found, an estimation method will be needed. For organic compounds Lydersen's method [108] is usually used for estimating the critical properties with sufficient accuracy for most design purposes.

$$T_c = T_b(0.567 + \Delta T - (\Delta T)^2)^{-1} \quad (A1.5)$$

$$P_c = MW(0.34 + \Delta P)^{-2} \quad (A1.6)$$

$$V_c = 40 + \Delta V \quad (A1.7)$$

$$Z_c = P_c * V_c / R * T_c \quad (A1.8)$$

where

T_c = critical temperature (K)

P_c = critical pressure (atm)

V_c = critical volume (cm^3/gmole)

T_b = normal boiling point (K)

ΔT = critical temperature increments

ΔP = critical pressure increments

ΔV = critical volume increments

The temperature, pressure and volume increments are evaluated by summation of the additive contributions for various atoms or groups of atoms given in Table 2-1 of Reference 135.

Estimation of Liquid Viscosity

At temperature T(K) liquid viscosity can be estimated by Morris´ method [135]. This method is a group contribution type method. The viscosity equations are given as follows:

$$\log \frac{\mu_L}{\mu^+} = j\,(1/T_r - 1.0) \qquad (A1.9)$$

$$j = \left[0.0577 + \sum_i (b_i n_i)\right]^{1/2} \qquad (A1.10)$$

where

μ_L = viscosity of liquid (cP)

μ^+ = the parameter constant for each compound class, and the values are listed in Table 9.9 in reference 135.

b_i = group contribution as determined in Table 9.10 of reference 135.

n_i = number of times group appears in molecule

T_r = the reduced temperature (T/T_c)

Estimation of Liquid Density

Generally, most liquid density data of chemical compounds are given at temperatures of 20°C or 25°C. Besides these two temperatures, if the data are not available, the liquid density can be estimated by many methods. This work selected the method of Goyal et al. [69], which was shown to be a very accurate method; for $T_r < 0.8$, the average and maximum errors are 2% and 4%, respectively. They expressed the density of liquid as a function of critical properties, this density expression is:

$$\rho_L = (P_c\, M/T_c)[(0.0653/(Z_c^{0.773})) - 0.09T_r] \qquad (A1.11)$$

where

ρ_L = density of liquid, gm/ml

M = molecular weight of liquid

T_r = the reduced temperature (T/T_c), K

P_c = critical pressure (atm)

Z_c = critical compressibility factor (P_cV_c/RT_c)

Estimation of Surface Tension

Surface tension values are usually difficult to find from the literature. Therefore, estimation methods will have to be used for most liquids. Sugden's method [156] is one of the methods which can be used to estimate the surface tension if reliable values of liquid and vapour density are available. This method estimates the surface tension from the Sugden parachor, which can be estimated by a group contribution method. The correlation of surface tension is given by

$$\sigma = [P_{ch}(\rho_L - \rho_V)/M]^4 \times 10^{-12} \qquad (A1.12)$$

where

σ = surface tension (dynes/cm)

P_{ch} = Sugden's parachor

ρ_L = liquid density (kg/m^3)

ρ_V = density of the saturated vapour (kg/m^3)

M = molecular weight

The vapour density can be neglected when it is small compared with the liquid density.

Estimation of Diffusion coefficients

Diffusion coefficients are needed in the design of mass transfer processes, such as absorption, distillation and liquid-liquid extraction. Experimental values for the more common systems can often be found in the literature, but for the B2 system both liquid and gas diffusivities have to be estimated.

For liquid diffusivity the published correlation of Wilke and Chang [172] was used:

$$D_L = (1.173 \times 10^{-13} (\varnothing\ M)^{\frac{1}{2}}\ T\ ) / \mu\ V_m^{0.6} \qquad \text{(A1.13)}$$

where

D_L = liquid diffusivity (m^3/s)

$\varnothing$ = association factor for the solvent

= 2.6 for water

= 1.9 for methanol

= 1.5 for ethanol

= 1.0 for unassociated solvents

M = molecular weight of solvent

μ = viscosity of solvent ($mN\ s/m^2$)

T = temperature (K)

V_m = molar volume of the solute at its boiling point ($m^3/kmol$)

For the prediction of gas diffusivity, the equation developed by Fuller et al. [58] is used:

$$D_v = \frac{1.013 \times 10^{-7}\ T^{1.75}\ (1/M_A + 1/M_B)^{1/2}}{P\ [(\sum_A v_i)^{1/3} + (\sum_B v_i)^{1/3}\ ]} \qquad \text{(A1.14)}$$

where

D_v = gas diffusivity (m^3/s)

T = temperature (K)

M_A, M_B = molecular weight of components a and b

P = total pressure (bar)

$\sum_A v_i$, $\sum_B v_i$ = the summation of the special diffusion volume coefficients for components a and b

and the diffusivity for the component A through a gaseous mixture B, C, D, etc. is given by the formula

$$D_{Amix} = \frac{1.0 - y_A}{(y_B/D_{AB})+(y_C/D_{AC})+(y_D/D_{AD})+\ldots} \qquad (A1.15)$$

where

y_A, y_B,... = mole fraction of components A, B,... in the gas phase

D_{AB},D_{AC},... = the diffusivity of component A in B and C...

Enthalpy, Heat Capacity of Gases and Liquids

Heat capacity (c_P) is the first derivative of enthalpy (Δh) with respect to temperature (T), differences in enthalpy are calculated by integrating the heat capacity:

$$\Delta h = \int c_p \, dT \tag{A1.16}$$

if T varies over the interval T_1 to T_2 and the pressure is constant, usually an atmospheric pressure. The integration result of equation A1.16 is then

$$\Delta h = c_p \, (T_2 - T_1) \tag{A1.17}$$

The heat capacity of gas varies with temperature which can be written as follows

$$\overset{o}{c}_p = A + B\,T + C\,T^2 + D\,T^3 \tag{A1.18}$$

In Appendix A of reference 135, the constants A, B, C and D are given for many compounds and allow the calculation of $\overset{o}{c}_p$ with equation A1.18. If these constants are not available, the specific heat can be estimated by the method of Rihani and Doraiswamy [186]. Table A1.1 shows constants A, B, C, and D for gases and solvents used in this work.

Liquid heat capacities (c_{pl}) are related to gas heat capacities by a correlation proposed by Sternling and Brown [187].

$$(c_{p1} - c_{p}^{o})/R = (0.5+2.2\ w)[3.67+11.64(1-T_r)^{4}+0.634(1-T_r)^{-1}]$$

where w is the acentric factor, R is gas constant and T_r is the reduced temperature (T/T_c).

Table A1.1 The constants A, B, C and D for equation A1.18

Compound	A	B	C	D
H_2	6.483	2.215E-3	-3.298E-6	1.826E-9
N_2	7.440	-0.320E-2	6.400E-6	-2.790E-9
CO	7.373	-0.300E-2	6.662E-6	-3.037E-9
Ar	4.969	-0.767E-5	1.234E-8	0.0
CH_4	4.598	1.245E-2	2.860E-6	-2.703E-9
CO_2	4.728	1.754E-2	-1.338E-5	4.097E-9
H_2S	7.629	3.431E-4	5.809E-6	-2.810E-9
Methanol	5.052	1.694E-2	6.179E-6	-6.811E-9
Selexol	22.238	25.590E-2	-1.095E-4	0.0306E-6
B2	4.0096	12.712E-2	-0.737E-4	0.0369E-6

Note. - For B2 and Selexol the value are estimated from the Rihani and Doraiswamy method [186].

- The unit of c_p is calories/gm-mole.

APPENDIX 2

SANDER ET AL.´S INTERACTION PARAMETERS AND THE DESCRIPTION OF THE COMPUTER PROGRAM

GROUP	1	2	3	4	5	6	7	8	9
	CH_3	CH_3'	CH_3''	CH_2	CH_2(C)	CH	CH(C)	C	ACH
1 CH_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-56.60
2 CH_3'	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-56.60
3 CH_3''	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-56.60
4 CH_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-56.60
5 CH_2(C)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-56.60
6 CH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-56.60
7 CH(C)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-56.60
8 C	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-56.60
9 ACH	-56.60	-56.60	-56.60	-56.60	-56.60	-56.60	-56.60	-56.60	-139.41
10 AC	-56.60	-56.60	-56.60	-56.60	-56.60	-56.60	-56.60	-56.60	-139.41
11 $ACCH_3$	99.70	99.70	99.70	99.70	99.70	99.70	99.70	99.70	48.50
12 $ACCH_2$	99.70	99.70	99.70	99.70	99.70	99.70	99.70	99.70	48.50
13 ACCH	99.70	99.70	99.70	99.70	99.70	99.70	99.70	99.70	48.50
14 OH	-39.60	-39.60	-39.60	-39.60	-39.60	-39.60	-39.60	-39.60	-245.50
15 H_2O	4.30	4.30	4.30	4.30	4.30	4.30	4.30	4.30	-
16 CH_3CO	-73.20	-73.20	-73.20	-73.20	-73.20	-73.20	-73.20	-73.20	-231.50
17 CH_2CO	-73.20	-73.20	-73.20	-73.20	-73.20	-73.20	-73.20	-73.20	-231.50
18 N_2	-70.90	-70.90	-70.90	31.30	9.90	200.50	176.90	176.90	-32.20
19 O_2	-88.70	-88.70	-88.70	-11.40	22.00	6.90	9.40	9.40	-73.90
20 H_2	-238.60	-238.60	-238.60	-151.10	-174.70	-219.60	-	-	-240.20
21 CO	148.20	-148.20	-148.20	-57.10	-74.10	90.80	50.50	50.50	-138.70
22 CO_2	209.10	209.10	209.10	256.00	257.50	330.60	293.30	293.30	177.80
23 H_2S	75.40	75.40	75.40	51.80	-	-	-	-	-46.80
24 CH_4	-60.20	-60.20	-60.20	-18.60	-21.20	-	-60.20	-60.20	-77.00
25 C_2H_6	-0.70	-0.70	-0.70	21.40	17.50	-	239.00	239.00	-34.10
26 C_2H_4	-3.80	-3.80	-3.80	29.10	-	93.00	-	-	-43.50
27 C_2H_2	363.30	363.30	363.30	374.70	383.70	-	-	-	280.20

GROUP	10 AC	11 $ACCH_3$	12 $ACCH_2$	13 ACCH	14 OH	15 H_2O	16 CH_3CO	17 CH_2CO	18 N_2
1 CH_3	-56.60	99.70	99.70	99.70	-39.60	4.30	-73.20	-73.20	-70.90
2 CH_3'	-56.60	99.70	99.70	99.70	-39.60	4.30	-73.20	-73.20	-70.90
3 CH_3''	-56.60	99.70	99.70	99.70	-39.60	4.30	-73.20	-73.20	-70.90
4 CH_2	-56.60	99.70	99.70	99.70	-39.60	4.30	-73.20	-73.20	31.30
5 CH_2 (C)	-56.60	99.70	99.70	99.70	-39.60	4.30	-73.20	-73.20	9.90
6 CH	-56.60	99.70	99.70	99.70	-39.60	4.30	-73.20	-73.20	200.50
7 CH(C)	-56.60	99.70	99.70	99.70	-39.60	4.30	-73.20	-73.20	176.90
8 C	-56.60	99.70	99.70	99.70	-39.60	4.30	-73.20	-73.20	176.90
9 ACH	-139.41	48.50	48.50	48.50	245.50	-	-231.50	-231.50	-32.20
10 AC	-139.41	48.50	48.50	48.50	245.50	-	-231.50	-231.50	3000.00
11 $ACCH_3$	48.50	213.70	213.70	213.70	-25.80	-	0.60	0.60	102.90
12 $ACCH_2$	48.50	213.70	213.70	213.70	-25.80	-	0.60	0.60	102.90
13 ACCH	48.50	213.70	213.70	213.70	-25.80	-	0.60	0.60	102.90
14 OH	-245.50	-25.80	-25.80	-25.80	-1312.00	-1440.00	-630.30	-630.30	3000.00
15 H_2O	-	-	-	-	-1440.00	-1576.00	-647.10	-647.10	-
16 CH_3CO	-231.50	0.60	0.60	0.60	630.30	-647.10	-392.70	-392.70	-4.80
17 CH_2CO	-231.50	0.60	0.60	0.60	-630.30	-647.10	-392.70	-392.70	-4.80
18 N_2	3000.00	102.90	102.90	102.90	3000.00	-	-4.80	-4.80	-250.00
19 O_2	-	79.60	79.60	79.60	741.00	-	-45.50	-45.50	-
20 H_2	-	-24.90	-24.90	-24.90	3000.00	-	-234.60	-234.60	-
21 CO	-	32.00	32.00	32.00	217.20	-	-153.00	-153.00	-
22 CO_2	1080.70	297.80	297.80	297.80	330.30	-	74.30	74.30	-
23 H_2S	844.00	128.40	128.40	128.40	-55.80	-	-	-	-
24 CH_4	437.80	86.20	86.20	86.20	312.40	-	-69.10	-69.10	-
25 C_2H_6	3.10	145.40	145.40	145.40	208.20	-	-18.80	-18.80	-
26 C_2H_4	-	122.30	122.30	122.30	118.90	-	-63.30	-63.30	-
27 C_2H_2	-	385.80	385.80	385.80	187.50	-	-	-	-

GROUP	19 O_2	20 H_2	21 CO	22 CO_2	23 H_2S	24 CH_4	25 C_2H_6	26 C_2H_4	27 C_2H_2
1 CH_3	88.70	-238.60	-148.20	209.10	75.40	-60.20	-0.70	-3.80	363.30
2 CH_3'	88.70	-238.60	-148.20	209.10	75.40	-60.20	-0.70	-3.80	363.30
3 CH_3''	-88.70	-238.60	-148.20	209.10	75.40	-60.20	-0.70	-3.80	363.30
4 CH_2	-11.40	-151.10	-57.10	256.00	51.80	-18.60	21.40	29.10	347.70
5 $CH_2(C)$	22.00	-174.70	-74.10	257.50	-	-21.20	17.50	-	383.70
6 CH	6.90	-219.60	90.80	330.60	-	-	-	93.00	-
7 CH(C)	9.40	-	50.50	239.30	-	-60.20	239.00	-	-
8 C	9.40	-	50.50	239.30	-	-60.20	239.00	-	-
9 ACH	-73.90	-240.20	-138.70	177.80	-46.80	-77.00	-34.10	-43.50	280.20
10 AC	-	-	-	1080.70	844.00	437.80	3.10	-	-
11 $ACCH_3$	79.60	-24.90	32.00	297.80	128.40	86.20	145.40	122.30	385.80
12 $ACCH_2$	79.60	-24.90	32.00	297.80	128.40	86.20	145.40	122.30	385.80
13 ACCH	79.60	-24.90	32.00	297.80	128.40	86.20	145.40	122.30	385.80
14 OH	741.00	3000.00	217.20	330.30	-55.80	312.40	208.20	118.90	187.50
15 H_2O	-	-	-	-	-	-	208.20	118.90	187.50
16 CH_3CO	-45.50	-243.60	-153.00	74.30	-	-69.10	-18.80	-63.30	-
17 CH_2CO	-45.50	-243.60	-153.00	74.30	-	-69.10	-18.80	-63.30	-
18 N_2	-	-	-	-	-	-	-	-	-
19 O_2	-260.00	-	-	-	-	-	-	-	-
20 H_2	-	-1000.00	-	-	-	-	-	-	-
21 CO	-	-	-380.00	-	-	-	-	-	-
22 CO_2	-	-	-	84.20	-	-	-	-	-
23 H_2S	-	-	-	-	-181.10	-	-	-	-
24 CH_4	-	-	-	-	-	-80.00	-	-	-
25 C_2H_6	-	-	-	-	-	-	0.00	-	-
26 C_2H_4	-	-	-	-	-	-	-	92.70	-
27 C_2H_2	-	-	-	-	-	-	-	-	243.20

Table 2.1 does not include interaction-energy parameters between the gases and water. Sander et al. provided these gas-water interaction parameters in temperature-dependent terms as follows:

$$u(\text{gas-water}) = u_o + u_1 / T$$

where T is temperature in Kelvins, u_o and u_1 are temperature independent parameters, these are presented in Table A2.2. These parameters can be applied to calculate gas solubilities in pure water and in water containing solvent mixtures at temperatures between 0 to 75°C.

Table A2.2 Gas-water interaction-energy parameters.

Gas	u_o	u_1 ($\times 10^{-5}$)
N_2	1260.4	-2.7416
O_2	1295.9	-3.0295
H_2	1503.3	-4.0130
CO	932.2	-2.4918
CO_2	980.1	-1.6895
H_2S	438.9	-0.7881
CH_4	1059.8	-2.3172
C_2H_6	821.9	-1.5496
C_2H_4	587.4	-1.0132
C_2H_2	721.4	-0.5545

The description of computer program (GASLOW) for low pressure gas solubility calculations (Sander et al. method)

The GASLOW.FOR program has been written to implement the UNIFAC-type Sander et al. method. It is written in the Fortran language and recorded on the diskette Number 1 in MSDOS (Microsoft disk operating system) format. It is for use on the IBM personal computer. GASLOW.FOR was compiled to generate an executable GASLOW.EXE program. These two programs are in the diskette Number 1 enclosed in the back cover of this thesis. To run the programs, type GASLOW. The program prompts you for all of the required input.

This section gives the schematic diagrams and necessary valiables used in the program. Figures A2.1 to A2.4 are simplified flow diagrams of the GASLOW.FOR program.

The GASLOW.FOR program (see Figure A2.1):

1. Asks for input values of temperature, pressure, the gas used, the name of solvent and the molecular weight of solvent.

2. Computes the reference Henry's constant $H_{2,r}$ from equation 1.27.

3. Asks for the input of constituent groups of the solvent from the list of 17 molecular groups displayed on the screen.

4. Computes the mole fraction of gas in the solvent (x)

by iteration until the following criteria are obtained.

$$f(x_2) = y_2P - x_2H_{2,r}\gamma_2/\gamma^{\infty}_{2,r} <= 0.0001$$

and

$$\Sigma x_i = 1.0$$

by using the Secant method (see Figures A2.2 and A2.3). Both γ_2 and $\gamma^{\infty}_{2,r}$ are calculated by using equations 2.11 to 2.21 (see Figure A2.4).

5. Asks for the boiling point and density of the solvent. If these are not available, the user has the option to estimate these values within the program. The boiling point and density are estimated by correlation proposed by Meissner [113] and Goyal et al. [69] respectively (see Appendix 1). The information required to make an estimation of boiling point include molar refraction, parachor and chemical classes of the solvent, and that for the density include critical temperature, critical pressure and critical compressibility factor. All these values are calculated by summation of the group additive contributions which are displayed on the screen for the user to enter the neccessary values.

6. Computes the volume of gas per volume of solvent solubility.

7. Prints results, and return to step 1.

Table of symbols

Problem Symbol	Program Symbol	Definition	Units
Main Program:			
T	T	Temperature	K
P	PP,P	Pressure	atm.
$H_{2,r}$	HENREF	Reference Henry´s constant	–
A	HENA(II)	constant for equation 1.27,	–
B	HENB(II)	and II identify gas used in	–
C	HENC(II)	the calculation.	–
	NK	the number of components, 2 for binary system.	
	NG	an amount of functional groups in the solvent	
	ITAB(I,J)	keep the information of the group´s number and the amount of groups for calculating interaction parameters in UNIFAC. I=1(gas) or 2(liquid), J = 1,27 (group´s number).	
T_b	TB	boiling point of solvent	K
ρ_L	DENSOLV	density of solvent	gm/ml
	MW	molecular weight of solvent	
x	XITER	the mole fraction of gas in the solvent.	

	GAMMA(I)	the activity coefficient
	GAMREF(I)	the reference activity coefficient

BLOCK DATA (Data area)

	ARR(I,J)	UNIFAC group interaction parameters I=1,27 and J=1,27
R_k	RR(I)	volume parameters, I=1,27
Q_k	QQ(I)	surface parameters, I=1,27
A	HENA(I)	constant A for equation 1.27
B	HENB(I)	constant B for equation 1.27
C	HENC(I)	constant C for equation 1.27
u_o	UO(I)	temperature-independent parameters of gas-water, see equation A2.1
u_1	U1(I)	temperature-independent parameters of gas-water, see equation A2.1

SUBROUTINE SYSTM

Q_k	Q(I)	surface area parameters, I=1,27
R_k	R(I)	group volume parameters, I=1,27
q_i	QS(I)	see equation 1.15
r_i	RS(I)	see equation 1.16
a_{ij}	PARA(I,J)	group interaction parameters, see equation 1.20. I=1,NG and J=1,NG
	ARR(I,J)	group interaction parameters data I=1,27 and J=1,27
	NY(I,J)	number of groups of type J in component I, see equations 1.15,1.16,

		1.17 and 1.18
u_o	UO(I)	temperature-independent parameters of gas-water, see equation A2.1
u_1	U1(I)	temperature-independent parameters of gas-water, see equation A2.1

SUBROUTINE GRES

X_m	XG(I)	the group fraction, I=1,NG
θ_1	TH(I)	group surface area fraction, I=1,NG
Γ_k	GAML(K)	activity coefficient of group K, see equation 1.18
	NY(I,J)	similar as in subroutine SYSTEM

SUBROUTINE GREF

	PARAB(M,N)	UNIFAC binary group interaction parameters for groups M and N relate to PARA(M,N)
$\Gamma_k^{(i)}$	GAM(I)	activity coefficient of group K in pure component I

SUBROUTINE GCOMB

$\Sigma\ q_j\ x_j$	QSS1	see equation 1.14
$\Sigma\ r_j\ x_j$	RSS1	see equation 1.21
	GAMMA(I)	the activity coefficient of combinatorial part

SUBROUTINE UNIFAC

	XA(I)	Activity coefficient of component I

SUBROUTINE ITER

	X1,X2	high and low guesses mole fraction of

		gas in the solvent	
	F1	f(X1) or f(x-high)	
	F2	f(X2) or f(x-low)	
	FR	f(XR) where XR=(X1+X2)/2	

SUBROUTINE FUNC

x_2	X(I)	mole fraction of gas in solvent	
	XITER	iteration value of mole fraction of gas in solvent	
γ_2	GAMMA(I)	activity coefficient of component I	
$\gamma_{2,r}^{\infty}$	GAMREF(I)	reference activity coefficient of component I	
$f(x\ )$	FCT	the objective function for iteration see above	
$H_{2,r}$	HENREF	reference Henry´s constant of gas I	

SUBROUTINE DENSITY

T_c	TC	critical temperature	K
P_c	PC	critical pressure	atm
V_c	VC	critical volume	cm^3/mole
Z_c	ZC	critical compressibility	
ΔT	DELTC	critical temperature increments (see equation A1.5)	
ΔP	DELPC	critical pressure increments (see equation A1.6)	
ΔV	DELVC	critical volume increments (see equation A1.7)	
	NGROUP(I)	group´s number	

	NAMOUNT(I)	the amount of group I	

SUBROUTINE BOILING

R_D	SUMRD	molar refraction, see equation A1.1.	
P	SUMPARA	parachor, see equation A1.1	
B	BCONST	the constant of chemical classes	
T_b	TB	boiling point	K

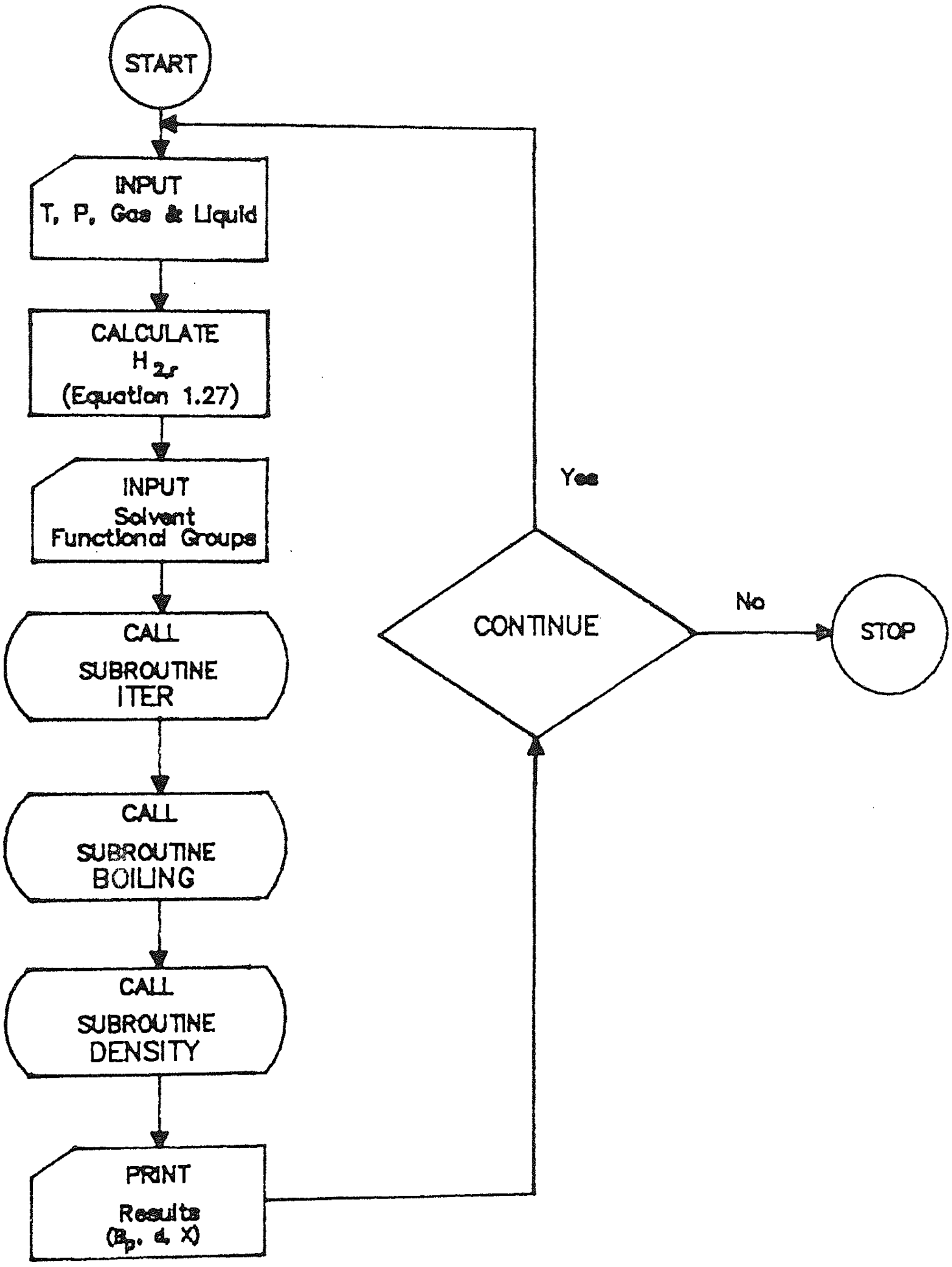


Figure A2.1 Solubility calculation flow diagram.

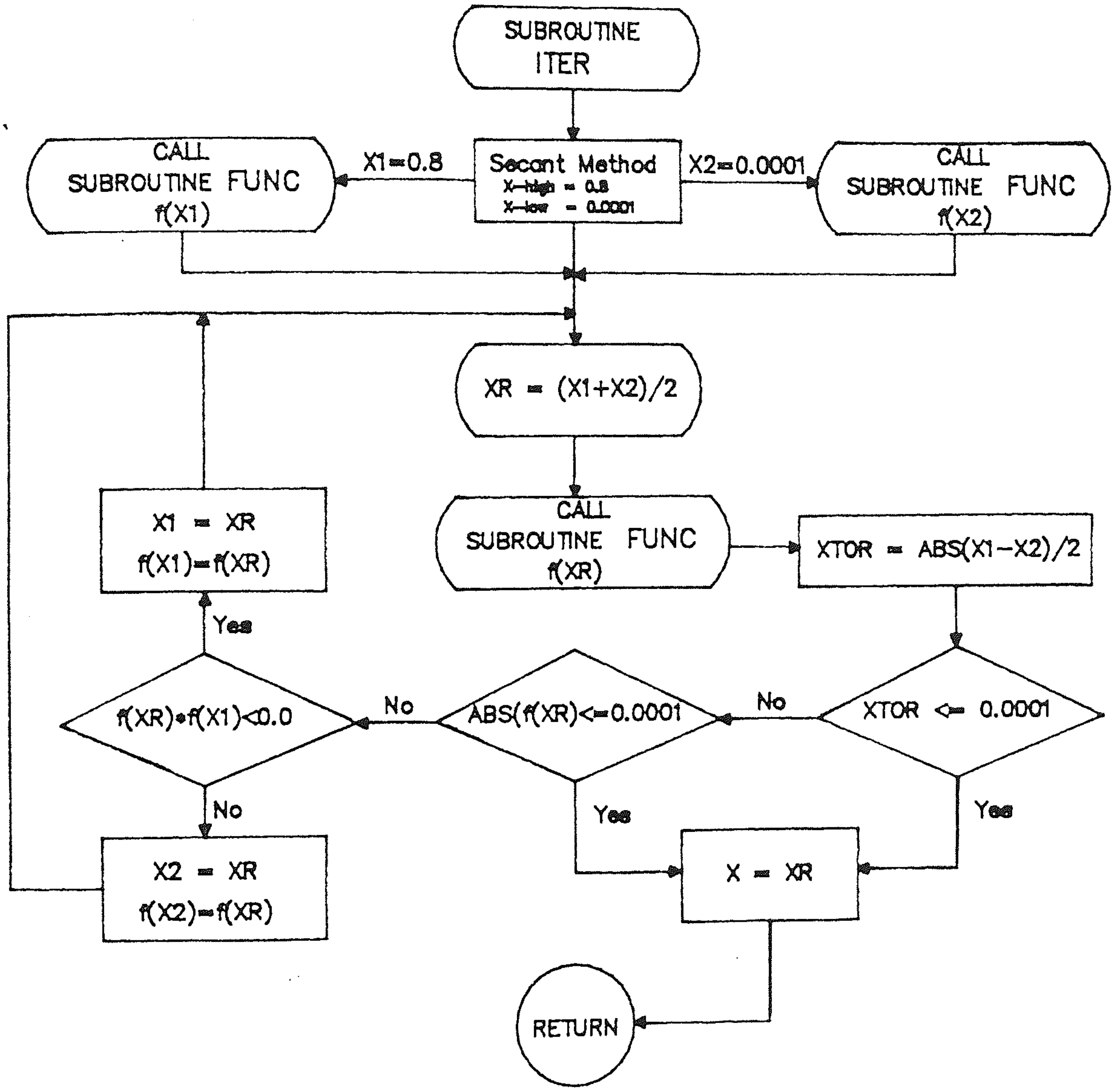


Figure A2.2 The flow diagram of SUBROUTINE ITER.

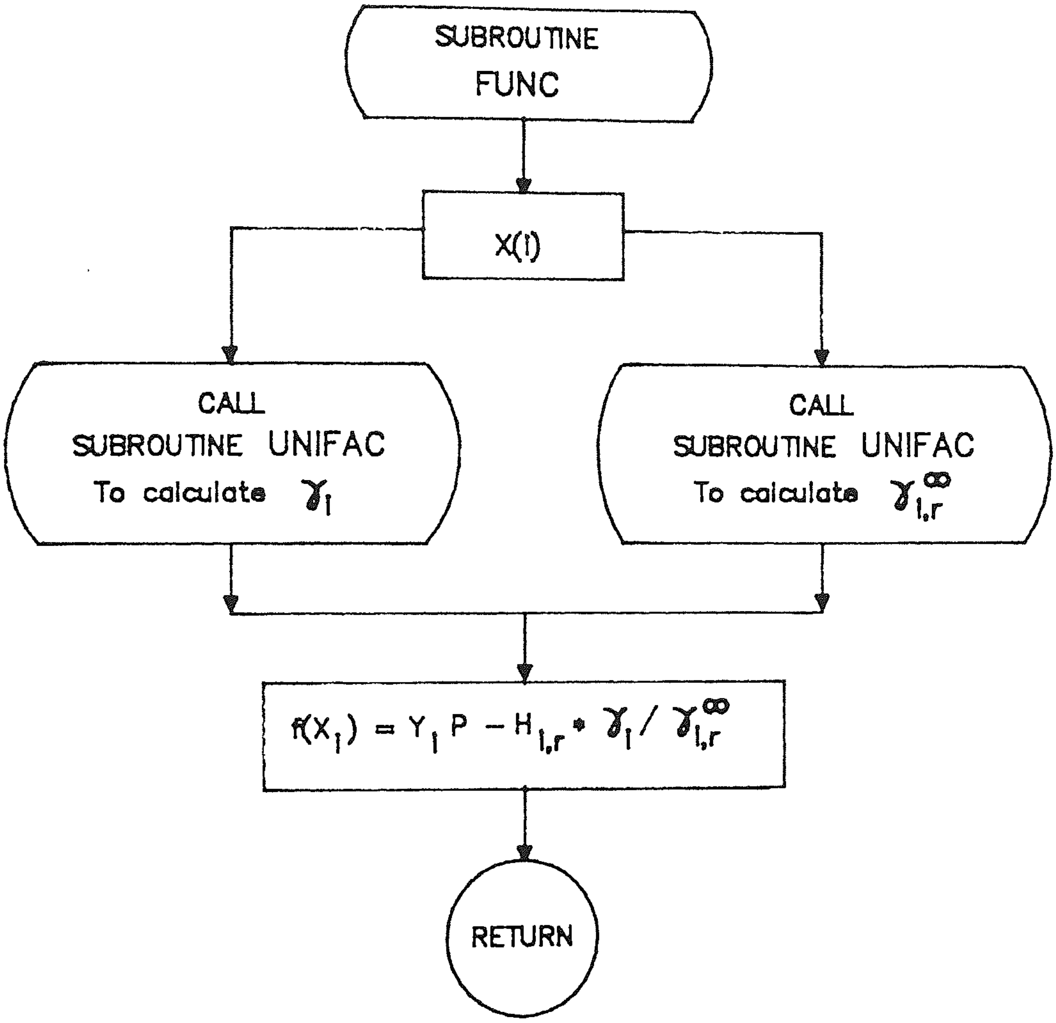


Figure A2.3 The flow diagram of SUBROUTINE FUNC.

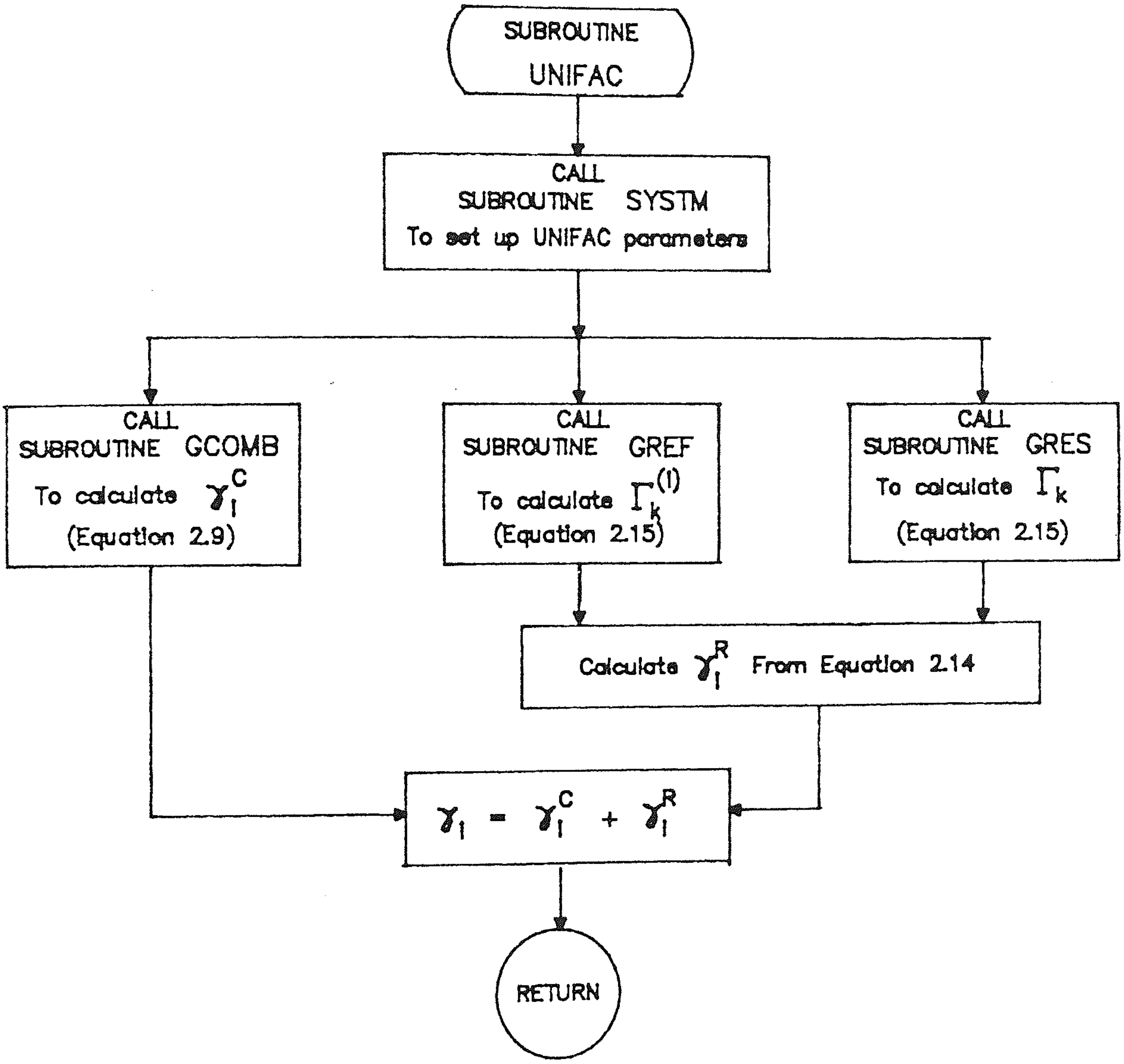


Figure A2.4 The flow diagram of SUBROUTINE UNIFAC.

APPENDIX 3

THE DESIGNED MOLECULES AND CARBON DIOXIDE SOLUBILITY

Table A3.1 The molecular structure and the solubility of carbon dioxide in solvents of class 1

(1). $CH_3-(CH_2)_4-CH_3$ (2). $CH_3-(CH_2)_5-CH_3$

(3). $CH_3-(CH_2)_6-CH_3$ (4). $CH_3-(CH_2)_7-CH_3$

(5). $CH_3-(CH_2)_8-CH_3$ (6). $CH_3-(CH_2)_9-CH_3$

(7). $CH_3-(CH_2)_{10}-CH_3$

GAS : CO_2 CLASS : 1

COMPOUND	MW	MOLE FRACTION	ccGAS/ccSOLVENT
1	86	0.0118	2.1819
2	100	0.0119	1.9661
3	114	0.0120	1.7993
4	128	0.0122	1.6666
5	142	0.0124	1.5586
6	156	0.0127	1.4691
7	170	0.0129	1.3932

Table A3.2 The molecular structure and the solubility of carbon dioxide in solvents of class 2

(1). $CH_3-(CH_2)_5-OH$

(2). $CH_3-(CH_2)_6-OH$

(3). $CH_3-(CH_2)_7-OH$

(4). $CH_3-(CH_2)_8-OH$

(5). $CH_3-(CH_2)_9-OH$

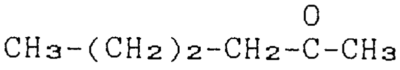
(6). $CH_3-(CH_2)_{10}-OH$

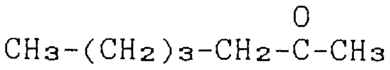
(7). $CH_3-(CH_2)_{11}-OH$

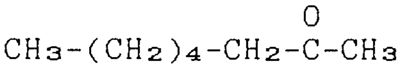
GAS : CO_2 CLASS : 2

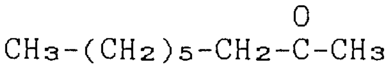
COMPOUND	MW	MOLE FRACTION	ccGAS/ccSOLVENT
1	102	0.0083	1.5058
2	116	0.0088	1.4132
3	130	0.0092	1.3380
4	144	0.0096	1.2755
5	158	0.0100	1.2219
6	172	0.0104	1.1758
7	186	0.0108	1.1350

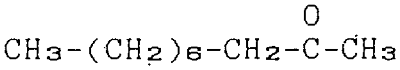
Table A3.3 The molecular structure and the solubility of carbon dioxide in solvents of class 3

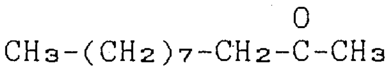
(1). 
$CH_3-(CH_2)_2-CH_2-\overset{O}{C}-CH_3$

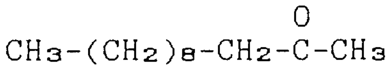
(2). 
$CH_3-(CH_2)_3-CH_2-\overset{O}{C}-CH_3$

(3). 
$CH_3-(CH_2)_4-CH_2-\overset{O}{C}-CH_3$

(4). 
$CH_3-(CH_2)_5-CH_2-\overset{O}{C}-CH_3$

(5). 
$CH_3-(CH_2)_6-CH_2-\overset{O}{C}-CH_3$

(6). 
$CH_3-(CH_2)_7-CH_2-\overset{O}{C}-CH_3$

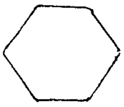
(7). 
$CH_3-(CH_2)_8-CH_2-\overset{O}{C}-CH_3$

GAS : CO_2 CLASS : 3

COMPOUND	MW	MOLE FRACTION	ccGAS/ccSOLVENT
1	100	0.0179	3.4319
2	114	0.0175	2.9751
3	128	0.0173	2.6391
4	142	0.0172	2.3810
5	156	0.0172	2.1774
6	170	0.0172	2.0121
7	184	0.0173	1.8756

Table A3.4 The molecular structure and the solubility of carbon dioxide in solvents of class 4

(1).



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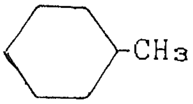

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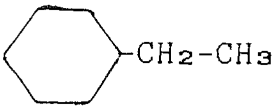

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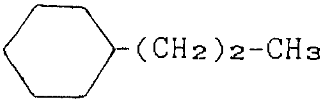

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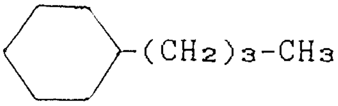

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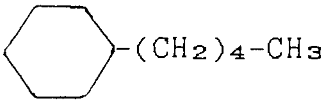
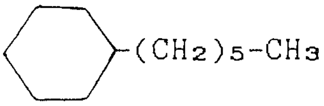


(7).

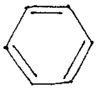


GAS : CO_2 CLASS : 4

COMPOUND	MW	MOLE FRACTION	ccGAS/ccSOLVENT
1	84	0.0075	1.7012
2	98	0.0083	1.6297
3	112	0.0094	1.6308
4	126	0.0097	1.5183
5	140	0.0101	1.4264
6	154	0.0105	1.3505
7	168	0.0108	1.2859

Table A3.5 The molecular structure and the solubility of carbon dioxide in solvents of class 5

(1).



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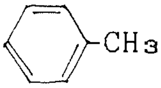
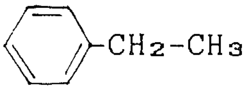
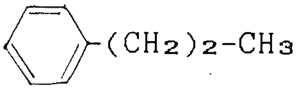


(3).



(4).



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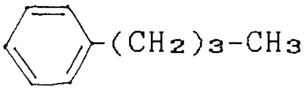

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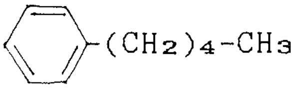

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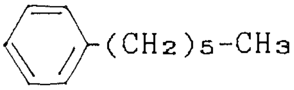
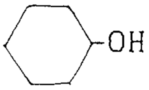


GAS : CO_2 CLASS : 5

COMPOUND	MW	MOLE FRACTION	ccGAS/ccSOLVENT
1	78	0.0097	2.7074
2	92	0.0100	2.3371
3	116	0.0113	2.2967
4	120	0.0115	2.0453
5	134	0.0117	1.8567
6	148	0.0119	1.7099
7	162	0.0122	1.5924

Table A3.6 The molecular structure and the solubility of carbon dioxide in solvents of class 6

(1).


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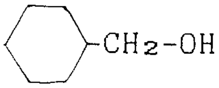

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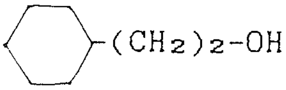

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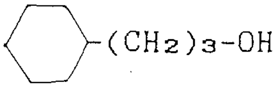
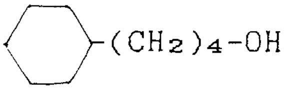


(5).


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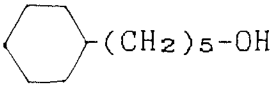

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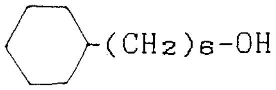
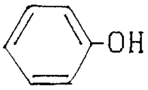


GAS : CO_2 CLASS : 6

COMPOUND	MW	MOLE FRACTION	ccGAS/ccSOLVENT
1	100	0.0059	1.1986
2	114	0.0064	1.1653
3	128	0.0070	1.1319
4	142	0.0075	1.1001
5	156	0.0080	1.0704
6	170	0.0084	1.0425
7	184	0.0089	1.0167

Table A3.7 The molecular structure and the solubility of carbon dioxide in solvents of class 7

(1).


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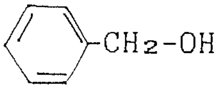

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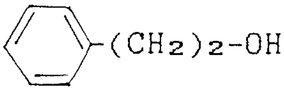

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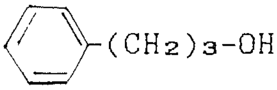

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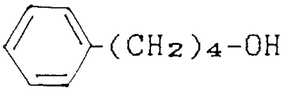

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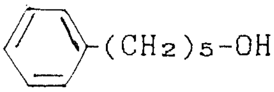

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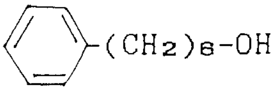
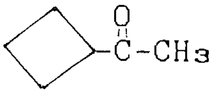


GAS : CO_2 CLASS : 7

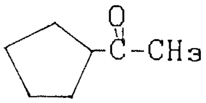
COMPOUND	MW	MOLE FRACTION	ccGAS/ccSOLVENT
1	94	0.0066	1.9035
2	108	0.0081	1.8308
3	122	0.0085	1.6543
4	136	0.0089	1.5245
5	150	0.0093	1.4237
6	164	0.0097	1.3428
7	178	0.0101	1.2761

Table A3.8 The molecular structure and the solubility of carbon dioxide in solvents of class 8

(1).



(2).



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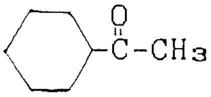
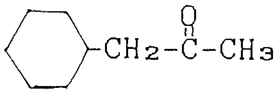


(4).



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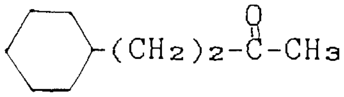
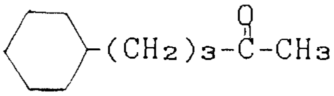


(6).



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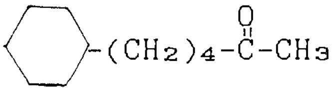
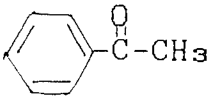


GAS : CO_2 CLASS : 8

COMPOUND	MW	MOLE FRACTION	ccGAS/ccSOLVENT
1	98	0.0145	3.1812
2	112	0.0144	2.7905
3	126	0.0144	2.5358
4	140	0.0145	2.2788
5	154	0.0146	2.0793
6	168	0.0148	1.9193
7	182	0.0150	1.7881

Table A3.9 The molecular structure and the solubility of carbon dioxide in solvents of class 9

(1).



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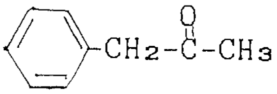
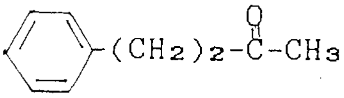
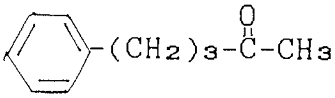


(3).



(4).



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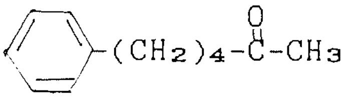
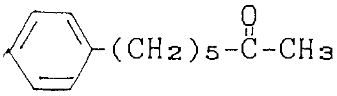
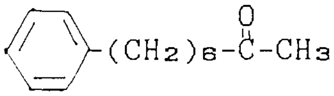


(6).



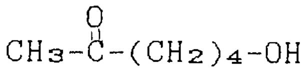
(7).

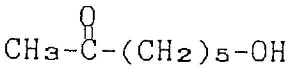


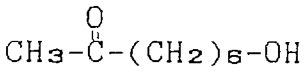
GAS : CO_2 CLASS : 9

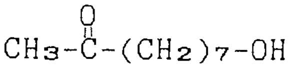
COMPOUND	MW	MOLE FRACTION	ccGAS/ccSOLVENT
1	120	0.0137	2.8057
2	134	0.0153	2.7419
3	148	0.0155	2.4654
4	162	0.0156	2.2472
5	176	0.0158	2.0711
6	190	0.0160	1.9260
7	204	0.0162	1.8044

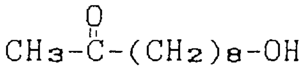
Table A3.10 The molecular structure and the solubility of carbon dioxide in solvents of class 10

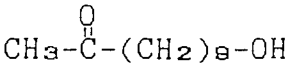
(1).

$CH_3-\overset{\overset{O}{\|}}{C}-(CH_2)_4-OH$

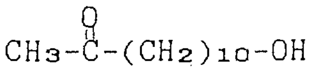
(2).

$CH_3-\overset{\overset{O}{\|}}{C}-(CH_2)_5-OH$

(3).

$CH_3-\overset{\overset{O}{\|}}{C}-(CH_2)_6-OH$

(4).

$CH_3-\overset{\overset{O}{\|}}{C}-(CH_2)_7-OH$

(5).

$CH_3-\overset{\overset{O}{\|}}{C}-(CH_2)_8-OH$

(6).

$CH_3-\overset{\overset{O}{\|}}{C}-(CH_2)_9-OH$

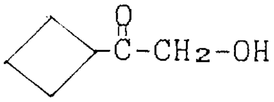
(7).

$CH_3-\overset{\overset{O}{\|}}{C}-(CH_2)_{10}-OH$

GAS : CO_2 CLASS : 10

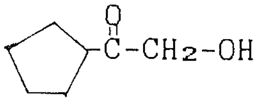
COMPOUND	MW	MOLE FRACTION	ccGAS/ccSOLVENT
1	116	0.0120	2.2261
2	130	0.0123	2.0212
3	144	0.0126	1.8627
4	158	0.0129	1.7359
5	172	0.0133	1.6516
6	186	0.0136	1.5443
7	200	0.0139	1.4696

Table A3.11 The molecular structure and the solubility of carbon dioxide in solvents of class 11

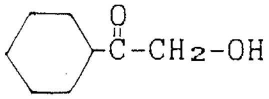
(1).



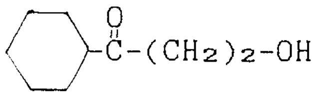
(2).



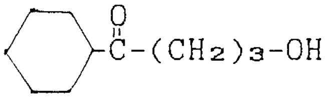
(3).



(4).



(5).



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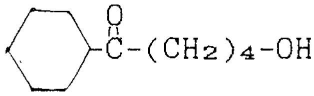

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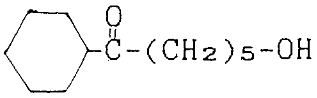
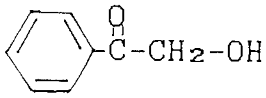


GAS : CO_2 CLASS : 11

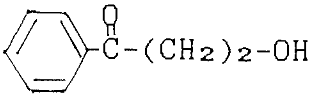
COMPOUND	MW	MOLE FRACTION	ccGAS/ccSOLVENT
1	114	0.0095	1.9763
2	128	0.0099	1.8537
3	142	0.0103	1.7531
4	156	0.0107	1.6319
5	170	0.0111	1.5337
6	184	0.0115	1.4523
7	198	0.0119	1.4928

Table A3.12 The molecular structure and the solubility of carbon dioxide in solvents of class 12

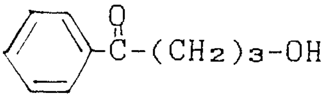
(1).



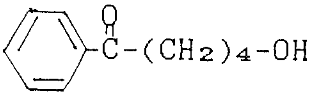
(2).



(3).



(4).



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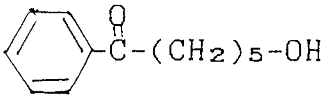

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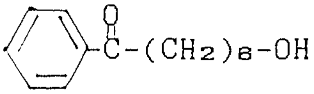

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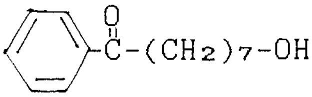
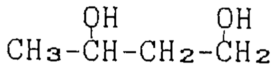


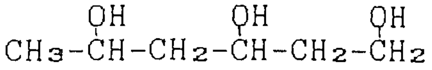
GAS : CO_2 CLASS : 12

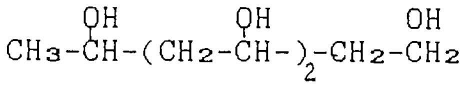
COMPOUND	MW	MOLE FRACTION	ccGAS/ccSOLVENT
1	136	0.0105	2.0476
2	150	0.0109	1.8691
3	164	0.0113	1.7301
4	178	0.0116	1.6177
5	192	0.0120	1.5256
6	206	0.0124	1.4473
7	220	0.0127	1.3807

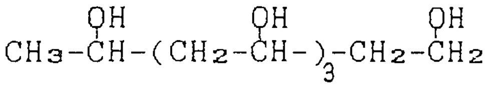
Table A3.13 The molecular structure and the solubility of carbon dioxide in alcohols (A-series).

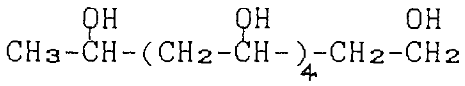
(1). CH_3-CH_2-OH

(2).

$CH_3-\overset{OH}{C}H-CH_2-\overset{OH}{C}H_2$

(3).

$CH_3-\overset{OH}{C}H-CH_2-\overset{OH}{C}H-CH_2-\overset{OH}{C}H_2$

(4).

$CH_3-\overset{OH}{C}H-(CH_2-\overset{OH}{C}H-)_2-CH_2-\overset{OH}{C}H_2$

(5).

$CH_3-\overset{OH}{C}H-(CH_2-\overset{OH}{C}H-)_3-CH_2-\overset{OH}{C}H_2$

(6).

$CH_3-\overset{OH}{C}H-(CH_2-\overset{OH}{C}H-)_4-CH_2-\overset{OH}{C}H_2$

GAS : CO_2 CLASS : A-series

COMPOUND	MW	MOLE FRACTION	ccGAS/ccSOLVENT
1	46	0.0063	2.5800
2	90	0.0050	1.1000
3	134	0.0050	0.7700
4	178	0.0052	0.6400
5	222	0.0055	0.5900
6	266	0.0058	0.5500

APPENDIX 4

THE PHYSICAL PROPERTIES OF THE DESIGNED SOLVENTS

TABLE A4.1 Estimated physical properties of the molecules in Class 1.

COMP.	MW	T_b	T_c	P_c	DENSITY	VAP.PRES	VIS
1	86.00	330.84	491.88	29.69	0.6436	0.30319	0.2661
2	100.00	359.40	522.84	26.87	0.6697	0.09907	0.3489
3	114.00	385.55	549.69	24.52	0.6897	0.03304	0.4537
4	128.00	409.79	573.46	22.54	0.7056	0.01109	0.5861
5	142.00	432.47	594.87	20.85	0.7185	0.00371	0.7534
6	156.00	453.85	614.47	19.38	0.7293	0.00123	0.9646
7	170.00	474.12	632.67	18.11	0.7384	0.00041	1.2315

TABLE A4.2 Estimated physical properties of the molecules in Class 2.

COMP.	MW	T_b	T_c	P_c	DENSITY	VAP.PRES	VIS
1	102.00	389.36	534.70	32.85	0.7493	0.01276	1.5556
2	116.00	410.60	555.07	29.32	0.7590	0.00409	2.1083
3	130.00	431.04	574.38	26.47	0.7674	0.00129	2.8387
4	144.00	450.70	592.75	24.13	0.7748	0.00040	3.8008
5	158.00	469.64	610.34	22.16	0.7812	0.00013	5.0676
6	172.00	487.90	627.29	20.49	0.7869	0.00004	6.7374
7	186.00	505.54	643.74	19.06	0.7918	0.00001	8.9448

TABLE A4.3 Estimated physical properties of the molecules in Class 3.

COMP.	MW	T_b	T_c	P_c	DENSITY	VAP.PRES	VIS
1	100.00	375.06	545.62	32.10	0.7710	0.04366	0.5259
2	114.00	397.36	566.52	28.73	0.7775	0.01594	0.6667
3	128.00	418.69	585.91	26.00	0.7834	0.00572	0.8441
4	142.00	439.12	604.01	23.73	0.7885	0.00202	1.0670
5	156.00	458.71	621.05	21.83	0.7930	0.00070	1.3471
6	170.00	477.54	637.22	20.21	0.7970	0.00024	1.6996
7	184.00	495.67	652.71	18.82	0.8005	0.00008	2.1445

TABLE A4.4 Estimated physical properties of the molecules in Class 4.

COMP.	MW	T_b	T_c	P_c	DENSITY	VAP.PRES	VIS
1	84.00	330.54	517.35	40.29	0.7687	0.30638	0.5817
2	98.00	359.62	549.39	34.76	0.7793	0.10287	0.7894
3	112.00	386.10	576.00	30.83	0.7885	0.03553	1.0347
4	126.00	410.54	599.13	27.69	0.7953	0.01246	1.3279
5	140.00	433.36	619.66	25.14	0.8005	0.00438	1.6778
6	154.00	454.83	638.21	23.01	0.8047	0.00153	2.0953
7	168.00	475.17	655.23	21.22	0.8081	0.00053	2.5942

TABLE A4.5 Estimated physical properties of the molecules in Class 5.

COMP.	MW	T_b	T_c	P_c	DENSITY	VAP.PRES	VIS
1	78.00	367.18	584.09	48.82	0.8822	0.07130	0.5698
2	92.00	392.55	608.03	41.38	0.8746	0.02581	0.5803
3	116.00	416.15	628.85	39.30	0.9480	0.00811	0.7151
4	120.00	438.30	647.29	31.72	0.8623	0.00349	0.8738
5	134.00	459.23	663.93	28.40	0.8586	0.00127	1.0608
6	148.00	479.12	679.17	25.72	0.8559	0.00046	1.2815
7	162.00	498.10	693.35	23.49	0.8538	0.00016	1.5425

TABLE A4.6 Estimated physical properties of the molecules in Class 6.

COMP.	MW	T_b	T_c	P_c	DENSITY	VAP.PRES	VIS
1	100.00	356.54	508.82	43.74	0.8329	0.06642	1.4544
2	114.00	381.91	534.92	37.70	0.8397	0.01902	2.1334
3	128.00	405.59	558.35	33.12	0.8442	0.00558	3.0330
4	142.00	427.85	579.72	29.53	0.8474	0.00165	4.2100
5	156.00	448.93	599.46	26.64	0.8497	0.00049	5.7376
6	170.00	468.97	617.94	24.26	0.8514	0.00015	7.7110
7	184.00	488.11	635.43	22.28	0.8528	0.00004	10.2556

TABLE A4.7 Estimated physical properties of the molecules in Class 7.

COMP.	MW	T_b	T_c	P_c	DENSITY	VAP.PRES	VIS
1	94.00	437.66	668.60	60.74	1.1001	0.00151	3.8494
2	108.00	452.44	640.15	44.90	0.9858	0.00036	6.6186
3	122.00	468.22	650.61	38.59	0.9613	0.00015	7.8837
4	136.00	484.35	661.92	33.83	0.9440	0.00006	9.5125
5	150.00	500.51	673.61	30.11	0.9311	0.00002	11.5633
6	164.00	516.52	685.49	27.12	0.9213	0.00001	14.1235
7	178.00	532.29	697.47	24.67	0.9136	0.00000	17.3128

TABLE A4.8 Estimated physical properties of the molecules in Class 8.

COMP.	MW	T_b	T_c	P_c	DENSITY	VAP.PRES	VIS
1	100.00	372.32	559.31	39.01	0.8692	0.04996	0.8307
2	112.00	398.47	589.79	35.15	0.8776	0.01653	1.2709
3	126.00	422.24	616.20	32.50	0.8969	0.00566	1.9173
4	140.00	442.23	632.35	29.03	0.8895	0.00214	2.3573
5	154.00	461.50	647.56	26.23	0.8839	0.00079	2.8846
6	168.00	480.08	662.00	23.92	0.8796	0.00028	3.5165
7	182.00	498.01	675.81	21.99	0.8762	0.00010	4.2753

TABLE A4.9 Estimated physical properties of the molecules in Class 9.

COMP.	MW	T_b	T_c	P_c	DENSITY	VAP.PRES	VIS
1	120.00	455.80	673.15	37.83	0.9878	0.00106	1.5333
2	134.00	472.66	683.35	33.23	0.9660	0.00045	1.7906
3	148.00	489.46	693.84	29.63	0.9497	0.00018	2.1001
4	162.00	506.04	704.40	26.73	0.9372	0.00007	2.4701
5	176.00	522.32	714.95	24.34	0.9272	0.00003	2.9116
6	190.00	538.25	725.48	22.34	0.9191	0.00001	3.4388
7	204.00	553.83	736.00	20.65	0.9125	0.00000	4.0700

TABLE A4.10 Estimated physical properties of the molecules in Class 10.

COMP.	MW	T_b	T_c	P_c	DENSITY	VAP.PRES	VIS
1	116.00	429.03	579.99	34.83	0.8694	0.00103	3.7525
2	130.00	445.07	593.09	30.87	0.8622	0.00039	4.7030
3	144.00	461.44	606.88	27.73	0.8580	0.00014	5.9733
4	158.00	477.83	620.98	25.16	0.8555	0.00005	7.6521
5	172.00	494.07	635.22	23.03	0.8541	0.00002	9.8638
6	186.00	510.08	649.52	21.23	0.8534	0.00001	12.7804
7	200.00	525.81	663.87	19.69	0.8531	0.00000	16.6398

TABLE A4.11 Estimated physical properties of the molecules in Class 11.

COMP.	MW	T_b	T_c	P_c	DENSITY	VAP.PRES	VIS
1	114.00	430.47	595.61	41.32	0.9600	0.00100	5.8073
2	128.00	449.65	615.49	37.60	0.9689	0.00033	8.5756
3	142.00	467.85	633.91	34.49	0.9767	0.00011	12.5413
4	156.00	483.26	645.31	30.65	0.9602	0.00004	15.6878
5	170.00	498.77	657.21	27.57	0.9478	0.00002	19.8345
6	184.00	514.21	669.41	25.05	0.9381	0.00001	25.2741
7	198.00	529.50	685.83	26.20	1.0042	0.00000	34.4467

TABLE A4.12 Estimated physical properties of the molecules in Class 12.

COMP.	MW	T_b	T_c	P_c	DENSITY	VAP.PRES	VIS
1	136.00	503.99	688.75	40.13	1.0762	0.00001	16.7330
2	150.00	515.71	694.07	35.07	1.0438	0.00000	18.5403
3	164.00	528.35	701.20	31.14	1.0194	0.00000	22.8767
4	178.00	541.49	709.53	27.99	1.0004	0.00000	27.6005
5	192.00	554.89	718.72	25.41	0.9854	0.00000	33.7730
6	206.00	568.37	728.56	23.26	0.9731	0.00000	41.8074
7	220.00	581.84	738.92	21.44	0.9631	0.00000	52.2811

TABLE A4.13 Estimated physical properties of the molecules in A-series.

COMP.	MW	T_b	T_c	P_c	DENSITY	VAP.PRES	VIS
A1	46.00	336.58	499.29	63.07	0.7669	0.16249	0.850
A2	90.00	361.48	483.71	49.31	0.8028	0.02916	1.699
A3	134.00	400.51	504.11	39.24	0.8421	0.00119	5.006
A4	178.00	439.66	539.00	32.37	0.8982	0.00004	21.024
A5	222.00	476.85	588.03	27.49	0.9630	0.00000	142.368
A6	266.00	511.83	656.08	23.86	1.0287	0.00000	1967.521

APPENDIX 5

CALCULATION OF GAS SOLUBILITIES FROM EXPERIMENTAL READINGS

The solubility of gas in the solvent can be defined as the mole fraction of gas (x_1) in the solvent. The mole fraction of gas in the solvent is given by

$$x_1 = \frac{ng}{ng + nl} \qquad \text{(A5.1)}$$

where

x_1 = mole fraction of gas in solvent

ng = number of moles of gas absorbed by solvent

nl = number of moles of solvent.

By taking a mass balance on the gas before and after being absorbed by the solvent:

$$ng = ng_i^G - ng_f^G \qquad \text{(A5.2)}$$

and from the second virial equation of state (V = RT/P + B), equation A5.2 can be written as;

$$ng = \frac{P_t \triangle V_G}{RT + B_1 P_t} + \frac{P_t \triangle V_L}{RT + B_m P_t} - \frac{y_1 P_t \triangle V_L}{RT + B_m P_t} \qquad \text{(A5.3)}$$

where

ng_i = initial number of moles of gas in the system before absorption take place.

ng_f = final number of moles of gas after absorption takes place.

P_t = total pressure of the system.

$\triangle V_G$ = volume of gas absorbed from the gas burette.

$\triangle V_L$ = volume of gas absorbed from the solution burette (= volume of solution).

T = temperature of the system.

B_1 = second virial coefficient of the gas in the gas burette.

B_m = second virial coefficient of the mixture in the solution burette.

R = gas constant

According to the equation of Lennard-Jones and Cook, B_m is given by

$$B_m = y_1^2 B_1 + y_2^2 B_2 + 2 y_1 y_2 B_{12} \qquad \text{(A5.4)}$$

where

B_{12} = second virial coefficient of interaction.

B_1 ,B_2 = second virial coefficients of the gas and the solvent.

y_1 ,y_2 = mole fraction in the gas phase of the gas and the solvent.

Subscript 1 refers to the gas.

2 refers to the solvent.

All variables in equations (A5.1) to (A5.4) are obtained from the experimental readings, except the second virial coefficients and the mole fraction of gas and solvent in the gas phase. For the second virial coefficients of gas and solvent (B_1 and B_2) and the second virial coefficient of interaction (B_{12}), the method of Hayden and O'Connell [184] is used. The mole fractions, y_1 and y_2, are obtained as below.

For a pure liquid solvent, at relatively low pressure, the relation between fugacity and the second virial coefficient can be evaluated from the following expression, using the pressure series of the virial equation of state:

$$\ln \left(\frac{F_2}{P_t} \right) = \frac{B_2 P_t}{RT} \qquad \text{(A5.5)}$$

where

F_2 = fugacity of the pure solvent

P_t = total pressure

and for a solvent in a mixture:

$$\ln \left(\frac{f_2}{y_2 P_t} \right) = \frac{\bar{B}_2 P_t}{RT} \qquad \text{(A5.6)}$$

where

f_2 = fugacity of solvent in the mixture.

$\bar{B}_2$ = partial molar second virial coefficient of solvent in the mixture.

Rearranging (A5.6),

$$y_2 = \frac{f_2}{P_t} \exp\left(- \frac{\bar{B}_2 P_t}{RT} \right) \qquad (A5.7)$$

Since the solvent contains a small amount of the gas, the solvent should obey Raoult's law expression, i.e.

$$f_2 = x_2 \overset{o}{F}_2 \qquad (A5.8)$$

and

$$\overset{o}{F}_2 = \overset{o}{P}_2 \exp\left(\frac{B_2 \overset{o}{P}_2}{RT}\right) \qquad (A5.9)$$

where

x_2 = mole fraction of solvent.

$\overset{o}{F}_2$ = fugacity at standard reference.

$\overset{o}{P}_2$ = solvent vapour pressure.

Substituting equations (A5.8) and (A5.9) into equation (A5.7) gives

$$y_2 = \frac{x_2 \overset{o}{P}_2}{P_t} \exp\left(\frac{B_2 \overset{o}{P}_2 - B_2 P_t}{RT}\right) \qquad (A5.10)$$

The partial molar second virial coefficient of the component can be obtained from the Lennard-Jones and Cook relationship.

$$B_2 = B_m + y_1\left(\frac{dB_m}{dy_2}\right)$$

$$= B_2 + y_1^2\ (2\ B_{12} - B_1 - B_2) \qquad (A5.11)$$

The mole fraction solubility of gas corresponding to a gas partial pressure of 1 atmosphere is obtained from the expression

$$X_1^{760} = x_1\left(1.0 + \frac{760 - P}{P_1}\right) \qquad (A5.12)$$

where

$P_1 = P\ (1.0 - y_2 - m)$

m = percentage of air in the system

The values of pure component vapour pressures are calculated from the Antoine equation. To calculate equation (A5.10) for y_2 which contains the term B_2 and this term itself depends on y_2, the iteration method was used to solve this problem.

APPENDIX 6

THE GROUP CONTRIBUTION EQUATION OF STATE MODEL (GCEOS)

Group contribution equation of state (GCEOS) model

In 1984, a group-contribution equation of state (GCEOS) model was developed by Skjold-Jorgensen [148]. This model was combined the group-contribution concept with the basic ideas of an equation of state. Skjold-Jorgensen suggested that the molar configuration Helmholtz function can be obtained from

$$\left(\frac{A^C}{RT}\right) = -\ln V + \left(\frac{A^R}{RT}\right)_{fv} + \left(\frac{A^R}{RT}\right)_{att} \tag{A6.1}$$

and the residual Helmholtz function at constant volume is the sum of two contributions, free-volume and attractive,

$$\left(\frac{A^C}{RT}\right)_{T,V,\underline{n}} = \left(\frac{A^R}{RT}\right)_{fv} + \left(\frac{A^R}{RT}\right)_{att} \tag{A6.2}$$

The free-volume contribution term is that for hard spheres derived by Mansoori and Leland [112].

$$\left(\frac{A^R}{RT}\right)_{fv} = 3(\lambda_1\lambda_2/\lambda_3)(Y-1)+(\lambda_2^3/\lambda_3^2)(-Y+Y^2-\ln Y)+n\ln Y \tag{A6.3}$$

where

$$\lambda_k = \sum_j^{NC} n_j d_j^k \tag{A6.4}$$

$$Y = (1 - \pi\lambda_3/6V)^{-1} \tag{A6.5}$$

The attractive term is based on the Van der Waals equation

$$\left(\frac{A^R}{RT}\right)_{att} = -a\rho \qquad (A6.6)$$

where the energy parameter has been defined as:

$$a = (z/2)\, g\, q^2 \qquad (A6.7)$$

to make it amenable for group contribution treatment. The parameter g is the characteristic attractive energy per segment, and q is the surface area parameter as defined in the UNIFAC method (Fredenslund [54]). The calculation of (A^R/RT) for mixtures is based on an expression similar to the NRTL equation, Renon and Prausnitz [138], but written in a group contribution form:

$$\left(\frac{A^R}{RT}\right)_{att} = -(z/2)\sum_{i}^{NC} n_i \sum_{j}^{NG} \upsilon_j^i\, q_i \sum_{k}^{NG} \theta_k (g_{kj}\, \tilde{q}/RTV)\, \tau_{kj} / \sum_{l}^{NG} \theta_l \tau_{lj} \qquad (A6.8)$$

where

$$\tilde{q} = \sum_{i}^{NC} n_i \sum_{j}^{NG} \upsilon_j^i q_j \qquad (A6.9)$$

$$\theta_j = (q_j/q) \sum_{i}^{NC} \upsilon_j^i n_i \qquad (A6.10)$$

$$\tau_{ji} = \exp(\alpha_{ji} \Delta g_{ji}\, \tilde{q}/RTV) \qquad (A6.11)$$

$$\Delta g_{ji} = g_{ji} - g_{ii} \qquad (A6.12)$$

As in the UNIFAC equation the interactions are considered to take place through the surface of the segments, and correspondingly surface fractions are used instead of mole fractions. The coordination number, z, which is the number of nearest-neighbour segments to any given segment in a lattice-like structure, is set to 10.

GCEOS parameters

The repulsive part of the GCEOS requires only pure-component parameters, namely the hard-sphere diameters. These are obtained from acentric factors, normal boiling points or particular vapour pressures. The hard-sphere diameter is assumed temperature-dependent following the generalized expression proposed by Ferminglia and Mollerup.

$$d = 1.065655\, d_c(1.0-0.12\exp(-2T_c/3T)) \qquad (A6.13)$$

where

$$d_c = (0.08943RT_c/P_c)$$

Besides pure-component parameters the GCEOS has group parameters and binary parameters.

The parameters are the group surface parameter and the attractive energy parameter between like segments (g_{ii}). The attractive parameter is assumed to be temperature-dependent:

$$g_{jj} = g^*_{jj}(1.0+g_{jj}(T/T^*_j - 1)+g_{jj}\ln(T/T^*_j)) \qquad (A6.14)$$

The binary parameters are the binary damping factor (α_{ij}), which are considered asymmetric, and the attractive energies between unlike segments (g_{ij}), which are defined as:

$$g_{ij} = k_{ij}(g_{ii}\ g_{jj})^{1/2} \qquad (A6.15)$$

where k_{ij} is a symmetric binary parameter, which is temperature dependent:

$$k_{ij} = k^*_{ij}(1 + k'_{ij}\ln(T/T^*_{ij})) \qquad (A6.16)$$

where $T^*_{ij} = (T^*_i + T^*_j)/2$ (A6.17)

The group parameters were estimated in the way explained by Skjold-Jorgensen. The pure group parameters are shown in Table A7.1, the binary parameters k_{ij} are shown in Table A7.2, and the binary damping factors are shown in Table A7.3.

Expression for fugacity coefficients and compressibility factors from GCEOS model

The properties neccesary for the phase-equilibrium calculations may be derived by differentiation of equation A6.1. The compressibility factors are derived by differentiation with respect to volume:

$$Z = -v \frac{\delta}{\delta v}(A^{C}/RT)_{T,\underline{n}} = Z_{fv} + Z_{att} + 1 \qquad (A6.18)$$

where

$$Z_{fv} = -v[3(\lambda_1 \lambda_2/\lambda_3) + (\lambda_2^3/\lambda_3^2)(2Y-1-\frac{1}{Y}) + \frac{n}{Y}](\frac{\delta Y}{\delta V})_{T,\underline{n}} \qquad (A6.19)$$

$$Z_{att} = -(z/2n)\sum_{j}^{NG} \bar{\upsilon}_j q_j (H_{5j} + H_{2j} - H_{2j} H_{6j}/H_{4j})/H_{4j} \qquad (A6.20)$$

$$\bar{\upsilon}_j = \sum_{i}^{NC} \upsilon_j^i n_i \qquad (A6.21)$$

The fugacity coefficients are derived from the expression for the residual Helmholtz function at constant volume, equation 2.25.

$$\ln \phi_i = \frac{\delta}{\delta n_i}(\frac{A^R}{RT})_{T,V,n_{k \neq i}} - \ln Z \qquad (A6.22)$$

$$= \ln \phi_{i,fv} + \ln \phi_{i,att} - \ln Z \qquad (A6.23)$$

where

$$\ln \phi_{i,fv} = 3(Y-1)(\frac{\lambda_1 \lambda_2}{\lambda_3})[\frac{\lambda_1'}{\lambda_1} + \frac{\lambda_2'}{\lambda_2} - \frac{\lambda_3'}{\lambda_3} + (\frac{Y'}{Y-1})]$$
$$+ (\frac{\lambda_2^3}{\lambda_3^2})(Y^2 - Y - \ln Y)(3\frac{\lambda_2'}{\lambda_2} - 2\frac{\lambda_3'}{\lambda_3})$$
$$+ (\frac{\lambda_2^3}{\lambda_3^2})(2Y - 1 - \frac{1}{Y})Y' + (\frac{n}{Y})Y' \qquad (A6.24)$$

with $\lambda'_k = d_i^k$ (A6.25)

$$Y' = Y^2 \Pi d_i^3/6V \qquad (A6.26)$$

and

$$\ln\phi_{i,att} = -\left(\frac{z}{2}\right)\left[\sum_j^{NG} PS_{ij}\, H_{2j}/H_{4j} + \sum_j^{NG} \theta_j\, (H_{3ij} + MS_i\, H_{5j})/H_{4j} - \sum_j^{NG} \theta_j\, H_{2j}\, (H_{7ij} - H_{4j}\, MS_i + H_{6j}\, MS_i)/H_{4j}^2\right] \qquad (A6.27)$$

The auxiliary quantities are defined as follows:

$$PS_{ij} = \nu_j^i\, q_j \qquad (A6.28)$$

$$MS_i = \sum_j^{NG} PS_{ij} \qquad (A6.29)$$

$$H_{2j} = \sum_k^{NG} \theta_k \tau_{kj} g_{kj}\ \tilde{q}/VRT \qquad (A6.30)$$

$$H_{3ij} = \sum_k^{NG} PS_{ik} \tau_{kj} g_{kj}\ \tilde{q}/VRT \qquad (A6.31)$$

$$H_{4j} = \sum_k^{NG} \theta_k\, \tau_{kj} \qquad (A6.32)$$

$$H_{5j} = \sum_k^{NG} \theta_k \tau_{kj}\, (g_{kj}\, \tilde{q}/VRT)\, \alpha_{kj}\quad g_{kj}\, \tilde{q}/VRT \qquad (A6.33)$$

$$H_{6j} = \sum_k^{NG} \theta_k\, \tau_{kj} \alpha_{kj} \Delta g_{kj}\, q/VRT \qquad (A6.34)$$

$$H_{7ij} = \sum_k^{NG} PS_{ik}\ \tau_{kj} \qquad (A6.35)$$

The details of GASHIGH.FOR program

In the previous section, the group contribution equation of state (GCEOS) was described in detail. This section describes the computer program which calculates the gas solubility at high pressure by using the GCEOS method. The program was written in Fortran under filename GASHIGH.FOR for the source program and GASHIGH.EXE for the executable program. Both programs are recorded on the diskette Number 1 enclosed in the back cover of this thesis.

Figure A6.1 shows a general flow diagram of the solubility calculation procedure . The GASHIGH.FOR program;

1. Reads three data files, STEEND1, STEEND2 and STEEND3. The STEEND1 contains data set for the gas-solvent used and is described in detail later in this section. The STEEND2 contains binary nonrandomness parameters α_{ij} and α_{ji} for the GCEOS method. The STEEND3 contains binary parameters k^{*}_{ij} and k'_{ij} for the GCEOS method. The pure-component group parameters, T*, q, g*, g′ and g′′, are in the BLOCK DATA within the program.

2. Calls subroutines DALPHA and KPARA to set the GCEOS parameters for the calculation.

3. Computes the gas phase compressibility factor z from the equation A6.18. Because equation A6.18 is an implicit expression for the molar volume, v, which must be solved iteratively, the equation is solved by the Secant method.

4. Computes the gas phase fugacity coefficient (ϕ_i^V)

equations A6.23 and A6.27.

5. Reads the guessed value of mole fraction in the liquid x_1.

6. Computes the liquid phase compressibility factor Z. The calculation of Z is similar to Step 3 above except that it uses the mole fraction in the liquid phase (x_1) instead of the mole fraction in the gas phase (y_1).

7. Computes the liquid phase fugacity coefficient (ϕ_i^L) from equations A6.23 and A6.27.

8. Computes the folowing equation

$$f(x_1) = y_1 \phi_i^V - x_1 \phi_i^L$$

9. Checks for convergence, i.e. $f(x_1) <= 0.0001$ and $\Sigma x_1 = 1.0$, continues to the next step when the convergence criteria are obtained; otherwise, sets $x_1 = y_1 (\phi_i^V / \phi_i^L)$ and returns to step 6.

10. Prints results when the convergence criteria are satisfied.

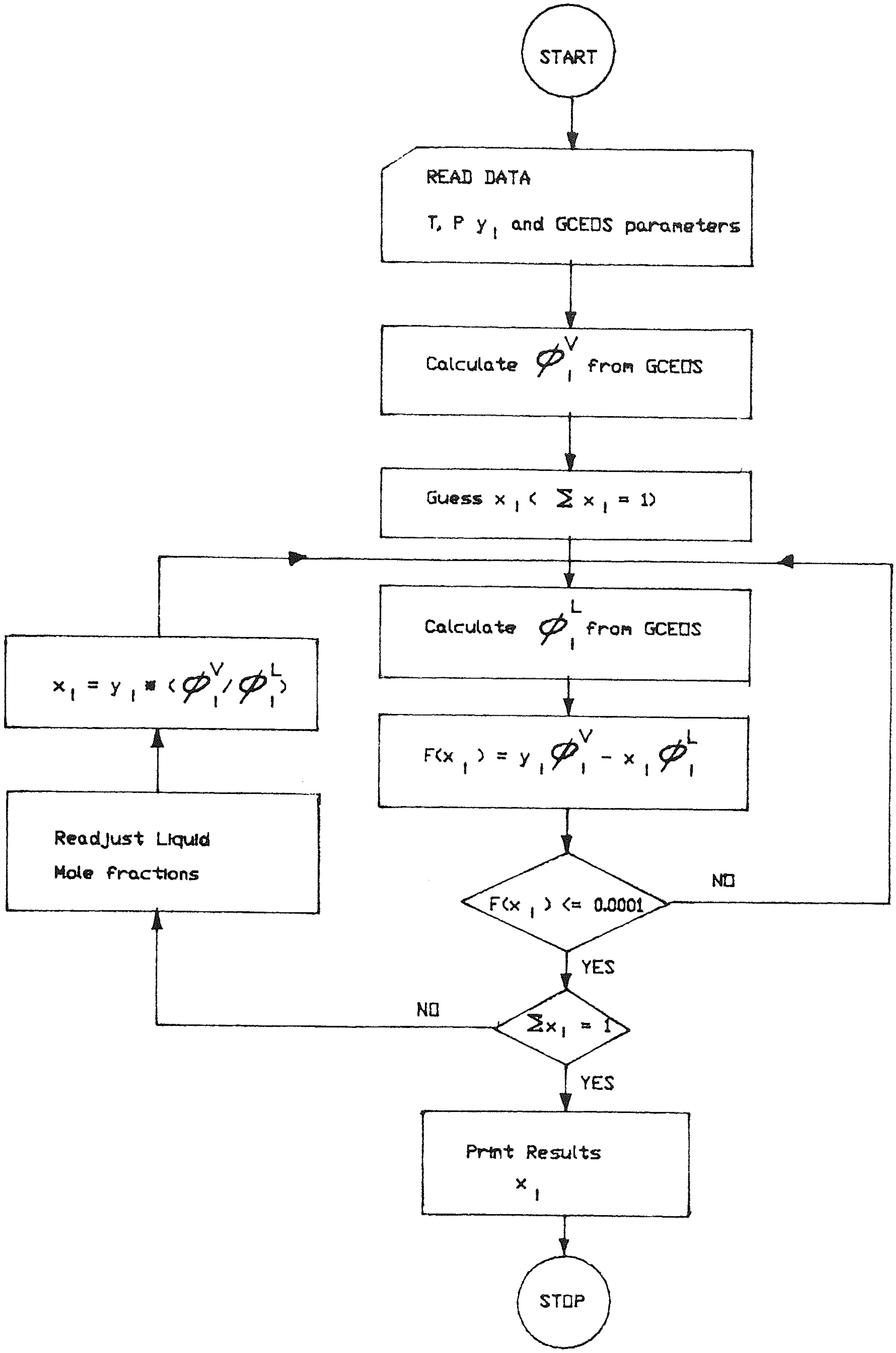


Figure A6.1 Schematic diagram of high pressure VLE calculation.

Table of Symbols

Problem Symbol	Program symbol	Definition	Units
Main Program:			
y_i	Y(I)	gas phase mole fraction	
x	X(I)	liquid phase mole fraction	
T_c	TC	critical temperature	K
P_c	PC	critical pressure	atm
V	VB	total volume	
z	Z	compressibility factor	
	NC	number of components	
	NG	number of groups	
	IP(I),NGR(I), NTAB(I), ITAB(I,J)	Readed data from data file STEEND1, these will be described later.	
T_i^*	TS(I)	GCEOS pure-component parameters	K
q_i	Q(I)	GCEOS pure-component parameters	
g^*	GS(I)	,, ,,	
g_i'	GD(I)	,, ,,	
g_i''	GDD(I)	,, ,,	
d_i	D(I)	The hard-sphere diameter, see equation A6.13	
d_c	DC(I)	see equation A6.13	
g_{jj}	G(J,J)	attractive-energy parameter between	

		like segment, see equation A6.14.
g_{ij}	G(I,J)	attractive-energy parameter between unlike segment, see equation A6.15.
T^{*}_{ij}	TTS(I,J)	see equation A6.17
k_{ij}	K(I,J)	a symmetric binary parameter, see equation A6.16
Δg_{ij}	DELG(I,J)	see equation A6.12
	VN(I,J)	group-composition variable
PS_{ij}	PS(I,J)	see equation A6.28
MS_i	MS(I)	see equation A6.29
	FUGV(I)	gas phase fugacity coefficient
	FUGL(I)	liquid phase fugacity coefficient
R	R	gas constant

SUBROUTINE CALZ

τ_{ij}	TAU(I,J)	exponential weighting factor, see equation A6.9
$\bar{\nu}_i$	VBAR(I)	see equation A6.21
n	NMOL(I)	number of mole of component i
λ	LAMDA(I)	see equation A6.4
Y	YB	see equation A6.5
$\hat{q}$	QBAR	see equation A6.9
θ_i	SETA(I)	surface fraction, see equation A6.10.
α_{ij}	ALPHA(I,J)	nonrandomness parameters
$H_{2,j}$	H2(J)	the auxiliary variable, see equa. A6.30
$H_{3,ij}$	H3(I,J)	,, ,, , see equa. A6.31
$H_{4,j}$	H4(J)	,, ,, , see equa. A6.32

$H_{5,j}$	H5(J)	,, ,, , see equa. A6.33
$H_{6,j}$	H6(J)	,, ,, , see equa. A6.34
$H_{7,ij}$	H7(I,J)	,, ,, , see equa. A6.35

SUBROUTINE FUGACITY

$\phi_{i,fv}$	GAMV(I)	free volume fugacity coefficient, see equation A6.24
$\phi_{i,att}$	GAMATT(I)	attractive-fugacity coefficient, see equation A6.27.
	FUG(I)	fugacity coefficient, see equa. A6.23
Y'	YD	see equation A6.26

SUBROUTINE DALPHA

	ALA(I,J)	GCEOS binary nonrandomness parameters, I=1,23, J=1,23
	ALPHA(I,J)	binary nonrandomness parameters between group I and J, I=1,NG and J=1,NG.

BLOCK DATA

T^*	TSS(I)	GCEOS pure-component parameters	K
q	QQ(I)		
g^*	GSS(I)	,, ,,	
g'	GGD(I)	,, ,,	
g''	GGDD(I)	,, ,,	

SUBROUTINE KPARA

k^*_{ij}	SK(I,J)	binary parameters of 23 groups, I=1,23 and J=1,23
k^*_{ij}	SKD(I,J)	binary parameters between groups I and J, where I=1,NG and J=1,NG

k'_{ij}	DK(I,J)	binary parameters of 23 groups, I=1,23 and J=1,23
k'_{ij}	DKD(I,J)	binary parameters between groups I and J, where I=1,NG and J=1,NG

Data file STEEND1

This data file can be modified to suit the system needs. It contains the variables which are described below.

Assumme the system consists of hydrogen, nitrogen carbon dioxide and n-pentanone.

COMPOUND	GROUP NUMBER	AMOUNT OF GROUP	T	P
Hydrogen	15	1	33.2	12.8
Nitrogen	16	1	126.2	33.5
Carbon dioxide	21	1	304.2	72.8
n-pentanone	1	1	564.0	38.4
	2	2		
	12	1		

(Note. n-pentanone consists of 3 groups i.e. groups 1, 2, and 12).

The following table shows the data input from the data file STEEND1 and variables in the GASHIGH.FOR program.

PROGRAM VARIABLE	**DATA INPUT IN STEEND1**
SYSNAME	H2 + N2 + CO2 + n-Propanone
NC,NG	4,6
VB	100.0
(IP(I),I=1,NG)	1,2,12,15,16,21
(NGR(I),I=1,NC)	1,1,1,3
I=1,NC	
TC(I),PC(I)	33.2,12.8
	126.2,33.5
	304.2,72.8
	564.0,38.4
I=1,NC	
(NTAB(J),ITAB(I,NTAB(J)), J=1,NGR(I))	15,1
	16,1
	21,1
	1,1,2,2,12,1
Z1,Z2	0.1,1.1

Notes:

NTAB(J) = variable for group´s number;

ITAB(I,NTAB(J))= amount of groups;

Z1 and Z2 are the guessed values of input data for the compressibility factor iterations.

APPENDIX 7

THE GCEOS PARAMETERS

Pure-component group parameters for the GC-EOS[a]

Group	Number	T^* (K)	q	g^*	g'	g''
CH_3	1	600.0	0.848	307640.0	−0.9804	0.0000
CH_2	2	600.0	0.540	355130.0	−0.9043	0.0000
CH	3	600.0	0.228	266290.0	−0.3426	0.0000
$Cy-CH_2$	4	600.0	0.540	468640.0	−0.5803	0.0000
Cy-CH[‡]	5	600.0	0.228	468640.0	−0.5803	0.0000
ACH	6	600.0	0.400	723210.0	−0.6060	0.0000
AC	7	600.0	0.285	723210.0	−0.6060	0.0000
$ACCH_3$	8	600.0	0.968	506290.0	−0.8013	0.0000
$ACCH_2$	9	600.0	0.660	506290.0	−0.8013	0.0000
CH_3OH	10	512.6	1.432	1109600.0	−0.9474	0.0000
CH_2OH	11	512.6	1.124	1109600.0	−0.9474	0.0000
CH_3CO	12	600.0	1.488	945860.0	−0.5840	0.0000
CH_2CO	13	600.0	1.180	945860.0	−0.5840	0.0000
H_2O	14	647.3	0.866	1697200.0	−0.6707	0.0000
H_2	15	33.2	0.571	179460.0	−0.0843	0.1351
N_2	16	126.2	0.985	330360.0	−0.1910	−0.0806
CO	17	132.9	1.060	309610.0	−0.1288	−0.1074
O_2	18	154.6	0.955	353780.0	−0.2750	0.0000
CH_4	19	190.6	1.160	402440.0	−0.2762	0.0221
C_2H_4	20	282.4	1.485	486510.0	−0.3724	0.0000
CO_2	21	304.2	1.261	531890.0	−0.5780	0.0000
C_2H_6	22	305.4	1.696	452560.0	−0.3758	0.0000
H_2S	23	373.2	1.163	780070.0	−0.3946	0.0000

[a] The units of the g^* parameters correspond to temperatures in Kelvin, volumes in $cm^3\,mol^{-1}$ and a gas constant $R = 82.05\ cm^3\,atm.mol^{-1}\,K^{-1}$.

Binary parameters k^*_{ij} and k'_{ij} for the GC-EOS [a]

Number	1	2	3	4	5	6	7	8	9	10	11	12
1		1.008	1.000	0.999	0.999	0.966	0.966	0.994	0.994	0.883	0.920	0.771
2	−0.003	–	1.000	0.999	0.999	1.024	1.024	0.994	0.994	0.883	0.920	0.806
3	0.000	0.000	–	1.019	1.019	1.218	1.218	1.353	1.353	0.883	0.920	0.806
4	0.000	0.000	0.000	–	1.000	0.990	0.990	1.002	1.002	0.778	0.544	0.811
5	0.000	0.000	0.000	0.000		0.990	0.990	1.002	1.002	0.778	0.544	0.811
6	0.000	0.000	0.000	0.000	0.000		1.000	1.007	1.007	0.861	0.837	0.913
7	0.000	0.000	0.000	0.000	0.000	0.000		1.007	1.007	0.861	0.837	0.913
8	0.064	0.064	0.000	0.000	0.000	0.000	0.000	–	1.000	0.794	0.715	0.826
9	0.064	0.064	0.000	0.000	0.000	0.000	0.000	0.000	–	0.794	0.715	0.826
10	−0.172	−0.172	−0.172	0.000	0.000	0.000	0.000	0.000	0.000	–	1.030	0.931
11	−0.162	−0.162	−0.162	0.000	0.000	0.000	0.000	0.000	0.000	0.000	–	0.745
12	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	−0.602	–
13	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	−0.602	0.000
14	0.000	0.000	0.000	0.000	0.000	n.a.	n.a.	n.a.	n.a.	0.000	0.000	−0.388
15	0.000	0.000	0.000	0.255	0.255	0.583	0.583	0.605	0.605	0.113	0.000	0.000
16	0.072	−0.089	−0.089	0.242	0.242	0.360	0.360	0.357	0.357	0.000	−0.387	0.000
17	0.099	−0.243	−0.243	−0.211	−0.211	0.086	0.086	0.086	0.086	−0.014	0.000	n.a.
18	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	−0.014	0.000	0.000
19	0.022	−0.063	−0.153	0.033	0.033	0.066	0.066	−0.182	−0.182	0.008	0.000	0.000
20	0.000	0.000	0.000	0.000	0.000	0.065	0.065	0.065	0.065	−0.122	0.000	0.000
21	−0.116	0.268	0.785	0.248	0.248	0.000	0.000	0.000	0.000	0.000	0.000	0.000
22	0.000	0.000	0.000	0.018	0.018	0.000	0.000	0.000	0.000	−0.236	−0.162	0.000
23	−0.089	−0.099	0.396	0.060	0.060	0.047	0.047	−0.141	−0.141	0.018	0.000	n.a.

Number	13	14	15	16	17	18	19	20	21	22	23
1	0.771	0.576	1.129	1.078	1.059	0.963	1.062	1.013	0.893	1.010	0.828
2	0.806	0.708	0.969	0.969	0.781	0.821	0.970	0.962	0.926	0.978	0.908
3	0.806	0.708	0.969	0.969	0.781	0.821	0.726	0.962	0.703	0.978	1.838
4	0.811	0.708	1.190	0.950	0.871	0.876	1.096	0.981	0.981	0.988	0.902
5	0.811	0.708	1.190	0.950	0.871	0.876	1.096	0.981	0.981	0.988	0.902
6	0.913	n.a.	1.243	1.071	0.953	0.875	1.059	1.019	1.028	1.032	1.005
7	0.913	n.a.	1.243	1.071	0.953	0.875	1.059	1.019	1.028	1.032	1.005
8	0.826	n.a.	1.169	1.071	0.953	0.839	1.003	1.019	0.935	0.964	0.915
9	0.826	n.a.	1.169	1.071	0.953	0.839	1.003	1.019	0.935	0.964	0.915
10	0.931	1.008	1.756	1.179	0.971	1.035	0.998	0.977	0.952	0.956	0.910
11	0.745	1.153	2.326	0.529	1.120	1.000	1.000	1.000	0.957	0.920	0.988
12	1.000	1.028	1.276	0.950	n.a.	0.694	0.905	0.918	1.295	0.836	n.a.
13	–	1.028	1.276	0.950	n.a.	0.694	0.905	0.918	1.295	0.836	n.a.
14	−0.338	–	1.172	1.395	1.339	0.769	1.390	1.021	0.847	0.917	0.952
15	0.000	0.000	–	0.999	1.013	n.a.	1.071	1.085	1.196	1.127	n.a.
16	0.000	−0.327	−0.100	–	1.000	1.019	0.978	0.962	1.045	0.994	0.855
17	n.a.	−0.219	−0.086	0.000	–	n.a.	0.959	n.a.	1.025	0.991	0.943
18	0.000	−0.061	n.a.	0.020	n.a.	–	n.a.	n.a.	0.967	n.a.	n.a.
19	0.000	−0.380	−0.067	0.009	−0.048	n.a.	–	0.977	0.832	1.009	0.953
20	0.000	−0.299	0.030	0.042	n.a.	n.a.	−0.017	–	0.950	0.994	n.a.
21	0.000	0.298	0.037	−0.002	0.000	−0.100	0.024	−0.029	–	0.880	0.928
22	0.000	−0.448	0.086	0.052	0.000	n.a.	0.007	0.025	0.000	–	0.917
23	n.a.	−0.122	n.a.	0.258	0.021	n.a.	0.000	n.a.	0.032	0.000	–

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[a] The k^*_{ij} values are found above while the k'_{ij} values are found below the diagonal ($k^*_{ij} = k^*_{ji}$ and $k'_{ij} = k'_{ji}$). Parameters which are not available are denoted by n.a.

Binary nonrandomness parameters α_{ij} for the GC-EOS [a]

Number	1	2	3	4	5	6	7	8	9	10	11	12
1	0.000	0.000	0.000	0.000	0.000	−0.077	−0.077	2.636	2.636	−0.044	0.811	0.692
2	0.000	0.000	0.000	0.000	0.000	−0.077	−0.077	2.636	2.636	2.408	2.585	0.692
3	0.000	0.000	0.000	0.000	0.000	−0.726	−0.726	−0.726	−0.726	2.408	2.585	0.692
4	0.000	0.000	0.000	0.000	0.000	−0.363	−0.363	−0.363	−0.363	0.781	4.495	0.784
5	0.000	0.000	0.000	0.000	0.000	−0.363	−0.363	−0.363	−0.363	0.781	4.495	0.784
6	−0.477	−0.477	−0.726	−0.778	−0.778	0.000	0.000	0.000	0.000	1.415	4.441	2.730
7	−0.477	−0.477	−0.726	−0.778	−0.778	0.000	0.000	0.000	0.000	1.415	4.441	2.730
8	2.636	2.636	−0.726	−0.778	−0.778	0.000	0.000	0.000	0.000	1.415	3.868	2.854
9	2.636	2.636	−0.726	−0.778	−0.778	0.000	0.000	0.000	0.000	1.415	3.868	2.854
10	0.412	−15.000	−15.000	4.049	4.049	1.415	1.415	1.415	1.415	0.000	0.000	14.560
11	0.161	−15.000	−15.000	−10.340	−10.340	4.441	4.441	3.868	3.868	0.000	0.000	1.840
12	4.699	4.699	4.699	5.696	5.696	29.680	29.680	4.701	4.701	4.433	1.840	0.000
13	4.699	4.699	4.699	5.696	5.696	29.680	29.680	4.701	4.701	4.433	1.840	0.000
14	−3.098	−3.098	−3.098	−3.098	−3.098	n.a.	n.a.	n.a.	n.a.	1.250	−0.778	−0.761
15	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	−0.624	0.000
16	−2.163	−2.163	−2.163	0.221	0.221	−0.312	−0.312	−0.312	−0.312	0.000	3.351	0.000
17	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.257	0.197	n.a.
18	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.190	0.356
19	−4.380	−4.380	−0.951	−5.693	−5.693	−0.598	−0.598	−2.148	−2.148	0.130	0.308	0.000
20	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	3.684	0.331
21	−0.743	−0.743	10.170	−2.898	−2.898	−2.803	−2.803	−2.803	−2.803	0.098	0.224	−0.996
22	0.000	0.000	0.000	0.000	0.000	−1.081	−1.081	−1.081	−1.081	−0.164	0.190	0.402
23	0.840	0.840	1.715	6.152	6.152	0.000	0.000	0.000	0.000	0.553	0.553	n.a.

Number	13	14	15	16	17	18	19	20	21	22	23
1	0.692	0.400	0.000	− 2.163	0.000	0.000	− 4.380	0.000	8.221	0.000	0.840
2	0.692	0.400	0.000	− 2.163	0.000	0.000	− 4.380	0.000	8.221	0.000	0.840
3	0.692	0.400	0.000	− 2.163	0.000	0.000	− 0.951	0.000	− 1.620	0.000	1.715
4	0.784	0.400	0.000	0.221	0.000	0.000	− 5.693	0.000	− 2.898	0.000	6.152
5	0.784	0.400	0.000	0.221	0.000	0.000	− 5.693	0.000	− 2.898	0.000	6.152
6	2.730	n.a.	0.000	− 0.312	0.000	0.000	− 0.598	0.000	− 4.258	− 1.081	0.000
7	2.730	n.a.	0.000	− 0.312	0.000	0.000	− 0.539	0.000	− 4.258	− 1.081	0.000
8	2.854	n.a.	0.000	− 0.312	0.000	0.000	− 2.148	0.000	− 4.258	− 1.081	0.000
9	2.854	n.a.	0.000	− 0.312	0.000	0.000	− 2.148	0.000	− 4.258	− 1.081	0.000
10	14.560	1.250	0.000	0.000	0.257	0.000	0.486	0.000	0.098	− 0.394	0.553
11	1.840	− 2.372	0.985	3.351	3.930	6.047	4.038	− 6.582	0.224	3.128	0.553
12	0.000	− 0.761	0.000	0.000	n.a.	0.356	0.000	0.331	− 7.800	− 1.296	n.a.
13	0.000	− 0.761	0.000	0.000	n.a.	0.356	0.000	0.331	− 7.800	− 1.296	n.a.
14	− 0.761	0.000	0.579	0.000	0.000	0.239	− 0.373	0.000	0.353	0.000	0.000
15	0.000	0.579	0.000	0.000	0.000	n.a.	0.000	0.000	0.000	0.000	n.a.
16	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.220
17	n.a.	0.000	0.000	0.000	0.000	n.a.	0.000	n.a.	0.000	0.000	0.000
18	0.356	0.239	n.a.	0.000	n.a.	0.000	n.a.	n.a.	− 0.782	n.a.	n.a.
19	0.000	− 0.373	0.000	0.000	0.000	n.a.	0.000	0.000	0.000	0.000	0.000
20	0.351	0.000	0.000	0.000	n.a.	n.a.	0.000	0.000	0.475	0.000	n.a.
21	− 0.996	0.353	0.000	0.000	0.000	− 0.782	0.000	0.475	0.000	1.272	0.000
22	0.402	0.000	0.000	0.000	0.000	n.a.	0.000	0.000	1.272	0.000	0.184
23	n.a.	0.000	n.a.	0.220	0.000	n.a.	0.000	n.a.	0.000	0.184	0.000

[a] Parameters which are not available are denoted by n.a.

APPENDIX 8

PRELIMINARY PROCESS DESIGN CALCULATIONS AND COMPUTER PROGRAM DESCRIPTION

Calculation for packed-column design

Absorption is a physical process that involves transfer of one or more components from the gas phase into a liquid solvent. It is one of the so-called stagewise or equilibrium stage operations. Normally there are three approaches used for evaluating the performance of absorption equipment. These three approaches are as follows.

1. The graphical procedure is simple, direct and easy to use for one or two components. It gives the user an explicit graphical presentation of the interrelationship of variables and parameters in the absorber. It has the disadvantage of becoming complex, tedious and time consuming for multicomponent absorption.

2. The approach using mass-transfer coefficients depends on the molecular diffusivity of the solute and the eddy diffusivity of the system (which is determined by the equipment used for the absorption process). The eddy diffusivity contribution is usually much larger than the molecular diffisivity contribution. This complicates the prediction of mass-transfer coefficients because they become significantly system-dependent.

3. The absorption-factor or overall approach generally attributed to Kremser [98]. This approach has the advantage of simplicity for multicomponent systems. However, accurate predictions require good estimates of temperature and vapour-liquid flowrate profiles for the column.

$$v_N = l_N/A_N \tag{A8.5}$$

where A_N is the absorption factor for stage N, $A = L/KV$. Substituting equation A8.5 into A8.1, gives

$$l_N = (l_{N-1} + v_1)A_N \tag{A8.6}$$

The internal flow rate l_{N-1} can be eliminated by successive substitution using material balances around successively smaller sections including the top of the column. For stages 1 through N-2,

$$l_{N-1} = (l_{N-2} + v_1)A_{N-1} \tag{A8.7}$$

Substituting equation A8.7 into A8.6, we have

$$l_N = l_{N-2}A_{N-1}A_N + v_1(A_N + A_{N-1}A_N) \tag{A8.8}$$

Continuing this process to the top stage, where $l_1 = v_1A_1$, ultimately converts equation A8.8 into

$$l_N = v_1(A_1A_2A_3\ldots A_N + A_2A_3A_4\ldots A_N + A_3A_4A_5\ldots A_N + \ldots\ldots + A_N) \tag{A8.9}$$

A more useful form is obtained by combining equation A8.9 with the overall component balance

$$l_N = v_{N+1} - v_1 \qquad (A8.10)$$

to give an equation for the exiting vapour in terms of the entering vapour and a recovery fraction

$$v_1 = v_{N+1}\,\phi_A \qquad (A8.11)$$

where, by definition, the recovery fraction is

$$\phi_A = \frac{1}{A_1A_2A_3..A_N + A_2A_3..A_N + ...+ A_N} \qquad (A8.12)$$

Equation A8.12 is the fraction of the species in the entering vapour that is not absorbed. In the group method, an average effective absorption factor A_e replaces the separation factors for each stage. Equation A8.12 then becomes

$$A_e = \frac{1}{A_e^{N} + A_e^{N-1} + A_e^{N-2} + ...+ A_e + 1} \qquad (A8.13)$$

when multiplied and divided by $(A_e - 1)$, equation A8.13 reduces to

$$\phi_A = (A_e - 1)/(A_e^{N} - 1) \qquad (A8.14)$$

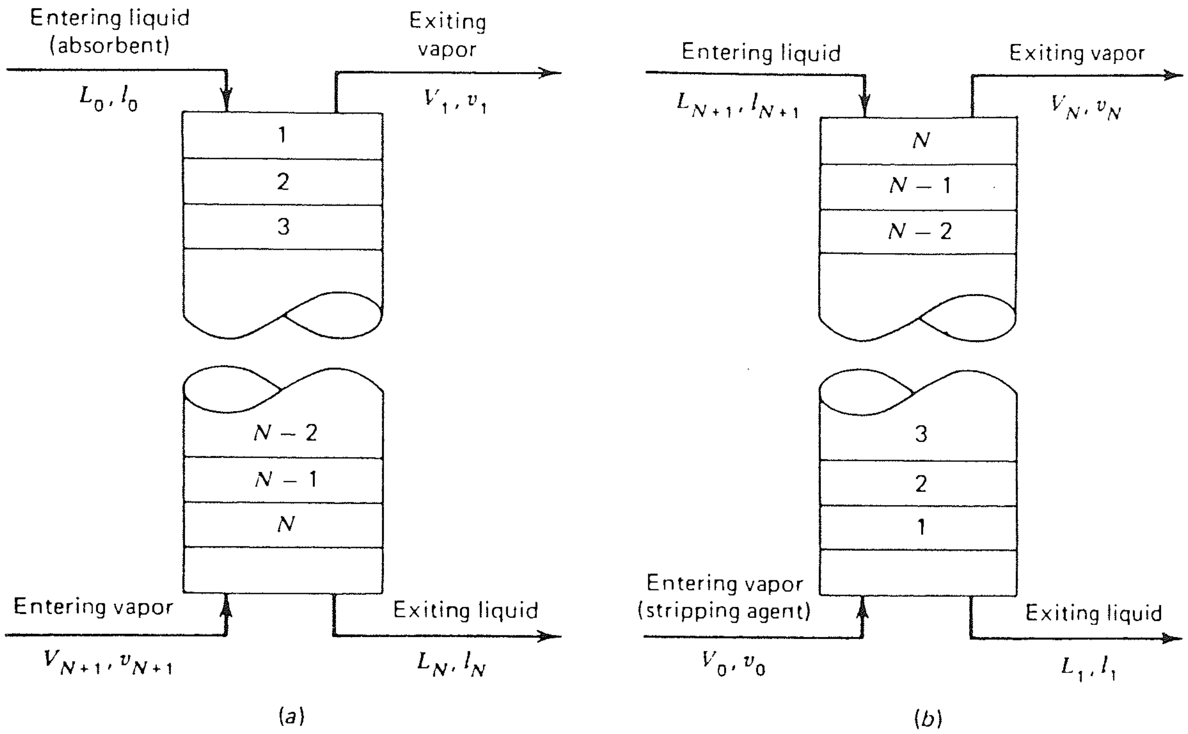

Figure A8.1 Countercurrent cascades of N adiabatic stages. (a) Absorber. (b) Stripper.

Consider next the countercurrent stripper shown in Figure A8.1b. In this case, stages are numbered from bottom to top to facilitate the derivation. The pertinent stripping equations follow in the manner analogous to the absorber equation. The results are

$$l_1 = l_{N+1} \phi_S \qquad (A8.15)$$

where

$$\phi_S = (S_e - 1)/(S_e^{N+1} - 1) \qquad (A8.16)$$

$$S = KV/L = 1/A \qquad (A8.17)$$

To obtain values of ϕ_A and ϕ_S for equations A8.14 and A8.16, expressions are required for A_e and S_e. These are conveniently obtained from equations derived by Edmister [41, 42].

$$A_e = [A_N(A_1 + 1) + 0.25]^{1/2} - 0.5 \qquad (A8.18)$$

$$S_e = [S_1(S_N + 1) + 0.25]^{1/2} - 0.5 \qquad (A8.19)$$

Absorbers are frequently coupled with strippers or distillation columns to permit regeneration and recycle of absorbent. Since the stripping action is sometimes not perfect, absorbent entering the absorber contains species present in the vapour entering the absorber. Vapour passing up through the absorber can strip these as well as the absorbed species introduced in the makeup absorbent. Therefore, a general equation of total balance in the absorber for components appearing in both entering vapour and entering liquid can be obtained from

$$v_1 = v_{N+1}\,\phi_A + l_0(1 - \phi_S) \qquad (A8.20)$$

The total flow rates can be estimated by the following equations of Horton and Franklin [88].

$$V_2 = V_1(V_{N+1}/V_1)^{1/N} \qquad (A8.21)$$

$$L_1 = L_0 + V_1 - V_1 \qquad (A8.22)$$

$$V_N = V_{N+1}(V_1/V_{N+1})^{1/N} \qquad (A8.23)$$

The temperature change in each stage can be obtained from

$$\frac{T_N - T_1}{T_N - T_0} = \frac{V_{N+1} - V_2}{V_{N+1} - V_1} \qquad (A8.24)$$

This equation is solved simultaneously with an overall enthalpy balance for T_1 and T_N

$$V_{N+1}H^V_{N+1} + L_0H^L_0 = V_1H^V_1 + L_NH^L_N \qquad (A8.25)$$

where H^V and H^L are the total enthalpy of gas and liquid streams respectively.

The minimum solvent flow rate, corresponding to an infinite number of stages, can be estimated from the following equation

$$(L_o)_{min} = K_k V_{N+1}(1 - \phi_{A_k}) \qquad (A8.26)$$

where k refers to the key component.

For the stripper, the vapour entering the column is often steam or another inert gas such as nitrogen. When the stripping agent contains none of the species in the feed liquid and is not condensed in the stripper, the only direction of mass transfer is from the liquid to the gas phase. The calculation of total flow rates can be obtained from

$$L_2 = L_1(L_{N+1}/L_1)^{1/N} \qquad (A8.27)$$

$$V_1 = V_0 + L_2 - L_1 \qquad (A8.28)$$

$$L_N = L_{N+1}(L_1/L_{N+1})^{1/N} \qquad (A8.29)$$

and the temperature change of the liquid is calculated from

$$\frac{T_{N+1} - T_N}{T_{N+1} - T_1} = \frac{L_{N+1} - L_N}{L_{N+1} - L_1} \qquad (A8.30)$$

This equation is also solved simultaneously with an overal enthalpy balance for T_1 and T_N. The minimum stripping gas flow rate, for a key component k corresponding to an infinite number of stages, can be obtained from

$$(V_0)_{min} = (L_{N+1}/K_k)(1 - \phi_{S_k}) \qquad (A8.31)$$

this equation assumes that K < 1 and the fraction of liquid feed stripped is small.

Calculation of column diameter

The first step in sizing a packed column involves predicting how large a shell diameter is necessary to pass the desired gas and liquid rates so that the gas will not simply blow the liquid back out ("flood"). Capacity depends on the resistance imposed by the packing. Liquid viscosity, liquid density, gas density, and packing size, type, surface and free space become the determining variables. Once the liquid and gas flow rates, and all the necessary data of the packing are known, the column cross-sectional area and diameter for the selected pressure drop can be determined from the generalised pressure-drop correlation given in Figure A8.2.

In order to simplify the calculation of diameter, for the computer program, we selected a pressure drop line of 42 mm of water per meter of packed height, and this line is linearised by the following equations:

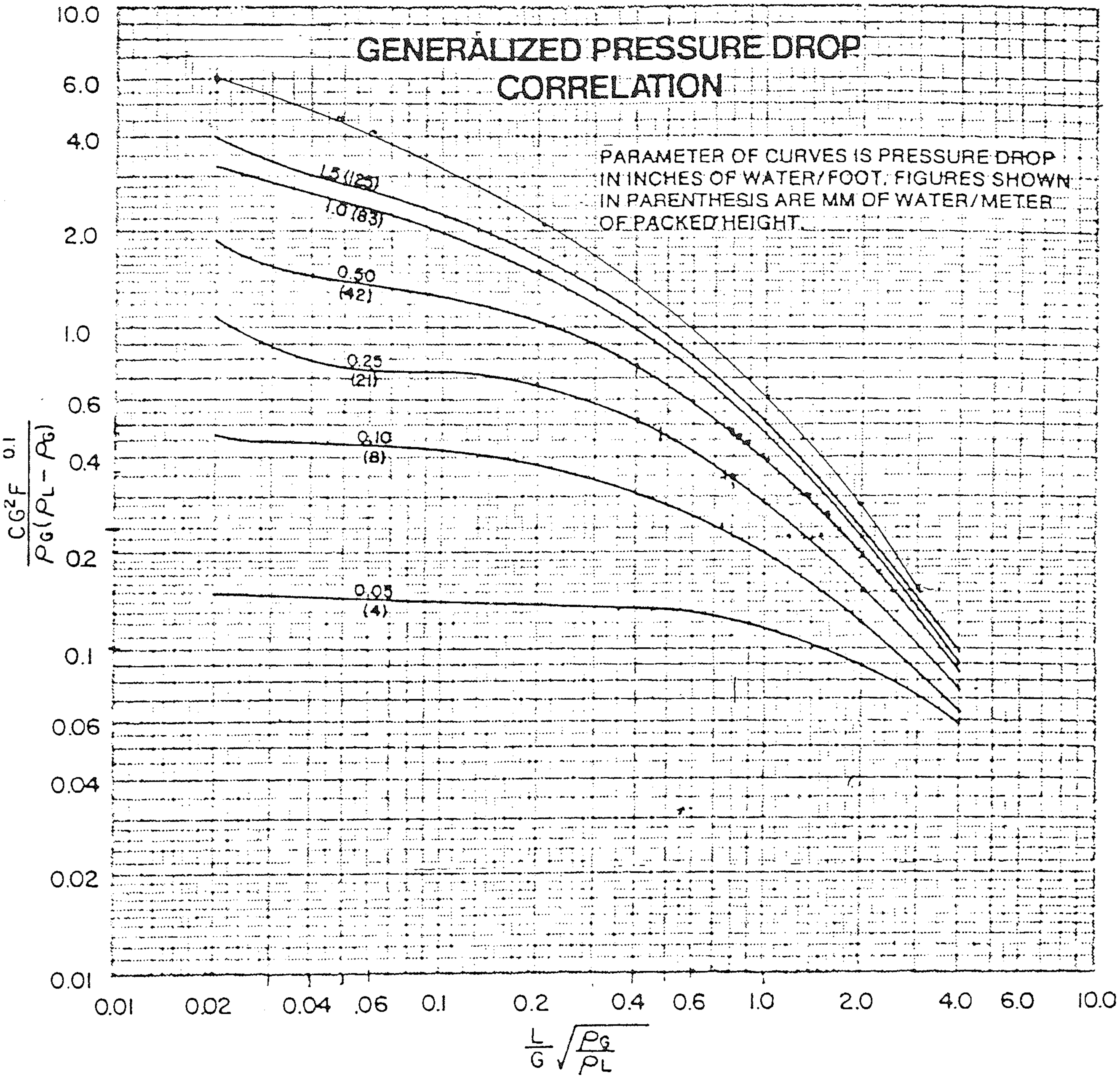

Figure A8.2 Generalized pressure drop correlation.

$$A_y = 4.9687-277.54A_x+7642.12A_x^{2}-72589.26A_x^{3} \qquad 0.02<A_x<0.04$$

$$A_y = 1.5481-3.1588A_x+3.8923A_x^{2}-2.6909A_x^{3}$$
$$+0.8923A_x^{4}-0.101048A_x^{5} \qquad 0.04<A_x<4.0$$

where

$$A_x = L/G(\rho_G/\rho_L)^{½} \qquad (A8.32)$$

$$A_y = \frac{10.764\, G'^{2}\, F\, \mu_L^{0.1}}{\rho_G(\rho_G-\rho_L)} \qquad (A8.33)$$

and the diameter of the packed tower can be calculated from the following expression

$$D = 1.13\ (G\ /\ G')^{½} \qquad (A8.34)$$

In order to find the percentage of flooding and flooding factor, the flooding line is also linearised by

$$A_f = 7.9068-116.81A_x+1186.9A_x^{2}-6505.4A_x^{3}+18790.0A_x^{4}$$
$$-28682.0A_x^{5}+22502.0A_x^{6}-8305.8A_x^{7}+1123.9A_x^{8} \qquad (A8.35)$$

Calculation of the height of column

In the case of a plate column, the height (z) is simply the product of the number of plates (N) required for the separation and the plate spacing. For a packed column, data are available for a number of systems providing the height equivalent to a theoretical plate (HETP).

$$z = N\ (HETP) \qquad (A8.36)$$

If the HETP data are unavailable, use is made of the mass transfer rate models. Such models must account for resistance in both vapour and liquid phases. To accomplish this, the transfer-unit concept is normally employed with the height of an overall transfer unit being given by:

$$H_{OG} = H_G + \lambda H_L \qquad (A8.37)$$

$$\lambda = m_e / m_o \qquad (A8.38)$$

where

H_{OG} = height of an overall transfer unit (HTU) in terms of vapour composition, m

H_G = height of a vapour-phase transfer unit, m

H_L = height of a liquid-phase transfer unit, m

λ = ratio of slopes of equilibrium to operating lines

m_e = slope of equilibrium line

m_o = slope of operating line

The use of H_G and H_L to obtain the height equivalent to a theoretical plate is straightforward:

$$HETP = (\ln\lambda / (\lambda - 1) H_{OG} \qquad (A8.39)$$

The calculation of equations A8.34 and A8.36 obviously needs the values of H_G and H_L. There are two major correlations to calculate H_G and H_L, i.e. the Monsanto (Cornell´s) model and the Onda model. This work selected the Monsanto model for the calculation of H_G and H_L. The Monsanto model was developed by Cornell et al. [185], it takes into account the physical properties of the system, the gas and liquid flowrates, and the column diameter and height. Cornell´s equations are:

$$H_G = \frac{0.011\,\psi\,(Sc)_V^{0.5}\,(D_c/0.305)^{1.11}\,(Z/3.05)^{0.33}}{(L_W^{*}\,f_1\,f_2\,f_3)^{0.6}} \qquad (A8.40)$$

$$H_L = 0.305\,\phi\,(Sc)_L^{0.5}\,K_3\,(Z/3.05)^{0.15} \qquad (A8.41)$$

where

H_G = height of a vapour-phase transfer unit, m

H_L = height of a liquid-phase transfer unit, m

$(Sc)_V$ = gas Schmidt number = $(\mu_V / \rho_V D_V)$

$(Sc)_L$ = liquid Schmidt number = $(\mu_L / \rho_L D_L)$

D_c = column diameter, m

z = column height, m

K_3 = percentage flooding correction factor (see Figure 8.3)

ψ = H factor (see Figures A8.4)

ϕ = H factor (see Figures A8.5)

L_w = liquid mass flow-rate per unit area column cross-sectional area, kg/m^{2}s

f_1 = liquid viscosity correction factor = (μ_w / μ_L)

f_2 = liquid density correction factor = (ρ_w / ρ_L)

f_3 = surface tension correction factor = (σ_w / σ_L)

The prefix w refers to the physical properties of water at 20°C. The terms $(D_c/0.305)$ and $(z/3.05)$ are included in the equations to allow for the effects of column diameter and packed height. For design purposes the diameter correction term should be taken as a fixed value of 2.3 for columns above 0.6 m diameter, and the height correction should only be included when the distance between liquid distributors is greater than 3 m.

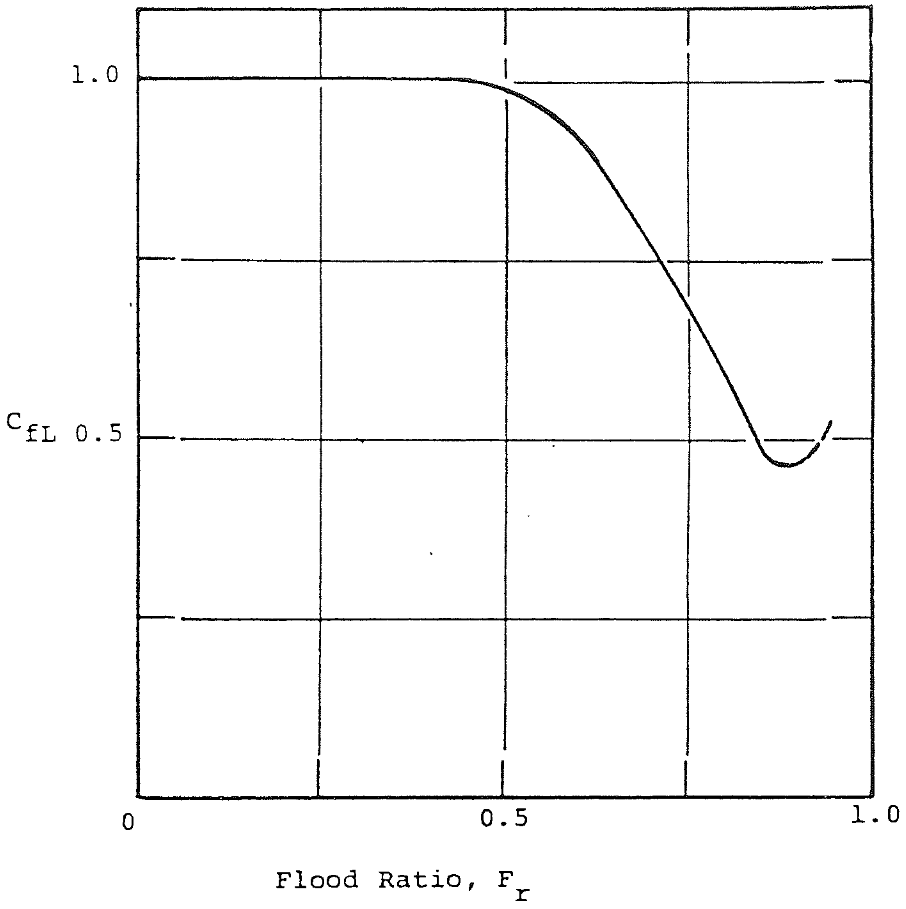

Figure A8.3 Vapour-load coefficient for liquid-phase mass transfer.

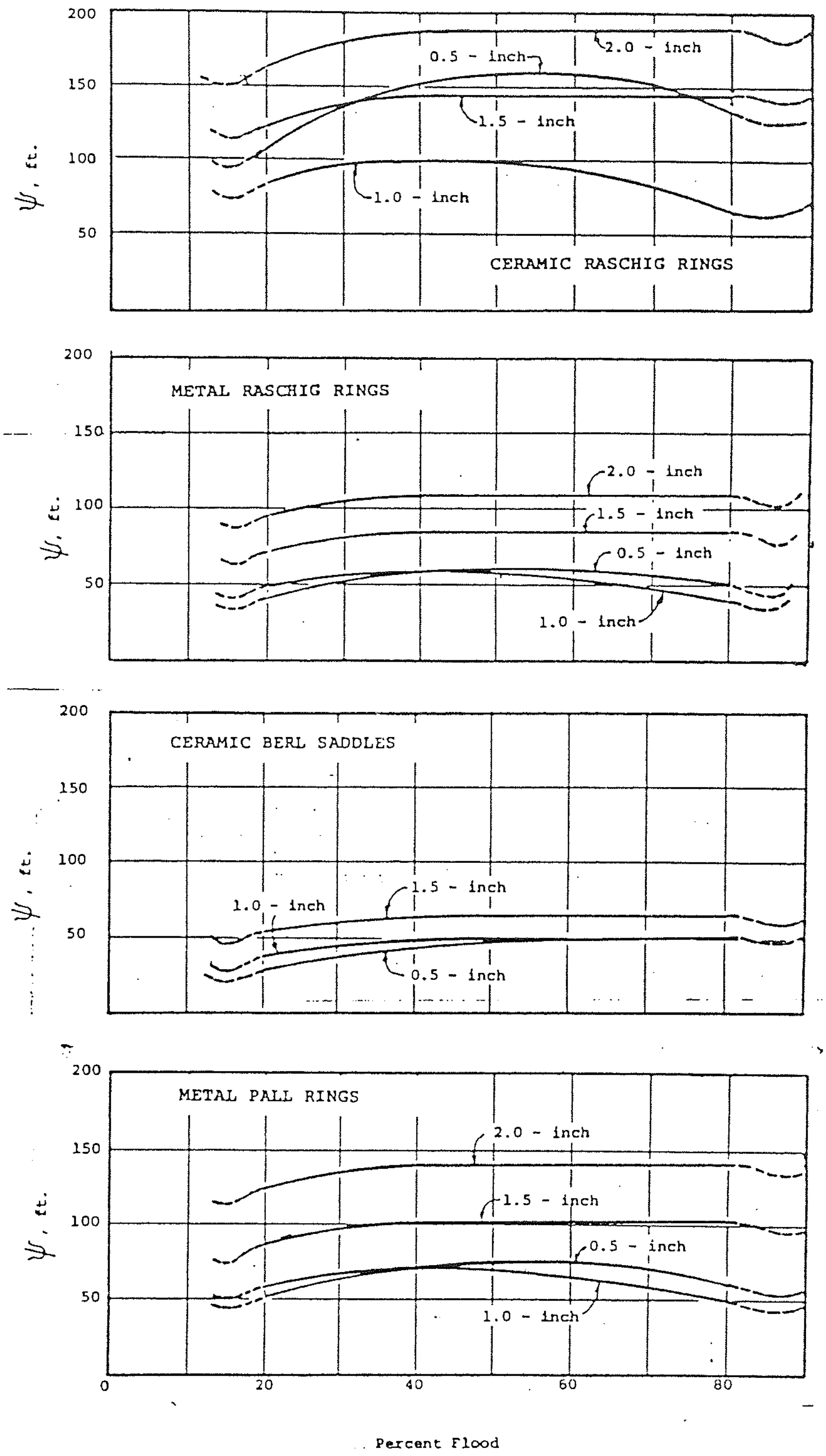

Figure A8.4 Improved packing parameters for vapour-phase mass transfer.

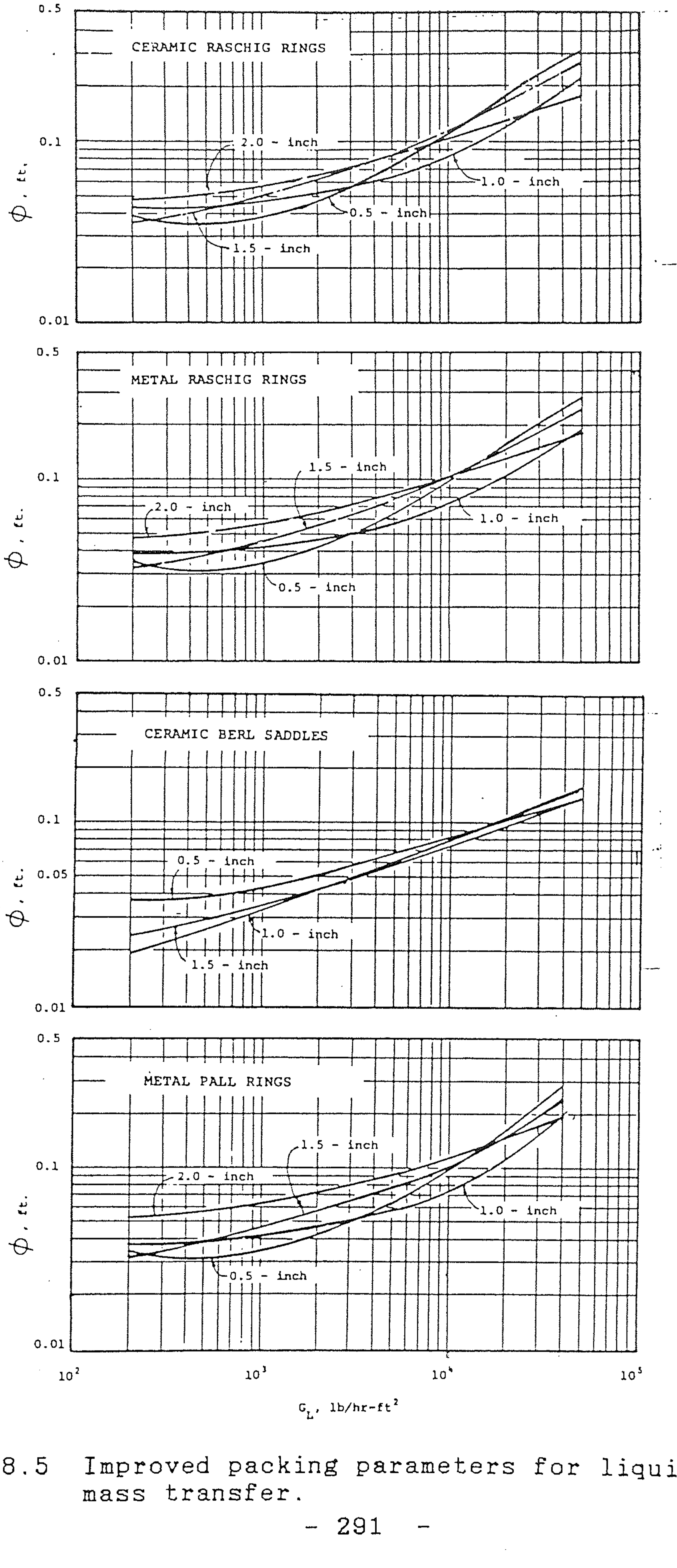

Figure A8.5 Improved packing parameters for liquid-phase mass transfer.

Cost of packed tower

In general, the cost of a packed tower depends on construction material, diameter, height and packing. Column diameter depends on the superficial velocity of the process gas, gas and liquid densities, liquid viscosity and the properties of the packing. The height of the tower depends on physical properties of liquid solvent and the solubilities of gases in the solvent. The cost of a packed column can be estimated from the following equations.

$$C_c = 717.0W_c^{0.183} \exp[0.023(\ln W_c)^2] \qquad (A8.42)$$

$$W_c = D_i(H_c + 0.8116D_i)\ T_s\ d \qquad (A8.43)$$

The amount of packing required and column height are primarily determined by the number of theoretical stages and the height equivalent to a theoretical plate (HETP).

$$H_c = N(HETP) + \triangle \qquad (A8.44)$$

where $\triangle$ is added height for such things as vapour and liquid separation, maintainance and inspection, typically 2-3 ft, plus 25% of the diameter.

$$T_s = (T_p + T_b)/2.0 + T_c \qquad (A8.45)$$

$$T_p = P\ R/(S\ E - 0.6P) \tag{A8.46}$$

$$T_b = T_w + T_g \tag{A8.47}$$

$$T_w = d_a V^2 (D_o + Z)\ Tl^2/(S\quad D\ ) \tag{A8.48}$$

$$T_g = P\ R/(2.0SE + 0.4P) \tag{A8.49}$$

where

Tl = Tangent-to-tangent length

T_s = Calculated wall thickness

T_p = Thickness to withstand design pressure

T_b = Thickness at the bottom of vertical vessel

T_c = Additional thickness for corrosion allowance

T_w = Thickness to withstand wind load

T_g = Thickness to withstand internal pressure when girth seam controls

d_a = Density of air

V = Wind velocity

W_c = Shell weight

D_i = Inside diameter

D_o = Outside diameter

Z = Allowance for cage ladders in wind-load calculation

S = Maximum allowable stress

E = Joint efficiency

R = Inside radius of vessel

P = Gauge pressure

The above cost of a packed column is based on using carbon steel as a material of construction. If the column material is other than carbon steel, the column cost (C_c), must be multiplied by a material cost factor, F_m. Selected values for Fm are listed in Table A8.1.

The cost of the column platform and ladder (C_{pl}), is calculated from

$$C_{pl} = 233.0\, D_i^{0.74}\, H_c^{0.707} \qquad (A8.50)$$

The total cost of the packed column can then be calculated from the sum of cost of column (C_c), cost of platform and ladder (C_{pl}), and cost of packing (C_p).

$$C_t = C_c + C_{pl} + C_p \qquad (A8.51)$$

Table A8.1 Constant material-of-construction factors

Material	Cost Factor, F_m
Stainless steel, 304	1.7
Stainless steel, 316	2.1
Carpenter 20CB-3	3.2
Nickle-200	5.4
Monel-400	3.6
Inconel-600	3.9
Incoloy-825	3.7
Titanium	7.7

Description of the computer program for process design

DESIGN.BAS is the program for preliminary process design calculations. The program has been written in Basic and is recorded on the diskette Number 2 which is enclosed in the back cover of this thesis. To run the program type DESIGN then follow the instructions displayed on the screen. The program calculates various information for the three services used, i.e. absorber, stripper and flash drums. The absorber and stripper calculations performed by the program DESIGN.BAS include material and heat balances, height of the overall gas transfer unit, the height equivalent to a theoretical plate, tower diameter, packed height and the cost of the tower. Figure A8.6 is a simplified flow diagram of the preliminary process design calculations. The program performance is illustrated by the following steps:

1. The program reads initial data from data files which depend on the selected process design. For using the solvent B2 in natural gas plant the program reads data from file DB2-1.BAS, for using the solvent B2 in ammonia plant the program reads data from file DB2-2.BAS, for using Selexol the program reads data from file DSELEXOL.BAS, and for using Rectisol the program reads data from file DCH3OH.BAS.

2. The program asks for operating temperature and pressure and the number of plates in the absorber.

3. Calculates the equilibrium constants (K_i) from the given temparature and pressure.

4. Material and energy balances around the absorber are solved simultaneously by iterative techniques. The equations for determining the design variables are explained in the previous section (equations A8.1 to A8.26). The iterations are performed until successive values of L are obtained within 0.1%, which is a satisfactory criterion for convergence (see computer flowsheet in Figure A8.6).

5. Prints the results for v and l (see Figure A8.1a). The program then asks for an option to continue to the next step or to change the number of plates and return to step 2.

6. Computes the diameter of the column from the generalised pressure-drop correlation given in Figure A8.1. The pressure drop of 42 mm of water per metre of packed height was selected for the calculation, and the diameter is calculated from equation A8.35.

7. Computes liquid and gas diffusivity (from equations A.13 to A1.15) to be used in packed height calculations.

8. This step calculates the packed height. The packed height is obtained by the multiplication of the number of plates and the height equivalent to a theoretical plate (HETP). The HETP is computed from equations A8.37 to A8.39 which are based on mass transfer rate models. The height of a vapour-phase transfer unit (H_G) and the height of liquid-phase transfer unit (H_L) are calculated from the Monsanto model (equations A8.40 and A8.41).

9. Calculates the cost of the absorber based on shell

weight, equations A8.42 to A8.51.

10. There are two choices in the program calculation for the rich solvent leaving the absorber. These are:

- the liquid is carried directly to the stripper, or
- it is fed to a flash drum to recycle some valuable gases to the absorber before the solvent is introduced to the stripper.

If the first choice is selected the calculation is continued to step 12, otherwise, continued to step 11.

11. Flash drum calculation is performed by

a. Input operating temperature (T) and pressure (P).

b. Guess the value of vapour flowrate (V_f) leaving the flash drum.

c. Calculates B = V_f/F (F = liquid feed stream rate)

d. Uses Newton-Raphson method to iterate equation 7.6.

e. Computes new value for B from equation 7.7 and checks for convergence.

f. Prints results when convergence criteria are satisfied; otherwise, sets new value for B from (e) and returns to step (c).

g. Checks the results. If T or P require change, it returns to step (a); otherwise continues to the next step.

h. If the process needs another flash drum then the program sets new values for F and z for liquid feed to the next flash drum, and returns to step (a).

Otherwise, it continues to step 12.

12. This step calculates the diameter, packed height, cost and stripping gas feed rate for the stripper. The calculation procedures are similar to those for the absorber described earlier and are therefore not explained in detail again.

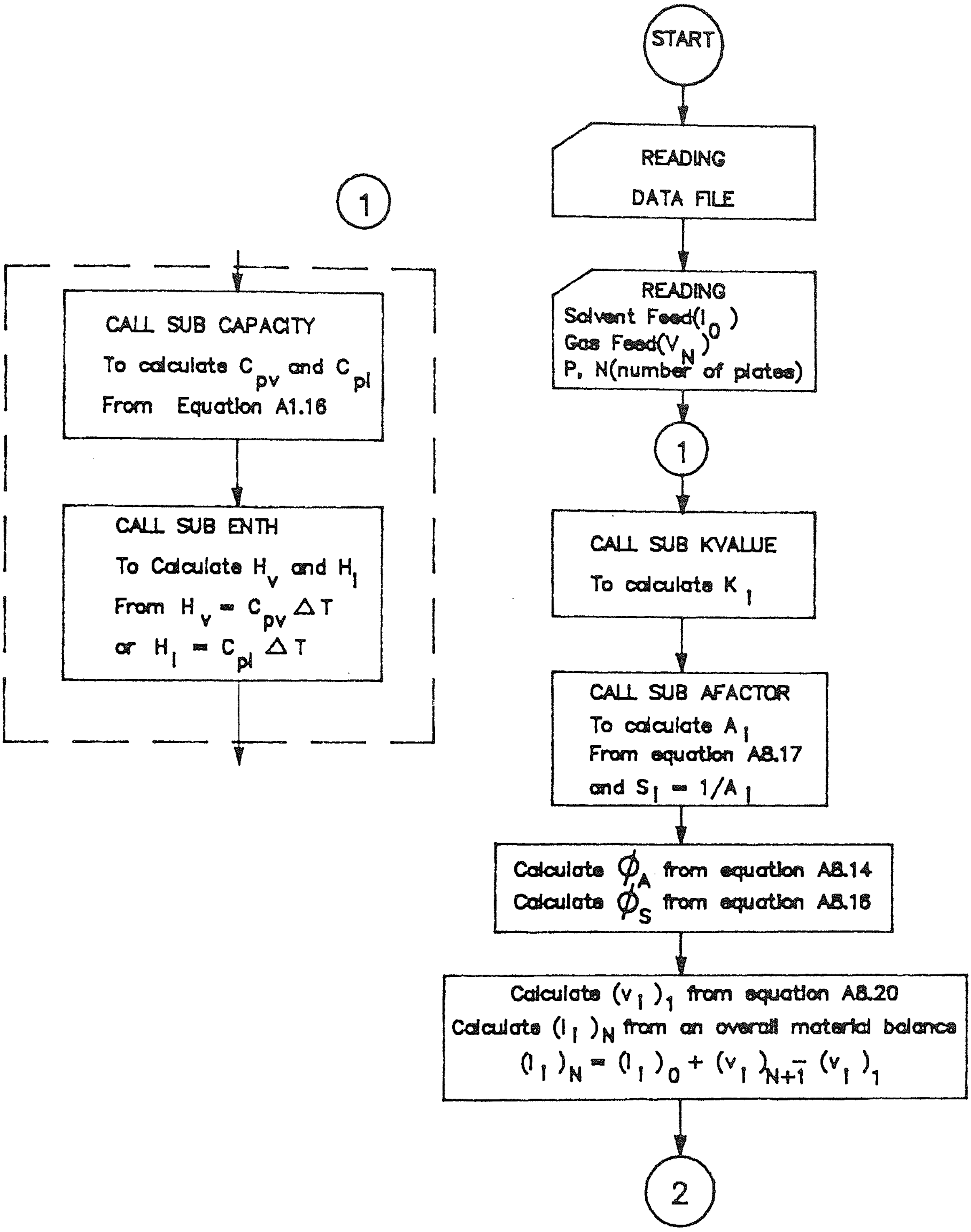

Figure A8.6 Schematic diagram of process design calculations.

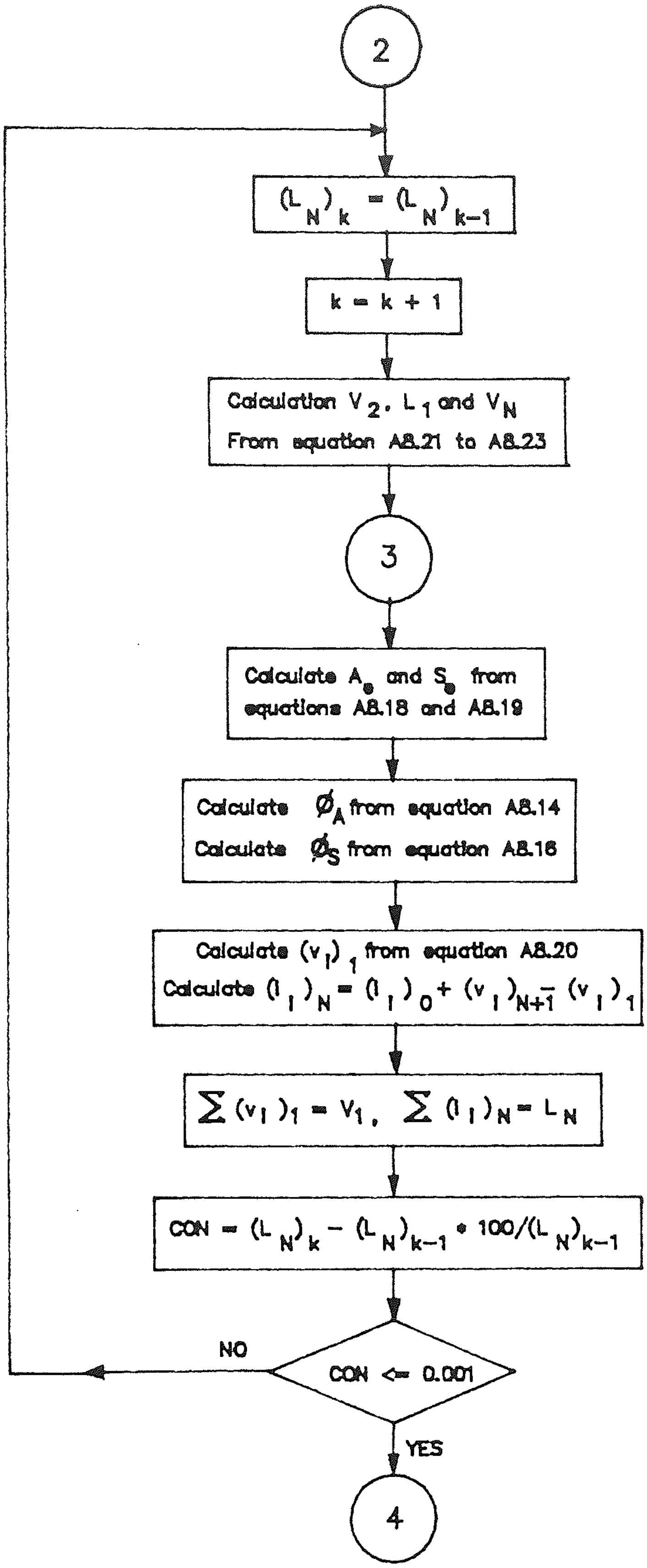

Figure A8.6 (Continued)

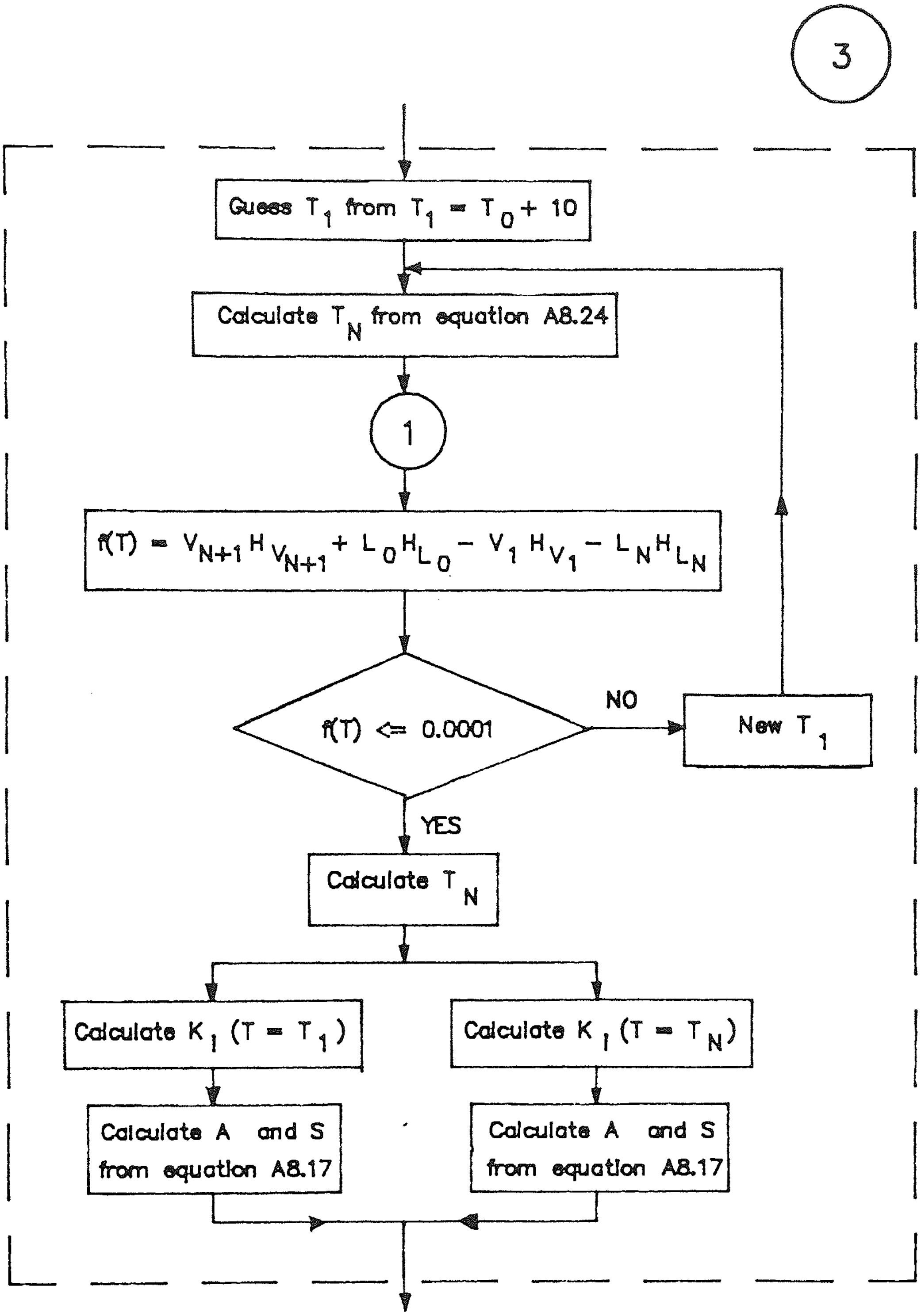

Figure A8.6 (Continued)

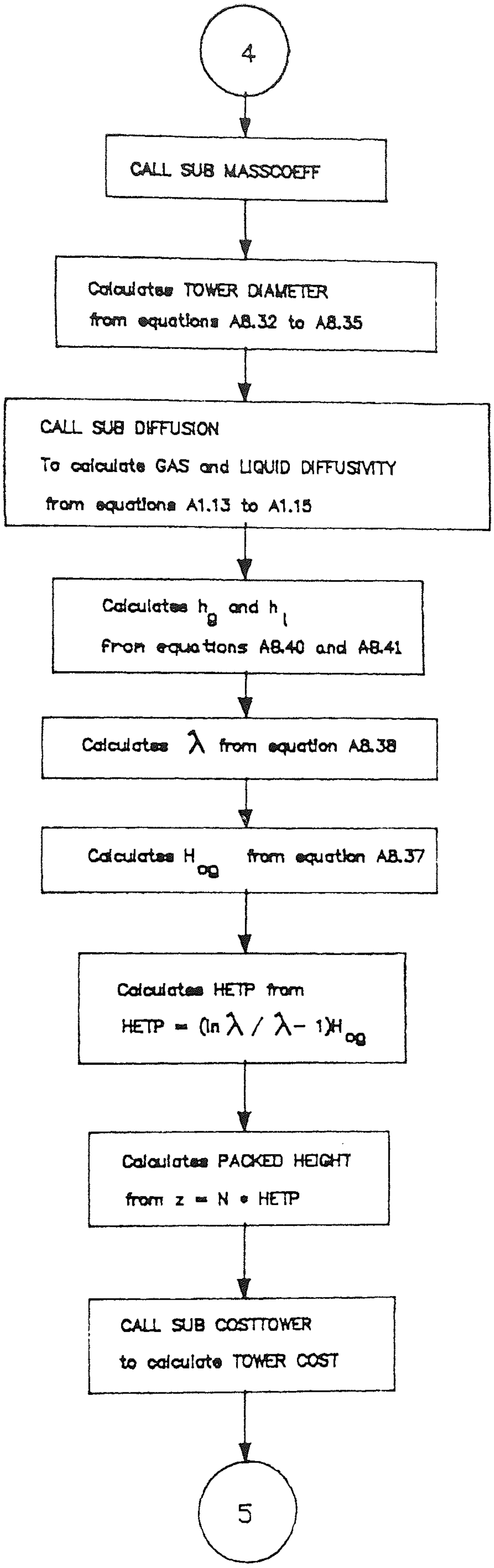

Figure A8.6 (Continued)

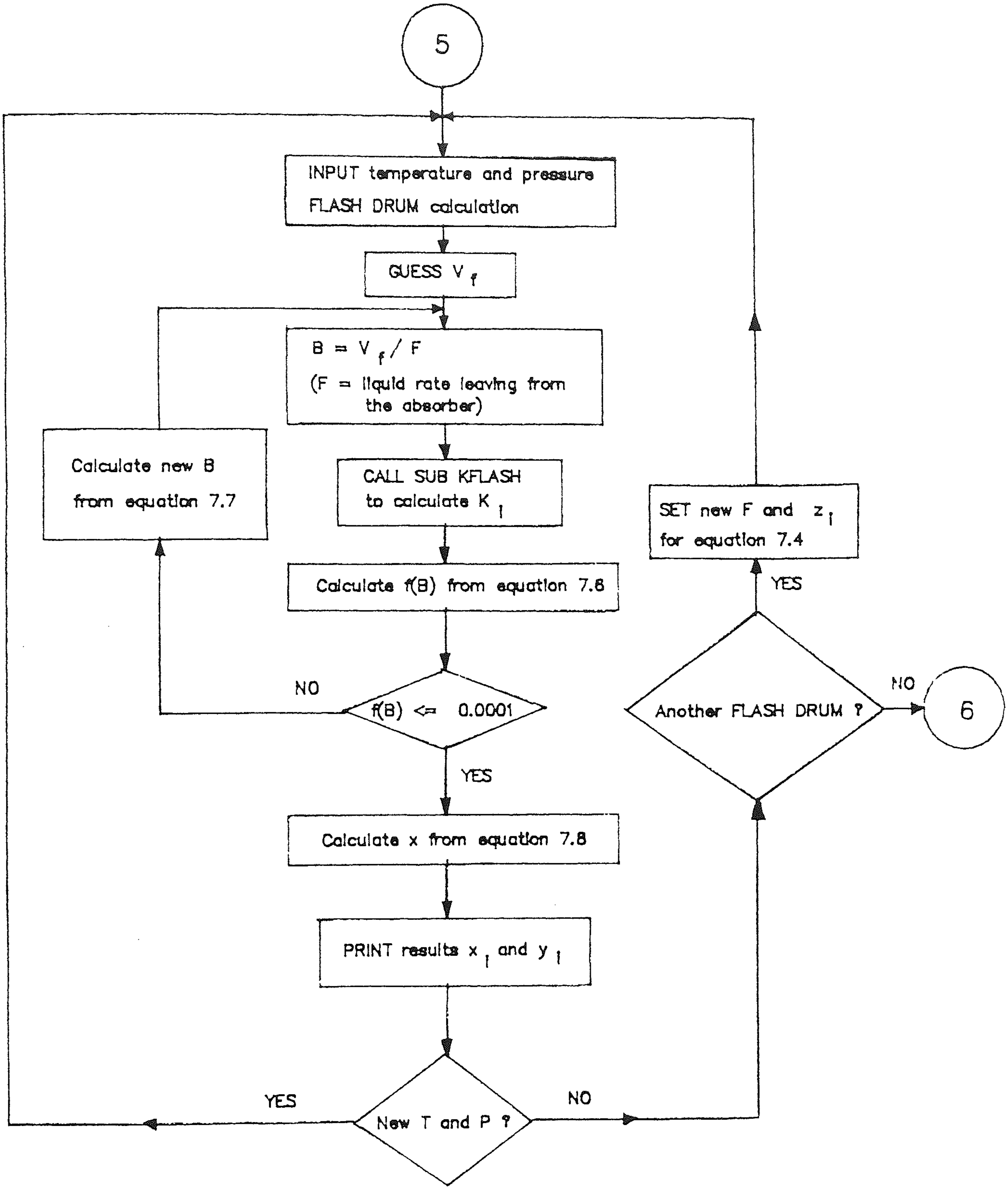

Figure A8.6 (Continued)

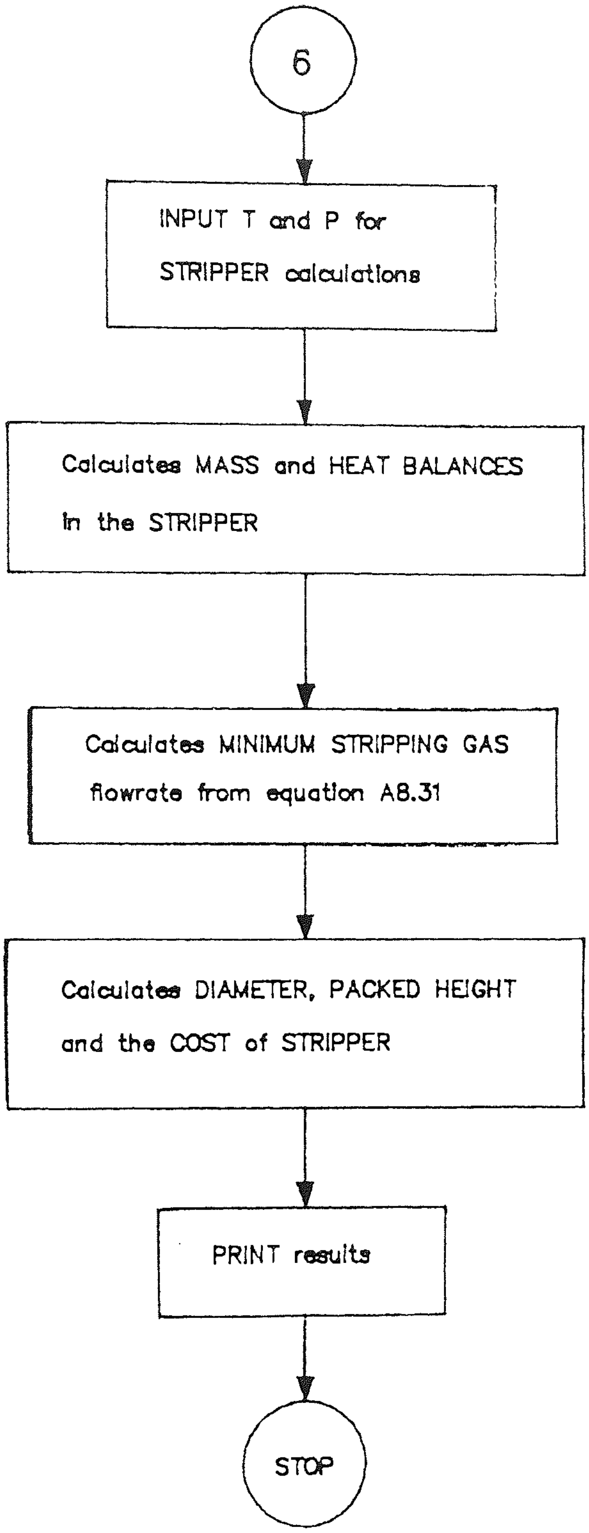

Figure A8.6 (Continued)

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