MODELS OF GAS-LIQUID SOLUBILITIES

Volume I

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Summary

A recent method for phase equilibria, the AGAPE method, has been used to predict activity coefficients and excess Gibbs energy for binary mixtures with good accuracy. The theory, based on a generalized London potential (GLP), accounts for intermolecular attractive forces. Unlike existing prediction methods, for example UNIFAC, the AGAPE method uses only information derived from accessible experimental data and molecular information for pure components. Presently, the AGAPE method has some limitations, namely that the mixtures must consist of small, non-polar compounds with no hydrogen bonding, at low to moderate pressures and at conditions below the critical conditions of the components.

Distinction between vapour-liquid equilibria and gas-liquid solubility is rather arbitrary and it seems reasonable to extend these ideas to solubility.

The AGAPE model uses a molecular lattice-based mixing rule. By judicious use of computer programs a methodology was created to examine a body of experimental gas-liquid solubility data for gases such as carbon dioxide, propane, n-butane or sulphur hexafluoride which all have critical temperatures a little above 298 K dissolved in benzene, *cyclo*-hexane and methanol.

Within this methodology the value of the GLP as an *ab initio* combining rule for such solutes in very dilute solutions in a variety of liquids has been tested. Using the GLP as a mixing rule involves the computation of rotationally averaged interactions between the constituent atoms, and new calculations have had to be made to discover the magnitude of the unlike pair interactions. These numbers have been seen as significant in their own right in the context of the behaviour of infinitely-dilute solutions. A method for extending this treatment to "permanent" gases has also been developed.

The findings from the GLP method and from the more general AGAPE approach have been examined in the context of other models for gas-liquid solubility, both "classical" and contemporary, in particular those derived from equations-of-state methods and from reference solvent methods.

Keywords: phase equilibria, intermolecular forces, AGAPE model, generalized London potential, activity coefficient model.

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Chapter 1 - Introduction and scope of research work

1.1 Introduction

In the chemical process industries, fluid mixtures are often separated into their components by diffusional operations such as distillation, absorption and extraction. Gas absorption is defined (Perry and Green, 1984) as a unit operation in which soluble components of a gas mixture (named the solutes) are dissolved in a liquid (called the solvent). The "stripping" process is the inverse of gas absorption, and is employed when transfer of volatile components from a liquid mixture is desired.

The equipment used for bringing a liquid and a gas stream into contact continuously is often of the packed tower type. A packed tower is a column filled with regular or irregular solid packing material. Another type of column is the plate-type unit containing a number of sieve plates, bubble-cap or other plates. In most installations the liquid and gas streams flow countercurrent, e.g., past each other, to obtain the highest rate of absorption, as this maximises the driving forces available.

An example of a process involving an absorber is shown in Figure 1.1 (from Perry and Green, 1984).

Figure 1.1. Gas absorber unit using a solvent regenerated by stripping. (a) Absorber. (b). Stripper.

The design of absorption (or stripping) towers can be divided into three steps.

1) Determine the quantity of either liquid (or gas) to absorb (or strip) the required amount of fluid, for this some data on the vapour-liquid phase equilibrium are needed.

2) Determine the required cross-sectional area and diameter of the equipment, for this data on the liquid-handling and vapour-handling capacities are needed.

3) Determine the necessary number of equilibrium stages; both equilibrium data and material balances are required.

Design of these separation operations then requires quantitative estimates of the partial equilibrium properties of fluid mixtures. Whenever possible, such estimates should be based on reliable experimental data for the particular mixture at conditions of temperature, pressure and composition corresponding to those of interest. Unfortunately, this is often not possible. In typical cases, no experimental data are available for the exact conditions and only fragmentary data at different temperatures, etc., are to hand. In such cases it is valuable to be able to predict or interpolate the process properties using models.

Since equilibrium properties are required for the design of separation operations, it is not surprisingly that a number of methods for prediction of phase equilibrium properties exist. Principal among them are the UNIFAC method (Fredenslund et al., 1975) (derived from the UNIQUAC method (Abrams and Prausnitz, 1975)), ASOG (Derr and Deal, 1969), and the solubility parameter theory of Scatchard and Hildebrand (Scatchard, 1931). These methods require some experimental vapour-liquid equilibrium data as they are semi-empirical.

The UNIFAC method is the most widespread method used by engineers, reducing as it does a vast body of data. Its underlying theory is derived from the lattice model devised by Guggenheim (1952) and its ideas can be used for a wider theoretical study involving real intermolecular forces.

Such a study has been made at Aston University by Homer et al. (1991) to give a procedure called AGAPE (**A** **G**eneral **A**pproach to **P**hase **E**quilibria). This has been applied to vapour-liquid equilibria. Since the distinction between vapour-liquid equilibria and gas-liquid solubility is rather arbitrary, it seems reasonable accordingly to extend the ideas of AGAPE to gas solubility.

This work begins from the semi-quantitative observations in the Ph.D. thesis of Mohammadi (1986) that a strong correlation exists between the solubility of permanent gases in a given solvent and the molecular buffeting effects relevant to their NMR shifts on passing from gas to liquid. Further, that some rationalisation of the differences in solubility of a range of gases in different solvents, including water, seemed to be possible in terms of van der Waals forces and that water might be considered to be less anomalous in its dissolving power for non-electrolytes than sometimes supposed.

Our approach to these ideas has been to seek to place them into the contexts of current knowledge of non-electrolyte solution thermodynamics and in particular within the immediate context of the AGAPE programme which uses a Generalized London Dispersion treatment of molecular interactions in devising its phase equilibrium equations.

1.2 Outline of Thesis

The work began with a review of the thermodynamic database for industrial gases in the liquid state at low temperatures and pressures. It sought to understand the frame work of vapour-liquid equilibria for low boiling compounds and by examining their mixing behaviour and excess thermodynamic functions to prepare the detailed basis of a suitable flexible mixing rule for all concentrations.

This thesis thus starts with an introduction to phase equilibrium and the equations for activity coefficients and excess Gibbs free energies using various existing prediction methods based on lattice models. It further demonstrates the use of equation-of-state procedures for calculating the thermodynamic excess functions, setting out the mixing rules and combining rules commonly used. For a better understanding of the underlying molecular interactions giving rise to those equations, some attention is paid to the ideas of intermolecular forces and how they effect aggregation in gases and liquids.

Since the behaviour of liquid mixtures is directly affected by the molecular interaction between like and unlike species it is desirable to relate thermodynamic excess functions to a realistic model of intermolecular forces. As has been demonstrated by a number of authors (e.g. Rowlinson and Swinton, 1982) the role of repulsion forces is primarily to determine the geometry and packing of liquids, and, since this is often relatively constant, it is practicable to treat the vapour-liquid behaviour of pure liquids and mixtures in terms mainly of an attractive potential. For many molecules the important potential is the London dispersion force and our attention has been focused on a modern form of this, suitable for multi-centred polyatomic molecules, the so-called **G**eneralized **L**ondon **P**otential (GLP) theory.

Application of this intermolecular potential can, in principle, be made to any statistical mixing rule for binary liquid mixtures. In practice, we have chosen to follow a molecular lattice-based mixing rule devised under the AGAPE model, already developed in this department for vapour-liquid equilibrium studies of organic liquids. By judicious use of some of the existing computer programs and by making suitable modifications, a methodology was created to examine a large body of experimental gas-liquid solubility data for gases such as ethane, ethylene, carbon dioxide, propane, n-butane or sulphur hexafluoride which all have critical temperatures a little above 298 K.

Within this methodology we have been able to test the value of the generalized London potentials as an *ab initio* combining rule for such solutes in very dilute solutions in a variety of liquids. Since the methods of using the GLP as a mixing rule involve the computation of rotationally averaged interactions between the constituent atoms, new calculations have had to be carried out in this work, and an analysis of best methods of computation done for this procedure to discover the magnitude of the unlike pair interactions. These numbers have been seen as significant in their own right in the context of the behaviour of infinite dilution solutions. A method for extending this treatment to "permanent" gases has also been developed.

The findings from the GLP method and from the more general AGAPE approach have been examined against the context of other models for gas-liquid solubility, both "classical" and contemporary, in particular those derived from equation-of-state methods and from reference-solvent methods.

Chapter 2 - Theoretical background

2.1 Introduction

To derive expressions which relate the concentrations of a given component in each phase of a vapour-liquid mixture in equilibrium, the first and second laws of thermodynamics are used. These expressions provide a basis for both theoretical and semi-empirical prediction methods of vapour-liquid equilibrium data from a minimum of information.

2.1.1 Criteria for equilibrium

The treatment outlined here follows closely that of Prausnitz et al. (1986), itself reflecting many early discussions.

In a closed system that interacts reversibly with its surroundings, the combination of the first and second law of thermodynamics gives

$$dU = T\,dS - P\,dV \tag{2.1}$$

Defining enthalpy, H as:

$$H = U + PV \tag{2.2}$$

and the Gibbs energy, G as:

$$G = H - TS \tag{2.3}$$

their differentiation gives

$$dH = T\,dS + V\,dP \tag{2.4}$$

$$dG = V\,dP - S\,dT$$

For an open system U is considered to be a function of entropy and volume and the mole numbers of the various components present. This is expressed formally as follows:

$$U = U(S, V, n_1, n_2, ..., n_m) \tag{2.5}$$

where m is the number of components.

Differentiation of this equation and combining with equation (2.1) yields

$$dU = T\,dS - P\,dV + \Sigma_i\,\mu_i\,dn_i \tag{2.6}$$

where μ_i is the chemical potential defined as

$$\mu_i \equiv \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_j} \tag{2.7}$$

From the definition of G it follows that

$$dG = V\,dP - S\,dT + \textstyle\sum_i \mu_i\,dn_i \tag{2.8}$$

and, further

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j} \tag{2.9}$$

From equation (2.6) the Gibbs-Duhem equation can be derived (e.g. Prausnitz et al., 1986)

$$S\,dT - V\,dP + \textstyle\sum_i n_i\,d\mu_i = 0 \tag{2.10}$$

It can be shown (e.g. Prausnitz et al., 1986) that for a closed, heterogeneous system consisting of π phases and m components the condition of equilibrium is

$$\begin{aligned} \mu_1{}^{(1)} &= \mu_1{}^{(2)} = \ldots\ldots\; \mu_1{}^{(\pi)} \\ \mu_2{}^{(1)} &= \mu_2{}^{(2)} = \ldots\ldots\; \mu_2{}^{(\pi)} \\ \mu_m{}^{(1)} &= \mu_m{}^{(2)} = \ldots\ldots\; \mu_m{}^{(\pi)} \end{aligned} \tag{2.11}$$

Important for phase equilibrium is the phase rule

$$F = m + 2 - \pi \tag{2.12}$$

where F is the number of degrees of freedom.

2.2 The problem

Introducing the chemical potential does not of itself enable the relationships between the concentrations of two or more phases in equilibrium to be formed. The chemical potential has to be transformed into a form dependent on temperature, pressure, and phase concentrations. This problem has been set out as in Figure 2.1 by Prausnitz et al. (1986).

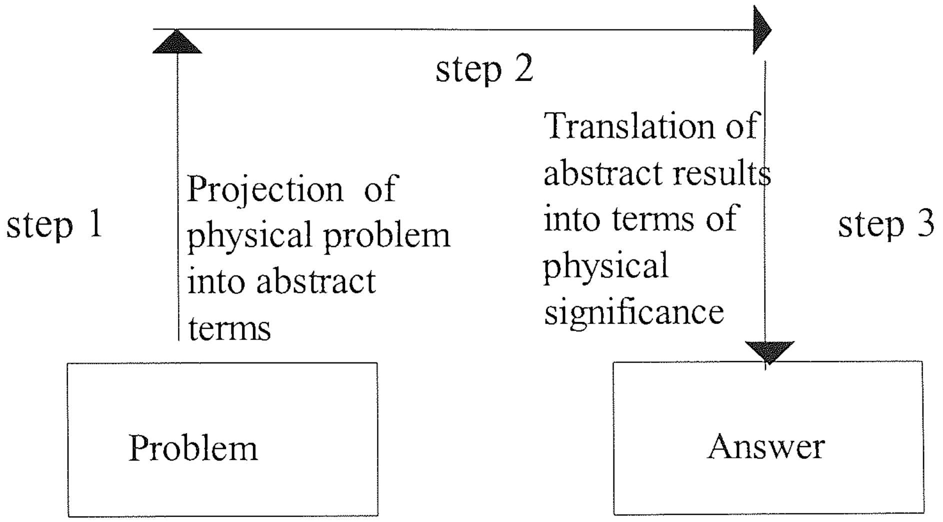


Figure 2.1. The problem to be solved.

In Step 1 a problem originally stated in terms of concentrations in the phases has been transformed into a statement involving the chemical potential. The specific relationship between pressure, temperature, concentrations, and the values of the chemical potentials makes it possible in Step 2 to achieve the goal in Step 1. The difficult step is Step 3 which involves a translation of the mathematical solution back into physically meaningful terms. For this purpose the terms fugacity, activity, and activity coefficient are introduced.

2.3 Fugacity, Activity, and Activity Coefficient

2.3.1 Definition of Fugacity, Activity, and Activity Coefficient

Fugacity was defined by Lewis in 1907 (Lewis, 1907) as

$$\mu_i - \mu_i^0 = RT \ln(f_i/f_i^0) \qquad (2.13)$$

where f_i is the fugacity of the i^{th} component and 0 indicates thermodynamic quantities at a so-called standard state with pressure P^0 and temperature T.

At equilibrium, the temperature is uniform throughout all phases of a system. It can then be shown (e.g. Prausnitz et al., 1986) that the criteria for phase-equilibria between phases α and β can be expressed as:

$$f_i^\alpha = f_i^\beta \qquad (2.14)$$

Further, Lewis named the ratio f_i/f_i^0 the activity a_i (Lewis, 1907). If f_i^0 changes, a_i^0 also changes, and the numerical value of the activity depends therefore among other things on the choice of the standard state. For solutions of non-electrolytes, the chosen standard state is that of the pure component at the temperature and pressure of the system. This always gives an activity of the pure component equal to unity.

$$(a_i)_{x_i=1} = f_i^0 \;/\; f_i^0 = 1$$

The activity coefficient of component i, γ_i, at some temperature, pressure, and composition is defined as the ratio of the activity of i to the mole fraction of i:

$$\gamma_i \equiv a_i / x_i \tag{2.15}$$

2.3.2 Ideal solution

An ideal solution is defined as a solution where both the vapour-phase and the liquid-phase solutions are ideal solutions, meaning that the fugacity for each component in each phase is proportional to the mole fraction. For a component in an ideal solution, it can be shown that the activity coefficient is equal to unity. The activity coefficient can thus be regarded as a correction factor for non-idealities in real solutions.

Combining the definitions of a_i and the activity coefficient gives

$$f_i = \gamma_i x_i f_i^0 \tag{2.16}$$

One important term is the fugacity coefficient of component i, φ_i, defined as

$$\varphi_i^V = f_i^V / (y_i P) \tag{2.17}$$

for the vapour phase (indicated by the superscript V). It can be shown (e.g. Prausnitz et al., 1986) that for a mixture of ideal gases $\varphi_i = 1$. The compressibility factor Z is defined as

$$Z \equiv Pv / (RT) \tag{2.18}$$

where v is the molar volume of the mixture.

Hence from equations (2.14), (2.16), and (2.17) we have

$$\gamma_i x_i f_i^0 = \varphi_i^V y_i P \tag{2.19}$$

This equation is a key equation for the calculation of vapour-liquid equilibrium using the activity coefficient approach (see section 2.10.3). We need an expression for f_i^0 to be able to use this equation.

Similar to the definition of the vapour-phase fugacity coefficient in equation (2.17), a liquid-phase fugacity coefficient can be defined

$$\varphi_i^L = f_i^L / (x_i P)$$

Inserting the definitions for the fugacity coefficient for both phases, one obtains

$$\varphi_i^L x_i = \varphi_i^V y_i \tag{2.20}$$

Again, this equation is a key equation for the calculation of vapour-liquid equilibrium in the equation-of-state approach (see section 2.10.2). We need to find an expression for both the liquid and the vapour phase fugacity coefficients.

2.4 Thermodynamic relationships

The terms introduced above are of use in solving step 3 in Figure 2.1. There is a choice of independent variables P and T or V and T, respectively.

2.4.1 Thermodynamic properties with independent variables P and T

Using the fundamental equations, of which equation (2.4) is one, the so-called Maxwell equations can be derived. The Maxwell equations are described in, for example, Prausnitz (Prausnitz et al., 1986) and using them the effect of the pressure on the enthalpy and entropy is expressed as

$$\frac{\partial H}{\partial P} = \left[V - T\left(\frac{\partial V}{\partial T}\right)_{P,\,n_T} \right]$$

$$\frac{\partial S}{\partial P} = -\left(\frac{\partial V}{\partial T}\right)_{P,\,n_T}$$

From these two equations Beattie (1949) derived

$$RT \ln \varphi_i = RT \ln \frac{f_i}{y_i P} = \int_0^P \left[\overline{v}_i - \frac{RT}{P} \right] dP \tag{2.21}$$

where $\overline{v}_i$ is the partial molar volume of i.

It is worth noticing that equation (2.21) is a general equation that can be applied not only to the vapour phase but also to the solid state and the liquid phase. It is convenient to separate equation (2.21) into two integrals, when calculating the fugacity for a pure solid or liquid at a given temperature T and pressure P. The first part gives the fugacity of the saturated vapour at T and the saturation pressure P^S, and the second part accounts for the compression of the condensed phase to the pressure P. Superscripts S and C refer to the saturation and the compressed phase, respectively, and equation (2.21) becomes

$$RT \ln \frac{f_i^C}{P} = \int_0^{P_i^S} \left[v_i - \frac{RT}{P} \right] dP + \int_{P_i^S}^{P} \left[v_i^C - \frac{RT}{P} \right] dP \tag{2.22}$$

As the fugacity of the saturated vapour, given by the first term on the right-hand side, is equal to the fugacity of the saturated condensed phase, this and a rearrangement give

$$f_i^C = P_i^S \varphi_i^S \exp\left(\int_{P_i^S}^{P} \frac{v_i^C dP}{RT} \right) \tag{2.23}$$

where $\varphi_i^S = f_i^S / P_i^S$.

Using the condensed phase as the standard phase in equation (2.19) makes it possible to replace f_i^0 with f_i^C as expressed by equation (2.23). Equation (2.23) can be further simplified. The exponential term, the Poynting correction, accounts for the liquid at a pressure P is different from P_i^S. At conditions remote from the critical conditions, the liquid is considered incompressible, and the simplified Poynting correction becomes

$$\exp\left[\frac{v_i^C \left(P - P_i^S \right)}{RT} \right]$$

2.4.2 Thermodynamic properties with independent variables V and T

This is based on the same use of the fundamental equations, the Maxwell equation and the equations derived by Beattie (1949) as in section 2.4.1. The result is (e.g. Prausnitz et al., 1986)

$$RT \ln \varphi_i = RT \ln \frac{f_i}{y_i P} =$$

$$\int_V^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - RT \ln Z \tag{2.24}$$

This equation is more useful for mixtures then equation (2.21).

Both equations (2.21) and (2.24) are useful for the equation-of-state approach to vapour-liquid equilibrium, as described in section 2.10.2. The key elements in this approach are the fugacity coefficients in both the liquid and the vapour phase.

2.4.3 Corresponding states theory

The law of corresponding states (Reid et al., 1987) was first proposed by van der Waals in 1873. The law of corresponding states expresses the generalization that equilibrium properties which depend on intermolecular forces are related to the critical properties in a universal way. Van der Waals showed the law to be theoretically valid for all pure substances whose pressure, temperature and volume properties could be expressed by a two-constant equation of state, such as the van der Waals equation of state (equation (2.31)). Later studies have shown that the law of corresponding states holds well for fluids containing simple molecules, and sufficiently well for substances where molecular orientation is not important.

Even though the relation of pressure to volume at constant temperature is different for different substances, the law of corresponding states states that the function relating reduced pressure to reduced volume becomes the same for all substances. The reduced properties are defined as the property divided by the critical property, e.g., reduced pressure, P_r, is expressed as $P_r = P / P_C$ and so on.

The law of corresponding states is illustrated in Reid et al. (1987), where the reduced pressure is plotted as a function of the reduced volume for two substances: methane and nitrogen. Only one of the isotherms is shown, but it agrees very well for the two substances.

The corresponding states principle has been employed to predict equilibrium constants for simple mixtures with reasonably accurate results (Leland et al., 1962).

2.5 Equation for vapour-liquid equilibrium

Inserting equation (2.23) into equation (2.19) using the simplified Poynting correction gives

$$\varphi_i y_i P = \gamma_i x_i P_i^S \varphi_i^S \exp\left[\frac{v_i^C\left(P - P_i^S\right)}{RT}\right]$$

The factor

$$\frac{\varphi_i^S}{\varphi_i} \exp\left[\frac{v_i^C\left(P - P_i^S\right)}{RT}\right]$$

is often near unity, when the total pressure P is sufficient low (Reid et al., 1987). Sufficient low usually means below 500 kPa, for some applications even up to 1000 kPa. At this low pressure the vapour phase is considered ideal, and then $\varphi_i^V \approx \varphi_i^S$. Setting the factor to 1.0 gives the basic equation for vapour-liquid equilibrium applicable at low total pressures

$$\gamma_i x_i P_i^S = y_i P \qquad (2.25)$$

Equation (2.25) is a key equation for calculating vapour-liquid equilibrium using the activity coefficient approach as described in section 2.10.3. The key element in the approach is the activity coefficient.

2.5.1. Auxiliary functions

For convenience in design work a number of alternative ways to express phase equilibrium are used.

One is the relative volatility α_{ij},

$$\alpha_{ij} = \frac{y_i x_j}{y_j x_i}$$

Another is the equilibrium ratio expressed as

$$K_i = y_i / x_i$$

or, in case of the equation-of-state approach as

$$K_i = \varphi_i^V / \varphi_i^L.$$

2.5.2 Raoult's law

If the activity coefficients for each individual compound in the liquid phase is unity, i.e., assuming that the liquid phase is ideal, equation (2.25) becomes

$$x_i P_i^S = y_i P$$

This equation is known as Raoult's law.

2.6 The Gibbs-Duhem equation

As mentioned earlier the Gibbs-Duhem equation

$$S\,dT - V\,dP + \sum_i n_i d\mu_i = 0 \qquad (2.10)$$

can be derived (e.g. Prausnitz et al., 1986) from differentiating equation (2.6). If variations in temperature and pressure are neglected the Gibbs-Duhem equation reduces to

$$\sum_i x_i \; d \ln \gamma_i = 0$$

This expression places a restrain on the way in which the composition can change in a given phase.

For the isobaric case equation (2.10) leads to the following useful thermodynamic relationship

$$\sum_i x_i \; d \ln \gamma_i = -\frac{h^E}{RT^2}\,dT$$

For the isothermal case the same equation gives

$$\sum_i x_i \; d \ln \gamma_i = \frac{v^E}{RT}\,dP \qquad P^0 = P_{system}$$

where superscript E in both cases stands for excess property.

2.7 Intermolecular forces

The need for development of VLE prediction models based on pure component data rather than experimental results has lead to the development of the AGAPE model.

The basis for the AGAPE model is that of London's dispersion forces (London, 1937). A short introduction of intermolecular forces based on that of Prausnitz et al. (1986) will be given in this section

2.7.1 Introduction to intermolecular forces

Thermodynamic properties of any pure substance are determined by intermolecular forces which operate between the molecules of that substance. Similarly, thermodynamic properties of a mixture depend on intermolecular forces which operate between the molecules of the mixture. The case of a mixture, however, is necessarily more complicated because consideration must be given not only to interaction between molecules belonging to the same component, but also to interaction between dissimilar molecules.

When a molecule is in proximity of another, forces of attraction and repulsion strongly influence its behaviour. If there were no forces of attraction, gases could not condense to form liquids, and in the absence of repulsive forces, condensed matter would not show resistance to compression.

2.7.2 Types of intermolecular forces

There are many different types of intermolecular forces. The most important ones may be classified as follows:

1. Electrostatic forces between charged particles (ions) and between permanent dipoles, quadrupoles, and higher multipoles.

2. Induction forces between a permanent dipole (or quadrupole) and an induced dipole.

3. Forces of attraction (dispersion forces) and repulsion between non-polar molecules.

4. Specific (chemical) forces leading to association and complex formation, i.e., to the formation of loose chemical bonds. The best example is that of hydrogen bonds.

2.7.3 Potential-Energy Functions

Molecules have kinetic energy as a result of their velocities relative to some fixed frame of reference. They also have potential energy as a result of their positions relative to one another.

Consider two simple, spherically symmetric molecules separated by the distance l. The potential energy Φ shared by these two molecules is a function of l. The force F between the molecules is related to the potential energy by

$$F = -\frac{d\Phi}{dl}$$

The negative of the potential energy, i.e., -Φ(l) is the work which must be done to separate two molecules from the intermolecular distance l to infinite separation. Intermolecular forces are almost always expressed in terms of potential-energy functions. The common convention is that a force of attraction is negative and a force of repulsion is positive.

In this simplified example it is assumed that the force acting between the two molecules depends on their relative position by the one co-ordinate, l. For a spherically symmetric molecule, such as an argon atom, this assumption is valid. For more complicated molecules, other co-ordinates, such as angles of orientation, may be required as additional independent variables of the potential-energy function.

2.7.4 Electrostatic forces

If we regard two point electric charges of magnitudes e_i and e_j, respectively, separated from one another *in vacuo* by the distance l, then the force between them is given by Coulomb's relation (sometimes called the inverse-square law):

$$F = \frac{e_i \quad e_j}{l^2}$$

Electrostatic forces can arise even for those particles which do not have a net electric charge. Asymmetric molecules possess permanent dipoles resulting from an uneven spatial distribution of electronic charges about the positively charged nuclei. Symmetric molecules, like argon and methane, have zero dipole moment, and those molecules having very little asymmetry generally have small dipole moments. The common unit for dipole moment is the debye. 1 debye is equivalent to 10^{-18} (erg $cm^3)^{1/2}$. This is not a SI unit, but is the unit used, when calculating dipole moments. In SI units 1 debye = 3.162 10^{-25} $(J/m^3)^{1/2}$.

It can be shown (e.g. Prausnitz et al., 1986) that the average potential energy Φ_{ij} between two dipoles i and j at a fixed separation l is found by averaging over all orientations with each orientation weighted according to its Boltzmann factor. When the Boltzmann factors are expanded in powers of $1/k_BT$, Φ_{ij} becomes

$$\overline{\Phi}_{ij} = -\frac{2}{3}\frac{m_i^2 \quad m_j^2}{l^6 \; k_BT} + \; . \; . \; . \tag{2.26}$$

Here m represents the dipole moment.

2.7.5 Induction forces between a permanent dipole and an induced dipole

A non-polar molecule such as argon or methane has no permanent dipole moment but when such a molecule is subjected to an electric field, the electrons are displaced from their ordinary positions and a dipole is induced. It can be shown (e.g. Prausnitz et al., 1986) that the general Debye formula for the mean potential energy due to induction by permanent dipoles, is

$$\overline{\Phi}_{ij} = -\frac{(\alpha_i \, m_j^2 + \alpha_j \, m_i^2)}{l^6} \tag{2.27}$$

where α is the polarizability, meaning the ease with which the molecule's electrons can be displaced by an electric field.

2.7.6 Intermolecular forces between non-polar molecules

It was shown by London (1937) that the so-called non-polar molecules are, in fact, non-polar only when viewed over a period of time. If an instantaneous photograph of such a molecule was taken, it would show that at a given instant the oscillations of the electrons about the nucleus had resulted in distortion of the electron arrangement sufficient to cause a temporary dipole moment. The dipole moment, rapidly changing its magnitude and direction, averages zero over a short period of time. However, these quickly varying dipoles produce an electric field which then induces dipoles in the surrounding molecules. The result of this induction is an attractive force.

London proposed that even for the simplest non-polar molecule the total potential energy between two simple, spherically symmetric molecules i and j at large distances can take the form

$$\Phi_{ij} = -\frac{3}{2}\frac{\alpha_i\,\alpha_j}{(R_{ij}^A)^6}\left(\frac{\hbar\,\nu_{0i}\;\hbar\,\nu_{0j}}{\hbar\,\nu_{0i} + \hbar\,\nu_{0j}}\right) \qquad (2.28)$$

where ν_{0i} is the frequency for molecule i in its unexcited state (corresponding to its "zero-point energy") and α_i is the polarizability for molecule i. R_{ij}^A is the distance between the centres of the two polarizable spheres (molecules i and j). The frequency is related to the variation of the index of refraction. It is this relationship between index of refraction and characteristic frequency which is responsible for the name "dispersion" for the attractive force between non-polar molecules.

For a molecule i, the product $\nu_{0i}\hbar$ is very nearly equal to its first ionization potential I_i. Equation (2.28) can therefore be written

$$\Phi_{ij} = -\frac{3}{2}\frac{\alpha_i\,\alpha_j}{(R_{ij}^A)^6}\left(\frac{I_i\,I_j}{I_i + I_j}\right) \qquad (2.29)$$

The important features of this potential for regular solution theory are: (1) the potential is temperature independent, (2) it is almost exactly additive, in pairs, non-specific, (3) it is short in range and, (4) its strength depends upon the number and "looseness" of the electrons. In the development of the Generalized London Potential which is the basis for the AGAPE model (section 2.11), it is assumed that the specific generalized London potential will not be independent of temperature. The dependency of temperature is an important feature in the success of the application of the AGAPE theory to predicting vapour-liquid equilibria.

To show the relative magnitude of dipole, induction and dispersion forces in some representative cases, London (1937) has presented calculated potential energies for a few simple molecules. His results are given in the form

$$\Phi_{ij} = \frac{J}{l^6}$$

where J is calculated separately for each contribution due to dipole, induction, and dispersion effect. In these calculations equations (2.26), (2.27) and (2.29) were used and the results are shown in Table 2-1 (Prausnitz et al., 1986)

Table 2-1. Relative magnitudes of intermolecular forces between two identical molecules at 273.15 K.

The computed values of J indicate that the contribution of induction forces is small and that even for strongly polar components, like ammonia, water or acetone, the contribution of dispersion forces is far from negligible.

Table 2-2 (Prausnitz et al., 1986) gives some calculated results for intermolecular forces between two molecules which are not alike. In these calculations equations (2.26), (2.27), and (2.29) were again used.

Table 2-2. Relative magnitudes of intermolecular forces between two different molecules at 273.15 K.

Again it is noticed that polar forces are not important when the dipole moment is less than 1 Debye and induction forces always tend to be much smaller than dispersion forces.

In London's original paper (London, 1937) he had included two more terms with opposite signs in equation (2.28). One of the terms accounts for the repulsive force. He assumed that at sufficient separation, these would cancel each other, because the terms had opposite signs.

In general it is necessary to take into account both repulsive and attractive forces between non-polar molecules and it is customary to assume that the total potential energy is the sum of two separate potentials, as we find in the Lennard-Jones potential (Lennard-Jones and Devonshire, 1937)

$$\Phi = 4\varepsilon\left[\left(\frac{\sigma}{l}\right)^{12} - \left(\frac{\sigma}{l}\right)^{6}\right] = \frac{j}{l^{12}} - \frac{k}{l^{6}} \qquad (2.30)$$

where $-\varepsilon = \Phi_{\text{minimum}}$, and where σ is the intermolecular distance when $\Phi = 0$. The Lennard-Jones potential relates the potential energy of two molecules to their distance of separation in terms of two parameters, an energy parameter ε which, when multiplied by -1.0 gives the minimum energy corresponding to the equilibrium separation, and a distance parameter σ that is equal to the intermolecular separation when the potential energy is zero. Parameters j and k are the repulsion constant and the attraction constant, respectively. In general, the characteristic Lennard-Jones parameter is the energy parameter ε.

An illustration of equation (2.30) is shown in Figure 2.2 from Prausnitz et al. (1986). For many treatments of liquids the Sutherland potential is effectively used. The variation of the London potential with separation looks similar to the Sutherland potential.

Figure 2.2. Potential functions with zero, one, or two adjustable parameters.

Figure 2.3 (from Prausnitz et al., 1986) illustrates the Mie's potential, where the Lennard-Jones potential is a variant (for n=12).

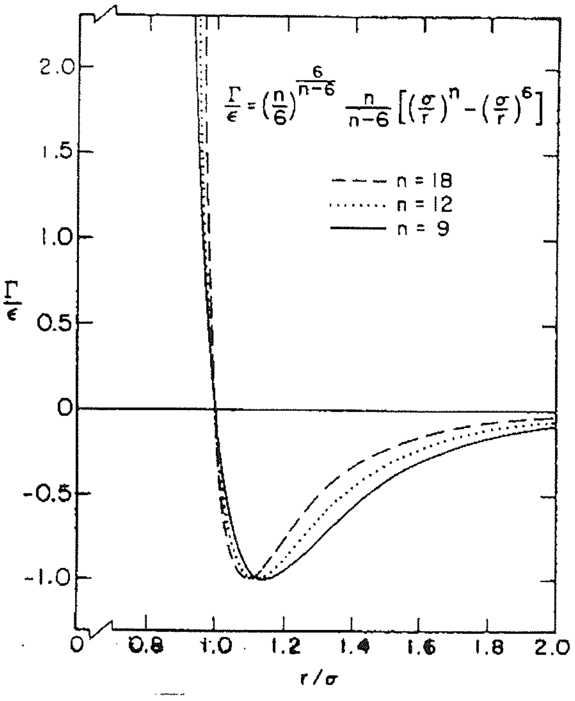


Figure 2.3. Three forms of Mie's potential for simple, non-polar molecules.

2.7.7 Specific (chemical) forces

In addition to the physical intermolecular forces briefly described here, there are specific forces of attraction that lead to the formation of new molecular species. These forces are called chemical forces. A good example of such force is the force that exists between ammonia and hydrogen chloride. In this case a new species, ammonium chloride, is formed. Another example is the hydrogen bond.

2.7.8 Summary

Both physical and chemical forces play an important role in determining properties of solutions. In some cases chemical forces can be neglected, but in other cases chemical forces predominate. The dissolved solution represents a state of wide versatility where in one extreme the solvent is merely a diluent with respect to the solute, while in the other extreme it is a chemical reactant.

The aim in applying thermodynamic methods to phase-equilibrium problems depends in large measures on the degree of the understanding of intermolecular forces which are responsible for the molecules' behaviour.

2.8 Models

In order to carry out step 3 in Figure 2.1 (the translation of abstract results into terms of physical significance) models for both the liquid phase and the vapour phase are required.

We limit the discussions to systems of one liquid phase and one vapour phase: for each a model is required which can be the same for both (the equation-of-state approach) or different (activity-coefficient approach) and only for binary mixtures consisting of components 1 and 2.

2.9 Models for the vapour phase

Two different types of model can be used to represent the vapour phase: the Lewis fugacity approach and the equation-of-state approach. Models for both are described in Prausnitz et al. (1986).

2.9.1 The Lewis fugacity model

Lewis (1907) defined the fugacity as

$$\mu_i - \mu_i^0 = RT \ln(f_i / f_i^0) \qquad (2.13)$$

where f_i is the fugacity of the ith component and 0 indicates thermodynamic quantities at a so-called standard state with pressure P^0 and temperature T. A pure, ideal gas is defined (e.g. Prausnitz et al., 1986) as a gas for which the fugacity is equal to the pressure. For a component i in a mixture of ideal gases, the fugacity of each component is equal to its partial pressure p_i defined as y_iP.

Since all systems, pure or mixed, approach ideal-gas behaviour at very low pressures, the definition of fugacity is completed by the limit

$$\frac{f_i}{y_iP} \rightarrow 1 \quad \text{as} \quad P \rightarrow 0$$

For an ideal gas, equation (2.13) becomes

$$\mu_i - \mu_i^0 = RT \ln(P / P^0)$$

This equation can be used to relate the abstract, thermodynamic quantity μ to a common, intensive property of the real world.

2.9.2 The equation-of-state model

As mentioned earlier, the vapour phase fugacity coefficients are usually calculated by use of equations of state. An equation of state is the mathematical relation between volume, pressure, temperature, and composition, often in the form of a cubic equation of state. The ideal gas law, stating PV = nRT is the earliest and often used as a starting point. However, since based on the ideal gas state it is not accurate enough to represent all gases. The problem increases as the pressure becomes large.

2.9.2.1 Van der Waals model

Introducing additional terms into the ideal gas law is one way to overcome the problem. One of the earliest equations is that of van der Waals (e.g. Prausnitz et al., 1986)

$$Z_{vW} = \frac{Pv}{RT} = \frac{v}{v - b'} - \frac{a'}{RTv} \qquad (2.31)$$

where a' and b' are the van der Waals constants and depend on composition. The parameter b' is interpreted as a measure for the size of the molecules (the hard sphere diameter), $(v\text{-}b')$ is the free volume and a' reflects the strength of attraction between two molecules which leads to negative pressures. It is important to notice that as well as constants a' and b' for each component i in the mixture, there are also the mixture constants a' and b'. The relation stating how the mixture constants a' and b' depend on composition is called a "mixing rule". The problem lies with the parameter a' for components i and j that are chemically non-identical and where no experimental data are available for the mixture i-j. In this case, a'_{ij} has to be expressed as a function of a'_i and a'_j. In fact, this reflects one of the key problems in thermodynamics. How are we able to predict the intermolecular forces of a mixture, when we have been given some information of the intermolecular forces for each of the fluids in the mixtures. Molecular forces are described in section 2.7. It is only due to a number of assumptions that the relation between the forces between two molecules i and j can be derived on the basis of the individual forces between molecule i and molecule j.

The simple geometric-mean assumption (e.g. Prausnitz et al., 1986) is

$$a'_{ij} = \sqrt{a'_i \; a'_j}\,. \qquad (2.32)$$

The AGAPE method (Homer et al., 1991) (described in detail in section 2.11) is a way of describing the intermolecular forces between molecules in a mixture given the forces for each of the two (or more) fluids. The theory is based on the London (1937) theorem (described in section 2.7). London showed that under certain conditions the geometric-mean concept is theoretically justified.

The attractive term in equation (2.31) is not accurately given by van der Waals a'. It can be expressed as a power series. However, for the purpose of the calculation of excess thermodynamics functions it is found that the standard cubic equations give a surprising cancellation of errors between the discrepancies in repulsion and attraction making cubic equations of state more accurate then they ought to be.

Because cubic equations of state are so much more convenient to use mathematically, much work has been done to develop these for the treatment of mixtures.

2.9.2.2 Mixing rules and combining rules

The term "mixing rule" has been used in the previous section and defined in section 2.9.2.1. A mixing rule is a relation that states how constants for the mixture depend on the composition. As an example a'_{mix} and b'_{mix} (van der Waals constants for the binary mixture, also written as a'_{ij} and b'_{ij}) were originally proposed by van der Waals as

$$a'_{mix} = x_1^2 a'_1 + 2x_1x_2\sqrt{a'_1a'_2} + x_2^2 a'_2$$
$$b'_{mix} = x_1 b'_1 + x_2 b'_2$$

where a'_1, a'_2, b'_1 and b'_2 are van der Waals parameters for the pure components 1 and 2. These equations are the so-called one-fluid rules.

Another example of a combining rule allowing us to obtain a'_{mix} from a'_1 and a'_2 and b'_{mix} from b'_1 and b'_2 is

$$(b'_{mix})^{1/3} = 0.5\left[(b'_1)^{1/3} + (b'_2)^{1/3}\right]$$

$$a'_{mix} = (b'_{mix})\left(\frac{a'_1\ a'_2}{b'_1\ b'_2}\right)^{1/2}(1 - k_{12})$$

where k_{12} is a binary parameter, which is small compared to 1, and the exponent 1/3 for the b′-parameter is due to the fact that the b′-parameter is proportional to the volume and hence the diameter in the third exponent.

These equations for the mixture parameters allow the use of van der Waals equation to derive the excess enthalpy from the excess Gibbs energy for mixtures of simple molecules. First, the molar excess Helmholtz energy, a^E (which is almost exactly equal to the excess Gibbs energy, g^E) is given by

$$\begin{aligned} a^E(T, x) &= a^E_{mix}(T, x, v_{mix}) - x_1\ a^E(T, x, v_1) \\ &\quad - x_2\ a^E(T, x, v_2) - RT(x_1 \ln x_1 + x_2 \ln x_2) \end{aligned}$$

where $v_{mix} = x_1\ v_1 + x_2\ v_2$.

McGlashan (1970) and Marsh et al. (1980a, 1980b, and 1980c) have performed calculations using this format to find the excess enthalpy, h^E

$$h^E = \left(\frac{\partial(g^E\ /\ T)}{\partial(1\ /\ T)}\right)_{P,x}$$

and also an expression for the excess molar volume, v^E. This shows results in good agreement for the following binary mixtures: nitrogen and oxygen, carbon monoxide and methane with $k_{12} = 0.989$ and 0.958, respectively. For the mixture benzene and carbon tetrachloride good agreement was obtained when using k_{12} very close to zero. For molecules of very different size or type, much less satisfactory results have been obtained.

2.9.2.3 Other cubic equations of state

For the moment, let us return to the equations of state. The most used equation of this type is due to Redlich and Kwong (1949) which was developed based on the van der Waals equation of state and is:

$$Z_{RK} = \frac{Pv}{RT} = \frac{v}{v - b} - \frac{a}{RT^{3/2}(v + b)} \qquad (2.33)$$

where a and b are characteristic constants differing from one fluid to another. Constants a and b are functions of the critical properties, although some treatments use them merely as empirical fitting parameters. The a factor is both temperature dependent and dependent on the acentric factor of Pitzer, ω, which reflects the anisotropy of the molecules. The fugacity coefficients can be derived (Redlich and Kwong, 1949) by inserting equation (2.33) into equation (2.24).

A number of improvements of the Redlich-Kwong equation have been developed, of which a major one is the Soave modification (Soave, 1972). It has been found that such cubic equations of state do not predict liquid density very well and different modifications are used to match different densities for pure liquids.

The Peng-Robinson (Peng and Robinson, 1976) equation of state is another example of a cubic equation of state where the pressure is calculated as

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

where, also, a and b are characteristic constants differing from one fluid to another. Constants a and b are functions of the critical properties and a is, as indicated, a function of temperature. Also in this case, the fugacity coefficients can be derived (Peng and Robinson, 1976).

An overview of four different cubic equations of state and their parameters is presented in Reid et al. (1987).

2.9.2.4 The virial equation of state

For gases the simplest equation-of-state approach is the virial equation (e.g. Prausnitz et al., 1986)

$$Z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \ldots$$

where B is the second virial coefficient, C the third virial coefficient and so forth. All the virial coefficients, for the pure components, are functions only of the temperature. The second virial coefficient accounts for the deviation from ideality resulting from interactions involving two molecules: the coefficient C deals with three molecules interaction, and so on. The importance of the virial equation of state lies in the fact, that there is a theoretical relation between the virial coefficients and the intermolecular potential. The virial equation is usually truncated after the second virial coefficient for pressures up to 1 MPa. In truncated form the virial equation (valid for pressures up to 1 MPa) becomes

$$Z = \frac{Pv}{RT} = 1 + \frac{B}{v} \tag{2.34}$$

For binary mixtures, B_{11}, B_{22}, B_{12}, as well as B_{mix} must be evaluated, often from experimental data. B_{mix} is considered a function of the other three second virial coefficients as

$$B_{mix} = \sum_{i=1}^{m} \sum_{j=1}^{m} y_i y_j B_{ij} \tag{2.35}$$

Inserting the truncated virial equation into equation (2.23), an expression by Beattie (1949) gives

$$\ln \varphi_i = \frac{2}{v} \sum_{j=1}^{m} y_j B_{ij} - \ln Z_{mix} \tag{2.36}$$

where Z_{mix} is given by

$$Z_{mix} = 1 - \frac{B_{mix}}{v} \tag{2.37}$$

This makes it possible to obtain the fugacity coefficients for the components in the vapour phase.

Truncating the virial equation of state after the third term gives

$$Z_{mix} = \frac{Pv}{RT} = 1 + \frac{B_{mix}}{v} + \frac{C_{mix}}{v^2} \tag{2.38}$$

and the fugacity coefficient for a component i in a mixture of m components can be written (Prausnitz et al., 1986)

$$\ln \varphi_i = \frac{2}{v} \sum_{j=1}^{m} y_j B_{ij} + \frac{3}{2v^2} \sum_{j=1}^{m} \sum_{k=1}^{m} y_j y_k C_{ijk} - \ln Z_{mix} \tag{2.39}$$

In both equations, Z_{mix} is the compressibility factor of the mixture, v is the molar volume of the mixture, and B_{mix} and C_{mix} are the virial coefficients of the mixture as given by equation (2.35) and a similar equation for C_{mix} accounting for interaction between three molecules. Note that the summations are over all components, including component i. As an example, the fugacity coefficients for a binary mixture become

$$\ln \varphi_1 = \frac{2}{v}(y_1 B_{11} + y_2 B_{12}) + \frac{3}{2v^2}(y_1^2 C_{111} + 2y_1 y_2 C_{112} + y_2^2 C_{122}) - \ln Z_{mix}$$

and

$$\ln \varphi_2 = \frac{2}{v}(y_2 B_{22} + y_1 B_{12}) + \frac{3}{2v^2}(y_2^2 C_{222} + 2y_1 y_2 C_{122} + y_1^2 C_{112}) - \ln Z_{mix} \qquad (2.40)$$

Data for the second virial coefficient are more plentiful in the literature then data for the third virial coefficient, and therefore it is more common to truncate the virial equation of state after the second term, leading to equation (2.34).

The fugacity coefficient for a component i can be expressed in volume-explicit form instead of the pressure-explicit form, as used throughout this description. In volume-explicit form, the virial equation of state is given by

$$Z = \frac{Pv}{RT} = 1 + B' P + C' P^2 + D' P^3 + \ldots$$

where the coefficients B′, C′, and D′ depend on temperature but are independent of pressure or density. Using this form of the virial equation-of-state to rewrite the fugacity coefficient of component i in a mixture of m components, and omitting the terms including the third virial coefficient C′ and higher order terms, the fugacity coefficient equation becomes

$$\ln \varphi_i = \left(2\sum_{j=1}^{m} y_j B'_{ij} - B'_{mix} \right) \frac{P}{RT} \qquad (2.41)$$

This equation has proved more useful than equation (2.36), as it uses pressure instead of the molar volume for the mixture as the independent variable, and the fact that assuming $C' = 0$ is a better assumption then assuming $C = 0$, as it is done in equation (2.36).

The virial equation of state is restricted to moderate densities.

2.9.2.5 Using potential functions to calculate the virial coefficients

As shown in the previous section, the virial equation can be used to calculate the fugacity of a component in the gaseous phase. As mentioned before, the virial equation of state is usually accurate enough at low to moderate densities to use in its truncated form (equation (2.36)).

Considering a binary mixture containing species i and j, the three types of two-molecule interactions are i-i, j-j, and i-j. The virial coefficient B_{ii} of the pure i then depends on the potential Φ_{ii}, B_{jj} depends on the potential Φ_{jj} for pure j, and B_{ij} depends on Φ_{ij}, the potential energy between molecules i and j.

If i and j are spherical symmetrical molecules, it can be shown that the relation between the second virial coefficient corresponding to the i-j interaction B_{ij} can be expressed as (Prausnitz et al., 1986)

$$B_{ij} = 2\pi L \int_0^\infty (1 - e^{-\Phi_{ij}(l)/k_B T}) l^2 dl$$

where l is the distance between molecular centres, k_B is the Boltzmann's constant, and L is Avogadro's number. The pure B_{ii} is found by substituting $\Phi_{ij}(l)$ with the potential energy of the pure ii, Φ_{ii}.

For a binary mixture, the second virial coefficient B_{mix} is a quadratic function of the mole fractions y_i and y_j (equation (2.35) for a binary mixture)

$$B_{mix} = y_i^2 B_{ii} + y_j^2 B_{jj} + 2 y_i y_j B_{ij}$$

Integration of the equation for B_{ij} has been carried out for many molecular models of the potential functions.

Ideal-gas potential.

Assuming $\Phi = 0$ (the simplest case) for all values of the intermolecular distance l, gives virial coefficients equal to zero, and reduces the virial equation to the ideal gas law.

Hard-sphere potential.

This model considers molecules to be like billiard balls. Further, it assumes no forces between the molecules when their centres are separated by a distance larger then the hard-sphere diameter, σ'. The potential function $\Phi(l)$ thus becomes

$$\Phi = \begin{cases} 0 & \text{for } l > \sigma' \\ \infty & \text{for } l \leq \sigma' \end{cases}$$

The second virial coefficient for a pure component, B_{ii} becomes

$$B_{ii} = \frac{2}{3} \pi L \sigma_{ii}'^{3}$$

and the mixed virial coefficient B_{ij} becomes

$$B_{ij} = \frac{2}{3} \pi L \left(\frac{\sigma_1' + \sigma_2'}{2} \right)^3$$

This model for the potential energy uses one adjustable parameter, σ', for each component.

Other models (such as the Lennard-Jones expression for the potential energy) for the intermolecular potential energy can be used to evaluate the integrals for both second and third virial coefficients if desired. In practice B is found to be temperature dependent being negative at low temperatures and positive at high temperature. The fugacity coefficients may be written in terms of the virial coefficient as expressed in equation (2.36) or equation (2.41). The fugacity coefficient may be close to zero for most systems at low pressures (100-300 kPa).

Measured values of B can be correlated using the ideas of the principle of corresponding states which allows us to normalise volume or pressure data as a function of temperature by referring the data to the critical properties of the fluids being examined. Thus a plot of B (which has the dimension of volume) divided by V_C against T/T_C (where V_C and T_C are critical volume and critical temperature, respectively) gives a widely valid relationship which permits B to be predicted given known values of V_C and T_C.

2.9.2.6 The conflict between mixing rules and combining rules

As may be seen from the many studies of thermodynamic functions of liquid mixtures by equations of state, there is always a need to define conditions dependent on concentrations for binary mixtures for the key parameters, e.g., the a′ and b′ of van der Waals equation of state, which then introduce the concept of separate parameters for 1,1, 2,2, and 1,2 interactions. The writing of the additional condition defining the 1,2 interaction in terms of the 1,1 and 2,2 parameters then requires a combining rule which assumes that the reality of the interactions is contained within it. If however, there are second order terms neglected in the equation of state for the pure liquids, then the combining rule may reflect this sensitivity. Thus for example studies of excess functions or phase equilibria for a homologous series of hydrocarbons against a reference compound, can show systematical deviation of parameters from "a norm" which leaves it unclear whether it is a mixing rule or the combining principle which is systematically varying.

The lattice model is no exception and part of the purpose of this work is to examine how far results from the dilute mixtures studied can throw light on the validity of the mixing rule as well as examine the usefulness of more sophisticated combining rules for binary interactions.

2.10 Models for the Liquid Phase

As for the vapour phase, two different models may be used to represent the liquid phase: the activity coefficient model and the equation-of-state model. Both models are described in Prausnitz et al. (1986) as well as elsewhere (Walas, 1985).

2.10.1 The liquid state

We all have an idea of what a liquid is, but how do we define it? The most common definition is (Rowlinson and Swinton, 1982) that a liquid is a substance that when it is placed in a vessel will conform to the shape of the vessel, but without filling it in full. The liquid state is between the solid state and the gaseous state. If a solid is heated, it loses regularity and becomes a liquid at a certain set of conditions, and heating the liquid even more will, at last, turn it into a gas whose molecules are individual.

It is not surprising that two different approaches of formulating a theory of liquids to describe their thermodynamic properties have been developed (Hildebrand et al., 1970). One direction is to extrapolate the properties for the liquid from the gaseous state, the other direction starts from the properties of the crystal (solid) lattice. Neither of these has led to the desired goal of formulating a theory of pure liquids. The extrapolation from the properties of gases involves the transition from the binary collisions that happen in the gaseous state to the multiple interactions that take place in the liquid state. The lattice theory assumes structures of the liquid that its properties show may be rather artificial.

Despite their failures to describe a liquid, the two models mentioned above are the two approaches that have been mainly used to formulate a theory of liquid mixtures. The method of extrapolating properties from the properties of gases is usually associated with equations of state for liquids. The approach from the solid state is associated with the lattice models for liquids, among them the UNIQUAC and the AGAPE model.

2.10.2 The equation-of-state model

The model uses an equation-of-state approach for the liquid phase as for the vapour phase (section 2.9). It is more convenient to substitute the chosen equation of state into equation (2.20) to calculate the fugacity coefficient for the liquid phase.

Equation-of-state models for the liquid phase have not been used very much, many more treatments are developed using the activity coefficient approach. This is caused by an inadequacy of the equations of state to predict accurate densities over any given range, especially at low to moderate pressures.

2.10.3 Activity coefficient models

Activity coefficients models are widely used for liquid mixtures at low pressures and are based on the relationship between the activity coefficient and the excess Gibbs energy.

Some new terms have to be introduced (e.g. Prausnitz et al., 1986). Excess functions are defined as thermodynamic properties of solutions that are in excess of those of an ideal solution at the same conditions. Thus the excess Gibbs energy is defined as

$$G^E = G_{(\text{actual solution at T, P, and x})} - G_{(\text{ideal solution at the same T, P, and x})}$$

Excess volume V^E, excess enthalpy H^E, excess entropy S^E, excess Helmholtz energy A^E, and excess internal energy U^E can be similarly defined. The same relationships as described in section 2.2 are valid for the excess properties. As an example the equation (2.2) in terms of the excess properties becomes

$$H^E = U^E + PV^E$$

Partial molar functions are defined, using Gibbs energy as an example by

$$\bar{g}_i \equiv \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}$$

The partial molar functions of entropy, enthalpy, etc., are defined similarly.

Partial molar excess functions are defined by

$$\bar{g}_i^E \equiv \left(\frac{\partial G^E}{\partial n_i}\right)_{T,P,n_j} \tag{2.42}$$

again using Gibbs energy as an example. We define the partial molar excess functions of entropy, enthalpy, etc., similarly.

Application of Euler's theorem that the order of differentiation in forming second partial derivatives is immaterial for continuous functions and their derivatives, gives (e.g. Prausnitz et al., 1986)

$$G = \sum_i n_i \bar{g}_i$$

and then

$$G^E = \sum_i n_i \bar{g}_i^E$$

This is equally valid for the other properties, excess or otherwise.

From the definition of G^E it follows that

$$\bar{g}_i^E \equiv \bar{g}_i - \bar{g}_{i,\,ideal} \tag{2.43}$$

Using the definition of the Gibbs energy given in section 2.1.1 which led to equation (2.9)

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} = \bar{g}_i$$

and the definition of the fugacity given as equation (2.13) in section 2.3

$$\mu_i - \mu_i^0 = RT \ln(f_i/f_i^0)$$

equation (2.43) can be written as

$$\bar{g}_i^E = RT \ln \frac{f_i}{f_{i,\,ideal}}$$

Since

$$f_i = \gamma_i x_i f_i^0 \tag{2.16}$$

and the ideal state is defined as the state where the activity coefficient is unity, it follows that

$$\left(\frac{\partial G^E}{\partial n_i}\right)_{T,P,n_j} = \bar{g}_i^E = RT \ln \gamma_i \tag{2.44}$$

Introducing a new parameter, the molar excess Gibbs energy, g^E, it follows that

$$g^E = RT\sum_i x_i \ln \gamma_i \tag{2.45}$$

The advantage of the activity coefficient models lies in the relationship between the excess Gibbs energy either in the molar or partial form and the activity coefficient. Many equations have been proposed to express g^E as a function of composition often based on some theory of the nature of liquids and liquid mixtures.

One simple approach is based on an assumption of the energy required to replace one molecule of the solvent with one molecule of the solute. Two models worth mentioning are the regular solution theory suggested by Hildebrand and Scott (1964) and the athermal approach. Both models use equation (2.3) written for the molar excess Gibbs energy as

$$g^E = h^E - Ts^E \tag{2.46}$$

Regular solution theory

The regular solution is associated with molecules of similar size and, for molecules of similar size, assumes $s^E = 0$ and that no volume change occurs on mixing, i.e.

$$g^E = h^E \tag{2.47}$$

The athermal approach is used, when considering molecules of very different size, and assumes that the non-ideality is due entirely to the entropy, i.e. $h^E = 0$ and

$$g^E = -Ts^E$$

The van Laar model.

The simplest of the regular solutions models is the van Laar model (e.g. Prausnitz et al., 1986). Van Laar calculated an energy change in each step in an assumed thermodynamic cycle, in which two liquids are expanded isothermally at a low pressure and then mixed ideally. Van Laar used the van der Waals equation of state (section 2.9.2.1). The derived equation does not account for the pressure and/or the temperature variations. Further, it is difficult to extend to multicomponent mixtures.

The Margules equations.

The van Laar equation has been modified by Margules to overcome some of its application problems. He developed the two-suffix Margules equations which have found some practical use for simple binary mixtures. The parameter A_M can be found from the activity coefficients at infinite dilution as shown:

$$\begin{aligned} \gamma_1^\infty &\equiv \lim_{x_1 \to 0} \gamma_1 = \exp\left(\frac{A_M}{RT}\right) \\ \gamma_2^\infty &\equiv \lim_{x_2 \to 0} \gamma_2 = \exp\left(\frac{A_M}{RT}\right) \end{aligned} \tag{2.48}$$

It is worth noticing that in the case of the symmetrical two-suffix Margules equation the activity coefficients at infinite dilution (equation (2.48)) for both components are equal. The three-suffix Margules equation contains two parameters, and the expressions for the activity coefficients are different from each other (see Table 2-4).

Scatchard-Hildebrand theory.

It is possible to derive Margules equations for ternary and higher mixtures, but the regular solution theory, also called the Scatchard-Hildebrand theory, is less tedious to use. The regular solution theory was developed by Scatchard (1931) and Hildebrand (1929) on the basis of both the van Laar and Margules equations.

A regular solution is one involving no entropy change when a small amount of one of its components is transferred to it from an ideal solution of the same composition, the total volume remaining unchanged (Hildebrand et al., 1970). Based on the following assumptions (1) the mutual energy of two molecules depends only upon the distance between them and their relative orientation, and not on the nature of the molecules around them or on the temperature, (2) the distribution of the molecules in position and in orientation is random, (3) the change of volume upon mixing at constant pressure is zero, Scatchard-Hildebrand introduced a parameter, the cohesive-energy density c, given by

$$c \equiv \frac{\Delta u_{vap}}{v^L}$$

where Δu_{vap} is the energy change upon isothermal vaporization of the saturated liquid to infinite volume (the ideal gas state) (Hildebrand et al., 1970). For a binary mixture, three c parameters have to calculated, one for each component (c_{ii}) and one for the mixture (c_{ij}). The molar energy change of mixing is equal to the excess energy of mixing and was derived to be (Hildebrand et al., 1970)

$$u^E = (c_{11} + c_{22} - 2c_{12})w_1 w_2 (x_1 v_1 + x_2 v_2)$$

where the volume fractions of component 1 and 2, w_1 and w_2 are defined as

$$w_1 \equiv \frac{x_1 v_1}{(x_1 v_1 + x_2 v_2)} \qquad w_2 \equiv \frac{x_2 v_2}{(x_1 v_1 + x_2 v_2)}$$

Scatchard-Hildebrand assumed that the attractive forces between the molecules are due primarily to dispersion forces (Hildebrand et al., 1970) and then c_{12} is related to c_{11} and c_{22} as suggested by London (1937)

$$c_{12} = \sqrt{c_{11}\ c_{22}}\ .$$

Defining the solubility parameters, δ_1 and δ_2

$$\delta_1 \equiv \sqrt{c_{11}} = \sqrt{\left(\frac{\Delta u_{vap}}{v}\right)_1} \qquad \delta_2 \equiv \sqrt{c_{22}} = \sqrt{\left(\frac{\Delta u_{vap}}{v}\right)_2} \qquad (2.49)$$

and using the definition of the regular solutions, the activity coefficients become

$$
\begin{aligned}
RT \ln \gamma_1 &= v_1 w_2^2 (\delta_1 - \delta_2)^2 \\
RT \ln \gamma_2 &= v_2 w_1^2 (\delta_1 - \delta_2)^2
\end{aligned}
\qquad (2.50)
$$

These equations are the regular solution equations.

The regular-solution equations are related to the van Laar equations by (e.g. Prausnitz et al., 1986)

$$A'_{VL} = \frac{v_1}{RT} (\delta_1 - \delta_2)^2 \qquad B'_{VL} = \frac{v_2}{RT} (\delta_1 - \delta_2)^2 \qquad (2.51)$$

The Gibbs excess energy and the activity coefficients as expressed by the van Laar equations are given in Table 2-4.

Flory-Huggins theory.

One theory was developed by Flory (1941, 1942) and Huggins (1941) and is based on the lattice theory that will be described in the next section. As mentioned previously the athermal approach for molecules of very different size assumes that the non-ideality is due entirely to the entropy, i.e. $h^E = 0$ and

$$g^E = - Ts^E$$

2.10.3.1 The lattice theory

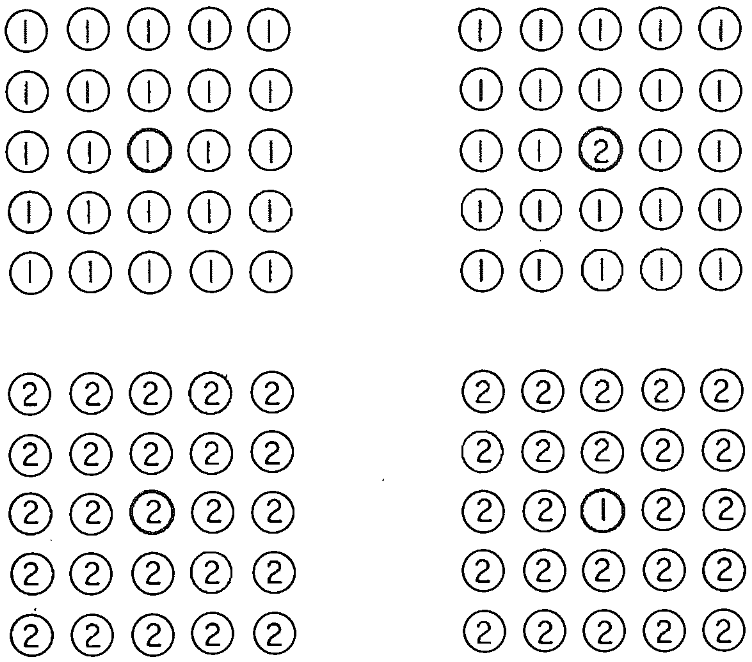
The liquid state is in some sense intermediate between the crystalline state and the gaseous state. One approach is to consider the liquid to be solid-like, in a quasicrystalline state, where the molecules do not translate fully into a chaotic manner as in the gas, but each molecule tends to stay in a small region, a more or less fixed position in space about which it vibrates back and forth. The quasicrystalline picture of the liquid state supposes molecules to sit in a regular array in space, called a lattice, hence the term lattice theory. A brief description of such a theory (from Prausnitz et al., 1986) follows.

Since the lattice theory of liquids assumes that molecules are confined to lattice positions, calculated entropies (an expression for the disorder) are low by what is called the "communal entropy". While this is a serious deficiency, it tends to cancel when lattice theory is used to calculate excess properties of liquid mixtures.

Molecular considerations suggest that deviations from ideal behaviour in liquid solutions are due primarily to the following effects: (i) the forces of attraction between unlike molecules are quantitatively different from those between like molecules, giving rise to a nonvanishing enthalpy of mixing; (ii) if the unlike molecules differ significantly in size or shape, the molecular arrangement in the mixture may be appreciably different from that for the pure liquids, giving rise to a nonideal entropy of mixing; and (iii) in a binary mixture, if the forces of attraction between one of three possible pair interactions are very much stronger (or very much weaker) than those of the other two, there are certain preferred orientations of the molecules in the mixture, which, in extreme cases, may induce thermodynamic instability and demixing.

Consider two simple liquids 1 and 2. Molecules of types 1 and 2 are small and spherically symmetric and the ratio of their sizes is close to unity. The arrangement of the molecules in each pure liquid is that of a regular array as indicated in Figure 2.4 (after Prausnitz et al., 1986). All the molecules are situated on lattice points which are equidistant from one another. Molecular motion is limited to vibrations about the equilibrium positions and is not affected by the mixing process. Further, it is supposed that for a fixed temperature, the lattice spacing for the two pure liquids and for the mixture are the same, independent of composition. In other words $v^E = 0$.

It is also assumed that the potential energy of a large number of molecules sitting on a lattice is given by the sum of the potential energies of all pairs of molecules which are situated immediately next to one another. Contributions to the total potential energy from pairs which are not nearest neighbours are neglected in this simple case.



BEFORE EXCHANGE

AFTER EXCHANGE

Figure 2.4. Physical significance of interchange energy. The energy absorbed in the process is 2w′.

Consider that each of N_1 molecules of type 1 and N_2 molecules of type 2 has z nearest neighbours. z is called the co-ordination number and may have a value between 6 and 12 depending on the way the molecules are arranged in three-dimensional space. For typical liquids at ordinary conditions z is close to 10. The total number of nearest neighbours is (z/2) (N_1+N_2) and there are three types of nearest neighbour interactions; 1-1, 2-2, 1-2. N_{ii} is the number of nearest neighbour pairs of type ii and N_{12} is the number of type 12. The numbers are restricted by the conservation equations:

$$z\ N_1 = 2\ N_{11} + N_{12}$$
$$z\ N_2 = 2\ N_{22} + N_{12}$$

The total potential energy of the lattice U_t, is then given by

$$U_t = N_{11}\ \Phi_{11} + N_{22}\ \Phi_{22} + N_{12}\ \Phi_{12}$$

where Φ_{11} is the potential energy of a 1-1 pair, Φ_{22} that of a 2-2 pair and Φ_{12} that of a 1-2 pair. Substitution of N_{11} and N_{22} from the above equation gives

$$U_t = \frac{z}{2} N_1 \Phi_{11} + \frac{z}{2} N_2 \Phi_{22} + \frac{w'}{2} N_{12} \tag{2.52}$$

where w′, called the interchange energy, is defined by

$$w' \equiv z [\Phi_{12} - \frac{1}{2} (\Phi_{11} + \Phi_{22})] \tag{2.53}$$

Equation (2.52) gives the potential energy of a binary mixture and also that of a pure liquid. In equation (2.52) the last term is the energy of mixing.

The physical significance of w′ is illustrated in Figure 2.4. z pairs of type 1 and z pairs of type 2 are separated to form 2z dissimilar 1-2 pairs. Therefore, the change in energy which accompanies the interchange process shown in Figure 2.4 is equal to 2w′.

From these equations it is possible to obtain thermodynamic properties in the manner given by Prausnitz et al. (1986). The lattice theory is the basis for many prediction models such as the UNIFAC and the AGAPE models. The major deficiency of the lattice theory is the need to take into account additional properties of the components beyond those which reflect molecular size and potential energy. The properties that the lattice theory lacks are manifested in P-V-T behaviour, in other words in an equation of state. A number of recently developed prediction models (the MHV2 model and the models by Sandler (Wong and Sandler, 1992)) use an activity coefficient model based on the lattice theory combined with an equation-of-state model in order to avoid the deficiencies of both models, and combine the best of both models.

The interchange energy.

Kohler (1957) has calculated the interchange energy from molecular properties. He assumed that for pure liquids, the distance between molecules can be written as a function of the molar volume in the power of 1/3 and that the distance between molecules in the mixture was the arithmetic mean of the distances for the pure components. He then wrote an expression for the London dispersion forces as

$$\Phi_{11} = -\frac{\alpha_1^2}{l_{11}^6}\kappa_1 \qquad \Phi_{22} = -\frac{\alpha_2^2}{l_{22}^6}\kappa_2$$

$$\Phi_{12} = -\frac{2\,\alpha_1\,\alpha_2}{(l_{11} + l_{22})^6}\,\frac{2\,\kappa_1\,\kappa_2}{(\kappa_1 + \kappa_2)} \tag{2.54}$$

where α is the polarizability and κ_i is calculated from the molar enthalpy of vaporization, $\Delta h_{i,vap}$, by

$$\kappa_i = \frac{2\,l_{ii}^6}{z\,\alpha_i^2}\left(\frac{\Delta h_{i,\,vap} - RT}{L}\right)$$

Substituting these equations into equation (2.53), Kohler was able to calculate the interchange energy. One advantage of his treatment is that the number of nearest neighbours, z, cancels out and that the three potentials,Φ_{11}, Φ_{22} and Φ_{12} are calculated separately. Table 2-3 shows some of Kohler's results (where 1) Data from Prausnitz et al. (1986) and 2) Data from Kohler (1957)) compared to experimental values of the excess Gibbs energies of four simple binary mixtures, each at the composition midpoint where $x_1 = x_2 = 0.5$.

		$g^E(x_1 = x_2)$ (J/mol)	
Mixtures	**T (K)**	**Lattice theory**	**Experimental**
$Ar + CH_4$ 1)	90.7	67.0	71.2
$N_2 + CH_4$ 1)	90.7	247	134
$C_6H_6 + CCl_4$ 2)	298	34.2	77.9
$C_6H_6 + c\text{-}C_6H_{12}$ 2)	298	174.2	321.5
$CCl_4 + c\text{-}C_6H_{12}$ 2)	298	55.3	70.8

Table 2-3. Experimental values of excess molar Gibbs energy for equimolar, binary mixtures and values calculated using Kohler's method.

Kohler's method is applicable to non-polar mixtures and to mixtures where the molecules of the two components are essentially spherical and similar in size.

The theory behind Kohler's method is very similar to the underlying theory of the AGAPE method (see section 2.11).

2.10.3.2 The athermal theory

Another application of lattice theory is the theory of Flory-Huggins (e.g. Prausnitz et al., 1986) which was introduced in this section to deal with polymer solutions showing considerable non-ideality.

2.10.3.3 Wilson's modification

Wilson (1964) modified the equations of Flory and Huggins by introducing the local mole fraction concept. Wilson considered that molecules in a mixture do not arrange themselves randomly, but partially segregate due to the effect of intermolecular forces, a subject introduced in section 2.7.

Wilson considered a binary solution of components 1 and 2. Focusing his attention on a central molecule of type 1, the probability of finding a molecule of type 2, relative to finding a molecule of type 1, about this central molecule, was in terms of the overall mole fraction and two Boltzmann factors

$$\frac{X_{21}}{X_{11}} = \frac{x_2 \exp\left(\frac{-\lambda'_{21}}{RT}\right)}{x_1 \exp\left(\frac{-\lambda'_{11}}{RT}\right)}$$

where the parameters λ'_{21} and λ'_{11} are, respectively, related to the potential energies of a 2-1 pair and 1-1 pair of molecules. An equation analogous to the above can be written for the probability of finding a molecule of type 1, relative to finding a molecule of type 2, about a central molecule 2, and it is

$$\frac{X_{12}}{X_{22}} = \frac{x_1 \exp\left(\frac{-\lambda'_{12}}{RT}\right)}{x_2 \exp\left(\frac{-\lambda'_{22}}{RT}\right)}$$

Wilson then defined the local volume fractions as

$$\xi'_1 \equiv \frac{v_1 X_{11}}{v_1 X_{11} + v_2 X_{21}} \qquad \xi'_2 \equiv \frac{v_2 X_{22}}{v_2 X_{22} + v_1 X_{12}}$$

and wrote the molar excess Gibbs energy of a binary system as

$$\frac{g^E}{RT} = x_1 \ln \frac{\xi'_1}{x_1} + x_2 \ln \frac{\xi'_2}{x_2}$$

From this equation an expression for the activity coefficients can be derived (Reid et al., 1987). The activity coefficients depend on the adjustable parameters $(\lambda'_{12} - \lambda'_{11})$ and $(\lambda'_{21} - \lambda'_{22})$, often obtained by fitting experimental data.

The Wilson equations cannot represent mixtures which exhibit partial miscibility.

2.10.3.4 The NRTL equations

Renon and Prausnitz (1968) considered that, in a real liquid, the distribution was ordered to some degree due both to the differences in molecular size and shape, and to the specific interactions. They developed the Non-Random, Two-Liquid (NRTL) theory by introducing a shape factor, which expresses the non-randomness element. This model is not discussed further here.

2.10.3.5 Overview of different activity coefficient models

The different activity coefficient models together with the expressions for both the excess Gibbs energy and the activity coefficients are listed in Table 2-4 (from Reid et al., 1987).

The UNIFAC method is the most used method for calculating activity coefficients. It is not shown among the thermodynamic methods in Table 2-4, but is a variation of the UNIQUAC method. The UNIFAC method is a group contribution method of the UNIQUAC method. Results obtained from a modified UNIFAC approach are compared in this work with those from the AGAPE method.

Name	g^E	Binary parameters	$\ln \gamma_1$ and $\ln \gamma_2$
Two-suffix[b] Margules	$g^E = Ax_1x_2$	A	$RT \ln \gamma_1 = Ax_2^2$
			$RT \ln \gamma_2 = Ax_1^2$
Three-suffix[b] Margules	$g^E = x_1x_2[A + B(x_1 - x_2)]$	A, B	$RT \ln \gamma_1 = (A + 3B)x_2^2 - 4Bx_2^3$
			$RT \ln \gamma_2 = (A - 3B)x_1^2 + 4Bx_1^3$
van Laar	$g^E = \frac{Ax_1x_2}{x_1(A/B) + x_2}$	A, B	$RT \ln \gamma_1 = A\left(1 + \frac{A}{B}\frac{x_1}{x_2}\right)^{-2}$
			$RT \ln \gamma_2 = B\left(1 + \frac{B}{A}\frac{x_2}{x_1}\right)^{-2}$
Wilson	$\frac{g^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(x_2 + \Lambda_{21}x_1)$	$\Lambda_{12}, \Lambda_{21}$	$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right)$
			$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right)$
Four-suffix[b] Margules	$g^E = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2]$	A, B, C	$RT \ln \gamma_1 = (A + 3B + 5C)x_2^2 - 4(B + 4C)x_2^3 + 12Cx_2^4$
			$RT \ln \gamma_2 = (A - 3B + 5C)x_1^2 + 4(B - 4C)x_1^3 + 12Cx_1^4$

Table 2-4. Some models for the excess Gibbs energy and subsequent activity coefficient relationships for binary mixtures (continued over).

NRTL[c]	$\frac{g^E}{RT} = x_1x_2\left(\frac{\tau_{21}G_{21}}{x_1+x_2G_{21}} + \frac{\tau_{12}G_{12}}{x_2+x_1G_{12}}\right)$ where $\tau_{12} = \frac{\Delta g_{12}}{RT} \qquad \tau_{21} = \frac{\Delta g_{21}}{RT}$ $\ln G_{12} = -\alpha_{12}\tau_{12} \qquad \ln G_{21} = -\alpha_{12}\tau_{21}$	$\Delta g_{12}, \Delta g_{21}, \alpha_{12}$[d]	$\ln \gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1+x_2G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2+x_1G_{12})^2}\right]$ $\ln \gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2+x_1G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1+x_2G_{21})^2}\right]$
UNIQUAC[e]	$g^E = g^E\text{ (combinatorial)} + g^E\text{ (residual)}$ $\frac{g^E\text{ (combinatorial)}}{RT} = x_1 \ln\frac{\Phi_1}{x_1} + x_2 \ln\frac{\Phi_2}{x_2} + \frac{z}{2}\left(q_1x_1 \ln\frac{\theta_1}{\Phi_1} + q_2x_2 \ln\frac{\theta_2}{\Phi_2}\right)$ $\frac{g^E\text{ (residual)}}{RT} = -q_1x_1 \ln\left[\theta_1 + \theta_2\tau_{21}\right] - q_2x_2 \ln\left[\theta_2 + \theta_1\tau_{12}\right]$ $\Phi_1 = \frac{x_1r_1}{x_1r_1 + x_2r_2} \qquad \theta_1 = \frac{x_1q_1}{x_1q_1 + x_2q_2}$ $\ln \tau_{21} = -\frac{\Delta u_{21}}{RT} \qquad \ln \tau_{12} = -\frac{\Delta u_{12}}{RT}$ r and q are pure-component parameters and coordination number $z = 10$	Δu_{12} and Δu_2	$\ln \gamma_i = \ln\frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln\frac{\theta_i}{\Phi_i} + \Phi_j\left(\ell_i - \frac{r_i}{r_j}\ell_j\right) - q_i \ln(\theta_i + \theta_j\tau_{ji}) + \theta_jq_i\left(\frac{\tau_{ji}}{\theta_i + \theta_j\tau_{ji}} - \frac{\tau_{ij}}{\theta_j + \theta_i\tau_{ij}}\right)$ where $i = 1 \quad j = 2$ or $i = 2 \quad j = 1$ $\ell_i = \frac{z}{2}(r_i - q_i) - (r_i - 1)$ $\ell_j = \frac{z}{2}(r_j - q_j) - (r_j - 1)$

---

[a] Reference 97 discusses the Margules, van Laar, Wilson, UNIQUAC, and NRTL equations. The UNIQUAC equation is also discussed in Ref. 4.

[b] Two-suffix signifies that the expansion for g^E is quadratic in mole fraction. Three-suffix signifies a third-order, and four-suffix signifies a fourth-order equation.

[c] NRTL = Non Random Two Liquid.

[d] $\Delta g_{12} = g_{12} - g_{22}$; $\Delta g_{21} = g_{21} - g_{11}$.

[e] UNIQUAC = *Uni*versal *Qua*si *C*hemical. Parameters q and r can be calculated from Eq. (8-10.52').

[f] $\Delta u_{12} = u_{12} - u_{22}$; $\Delta u_{21} = u_{21} - u_{11}$.

Table 2-4. Some models for the excess Gibbs energy and subsequent activity coefficient relationships for binary mixtures.

2.10.3.6 The UNIQUAC equations

The UNIFAC method for calculation of phase equilibria is based on the UNIQUAC equations for calculation of the activity coefficients of a (in this case) binary mixture.

The derivation of the UNIQUAC equations is described in Prausnitz et al. (1986). The derivation is very analogous to the derivation of the AGAPE equations (described in section 2.11). The resulting equations are (the symbols are explained in the list of symbols)

$$\left(\frac{g^E}{RT}\right)_{T,P} = \left(\frac{g^E}{RT}\right)^{\text{combinatorial}} + \left(\frac{g^E}{RT}\right)^{\text{residual}} \tag{2.55}$$

where

$$\begin{aligned}\left(\frac{g^E}{RT}\right)^{\text{combinatorial}} &= x_1 \ln \frac{\Theta_1^*}{x_1} + x_2 \ln \frac{\Theta_2^*}{x_2} \\ &+ \frac{1}{2} z \left(q_1^* x_1 \ln \frac{\theta_1^*}{\Theta_1^*} + q_2^* x_2 \ln \frac{\theta_2^*}{\Theta_2^*} \right)\end{aligned} \tag{2.56}$$

and

$$\begin{aligned}\left(\frac{g^E}{RT}\right)^{\text{residual}} &= - x_1 q_1^* \ln\left[\theta_1^* + \theta_2^* \exp\left(\frac{-\Delta u_{21}}{RT}\right)\right] \\ &- x_2 q_2^* \ln\left[\theta_2^* + \theta_1^* \exp\left(\frac{-\Delta u_{12}}{RT}\right)\right]\end{aligned} \tag{2.57}$$

where

$$\Theta_1^* = \frac{r_1 x_1}{r_1 x_1 + r_2 x_2} \qquad \theta_1^* = \frac{x_1 q_1^*}{x_1 q_1^* + x_2 q_2^*}$$

and similarly for Θ_2^* and θ_2^*.

Equations (2.56) and (2.57) are the UNIQUAC equations.

The UNIQUAC interaction parameters Δu_{12} and Δu_{21} represent a problem in themselves as they have little or no physical relation to physical parameters. Recent developments to determine them from molecular information have proved successful for a limited number of ketones and alkanes (Jónsdóttir et al., 1994).

From the UNIQUAC equations, the UNIFAC (Universal Functional Activity Coefficient) equations are derived.

2.10.3.7 The UNIFAC method

The UNIFAC method (Fredenslund et al., 1975) is a general method for estimating activity coefficients. It is a group-contribution method where a molecule is divided into functional groups. Molecule-molecule interactions are considered to be properly weighted sums of group interactions. Once quantitative information on the necessary group-group interactions is obtained, it is then possible to calculate molecule-molecule interactions for molecular pairs, where no experimental data are available.

The UNIFAC equation for activity coefficient for compound i is obtained (Fredenslund, 1993) as

$$\ln \gamma_i = \ln \gamma_i^{\text{combinatorial}} + \ln \gamma_i^{\text{residual}} \tag{2.58}$$

where

$$\begin{aligned}\ln \gamma_i^{\text{combinatorial}} &= \left(\ln \frac{\theta_i}{x_i} + 1 - \frac{\theta_i}{x_i}\right) \\ &\quad - \frac{1}{2} z q_i^U \left(\ln \frac{\theta_i}{\Theta_i} + 1 - \frac{\theta_i}{\Theta_i}\right)\end{aligned} \tag{2.59}$$

and

$$\theta_i = \frac{x_i \, r_i^U}{\sum x_j \, r_j^U} \qquad \Theta_i = \frac{x_i \, q_i^U}{\sum x_j \, q_j^U} \tag{2.60}$$

where the summation is over all components

$$r_i^U = \sum_k \nu_{ki} \, R_k^U \qquad q_i^U = \sum_k \nu_{ki} \, Q_k^U \tag{2.61}$$

here the summation is over all groups and

R^U_k = volume parameter for group k

Q^U_k = surface area parameter for group k

ν_{ki} = number of groups of type k in molecule i

x_i = liquid mole fraction of component i

z = co-ordination number = 10.

$$\ln \gamma_i^{\text{residual}} = \Sigma_k \; \nu_{ki} \; (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \qquad (2.62)$$

where the summation is over all groups

$$\ln \Gamma_k = Q_k^U \left[1 - \ln(\Sigma_m \theta_m \; \psi_{mk}) - \Sigma_m \left(\frac{\theta_m \; \psi_{km}}{\Sigma_n \; \theta_n \; \psi_{nm}} \right) \right] \qquad (2.63)$$

and

$$\psi_{nm} = \exp(- \frac{a^U_{nm}}{T}) \qquad (2.64)$$

$$\theta_m = \frac{Q^U_m \; X^U_m}{\Sigma_n \; Q^U_n \; X^U_n} \qquad X^U_m = \frac{\Sigma_j \; \nu_{mj} \; x_j}{\Sigma_j \; \Sigma_n \nu_{nj} \; x_j}$$

a^U_{nm} = group interaction parameter for the interaction between groups m and n

$\rightarrow \Gamma_k^{(i)}$

2.10.3.8 Limitations of the UNIFAC method

The UNIFAC equations are limited as given below (Fredenslund, 1993)

1. UNIFAC cannot distinguish between isomers due to the assumptions of the solution-of-groups method.

2. Assuming gas-phase ideality limits UNIFAC to applications below 1000-1500 kPa pressure.

3. The interaction parameters are assumed independent of temperature. This limits the temperature range to temperatures approximately between 275 and 425 K.

4. In principle it should be possible to apply the UNIFAC model to liquid-liquid equilibrium (LLE) using the same interaction parameters. At the moment it is only possible to predict LLE using UNIFAC and interaction parameters specifically developed for handling LLE predictions at 298.15 K (Magnussen et al., 1981). This discrepancy indicates a fundamental deficiency of the solution-of-groups approach.

5. When two or more strongly polar groups are situated on the same or on adjacent atom, they do not have the properties as if they were separated by several carbon atoms. A proximity effect occurs.

6. Not included at the moment are: non-condensable gases, electrolytes, and polymers.

The UNIFAC interaction parameters (a^U_{nm}) represent a problem in themselves as they have little or no physical relation to physical parameters.

2.10.3.9 Modified UNIFAC

An attempt to overcome limitation 3 has been the development of the Modified UNIFAC equations. The Modified UNIFAC model offers only a marginal improvement over the original UNIFAC model for VLE predictions (see Larsen et al., 1987). The force of the modified UNIFAC model lies in its ability to predict excess enthalpy (H^E). The equations for the modified UNIFAC model are different from the original UNIFAC equations as given below

The combinatorial term becomes

$$\ln \gamma_i^{\text{combinatorial}} = \left(\ln \frac{\omega_i^U}{x_i} + 1 - \frac{\omega_i^U}{x_i} \right) - \frac{1}{2} z q_i^U \left(\ln \frac{\theta_i}{\Theta_i} + 1 - \frac{\theta_i}{\Theta_i} \right) \qquad (2.65)$$

where

$$\omega_i^U = \frac{x_i \ (r_i^U)^{2/3}}{\Sigma x_j \ (r_j^U)^{2/3}}$$

The residual term is the same, except the group-interaction parameter is considered to be the following function of temperature (T):

$$a_{ij}^U(T) = a_{ij}^{U(0)} + a_{ij}^{U(1)} (T - T_0) + a_{ij}^{U(2)} \left(T \ln\frac{T_0}{T} + T - T_0 \right) \qquad (2.66)$$

where T_0 is an arbitrary reference temperature.

2.10.3.10 The MHV2 method

The MHV2 method is described by Dahl et al. (Dahl et al., 1991, and Dahl and Michelsen, 1990). The MHV2 method tries to overcome the second limitation in the UNIFAC (previous section) that the pressure should be below 1000-1500 kPa due to the assumption of vapour phase ideality.

The MHV2 method is used in this thesis to give predictions with which to compare the results obtained from solubility calculations using the AGAPE method. The derivation of the MHV2 equations is briefly described in this chapter.

The MHV2 method is a group-contribution equation of state based on the modified Huron-Vidal (Huron and Vidal, 1979) mixing rule. It combines the Soave-Redlich-Kwong (SRK) equation of state with a model for the excess Gibbs energy, which in Dahl and co-workers is the modified UNIFAC model (described in section 2.10.3.9). The MHV2 model can be used to predict vapour-liquid equilibrium (VLE) and gas solubilities at high and low pressures.

The Soave-Redlich-Kwong (SRK) (Soave, 1972, and Redlich and Kwong, 1949) equation of state can be written as follows:

$$P = \frac{R\,T}{v - b} - \frac{a}{v(v + b)} \qquad (2.67)$$

where the mixture b parameter is derived from the conventional linear mixing rule

$$b = \sum_{i=1}^{c} z_i \, b_{ii}$$

using for the corresponding pure component parameter

$$b_{ii} = \frac{0.08664\,R\;T_{ci}}{P_{ci}}$$

where P_{Ci} and T_{Ci} are the critical pressure and critical temperature, respectively, of component i.

The pure component a parameter (a_{ii}) is given by

$$a_{ii} = \frac{0.4286\;R^2\;T_{ci}^2\;f(T_{ri})^2}{P_{ci}}$$

where $f(T_{ri})$ is a function of the reduced temperature for the individual component and given in Mathias and Copemann (1983).

The problem lies in finding an expression for the a parameter for the mixture. Following the procedure as described in Dahl and Michelsen (1990), the MHV2 mixing rule is as follows:

$$q_1^{HV}\left(\alpha_{mix}^{HV} - \sum_{i=1}^{m} x_i\,\alpha_{ii}^{HV}\right) + q_2^{HV}\left((\alpha_{mix}^{HV})^2 - \sum_{i=1}^{m} x_i\,(\alpha_{ii}^{HV})^2\right) = \frac{g^E}{R\,T} + \sum_{i=1}^{m} x_i \ln\left(\frac{b}{b_{ii}}\right) \qquad (2..68)$$

where

$$\alpha_{mix}^{HV} = \frac{a_{mix}}{b\,R\,T} \qquad \alpha_{ii}^{HV} = \frac{a_{ii}}{b_{ii}\;R\,T} \tag{2.69}$$

Dahl and Michelsen (1990) determined the values of q^{HV}_1 and q^{HV}_2 as q^{HV}_1= -0.478 and q^{HV}_2= -0.0047.

Since all the parameters in equation (2.68) are known and since g^E can be calculated using the modified UNIFAC model as described in section 2.10.3.9, equation (2.68) can be solved for the α_{mix} yielding the mixture parameter for the equation of state. Then the molar volume, v can be calculated from equation (2.67), where α^{HV} is substituted as $a_{mix} = \alpha_{mix}{}^{HV}$ bRT to obtain:

$$\frac{P}{R\,T} = \frac{1}{v - b} - \alpha_{mix}^{HV}\left(\frac{1}{v} - \frac{1}{v + b}\right)$$

Inserting equation (2.65) into equation (2.24) the fugacity coefficient can be derived as:

$$\ln \varphi_i = \ln\left(\frac{R\,T}{P\,(v - b)}\right) + \left(\frac{1}{v - b} - \frac{\alpha_{mix}^{HV}}{v + b}\right) b_{ii} - \ln\left[\left(\frac{v + b}{v}\right)\left(\frac{\partial(n\,\alpha_{mix}^{HV})}{\partial n_i}\right)\right]_{T,\,n_j} \tag{2.70}$$

The composition derivative of $n\alpha_{mix}{}^{HV}$ can be calculated from the mixing rule, equation (2.68). The equation of the derivative and a procedure for the calculation of the fugacity coefficients are both described in Dahl and Michelsen (1990).

2.10.3.11 Mixing rules by Wong and Sandler

The MHV2 is only one example of a mixing rule. Another example is the mixing rule as developed by Wong and Sandler (1992), the so-called W-S mixing rule. The authors claim it to be more theoretically correct then the previously discussed MHV2 mixing rule, and therefore the results obtained by the W-S mixing rule are likely to be more accurate then the results obtained using the MHV2 method.

In their paper (Wong and Sandler, 1992) they showed that by the simple expedient of considering the Helmholtz free energy, they were able to develop a new class of density-independent mixing rules which can be applied to give the two a and b parameters in any cubic equation of state. They use statistical mechanics to write the second virial coefficient B in terms of a quadratic composition dependence. They are then able to equate the excess Helmholtz free energy at infinite pressure from an equation of state to that from an activity coefficient model.

In the paper by Wong et al. (1992) they state that the parameters in the W-S mixing rule model obtained from a low pressure-low temperature isotherm can be used to make accurate predictions at conditions hundreds of degrees and hundreds of 10^5Pa above the experimental data used to obtain those parameters.

Their method is further discussed in Orbey et al. (1993) and Huang and Sandler (1993).

Other mixing rules have been developed recently. Among them is Apostolou et al. (1995). Neither this nor the W-S mixing rule have been used in this work, as they were developed later then the work described in section 4.6.

2.10.3.12 The ASOG method

Another method for predicting the activity coefficients of a binary vapour-liquid equilibrium based on groups contribution is the so-called Analytical Solution of Groups (ASOG) method (Derr and Deal, 1969). As with the UNIFAC method, the parameters used in the ASOG method are calculated from experimental data. The ASOG method has not managed to obtain the reputation of the UNIFAC method, and does not include interaction parameters for as many groups as the UNIFAC method does, although an advanced version is in use in-house by Shell. The method will not be used in this work. The derivation and the equations for the base method are given in Derr and Deal (1969).

2.10.3.13 Application of the ASOG and the UNIFAC equations

Both the ASOG and the UNIFAC methods are applied to predict the activity coefficients of a multicomponent mixture in much the same way. Firstly, the groups to be dealt with and their respective group numbers have to be defined. Secondly, the group interaction parameters have to be calculated from experimental data involving the groups of interest. Finally, the activity coefficients for new mixtures are calculated.

2.10.3.14 Dilute solutions and activity coefficients at infinite dilution

In his book on mixtures Guggenheim (1952) develops the equations for a strictly regular solution under the conditions of extreme dilution where there are actually no solute-solute interactions.

The result is that for the solvent 2

$$p_2 / p^0_2 = 1 - x_1$$

i.e. the solvent obeys Raoult's law.

For the solute 1

$$p_1 \ / \ p_1^0 \ = \ x_1 \ \exp(w' \ / \ RT) \qquad (2.71)$$

where w' is the usual free interchange energy. The above equation for the solute can be rearranged to

$$p_1 \ = \ x_1 \left[p_1^0 \ \exp(w' \ / \ RT) \right] \qquad (2.72)$$

where the term in the squared brackets is the equivalent of the Henry's constant (a subject to be introduced in connection with the solubility of gases in liquids in Chapter 3). Since a strictly random solution can be taken to conform to a two suffix Margules equation

$$g^E = A_M \, x_1 \, x_2$$

we obtain equation (2.47). At infinite dilution of each component, the equation reduces to (equation(2.48))

$$\gamma_1^\infty \equiv \lim_{x_1 \to 0} \gamma_1 = \exp\left(\frac{A_M}{RT}\right)$$

$$\gamma_2^\infty \equiv \lim_{x_2 \to 0} \gamma_2 = \exp\left(\frac{A_M}{RT}\right)$$

or

$$g^E = RT\ x_1\ x_2\ \ln \gamma_1^\infty$$

In the equation for g^E it does not matter whether $\gamma^\infty{}_1$ or $\gamma^\infty{}_2$ is used, as equation (2.48) shows that they are equal.

Although many solutions approximate to $g^E = A_M\ x_1\ x_2$, when examined in detail they more commonly fit the van Laar equations (see Table 2-4)

$$g^E = \frac{x_1\ x_2}{\left(\dfrac{x_1}{A'_{VL}} + \dfrac{x_2}{B'_{VL}}\right)}$$

and the activity coefficients are given in Table 2-4. At infinite dilution the equations for the activity coefficients reduce to

$$\ln \gamma_1^\infty = A'_{VL} \text{ and } \ln \gamma_2^\infty = B'_{VL}$$

These differences are illustrated by the application of the Hildebrand-Scatchard equations (2.51) in which

$$A'_{VL} = \frac{v_1}{RT}(\delta_1 - \delta_2)^2 \text{ and } B'_{VL} = \frac{v_2}{RT}(\delta_2 - \delta_1)^2$$

thus

$$\frac{\ln \gamma_1^\infty}{\ln \gamma_2^\infty} \cong \frac{v_1}{v_2}$$

using this model.

Since both the excess Gibbs function and the limiting activity coefficients are defined in terms of the same constants, they are defined in terms of the same two parameters in any of the activity coefficient models and experimental data for both properties should give rise to consistent parameters. Equations for gas solubility are often derived in terms of $\gamma^\infty{}_{solute}$ as seen in Chapter 3.

2.10.3.15 Prediction of activity coefficients at infinite dilution

The activity coefficient at infinite dilution, γ_i^∞, is mentioned in the solubility section, especially in the chapter on Henry's law (section 3.2.4). The activity coefficient at infinite dilution is a valuable tool in separation process design. Infinite dilution activity coefficient data have been used to generate binary data used for the accurate prediction of multi-component vapour-liquid equilibrium data for completely miscible systems (Howell et al., 1989).

Limiting activity coefficients provide valuable information of the solute-solvent interactions in the absence of solute-solute interactions. Another important feature regarding the infinite dilution is that the excess Gibbs energy is not dependent on the composition. Considerations about the excess Gibbs energy can then take into account the type and strength of interactions instead of evaluating how the separate contributions add up.

Many of the previous described methods for predicting vapour-liquid equilibrium data have been used to predict infinite dilution activity coefficients. The ASOG method (section 2.10.3.12), the UNIFAC method (section 2.10.3.7) and the MOSCED method (Thomas and Eckert, 1984) are examples of methods for predicting infinite dilution activity coefficients. The MOSCED method is an extension of the regular solution theory (section 2.10.3) to mixtures with highly polar and chemical interactions.

2.10.3.16 The MOSCED method

The Modified Separation of Cohesive Energy Density (MOSCED) method, described by Thomas and Eckert (1984) takes into account all four types of interaction mentioned in chapter 2.7. It accounts for the dispersion interaction, the induction/polarity interaction, the chemical interactions as well as interactions arising from size difference of the molecules in the mixture. The basic assumption of the MOSCED method is that the forces contributing to the cohesive energy density act independently and are additive.

The MOSCED expression for the activity coefficient of component 2 infinitely diluted in solvent 1 is (Thomas and Eckert, 1984)

$$\ln \gamma_2^\infty = \frac{v_2}{RT}\left[(\lambda_1 - \lambda_2)^2 + \frac{m_1^2 m_2^2(\alpha_1 - \alpha_2)^2}{o} + \frac{(ac_1 - ac_2)(bc_1 - bc_2)}{\chi}\right] + \ln\left[\frac{v_2}{v_1}\right]^{aa} + 1 - \left[\frac{v_2}{v_1}\right]^{aa} \tag{2.73}$$

where

λ, the dispersion parameter, is a measure of a molecule's polarizability

α represents its polarity

m is a measure of dipole-induced dipole interaction

ac is a measure of the molecule's acidity

bc is a measure of the molecule's basicity

o and χ are interaction asymmetry parameters (as opposed to shape)

v_i is the molar volume of component i

aa is a correction exponent (calculated from solute properties)

The last three terms in equation (2.73) account for the differences in molecular size and comprise the size ratio term (often referred to as the combinatorial term). Dispersion contributions are calculated using index of refraction, the size term is calculated with a modified Flory-Huggins type expression, and the polar contribution is a model parameter.

The development of the original MOSCED method (Thomas and Eckert, 1984) was limited by the scarcity of the measured data on infinite dilution activity coefficients and by lack of any accurate measure of molecular acidity and basicity. In the original MOSCED model, α was treated as an adjustable parameter.

Of particular interest is the dispersion parameter, λ. In Thomas and Eckert (1984) it is a function of the refractive index n_D

$$
\begin{aligned}
f(n_D) &= \left(\frac{n_D^2 - 1}{n_D^2 + 2}\right) \\
\lambda_{\text{non - aromatic}} &= 20.3f(n_D) + 3.02 \qquad (2.74) \\
\lambda_{\text{aromatic}} &= 19.5f(n_D) + 2.79
\end{aligned}
$$

An attempt to evaluate a possible relation between the MOSCED dispersion parameter and the London potential will be described in section 4.8.

There are two ways the MOSCED equation can be used to predict infinite dilution activity coefficients: (1) interpolation and (2) extrapolation. Interpolation predictions are predictions of γ_i^∞ for which MOSCED parameters have been obtained for both components but data for that particular binary system were not used in parameter determination. Extrapolation predictions are predictions of γ_i^∞ for which MOSCED parameters have not been obtained for one or both of the components.

Howell et al. (1989) report on improved predictions of infinite dilution activity coefficients using a developed scale of hydrogen bond acidity/basicity and dipolarity/polarizability to determine solvatochromic parameters. The scale is based on extensive spectroscopic measurements.

A recent prediction method, the SPACE (Solvatochromic Parameters for Activity Coefficient Estimation) predictor (Hait et al., 1993) has been developed based on the MOSCED method. The SPACE method uses solvatochromic parameters for dipolarity/polarizability and for hydrogen bonding. This presents an advantage of including explicitly "chemical" interactions. The method claims to be somewhat more accurate then the UNIFAC method.

2.10.3.17 Binary VLE data from infinite dilution activity coefficients

As mentioned in the previous chapter, it is possible to predict binary VLE data from infinite dilution activity coefficients.

Table 2-5 shows the expressions for the activity coefficients at infinite dilution for different excess Gibbs energy models and thereby the dependency of the binary parameters in the models and the infinite dilution activity coefficients.

Type of equation	$\ln \gamma_1^\infty$ $\ln \gamma_2^\infty$
Margules	A_M A_M
van Laar	A'_{VL} B'_{VL}
Wilson	$1 - \ln \Lambda_{12} - \Lambda_{21}$ $1 - \ln \Lambda_{21} - \Lambda_{12}$
NRTL	$\tau_{21} + \tau_{12} \exp(- \alpha_{12}\tau_{12})$ $\tau_{12} + \tau_{21} \exp(- \alpha_{21}\tau_{21})$
UNIQUAC	$\ln\left(\frac{r_2}{r_1}\right) + q_2\left[\frac{z}{2} \ln\left(\frac{q_2 r_1}{q_1 r_2}\right) - \ln \tau_{12} + 1 - \tau_{21}\right] + l_2 - \frac{r_2}{r_1} l_1$ $\ln\left(\frac{r_1}{r_2}\right) + q_1\left[\frac{z}{2} \ln\left(\frac{q_1 r_{21}}{q_2 r_1}\right) - \ln \tau_{21} + 1 - \tau_{12}\right] + l_1 - \frac{r_1}{r_2} l_2$
Notes Wilson	$\Lambda_{12} = \frac{v_1}{v_2} \exp(- \frac{\lambda_{12} - \lambda_{11}}{RT})$ $\Lambda_{21} = \frac{v_2}{v_1} \exp(- \frac{\lambda_{21} - \lambda_{22}}{RT})$
NRTL	$\tau_{12} = \frac{g_{12} - g_{22}}{RT}$ $\tau_{21} = \frac{g_{21} - g_{11}}{RT}$
UNIQUAC	$\tau_{12} = \exp(- \frac{u_{12} - u_{22}}{RT})$ $\tau_{21} = \exp(- \frac{u_{21} - u_{11}}{RT})$ $l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1)$

Table 2-5. Activity coefficients at infinite dilution for different g^E models.

Please note, that not all symbols in Table 2-5 are consistent with the symbols used in the sections, where the models are described.

2.10.3.18 Limitations to activity coefficient models

After discussing the activity coefficient models, it is reasonable to ask the question, are they able to predict all excess thermodynamic functions with as good an accuracy as they predict the phase equilibrium ?

In the years before and since the UNIFAC model, many authors have attempted to explore the underlying lattice treatment making it more physically realistic.

In a paper (Bruin and Prausnitz, 1971) it was shown that when the excess Gibbs energy was expressed in terms of volume fractions, a very wide range of g^E values could be correlated in terms of a simple interaction parameter which correlated with molecular structure.

In 1964 and 1970 Flory (Flory et al., 1964 and Flory, 1970) drew attention to the need for lattice models to take account of the normalization of parameters using the principle of corresponding states, i.e., comparisons to be made at "equivalent" temperatures and densities with reference to the critical temperatures and volumes.

Brandani and Prausnitz (1981) attempted to take account of Flory's ideas in seeking to allow for the free volume and compressibility effects in real liquid mixtures using a two disposable parameter model in which the parameters are not correlated. One parameter is an energy parameter, the other a structure parameter. Although this model correlates the excess Gibbs energies well, it was not applied to other thermodynamics properties.

Goates et al. (1980) have provided much data with which to test a variety of models by seeking to fit g^E, the excess enthalpy h^E, the limiting activity coefficients γ^∞ and liquid-liquid data. Such models show the need for the original parameters to become temperature dependent with a number of such parameters.

In 1990 there remained a hope that by more precise definition of the lattice parameters a similar analysis of thermodynamic data might be possible. It was in that hope that the AGAPE model was launched.

The question proposed above, has to be answered in the negative. The prediction models based on a lattice model have some difficulty in predicting excess thermodynamic functions with a similar accuracy as they predict phase equilibria.

2.11 The AGAPE model

The AGAPE model is also an activity coefficient model, but it will be described in a separate subchapter as it is the model used throughout this research work.

The UNIFAC model is currently the most important model for the prediction of vapour-liquid equilibrium data. As explained previously, the binary UNIFAC interaction parameters lack a clear physical meaning. The UNIFAC method has stimulated the development of a prediction model based on molecular parameters. The AGAPE model represents such an attempt to find a model with improvements in realism in comparison to UNIFAC. It makes use of a theoretically sound interaction potential to create its equations. Recent developments to determine UNIQUAC interaction parameters from molecular information have proved successful for ketones and alkanes (Jónsdóttir et al., 1994), and could lead the way to meaningful physical UNIFAC interaction parameters.

2.11.1 The generalized London potential

The total potential energy between two simple, spherically symmetric molecules i and j at large distances can take the form

$$\Phi_{ij} = -\frac{3}{2}\frac{\alpha_i\,\alpha_j}{(R_{ij}^A)^6}\left(\frac{\hbar\,\nu_{0i}\;\hbar\,\nu_{0j}}{\hbar\,\nu_{0i} + \hbar\,\nu_{0j}}\right) \qquad (2.75)$$

according to London. This is valid even for the simplest non-polar molecule. ν_{0i} is the frequency for molecule i in its unexcited state and α_i is the polarizability for molecule i. R_{ij}^A is the separation between molecules i and j.

In the general form of London's dispersion theorem used in the AGAPE model it is presumed that equation (2.75) continues to hold at separations down to the intermolecular equilibrium separation between the molecules in the liquid state. This separation is hereafter written as R^A.

For a molecule i, the product $\nu_{0i}\hbar$ is very nearly equal to its first ionization potential I_i. Equation (2.75) can therefore be written

$$\Phi_{ij} = -\frac{3}{2}\frac{\alpha_i\alpha_j}{(R^A)^6}\left(\frac{I_i I_j}{I_i + I_j}\right) \qquad (2.76)$$

Homer and Mohammadi (1987a) have derived a generalized form of London's dispersion theorem (GLP) for polyatomic molecules, and used only the attractive forces as indicated by equations (2.75) and (2.76) to calculate the latent heat of vaporization for pure compounds (Homer and Mohammadi, 1987b) and solvent-induced NMR chemical shifts (Homer and Mohammadi, 1988) for binary mixtures. Their results indicate that London was right in his hypothesis assuming that the two terms with opposite signs virtually cancel each other.

Any theory used to describe the physical properties of liquid mixtures has to solve two problems, an entropy-based problem and an energy-interaction based problem. The first is how to describe quantitatively the structures of liquids in terms of the arrangement in space of the molecules of a liquid mixture. The second is how to quantify the net attractive energy between like and unlike molecules.

Combining the theory of London's dispersion forces with a modification of Wilson's local composition concept (Wilson, 1964) and Guggenheim's quasi-chemical theory (Guggenheim, 1952) has lead to the approach, AGAPE, to describe phase equilibria.

2.11.2 Mean-square moment

Homer and Mohammadi (1987a) have tested the hypotheses that certain molecular properties can be predicted from the sum of the corresponding values of the inert-gas atom counterparts of the bonded constituent atoms. They showed that for bonded atoms the mean-square moment $<m^2>$, which is equal to the product $\alpha\nu_0\hbar$, can be predicted with precision. Such efforts can be added up for the constituent atoms in a molecule, if the electronic properties of molecules are considered to be functions of the electronic properties of the inert-gas atoms, whose structures have been achieved. In other words, from an electronic standpoint, each atom of a molecule may be replaced by its inert-gas counterpart.

It still leaves the problem of averaging distances for the atoms, some of which are nearer and some farther then the equilibrium separation, R^A apart. The averaging distances are in general given by r_{ij} which stems from considering molecular electronic, vibrational, rotational and translational motions in order to characterize the equivalent of $(R^A)^{-6}$ in equation (2.76).

Homer and Mohammadi (1987b) showed that averaging of the inverse sixth power of r_{ij} $\{r_{ij}^{-6}\}$ gives $(R^A)^{-6}$. They expressed it as

$$\{r_{ij}^{-6}\} = (R^A)^{-6} F^A$$

where F^A is assigned to account for the molecular rotations. Their best Monte Carlo-derived expression for F^A is given by

$$(F^A)^{-1} = 1 + 0.727\left(\frac{d_i + d_j}{2R^A}\right) - 17.509\left(\frac{d_i + d_j}{2R^A}\right)^2 + 24.550\left(\frac{d_i + d_j}{2R^A}\right)^3 \qquad (2.77)$$

for $0 < (d_i+d_j)/2R^A < 0.43$.

Figure 2.5 (from Homer and Mohammadi, 1987b) shows the relationship between the averaging distance, r_{ij}, the equilibrium separation, R^A, and the equilibrium separations of the atoms from the centres of mass, d_i and d_j. Figure 2.5(a) is at time t_0 and Figure 2.5(b) at time t_1, where t_0 and t_1 refer to instances of time on the rotational time scale during which the intermolecular separation, R^A is fixed.

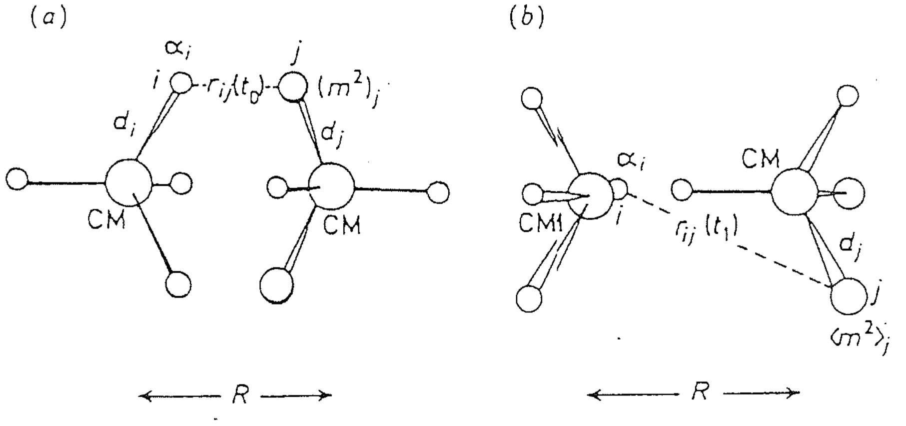


Figure 2.5. Two mutual orientations of two interacting molecules in the liquid phase.

For each component (i) there is only one equilibrium distance R^A_i, while there for a multi-atom molecule are several equilibrium distances from the centre of mass, d_j and r_{ij}, distances between atoms in two rotating molecules.

For all the W_j atoms acting on any single atom i in the other molecule the mean-square value of the dispersion field (only the rotational dependence) $< \overline{E}^2 >$ is given by Homer and Mohammadi (1987b) as

$$< \overline{E}^2 > (\text{pair}) = 2(R^A)^{-6} \sum_j W_j < m^2 >_j F^A \quad (2.78)$$

where <> represents electronic time averaging and $<m^2> = 3\alpha v_0 \hbar/2$, the bonded atom mean square moment.

If we assume additivity of the dispersion forces (equation (2.75)) and say that we have z nearest neighbours, equation (2.78) becomes (Homer and Mohammadi, 1987b)

$$< \overline{E}^2 > (\text{pair}) = 2z(R^A)^{-6} \sum_j W_j < m^2 >_j F^A$$

From this equation it may be shown (Homer and Mohammadi, 1987b) that the total London dispersion potential from all W_i of the type i in the central molecule (Φ_{ij}) is given by

$$\Phi_{ij} = \Phi(\text{pair}) = -0.25\ (R^A)^{-6} \sum_i \sum_j (\alpha_i < m^2 >_j + \alpha_j < m^2 >_i) F^A\ W_i\ W_j \tag{2.79}$$

which defines the net attractive potential for liquids, with the long-range repulsion contribution included. The summation should be taken over all atoms i and j in the component. At equilibrium separations in the condensed phase the short-range repulsive forces are neglected. The pair potential is called the unlike pair potential for $i \neq j$ and the like pair potential for $i = j$.

For practical use the equilibrium separation R^A can be derived using a probabilistic approach from the molecular volume V^m (Homer and Mohammadi, 1987b) as

$$R^A = 2\,(0.17\ V^m)^{1/3} \tag{2.80}$$

Equation (2.80) is valid for a single component. Mohammadi (1986) tried to apply a number of different equations for the values of R^A. In fact, he did an extensive investigation. He found that equation (2.80) was the most accurate, when the calculated separations were compared with experimental results. Using conversion factors and Avogadro's number to calculate the relationship between the molecular volume and the molar volume, equation (2.80) becomes

$$v\ (\text{cm}^3/\text{mol}) = 0.4429\ (R^A)^3$$

where R^A is in Å.

Another alternative is to calculate R^A from the heat of vaporization. The total potential as given in equation (2.79) was tested in Homer and Mohammadi (1987b) by using it to calculate the latent heat of vaporization for several pure compounds. Their results were relatively accurate compared with experimental data. There is no reason why the opposite cannot be applied: from a known value of the heat of vaporization, the equilibrium separation R^A can be derived. It is worth noticing that Homer and Mohammadi (1987b) used non-consistent parameters in their calculations. They used the R^A distance from solid-state studies, and compared the calculated heat of vaporization results with experimental values at the boiling point.

Assuming that the major part of the cohesion energy is due to immediate interactions between nearest neighbours, of which each molecule in a liquid has z giving the number of nearest neighbour pairs to z L /2, the molar potential energy for the pure component can be written as

$$U_{\text{molar}} = -LzU_{\text{like pair}} / 2 + RT$$

This molar potential approximates the latent heat of vaporization H_{vap}. The heat of vaporization for the single compound can be written as

$$\Delta H_{vap} = -60.24 \; L \; z \; \Phi_{\text{like pair}} / 2 + RT \qquad (2.81)$$

where the constant 60.24 takes into account different conversion factors. The constant allows for ΔH_{vap} calculated in kJ/mol, R^A in Å, α_i in Å^3, and $<m^2>$ in 10^{-36} erg cm^3, respectively. Using this equation for a given value of the heat of vaporization depending on the temperature, it is possible to determine a value for R^A that satisfies the equation.

The heat of vaporization values are calculated from the so-called Watson's correlation (Reid et al., 1987). This method will be described in Appendix 13 where the heat of vaporization as calculated by the POT method (equation (2.81)) will be critically reviewed. A more accurate option would have been to calculate the heat of vaporization from the slope of the saturated vapour pressure curve.

The molar volume is calculated by the Yen-Woods method (Yen and Woods, 1966) which has proved to give relatively accurate density results for organic liquids. The method of Rackett (Reid et al., 1987) has shown to give more accurate density results. The method by Yen and Woods (1966) will be critically reviewed in Appendix 14.

Despite the more accurate methods available, the use of Watson's correlation for the heat of vaporization calculations and the Yen-Woods method for the calculation of the molar volume was continued so as to provide consistency between the vapour-liquid equilibria prediction results (Kakhu and Homer, 1996a) and the results obtained in this study.

2.11.3 Combining rules

Representing the potential energy for the unlike molecules as done by London (1937) is only one way of calculating the unlike potential. It is relatively easy to find expressions for the like molecules. The way of combining two different like potentials to form an expression for the unlike potential is called a combining rule.

One of the most common combining rules for energies is the geometric mean, also called the Berthelot combining rule (Hudson and McCoubrey, 1960)

$$\Phi_{ij} = -\sqrt{\Phi_{ii}\Phi_{jj}} \tag{2.82}$$

The London combining rule can be described in general engineering combining terms as

$$\Phi_{ij} = -\sqrt{\Phi_{ii}\Phi_{jj}}(1 - k_{ij})$$

where k_{ij} is a characteristic binary constant and represents the deviation from the geometric mean. Another way of approximately representing the London combining rule is by a harmonic mean rule (Hicks and Young, 1975)

$$\Phi_{ij} = \frac{2\Phi_{ii}\Phi_{jj}}{\Phi_{ii} + \Phi_{jj}}$$

Hudson and McCoubrey (1960) give a more accurate but approximate combining rule based on elimination of the polarizabilaties from the London dispersion forces which includes a relative size term.

It is important to notice that the Φ_{ij} thus is a function of Φ_{ii} and Φ_{jj}.

Combining rules for molecular separations are usually assessed by the so-called Lorentz combining rule that states

$$\sigma'_{ij} = \frac{\sigma'_i + \sigma'_j}{2} \text{ or } v_{ij}^{1/3} = \frac{v_i^{1/3} + v_j^{1/3}}{2}$$

2.11.4 Excess Gibbs energy and activity coefficients

The derivation of the VLE equations for a binary mixture with components 1 and 2 from the AGAPE theory (Homer et al., 1991) follows here. The equations for a multicomponent mixture are given in Appendix 1.

The excess Helmholtz energy (a^E) at constant temperature and volume at low to moderate pressures is nearly equal to the excess Gibbs free energy at constant pressure and temperature thus (after Hildebrand and Scott, 1964)

$$\left(\frac{a^E}{R\,T}\right)_{T,\,V} \approx \left(\frac{g^E}{R\,T}\right)_{T,\,P} \tag{2.83}$$

The number of nearest neighbours z is also called the co-ordination number, and it is constant in most organic liquids. Introducing $t^W{}_2$ as the number of whole molecular contacts that a central molecule 1 makes with molecules of type 2 in its co-ordination shell and $t^W{}_1$ as the corresponding number that the same central molecule 1 makes with molecules of type 1 in its co-ordination shell, the pure compound co-ordination number z is given by

$$z = t_1^W + \frac{V_2^m\ t_2^W}{V_1^m} \qquad \text{(symmetric convention)}$$

A similar definition applies of course to a molecule type 2 centred cell. Using symbols $m^W{}_1$ and $m^W{}_2$ for the numbers of whole contacts, the pure compound co-ordination number becomes

$$z = m_2^W + \frac{V_1^m\ m_1^W}{V_2^m} \qquad \text{(symmetric convention)}$$

Following the procedure suggested by Wilson (1964), the local composition in a cell with a molecule of type 1 at its centre can be expressed as

$$\frac{X_{21}}{X_{11}} = \frac{x_2}{x_1}\exp\left[-\frac{(\Phi_{21} - \Phi_{11})}{k_B\ T}\right]$$

where X_{12} and X_{11} are the fractions of the total number of molecules around the central 1 that are of type 2 or 1, and Φ_{11} and Φ_{21} are the relevant molecular pair of interaction energies (as defined by equation (2.79)).

Wilson's principle assumes that energetics of bulk liquids may be adequately characterised through a shell model in which each molecule is surrounded by a spherical co-ordination shell of other molecules. This principle is illustrated in Figure 2.6 (from Kakhu and Homer, 1996a). Figure 2.6(a) shows the co-ordination shell structure for a pure liquid 1 when the molecules of type 2 are introduced, a local composition is achieved (Figure 2.6(b)) that is not necessarily the same as that of the bulk mixture.

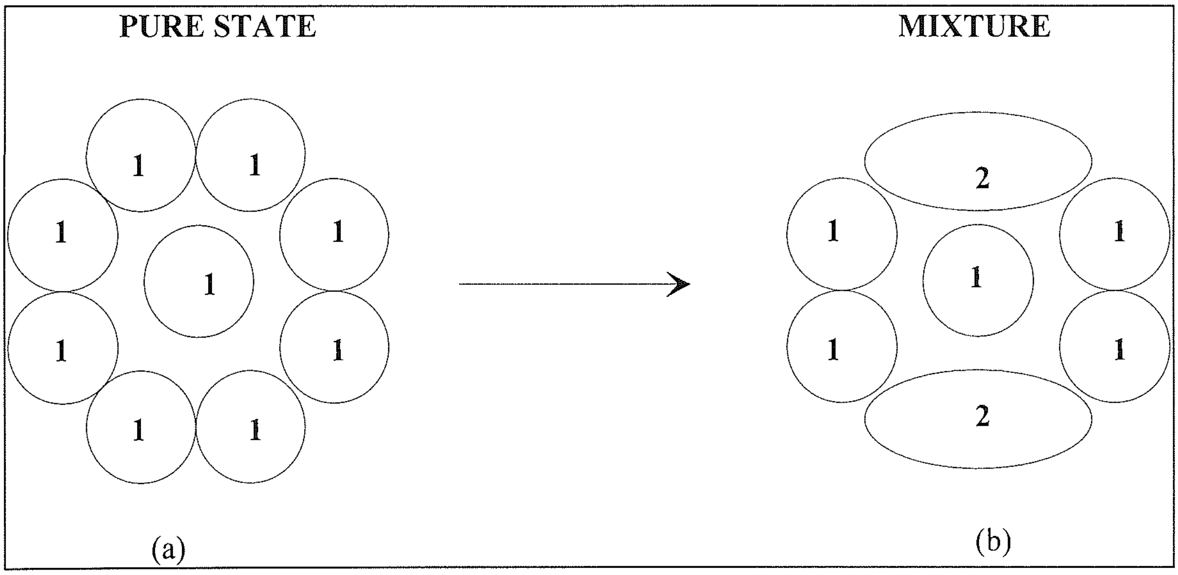


Figure 2.6. Representation of the change in the composition of the solvation shell of molecule 1 when one molecule of 2 is assumed to replace two molecules of 1.

X_{21} and X_{11} are related to t^W_1 and t^W_2 through their definitions by

$$X_{21} = \frac{t_2^W}{t_1^W + t_2^W}$$

$$X_{11} = \frac{t_1^W}{t_1^W + t_2^W}$$

Substitution and replacement gives

$$t_1^W = \frac{z}{1 + \frac{V_2^m \ x_2}{V_1^m \ x_1} \exp\left[- \frac{(\Phi_{21} - \Phi_{11})}{k_B \ T} \right]}$$

as an expression for $t^W{}_1$. Similar arguments give

$$m_2^W = \frac{z}{1 + \frac{V_1^m \ x_1}{V_2^m \ x_2} \exp\left[- \frac{(\Phi_{12} - \Phi_{22})}{k_B \ T} \right]}$$

where $\Phi_{12} = \Phi_{21}$.

If we have a mixture containing Avogadro's number of molecules, L, London (1937) stated that the sum of the interaction energies of all the radial molecular pairs in the solvation shells is equal to the potential energy (U). This gives the following equation

$$U = \frac{1}{2} x_1 \ L (t_1^W \ \Phi_{11} + t_2^W \ \Phi_{21}) + \frac{1}{2} x_2 \ L (m_2^W \ \Phi_{22} + m_1^W \ \Phi_{12}) \tag{2.84}$$

The factor of ½ is introduced so that pair interactions are not counted twice.

The change in total molar energy due to mixing (ΔU) is given by

$$\Delta U = U - (\frac{1}{2} x_1 \ L z \ \Phi_{11} + \frac{1}{2} x_2 \ L z \ \Phi_{22}) \tag{2.85}$$

As the molar excess energy (U^E) is equal to ΔU, and inserting equation (2.85) in equation (2.84) gives

$$U^E = \frac{1}{2} L \left[x_1 \ \Delta \ U_{11} \ (t_1^W - z) + x_2 \ \Delta \ U_{22} \ (m_2^W - z) \right] \tag{2.86}$$

where

$$\Delta \ U_{11} = \Phi_{11} - \frac{\Phi_{21} \ V_1^m}{V_2^m} \tag{2.87}$$

and

$$\Delta \ U_{22} = \Phi_{22} - \frac{\Phi_{12} \ V_2^m}{V_1^m} \tag{2.88}$$

At constant volume and composition (Prausnitz et al., 1986)

$$\frac{a^E}{T} = \int U \, d\left(\frac{1}{T}\right) + \text{constant of integration} \tag{2.89}$$

Guggenheim (1952) showed that for a binary mixture of the smaller molecule (1), occupying one lattice site and the larger molecule (2), occupying r lattice sites, equation (2.89) can be expressed as

$$\begin{aligned} \left(\frac{a^E}{R\,T}\right)_{\text{athermal}} &= x_1 \ln\left(\frac{w_1^m}{x_1}\right) + x_2 \ln\left(\frac{w_2^m}{x_2}\right) \\ &+ \frac{1}{2} z\,(x_1 + x_2\, q) \ln\left[\frac{x_1 + r\, x_2}{x_1 + q\, x_2}\right] \\ &- \frac{1}{2} z\, q\, x_2 \ln\left(\frac{r}{q}\right) \end{aligned} \tag{2.90}$$

where w^m_1 and w^m_2 are the volume fractions of components 1 and 2 respectively, r represents the difference in sizes of the molecular volumes between molecule 1 and 2, and q represents the relative contact surface areas of the two molecules.

Inserting equation (2.90) in equation (2.83) gives the following expression for the excess Gibbs free energy

$$\begin{aligned} \left(\frac{g^E}{R\,T}\right) &= x_1 \ln\left(\frac{w_1^m}{x_1}\right) + x_2 \ln\left(\frac{w_2^m}{x_2}\right) \\ &+ \frac{1}{2} z\,(x_1 + x_2\, q) \ln\left[\frac{x_1 + r\, x_2}{x_1 + q\, x_2}\right] \\ &- \frac{1}{2} z\, q\, x_2 \ln\left(\frac{r}{q}\right) \\ &+ \left(\frac{L\,z}{2\,R}\right)\left(\frac{x_1\, \Delta\, U_{11}}{b_1^A}\right) \ln\left(\frac{1 + a^A \exp\left(-\frac{b_1^A}{T}\right)}{1 + a^A}\right) \\ &+ \left(\frac{L\,z}{2\,R}\right)\left(\frac{x_2\, \Delta\, U_{22}}{b_2^A}\right) \ln\left(\frac{1 + (a^A)^{-1} \exp\left(-\frac{b_2^A}{T}\right)}{1 + (a^A)^{-1}}\right) \end{aligned} \tag{2.91}$$

where

$$
\begin{aligned}
w_1^m &= \frac{x_1 V_1^m}{x_1 V_1^m + x_2 V_2^m} \\
w_2^m &= \frac{x_2 V_2^m}{x_1 V_1^m + x_2 V_2^m} \\
a^A &= \frac{x_2 V_2^m}{x_1 V_1^m} \\
b_1^A &= \frac{L(\Phi_{21} - \Phi_{11})}{R} \\
b_2^A &= \frac{L(\Phi_{12} - \Phi_{22})}{R} \\
\text{and} \quad r &= \frac{V_2^m}{V_1^m}
\end{aligned}
\tag{2.92}
$$

The r parameter can also be defined as the ratio of the van der Waals volumes (or some other characteristic volume) of the molecule (the monomer) chosen to define the characteristic unit size of the lattice. The parameter q arises from the Guggenheim terms (mentioned earlier), and is defined as

$$q = A_{W2} / A_{W1}$$

where A_{Wi} is the van der Waals surface area of molecule i.

2.11.5 Equations for the activity coefficients

The activity coefficient can be found by differentiating equation (2.91) as required in equation (2.44). By doing this the activity coefficient for compound 1 can be expressed as

$$\begin{aligned}
\ln \gamma_1 \; = \; & \ln\left(\frac{w_1^m}{x_1}\right) + x_2 \left(\frac{r - 1}{x_1 + r\, x_2}\right) \\
& + \frac{1}{2}\, z \left[\frac{x_2\, (q - r)}{x_1 + r\, x_2} + \ln\left(\frac{x_1 + r\, x_2}{x_1 + q\, x_2}\right)\right] \\
& + \left(\frac{L\, z}{2\, R}\right) \left(\frac{\Delta\, U_{11}}{b_1^A}\right) \left[\frac{a^A (1 + a^A) \left(1 - \exp\left(- \frac{b_1^A}{T}\right)\right)}{1 + a^A \exp\left(- \frac{b_1^A}{T}\right)}\right] \\
& + \left(\frac{L\, z}{2\, R}\right) \left(\frac{\Delta\, U_{11}}{b_1^A}\right) \ln \left(\frac{1 + a^A \exp\left(- \frac{b_1^A}{T}\right)}{1 + a^A}\right) \\
& + \left(\frac{L\, z}{2\, R}\right) \left(\frac{\Delta\, U_{22}}{b_2^A}\right) \frac{V_1^m}{V_2^m} \left[\frac{\left(\exp\left(- \frac{b_2^A}{T}\right) - 1\right) (1 + (a^A)^{-1})}{1 + (a^A)^{-1} \exp\left(- \frac{b_2^A}{T}\right)}\right]
\end{aligned} \tag{2.93}$$

That for compound 2 is then

$$\begin{aligned}
\ln \gamma_2 \; = \; & \ln\left(\frac{w_2^m}{x_2}\right) + x_1 \left(\frac{r - 1}{x_1 + r\, x_2}\right) \\
& + \frac{1}{2}\, z \left[\frac{x_1\, (r - q)}{x_1 + r\, x_2} + q \ln \left(\frac{q\, (x_1 + r\, x_2)}{r\, (x_1 + q\, x_2)}\right)\right] \\
& + \left(\frac{L\, z}{2\, R}\right) \left(\frac{\Delta\, U_{22}}{b_2^A}\right) \left[\frac{(a^A)^{-1} (1 + (a^A)^{-1}) \left(1 - \exp \left(- \frac{b_2^A}{T}\right)\right)}{1 + a^{-1} \exp\left(- \frac{b_2^A}{T}\right)}\right] \\
& + \left(\frac{L\, z}{2\, R}\right) \left(\frac{\Delta\, U_{22}}{b_2^A}\right) \ln\left(\frac{1 + (a^A)^{-1} \exp\left(- \frac{b_2^A}{T}\right)}{1 + (a^A)^{-1}}\right) \\
& + \left(\frac{L\, z}{2\, R}\right) \left(\frac{\Delta\, U_{11}}{b_1^A}\right) \frac{V_2^m}{V_1^m} \left[\frac{\left(\exp\left(- \frac{b_1^A}{T}\right) - 1\right) (1 + a^A)}{1 + a^A \exp\left(- \frac{b_1^A}{T}\right)}\right]
\end{aligned} \tag{2.94}$$

Equations (2.93) and (2.94) can be used, together with equation (2.25), if the vapour pressures of the pure liquids are known, to predict vapour-phase compositions and/or total vapour pressures for given liquid phase compositions (x_i).

Compared to the similar equations in Table 2-4, the AGAPE equations look similar to the UNIQUAC equations, especially in complexity. There is, though, one very important difference, the AGAPE equations use only molecular and volume parameters for the pure compounds, whereas UNIQUAC includes binary parameters.

2.11.6 Equilibrium separation distances

The equilibrium separation (R^A) is a very important parameter in the AGAPE model. For each component there is one separation. For a binary mixture consisting of components 1 and 2, the equilibrium separation is calculated using the Lorentz combining rule (Mohammadi, 1986)

$$R^A_{mix} = (R^A_1 + R^A_2) / 2 \qquad (2.95)$$

In some cases, Mohammadi (1986) used R^A_{mix} as the maximum of the two separations. In the following the R^A_{mix} will be calculated from the above equation.

Equation (2.79) defined the net attractive potential for a component. It is worth noticing that for a binary mixture, consisting of components 1 and 2, there are three net attractive potentials, one for each of the pure components, named the like potential calculated from equation (2.79) using the equilibrium separation unique to each component and with the notation Φ_{11} or Φ_{22}, respectively. The net potential for the mixture is also calculated using equation (2.79), but with the above expression for the separation for the mixture. This potential is named the unlike potential and Φ_{12} is the symbol for that. The unlike potentials Φ_{12} and Φ_{21} are equal to each other.

2.11.7 Limitations

At the present time AGAPE enables us to predict VLE and excess Gibbs free energy for binary or multicomponent mixtures. But because of the limitations in the generalized London potential, the AGAPE equations are limited to the following compounds:

- small compounds (less than C6)

- non-polar compounds
- no hydrogen bonds

Because of the assumption used to derive equation (2.25) from equation (2.19),

- low pressure

is also a limitation.

A final limitation occurs because neither the molecular volume nor the heat of vaporization has a value above the critical temperature or the critical pressure, and then it is not possible to determine a value for the equilibrium separation at conditions above the critical conditions

- conditions have to be below the critical conditions of each pure component.

2.11.8 Compounds included in the AGAPE database

Table 2-6 shows a list of the compounds presently included in the AGAPE data base.

AGAPE library number	**component formula**	**chemical name**
1	$c\text{-}C_6H_{12}$	*cyclo* hexane
2	CCl_4	carbon tetrachloride
3	$C(CH_3)_4$	neo-pentane
4	C_6H_6	benzene
5	N_2	nitrogen
6	Ar	argon
7	CH_4	methane
8	O_2	oxygen
9	Kr	krypton
10	CS_2	carbon disulphide
11	$c\text{-}C_5H_{10}$	*cyclo* pentane
12	$SiCl_4$	silicon tetrachloride
13	$CHCl_3$	chloroform
14	CH_2Cl_2	dichloromethane

Table 2-6. The compounds presently included in the AGAPE data base (continued over).

AGAPE library number	**component formula**	**chemical name**
15	C_2H_6	ethane
16	C_3H_8	propane
17	CO	carbon monoxide
18	C_2H_4	ethylene
19	Xe	xenon
20	CH_3I	methyl iodide
21	CF_4	carbon tetrafluoride
22	$n\text{-}C_6H_{14}$	n-hexane
23	$1,1\text{-}C_2H_4Cl_2$	1,1-dichloroethane
24	$1,2\text{-}C_2H_4Cl_2$	1,2-dichloroethane
25	C_2HCl_3	trichloroethylene
26	CH_3OH	methanol
27	C_2H_5OH	ethanol
28	CHF_3	fluoroform
29	CO_2	carbon dioxide
30	$n\text{-}C_4H_{10}$	n-butane
31	H_2	hydrogen (normal)
32	C_2Cl_4	tetrachloroethylene
33	C_2F_6	perfluoroethane
34	C_3H_6O	acetone
35	C_2H_4O	acetaldehyde
36	C_3H_6O	propionaldehyde
37	C_3H_8O	1-propanol
38	C_4H_8O	methyl ethyl ketone (2-butanone)
39	H_2O	water
40	Br_2	bromine
41	I_2	iodine
42	Cl_2	chlorine
43	BrF_3	bromine trifluoride (...no critical data)
44	D_2	deuterium (normal)
45	Ne	neon
46	SF_6	sulphur hexafluoride

Table 2-6. The compounds presently included in the AGAPE data base (continued over).

AGAPE library number	**component formula**	**chemical name**
47	H_2S	hydrogen sulfide
48	SO_2	sulphur dioxide
49	NH_3	ammonia
50	C_2H_2	acetylene
51	Ra	radon

Table 2-6. The compounds presently included in the AGAPE data base.

The list is continuously being expanded with new compounds. The components chosen in this study have been chosen from the list of included components available at that specific time. The list shows several components that are either polar or contain hydrogen bondings. Despite the limitations of the AGAPE theory, these compounds have been included. By including them in the calculations and see how inaccurate the results are compared with experimental data, it may be possible to define additional terms which would bring them within the scope of the AGAPE approach.

2.11.9 Advantages of the AGAPE method

The AGAPE model can predict vapour-liquid equilibrium data from only pure component data, meaning it provides a truly *ab initio* procedure, and it is based on a *whole* molecule approach as opposed the UNIFAC method that is based on a group contribution approach. Because of the incorporating of the generalized London potential theorem, the AGAPE model is able to differentiate between geometric isomers, like the *cis* and *trans* configurations of the same molecule. Further, the AGAPE model can handle small molecules and inert atoms like Ar and O_2.

Recently research has shown that the AGAPE model can be used to predict liquid-liquid equilibrium as well as vapour-liquid equilibrium and enthalpy data from the same set of parameters (Kakhu and Homer, 1996b).

2.11.10 Computer programs

A suite of computer programs has been developed based on the above mentioned equations. In the following the notation P11, P22 will be equivalent to Φ_{11} and Φ_{22} (equation (2.79) where i=j). P12 will be used as a notation for the unlike pair potentials for a binary mixture, Φ_{12} (equation (2.79)). P12-GLP indicates that the value is calculated using the London combining rule (equation (2.79)). P12-GM indicates that the value was derived by applying the geometric mean combining rule (equation (2.82)). This notation has been used to differentiate between the various values that have been calculated by running the different computer programs. R, the equilibrium distance (often in the form of R1 or R2) is similar to the parameter R^A in the previous section (equation (2.80)). R1 and R2 are, of course, the equilibrium distances for component 1 and component 2, respectively.

MENU OF AGAPE PROGRAMS

** With the exception of VLE, all the programs accept non-library compounds **

GLP	calculates the pair potentials (P11, P22, P12) and the heats of vaporisation of the pure compounds for a binary mixture using the GLP equation. R is calculated from the molar volumes.
MOHV	calculates the molar volumes and heats of vaporisation for pure compounds at any given temperature using suitable correlations.
GAMV	calculates gammav = (dp/dt)v = internal pressure coefficient for pure compounds using the Redlich-Kwong equation of state.
PP	calculates pair potentials (P11, P22, P12) for a binary mixture. P11 and P22 are calculated from either the heats of vaporization or the molar volumes or user-specified values of R

	of the pure compounds while P12 is calculated either by the GLP or the geometric mean.
LOCAL	uses AGAPE to calculate the number of whole molecular contacts and local compositions for a binary mixture. P12 is calculated either from the GLP or using the fitted parameters obtained from FIT (see section 2.11.13).
VLE	predicts VLE data using AGAPE and GLP. r is calculated from the molar volumes or the van der Waals volumes.

2.11.11 Input parameters needed for the pure compounds

A number of input parameters for the pure compounds are needed. Among them are the heat of vaporization, molar volume, critical properties, boiling point, and information on equilibrium distances.

2.11.12 Options

The parameters needed for calculating the activity coefficients by the AGAPE model are:

R1	the equilibrium separation for component 1
R2	the equilibrium separation for component 2
P12	the unlike pair potential for the mixture
r	the difference in sizes of volumes between molecule 1 and 2
z	number of nearest neighbours

All these parameters are either calculated from several options or can be given different values.

R1, R2	- calculated from the molar volume at the relevant temperature - calculated from the heat of vaporization at the relevant temperature - independent of temperature, meaning any convenient values can be used

The chosen option for the calculation of the R1 and R2 values changes the P11 and P22 values, of course. So the P11 and P22 values can be calculated from the following options

P11, P22 - calculated from the molar volume at the relevant temperature
- calculated from the heat of vaporization at the relevant temperature
- independent of temperature, meaning any convenient values can be used

These options give different values for the unlike pair potential, P12.

P12 - calculated from the molar volume at the relevant temperature
- calculated from the heat of vaporization at the relevant temperature
- independent of temperature, meaning any convenient values (independent of P11 and P22) can be used

The P12 can be derived either from the London theory, or a geometric mean unlike pair potential, P12-GM can be used. The geometric mean value for the unlike pair potential is calculated from the Berthelot theory,

$$P12 - GM = -\sqrt{P11 * P22}$$

This gives two different options for the unlike pair potential

P12 - calculated from the London theory
- calculated from the Berthelot theory

and of course, the options as mentioned for P12 can still be used.

The number of nearest neighbours, z is usually set to the value of 11, but other values of 7 or 4 can be found in the literature (Moelwyn-Hughes, 1961).

z - set to 11.0
- set to 7.0
- set to 4.0

The r value can be calculated from the molar volumes (at the relevant temperature) for the compounds, or from the van der Waals volumes of the compounds.

r	- calculated from the molar volumes for the compounds at the relevant temperature - calculated from the van der Waals volumes for the compounds at a fixed temperature - independent of the compounds, meaning any convenient value can be used

Testing all these different options to the full extent possible has not been carried out. Some parameters have been fixed in certain calculations in an attempt to minimise the influence from these parameters.

2.11.13 The AGAPE-FIT method

This section (2.11) describes the AGAPE method for prediction of vapour-liquid equilibrium data and some of the excellent results obtained by the method. As it can be seen from the tables of presently included compounds, the numbers of compounds for which the AGAPE method can be used is limited. Not surprisingly, this problem has been attacked and resulted in the development of an extension of the AGAPE method named the AGAPE-FIT method (McCoubrey et al., 1993 and Kakhu and Homer, 1996a). The AGAPE-FIT method has been applied to binary mixtures with good results (Kakhu and Homer, 1996a).

The AGAPE equations involve two parameters, a structural parameter, r, (the difference in size of the molecular volumes between two molecules) and an energy term parameter (the unlike London potential, Φ_{12}). Both parameters have the advantage of having a clear physical meaning, and they can be obtained independently of each other. Furthermore, the two parameters are uncorrelated (Kakhu and Homer, 1996a).

The interaction parameters in the UNIFAC and also in the UNIQUAC models are derived from a large body of experimental data and have no clear physical meaning.

Recent research attempting to derive a physical meaning for the UNIQUAC parameters (Jónsdóttir et al., 1994) has been quite successful for ketones and alkanes mixtures. Looking at the derived UNIQUAC parameters in Jónsdóttir et al. (1994) compared with the current UNIQUAC parameters, there seems to be quite a difference between them. Some parameters even change sign. This could indicate that the actual values of the UNIQUAC interaction parameters are not important, in fact, any convenient values of the parameters could be used. If this is the case for the UNIQUAC model, this could well be true for the UNIFAC model, which is derived based on the UNIQUAC model.

The AGAPE-FIT method uses one experimental data point of an excess thermodynamic property (usually at the equimolar concentration value).

In case of one known value of excess Gibbs energy, the r is then fixed as the ratio of the van der Waals volumes (or the temperature-dependent molar volumes) and the excess Gibbs energy equation (2.91) is then matched to this experimental point to yield a fitted value of Φ_{12} by employing a straight forward secant algorithm.

If one single value of the excess enthalpy is known, besides one single value of the excess Gibbs energy (both values at the same molar composition), it is necessary to carry out a simultaneous g^E - h^E fit (equations 2.91 and 2.86) to obtain r and Φ_{12}. This procedure is more complicated then the g^e fit procedure and involves a Newton-Raphson technique.

The AGAPE-FIT method has the advantage of being applicable to many more compounds without the limitations introduced by use of the generalized London potential. It can as well be used without the temperature limitation below the critical temperature of the pure compounds.

McCoubrey et al. (1993) have tried to use the values of the unlike London potential obtained when predicting VLE data using the AGAPE-FIT method, to obtain information of the pure compound like potential and, indirectly, of the intermolecular forces. This proved a difficult task.

2.11.14 Computer programs for the AGAPE-FIT method

A series of computer programs have been developed based on the above mentioned method. Again, the notation of P11, P22 and P12 will be used as a notation for the different potentials. P12-GLP indicates that the value is calculated using the London combining rule (equation (2.79)). P12-GM indicates that the value was derived by applying the geometric mean combining rule (equation (2.82)).

MENU OF AGAPE-FIT PROGRAMS

P12	uses AGAPE, with a constant value of r (from molar volume or van der Waals volume), to determine P12 that fits the experimental G^E, and then predicts U^E (and H^E) with the derived P12. Similar procedure from experimental H^E to predicted G^E.
FIT	uses AGAPE to determine values of r and P12 that simultaneously fit one single experimental data point for G^E and H^E for a given value of z
VLEF	predicts VLE and Enthalpy data using AGAPE and fitted parameters obtained from program FIT or P12. Parameters needed are z, r and the P12-ratio.

2.11.15 Prediction results

Prediction results employing both the AGAPE method and the AGAPE-FIT method are shown below and more in Appendix 2. All data are from Kakhu et al. (1995).

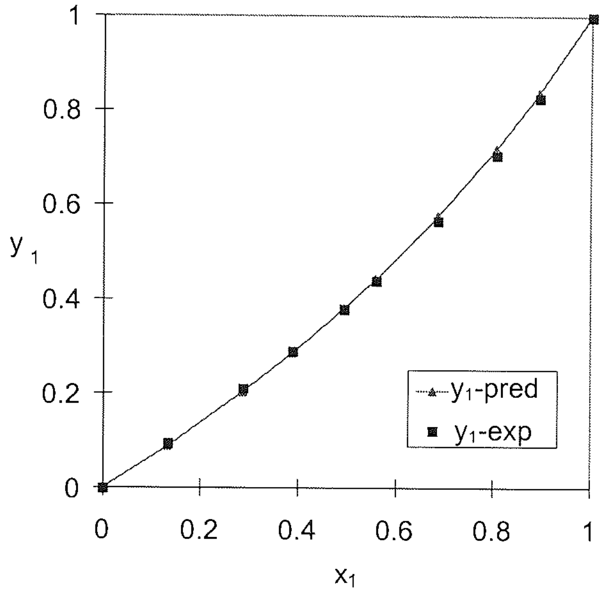


Figure 2.7. Nitrogen (1) and carbon monoxide (2) at 83.82 K. Vapour mole fractions predicted by the AGAPE method (line and ▲) and experimental values (■).

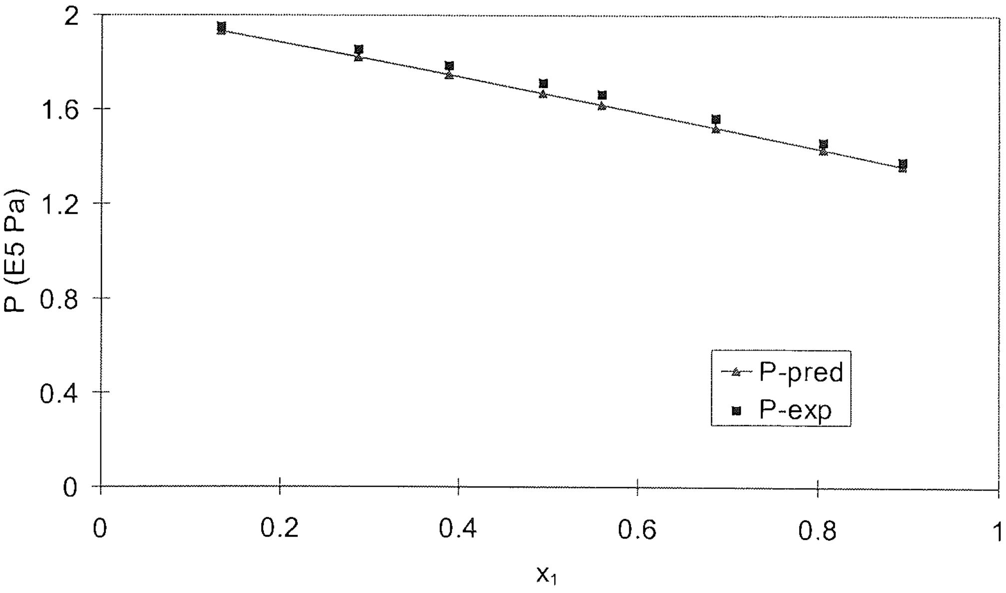


Figure 2.8. Nitrogen (1) and carbon monoxide (2) at 83.82 K. Total pressure predicted by the AGAPE method (line and ▲) and experimental values (■).

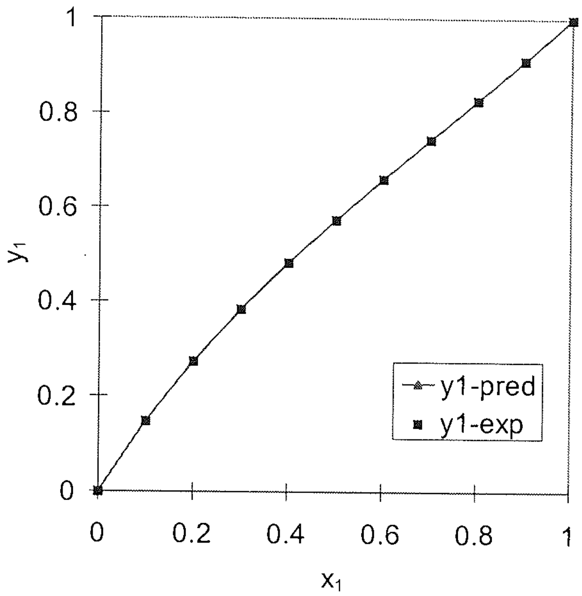


Figure 2.9. Argon (1) and oxygen (2) at 84 K. Vapour mole fractions predicted by the AGAPE-FIT method (line and ▲) and experimental values (■).

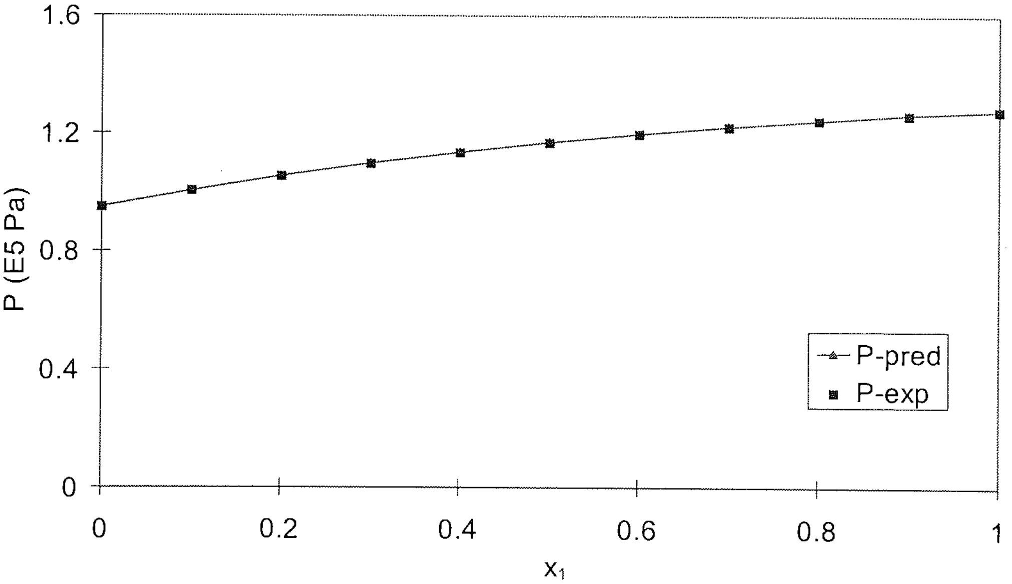


Figure 2.10. Argon (1) and oxygen (2) at 84 K. Total pressure predicted by the AGAPE-FIT method (line and ▲) and experimental values (■).

Chapter 3 - Solubility

3.1 Solubility of gases in liquids

In general, the phrase "solubility of gases in liquids" refers to the liquid phase concentration of components which could not exist as pure liquids at the system temperature, T, and the pressure, P, either because T is higher then their critical temperatures, T_C, or P is much lower then their saturated vapour pressures, P^s (O'Connell, 1980). In other words, at least one of the components is supercritical. The liquid mole fraction of such substances is usually low, but for solvents with very high critical temperatures and at pressures 50-100 MPa, the liquid mole fraction of the solute can be as large as 0.3.

Vapour-liquid equilibrium and solubility of gases in liquids are connected. As noted in Chapter 2, the distinction between vapour-liquid equilibria and the solubility of gases in liquids is arbitrary. It is generally accepted that equilibrium up to 300 K between a typical gas as argon and a liquid such as water is gas-liquid solubility, whereas that between hexane and *cyclo*-hexane at 350 K is an example of vapour-liquid equilibrium. The equilibrium between methane and propane above the critical temperature of methane and below the critical temperature of propane can be classed as vapour-liquid equilibrium or gas-liquid solubility depending on the particular range of pressure considered. In general, the solubility of a gaseous component in a liquid phase is small, below 0.10 mole fraction, but no firm rule exists. The vast majority of gas-liquid solubilities is measured at room temperature. Common examples of gas-liquid solubilities from nature are the solution of oxygen in blood and that of oxygen in water.

Despite the arbitrary distinction, the objective in predicting gas-liquid solubilities is different to the objective in predicting vapour-liquid equilibrium. Due to the small solubility of a gas in a liquid, the gas phase is very close to ideal, and the gas phase composition is therefore much less important then in vapour-liquid equilibrium prediction, where the objective in by far the majority of calculations is to predict the vapour-phase compositions.

We have a gas, component 1 dissolving in a liquid, component 2 at constant temperature. We assume that the fugacity of the gas is 101.325 kPa and that the temperature is well below the critical temperature of the solvent. The dissolution process is followed by a change in enthalpy and entropy, and, what distinguishes the dissolution of a gas in a liquid from the dissolution of a liquid in a liquid, a large decrease in volume of the solute.

3.1.1 Ideal solubility

The solubility of a gas dissolved in a liquid is determined by the equations of phase equilibrium as discussed in chapter 2. If a gaseous phase and a liquid phase are in equilibrium, then for any component i the fugacities in both phases must be the same:

$$f_i^G = f_i^L \tag{3.1}$$

The simplest way to reduce equation (3.1) to a useful form is to rewrite it in a matter suggested by Raoult's law. Raoult's law is discussed in section 2.5.1. Neglecting all gas-phase nonidealities as well as the effect of pressure on the condensed phase, and also any nonidealities due to the solvent-solute interaction, the equation of equilibrium can be simplified to:

$$p_i = y_i P = x_i P_i^S \tag{3.2}$$

p_i is the partial pressure of component i in the gas phase, and P_i^S is the saturation (vapour) pressure of pure liquid i at the temperature of the solution. The solubility x_i as given by equation (3.2) for the gaseous component is called the ideal solubility of the gas.

A difficulty arises when we have to find a value for P_i^S whenever the solution temperature is above the critical temperature of pure i. This is often the case, and it has been customary to extrapolate the saturation pressure of pure liquid i beyond its critical temperature to the solution temperature.

If the ideal solubility is calculated using equation (3.2) and the extrapolation of the vapour pressure, a correct order-of-magnitude result is obtained. The partial pressure of the gas must not be large, and the solution temperature must not be markedly above the critical temperatures of both the liquid and, more importantly, the gaseous solute.

Table 3-1 (Prausnitz et al., 1986) compares some ideal and observed solubilities. The table shows that the ideal solubility is significantly different from the observed solubilities, but is of the right order of magnitude.

	ideal	n-C_7F_{16}	n-C_7H_{16}	CCl_4	CS_2	$(CH_3)_2CO$
H_2	8	14.01	6.88	3.19	1.49	2.31
N_2	10	38.7		6.29	2.22	5.92
CH_4	35	82.6		28.4	13.12	22.3
CO_2	160	208.8	121	107	32.8	

Table 3-1. Solubilities of gases in several liquid solvents at 298.15 K and 101.325 kPa partial pressure (mole fractions x 10000).

The ideal solubility suffers from being independent of the solvent. The ideal solubility is defined to be the same for one solute dissolved in various solvents. This is far from true, as indicated in Table 3-1. The ideal solubility also decreases with rising temperatures at constant partial pressures due to the extrapolation. This is usually correct, but not always.

Despite these two defects, the ideal solubility never the less provides a rough estimate of gas solubility and gives remarkably good relative values for different solutes.

3.1.2 Real Solutions

No known liquid solutions are ideal (e.g. Mohammadi, 1986) though hydrocarbon/hydrocarbon or alcohols/alcohols come close. In fact, ideal solutions, particularly for liquids, do not exist (Gerrard, 1980), but as the components of a solution approach one another in molecular size, shape, chemical type (electron configuration), and mass, the behaviour of all components in the solution approaches equation (3.2) as a limit.

Deviations from the ideal solution are observed in many solutions in which the components showed marked differences in size, shape, and especially chemical nature. The deviations from ideal solution are quantified by the activity coefficient γ_{solute} expressed by:

$$\gamma_{solute} = \frac{P_{solute}}{x_{solute}\ P^{0}_{solute}} \qquad \text{where} \qquad \begin{array}{lllll} \gamma_{solute} & = & 1, \text{ if } x_{solute} & = & x^{ideal}_{solute} \\ \gamma_{solute} & < & 1, \text{ if } x_{solute} & > & x^{ideal}_{solute} \\ \gamma_{solute} & > & 1, \text{ if } x_{solute} & < & x^{ideal}_{solute} \end{array}$$

Figures 3.1 and 3.2 show solubility of propane and n-butane in n-alkanes at 298.15 K and at 101.325 kPa partial pressure of the gas (from Hayduk, 1986 (IUPAC Solubility Data Series, vol. 24), the numbers refer to references in the actual volume). These figures illustrate that the solubility varies very little with the solvent (for these n-alkanes).

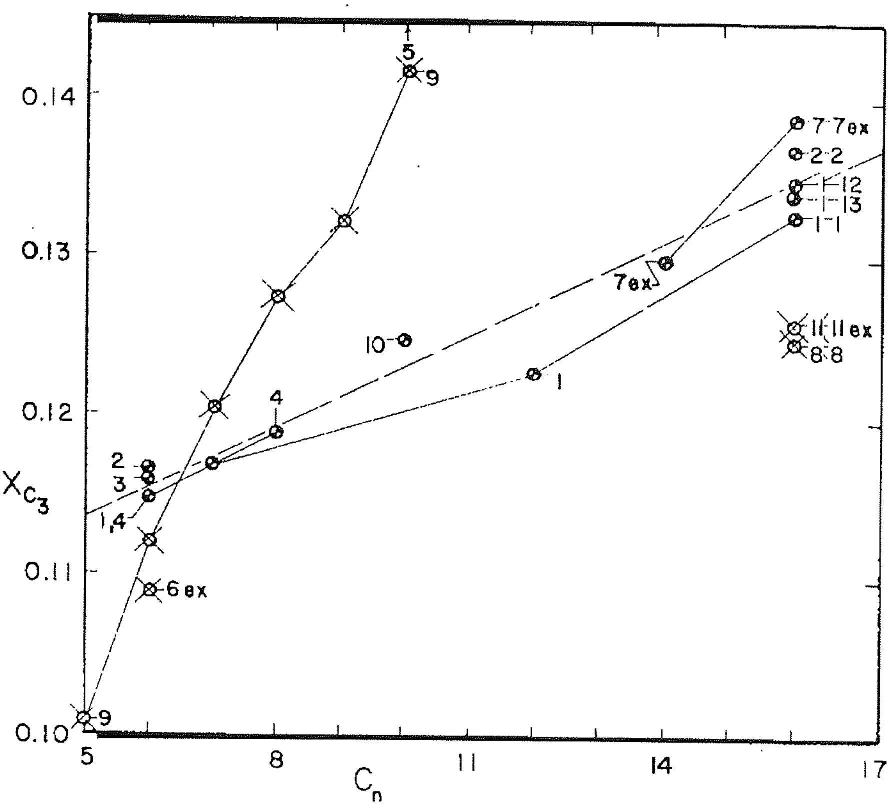


Figure 3.1. Solubility of propane in n-alkane solvents at 298.15 K and 101.325 kPa partial pressure of the gas.

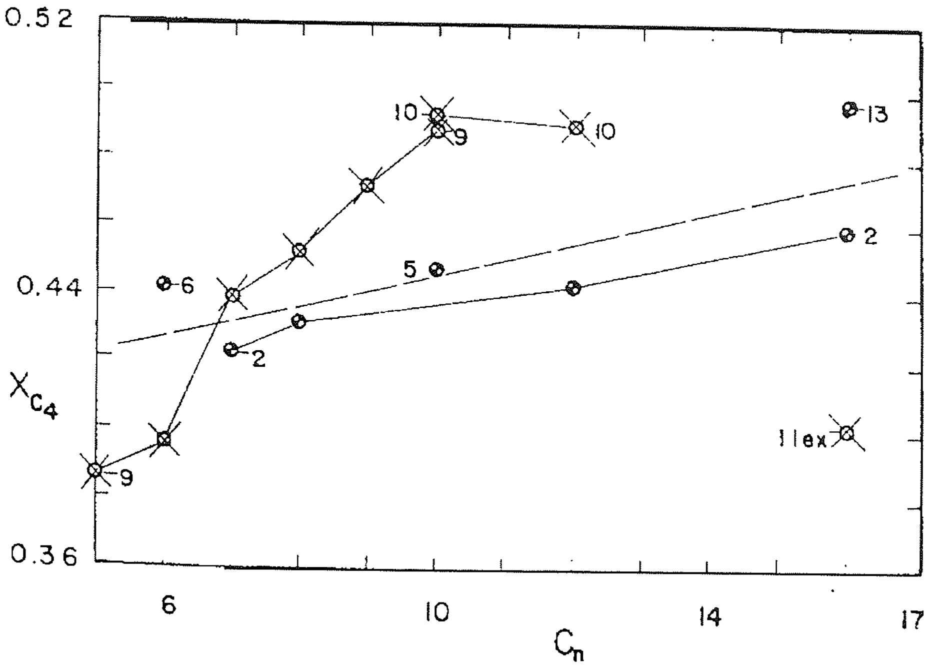


Figure 3.2. Solubility of n-butane in n-alkane solvents at 298.15 K and 101.325 kPa partial pressure of the gas.

Figure 3.3 (from Prausnitz et al., 1986) shows the solubility of Freon-21 in a number of liquid solvents at 305.35 K. The ideal solubility of Freon-21 is calculated using equation (3.2). The figure illustrates that for hydrogen bonding solutes, already associated solvents are poor dissolvers while hydrogen bonding acceptors are much better then the ideal value. Solvent/solute interaction thus is very important in such cases.

In figure 3.3 the solvents are: 1. Ethylene glycol, 2. Trimethylene, 3. Decalin, 4. aniline, 5. Benzofluoride, 6. Nitrobenzene, 7. Tetralin, 8. Bis-β methylthioethyl sulphide, 9. Dimethylaniline, 10. Dioxan, 11. Diethyl oxalate, 12. Diethyl acetate, 13. Tetrahydrofurfuryl laurate, 14. Tetraethyl oxamide, 15. Dimethyl ether of tetraethylene glycol.

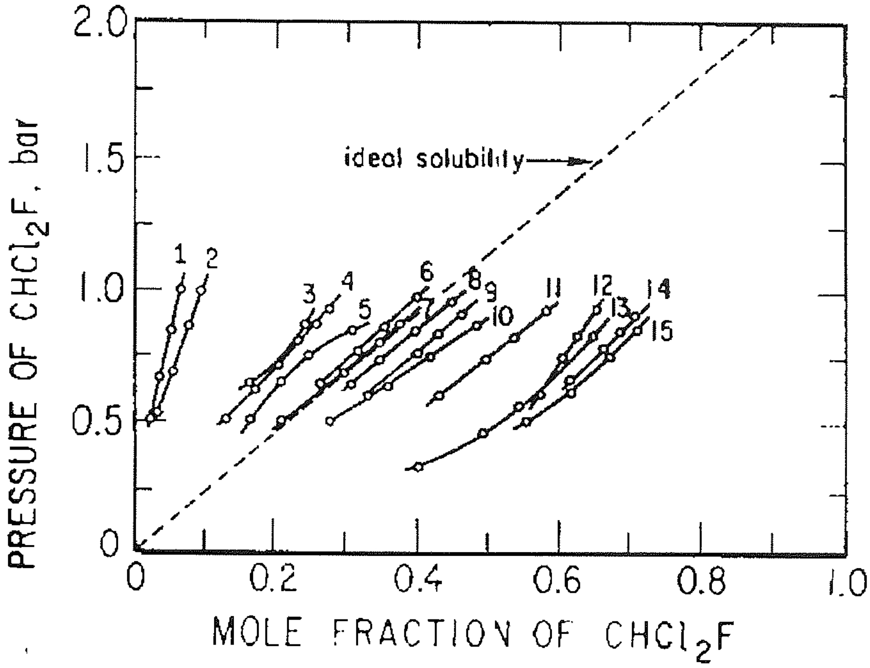


Figure 3.3. Solubility of Freon-21 in liquid solvents at 305.35 K.

The AGAPE model can only handle a very few of these solvents (and neither the solute Freon-21).

3.1.3 Dilute solutions

Guggenheim (1952) has defined dilute solutions as a solution where the solvent is present in large excess compared to the solute. The characteristic of a dilute solution is that the mutual interactions of solute molecules should be negligible. His condition for a binary solution to be dilute is that the product of the liquid mole fraction of the solute times the number of nearest neighbours should be less then 10, in other words, the solubility, $x_{solute} < 0.1$.

3.2 Methods for expressing solubility

There are different methods of expressing measured solubilities.

3.2.1. Mole fraction solubility

A small database for the low-boiling industrial gases dissolved in a number of ordinary solvents has been set up (Appendix 3). The data are presented as mole fraction solubilities, where the mole fraction solubility of a gas x_{solute} dissolved in a solvent is given by

$$x_{solute} = \frac{n_{solute}}{n_{solute} + n_{solvent}} \tag{3.3}$$

where n is the number of moles.

3.2.2 Ostwald coefficient

Other measurements of solubilities use the Ostwald coefficient to express the results obtained. The Ostwald coefficient is usually defined as the ratio of the volume of gas absorbed to the volume of the absorbing liquid, both volumes being measured at the same temperature. Conversion of the measured Ostwald coefficients to mole fractions assumes ideal gas behaviour, and is often not accurate enough (Fogg and Gerrard, 1991).

3.2.3 Bunsen coefficient

A previous popular coefficient to measure was the Bunsen coefficient that is, the volume of gas, reduced to 273.15 K and 101.325 kPa which is absorbed by a unit volume of solvent at a stated temperature under partial pressure of gas of 101.325 kPa. Again, conversion to mole fractions usually assumes ideal gas behaviour (Fogg and Gerrard, 1991).

3.2.4 Henry's law and Henry's law constant

Henry's law constant is the proportionality constant between the concentration of gas in the liquid phase and the partial pressure of the dissolved gas (as above)

$$p_g = x_g H \tag{3.4}$$

where subscript g stands for the gas phase (solute) and H is the Henry's law constant. The relationship is usually valid for mole fractions (x_g) below 0.01 (Fogg and Gerrard, 1991). Values of Henry's law constant found in literature are often given without stating the exact method of evaluation.

Comparing equation (3.4) with the fugacity-equation (3.1) shows that Henry's law assumes that the gas phase is ideal by replacing the fugacity of the vapour phase with the partial pressure of the vapour. Similarly the fugacity of the liquid phase is assumed to be proportional to the mole fraction (in the liquid phase). The proportionality constant $H_{\text{solute, solvent}}$ can be restated using the concept of an activity coefficient and a fugacity at some standard state as

$$H_{\text{solute, solvent}} = \gamma_{\text{solute}}\, f_{\text{solute}}^{0} \qquad (3.5)$$

From the discussion of the fugacity in chapter 2, it follows that f_{solute}^{0} is a constant independent of the solute mole fraction in the liquid phase, x_{solute}. From the above equation it then follows that the activity coefficient γ_{solute} must also be independent of x_{solute}. The constancy of the activity coefficient of the solute at the low concentrations considered is the essential assumption of Henry's law.

For Henry's law to be valid, the mole fraction of the solute must be small. What is meant by "small" depends on the mixture, but for most mixtures, Henry's law gives good values compared with experimental data when the solute mole fraction in the liquid phase is below 0.01 (Fogg and Gerrard, 1991). The theoretical explanation for this can be illustrated by expressing a normalised activity coefficient as a power series in $(1-x_{\text{solute}})$

$$RT \ln \gamma_{\text{solute}} = A^{S}(1-x_{\text{solute}})^{2} + B^{S}(1-x_{\text{solute}})^{3} + \ldots \qquad (3.6)$$

This normalized activity coefficient can be seen to approach unity, when the mole fraction of the solute goes to unity.

If we retain only the first term and neglect the higher terms, the coefficient A^{S} can be regarded as a measure of non-ideality. A positive value of A^{S} indicates a "dislike" between the solute and the solvent. A negative value of A^{S} indicates a liking of the solute and the solvent to form a complex, and its absolute value can be used as a measure for this tendency. A value of A^{S} equal to zero gives an ideal solution, for which Henry's law holds for the entire range of composition $0 \leq x_{\text{solute}} \leq 1$. If the absolute value of A^{S}/RT is small compared to unity, then Henry's law holds, even for appreciable values of x_{solute}. If the absolute value of A^{S}/RT is large, then even a small x_{solute} can produce a change in the activity coefficient with composition, meaning that Henry's law is unlikely to hold.

As mentioned, Henry's law assumes gas-phase ideality. This assumption is not necessary, and introducing the gas-phase fugacity coefficient (equation (2.19)) in equation (3.1) gives

$$f_i = \varphi_i \, y_i \, P = H_{i,\,solvent} \, x_i \qquad (3.7)$$

O'Connell (1980) has shown how to overcome the problem of the standard liquid fugacity of component i by replacing it with Henry's constant, $H_{iR}(T)$, in a reference solvent, R

$$H_{iR}(T) \equiv \lim_{x_R \to 1} \left(\frac{f_i}{x_i} \right)$$

and using the activity coefficient in the unsymmetric convention, γ^*_i

$$\lim_{x_R \to 1} \gamma^*_{iR} = 1$$

Correlation and prediction of Henry's constant in a reference solvent.

According to O'Connell (1980) the theories for correlating and predicting Henry's constant in a reference solvent can be divided into three categories.

(1) the theories which correlate the temperature dependency by using a known value of H_{iR} at a single temperature

(2) the theories which fit one or more parameters of a theory

(3) the theories which only predict H_{iR} from other quantities.

Fugacity of the liquid.

The extrapolation of the saturated vapour pressures illustrates the difficulty that arises from the fundamental solubility equation (3.5)

$$H^T_{2,1} = f^T_2 \, \gamma^T_{2(in\ 1)}.$$

This equation includes the fugacity of the solute at the solution temperature, which is (often the case) higher then the critical temperature of the solute. This represents a problem in itself and the customary solution has been to extrapolate the saturation vapour pressure of the solute to above the critical temperatures as shown in Figures A12.1 and A12.2. This method has no sound theoretical basis, but is dedicated by convenience. From the extrapolated saturated vapour pressure it is then possible to calculate the fugacity of the hypothetical liquid at the solution temperature.

3.2.5 Ideal dilute solution

An ideal solution was defined in section 2.3.2. An ideal dilute solution is defined as a solution where

$$\lim_{x_{solute} \to 0} \frac{f_{solute}}{x_{solute}} = H_{solute,\, solvent}$$

using the boundary condition of the infinitely dilute solution. For the solvent which is present in excess the similar boundary condition is

$$\lim_{x_{solute} \to 0} \frac{f_{solvent}}{x_{solvent}} = f_{pure\ liquid\ solvent}$$

The use of an ideal dilute solution has been found useful (Prausnitz et al., 1986) whenever the liquid mixture cannot exist over the entire composition range. If the temperature is higher then the critical temperature of the solute, then the liquid phase cannot exist as the solute liquid mole fraction goes to unity. This means that introducing a hypothetical liquid state for the solute has been necessary for using the relationships based on Raoult's law.

3.2.6 The activity coefficient described in the symmetric and unsymmetric way

The activity is conveniently defined in such a way that for an ideal solution, the activity coefficient is unity. One way of describing ideality leads to Raoult's law (see section 2.5.2), another leads to Henry's law. The activity coefficient can be defined using the two different ways of ideality (Prausnitz et al., 1986).

If the activity coefficients are defined with reference to an ideal solution in the sense of Raoult's law, then the normalisation for each component i is

$$\gamma_i \rightarrow 1 \text{ as } x_i \rightarrow 1$$

This normalisation holds for both the solute and the solvent and is referred to as the symmetric convention for normalisation.

On the other hand, if the activity coefficients are described with reference to an ideal dilute solution, then the normalisation of the activity coefficients is

$$\begin{aligned} &\gamma_{\text{solvent}} \rightarrow 1 \quad \text{as} \quad x_{\text{solvent}} \rightarrow 1 \\ &\gamma_{\text{solute}} \rightarrow 1 \quad \text{as} \quad x_{\text{solute}} \rightarrow 0 \end{aligned} ,$$

so here the activity coefficients are not normalized in the same way. This is the unsymmetric convention for normalisation.

Usually, the activity coefficient of a component which approaches unity as its mole fraction goes to zero is denoted with an asterix, so that the unsymmetric convention becomes

$$\begin{aligned} &\gamma_{\text{solvent}} \rightarrow 1 \quad \text{as} \quad x_{\text{solvent}} \rightarrow 1 \\ &\gamma^{*}_{\text{solute}} \rightarrow 1 \quad \text{as} \quad x_{\text{solute}} \rightarrow 0 \end{aligned}$$

For extension of the symmetric and the unsymmetric conventions to multicomponent mixtures see Prausnitz et al. (1986).

3.2.7 Pressure dependency of solubilities

As can be seen from the previous section, Henry's constant is not a function of the composition, but it depends on the temperature, and to a lesser degree, on the pressure.

From section 2.4.1 it follows that the fugacity coefficient's variation with pressure can be expressed as

$$\left(\frac{\partial \ln f_i^L}{\partial P}\right)_{x,T} = \frac{\overline{v}_i}{RT}$$

where $\overline{v}_i$ is the partial molar volume of component i in the liquid phase. Using the thermodynamic definition of Henry's constant equation (3.5) gives

$$\left(\frac{\partial \ln H_{i,\text{solvent}}}{\partial P}\right)_{T} = \frac{\overline{v}_i^{\infty}}{RT}$$

where ∞ indicates the value should be taken at infinite dilution. Integration gives

$$\ln \frac{f_i}{x_i} = \ln H_{i,\,\mathrm{solvent}}^{(P')} + \frac{\int_{P'}^{P} \overline{v}_i^{\infty}\, dP}{RT}$$

where $H_{i,\,\mathrm{solvent}}^{(P')}$ is Henry's constant taken at some arbitrary reference pressure P', usually set to the vapour saturation pressure of the solvent, P_{solvent}^{S}.

$\overline{v_i^{\infty}}$ can be assumed independent of pressure for temperatures well below the critical temperature of the solvent, turning the above equation into the Krichevsky-Kasarnovsky equation

$$\ln \frac{f_{\mathrm{solute}}}{x_{\mathrm{solute}}} = \ln H_{\mathrm{solute,\,solvent}}^{(P_{\mathrm{solvent}}^{S})} + \frac{\overline{v}_{\mathrm{solute}}^{\infty}(P - P_{\mathrm{solvent}}^{s})}{RT} \qquad (3.8)$$

Another important equation for the dependency of solubility with pressure is the so-called Krichevsky-Illinskaya equation. It is derived from the variation of the activity coefficient of the solute (component 2) with the mole fraction assuming that the activity coefficient of the solvent (component 1) is given by a two-suffix Margules equation (see section 2.10.3)

$$\ln \gamma_1 = \frac{A_M}{RT} x_2^2$$

thus A_M (the Margules parameter) is an empirical constant accounting for the intermolecular forces in the solution and weakly dependent on temperature. From the Gibbs-Duhem equation (see section 2.6) the activity coefficient of the solute in the unsymmetric convention, γ_2^* can be found as

$$\ln \gamma_2^* = \frac{A_M}{RT}(x_1^2 - 1)$$

At pressure P_1^S the fugacity coefficient of the solute is then

$$f_2 = \gamma_2^* H_{2,1}^{(P_1^S)} x_2$$

From this the Krichevsky-Illinskaya equation can be derived instead of the Krichevsky-Kasarnovsky equation

$$\ln \frac{f_2}{x_2} = \ln H_{2,1}^{(P_1^S)} + \frac{A_M}{RT}(x_1^2 - 1) + \frac{\overline{v}_2^{\infty}(P - P_1^S)}{RT} \qquad (3.9)$$

This equation contains three parameters. Where pertinent experimental data are absent, the three parameters can be calculated from a reliable equation of state that is valid for the dilute mixture for the entire density range from zero to the inverse of v_1^S. For more details, see Bender et al. (1984) or Prausnitz et al. (1986). Bender et al. (1984) describes a procedure for evaluation of Henry's constant from gas solubility measurements using the Krichevsky-Illinskaya equation combined with either the Peng-Robinson equation of state or the Redlich-Kwong equation of state. The procedure involves numerical or graphical interpolation and extrapolation to obtain a first guess of Henry's constant and iteration of the fugacities.

3.2.8 Temperature dependency of solubilities

Commonly, it is believed that when the temperature rises, the solubility falls (Prausnitz et al., 1986). This is not true, as experimental data are able to show. The rare gases are good examples of the types of gas solubility dependence that can be observed (Battino and Clever, 1966). All the noble gases have a negative temperature coefficient of solubility in water around room temperature and at atmospheric pressure. The temperature coefficient goes through a zero and becomes positive at high temperatures and pressures. Figure 3.4 which shows Henry's constant as a function of temperature for nine binary mixtures illustrates this (from Prausnitz et al., 1986). As can be seen from the figure, the effect of temperature differs qualitatively from one mixture to an other.

For gases dissolved in non-polar solvents Hildebrand and Scott (1962) have found the temperature dependency of gas solubilities as follows. For a sparingly soluble gas (component 2) that obeys Henry's law (the activity coefficient of the solute is independent of the mole fraction) the entropy of solution is

$$\frac{\bar{s}_2^L - s_2^G}{R} = \left(\frac{\partial \ln x_2}{\partial \ln T}\right)_P$$

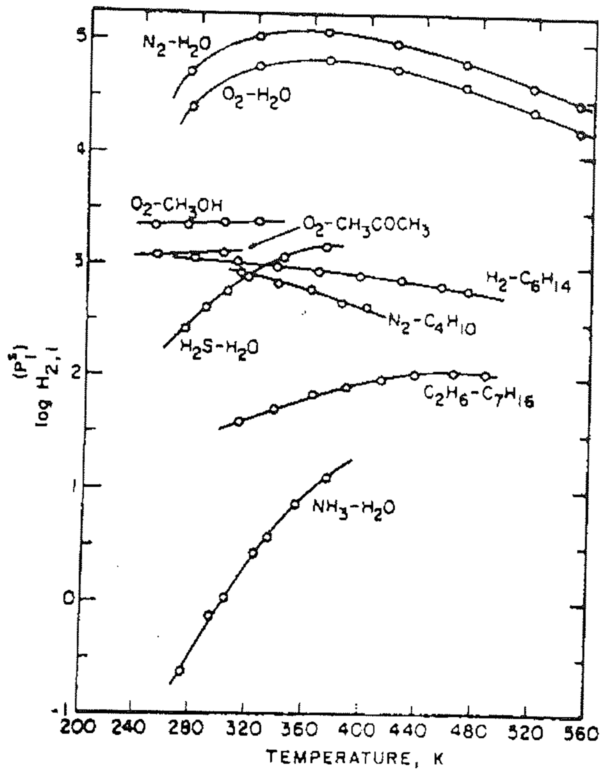


Figure 3.4. Base 10 logarithmic of Henry's constants (10^5 Pa) for typical gases range over five orders of magnitude.

Writing the entropy change as two parts gives

$$\bar{s}_2^L - s_2^G = (s_2^L - s_2^G) + (\bar{s}_2^L - s_2^L)$$

where s_2^L is the entropy of the hypothetical pure liquid at the temperature of solution. The first term of the above equation is then the entropy of condensation of the pure gas. This term is, in general, negative due to the fact that the entropy of a liquid is lower than the entropy of a saturated gas at the same temperature, bearing in mind that entropy is an expression for the disorder of the system. The second term is the partial molar entropy of solution of the condensed solute. Assuming ideal entropy of mixing for the two liquids, the term can be rewritten as

$$\bar{s}_2^L - s_2^L = -R \ln x_2$$

The solubility x_2 is less then 1, and the second term is then positive. With the first term negative and the second term positive, the temperature dependency of the solubilities depends on the actual solubility. For gases that are sparingly soluble (very small x_2) a positive temperature coefficient would be expected, whereas a negative temperature coefficient would be expected for gases which are readily soluble (relatively large x_2). This semiquantitative argument agrees well with experimental observations (Hildebrand and Scott, 1962).

The enthalpy change of solution can be written as (Hildebrand and Scott, 1962), assuming again that the activity coefficient of the solute is independent of the mole fraction

$$\frac{\bar{h}_2^L - h_2^G}{R} = -\left(\frac{\partial \ln x_2}{\partial (1 / T)}\right)_P$$

This can divided into two terms

$$\bar{h}_2^L - h_2^G = (h_2^L - h_2^G) + (\bar{h}_2^L - h_2^L)$$

where h_2^L is the enthalpy of the hypothetical pure liquid at the temperature of the solution. The first term is the enthalpy of condensation of pure solute. This term is usually negative as the enthalpy of a liquid is lower then the enthalpy of a gas at the same temperature. The second term is the partial enthalpy of mixing for the liquid solute and depends on the solute-solvent interaction. For mixtures where the regular solution theory holds, the larger the difference between the cohesive energy density of the solute and that of the solvent, the larger the enthalpy of mixing. Therefore, if the difference is very large, the enthalpy change of solution becomes positive, and the solubility increases with rising temperature. If the difference in cohesive energy densities is very small, the enthalpy change of solution becomes negative, and the solubility falls with rising temperature.

A study of solubilities of gases in liquids has shown that the best fit for Henry's constant as a function of temperature can be expressed as (the study is referred to in Prausnitz et al., 1986)

$$\ln H_{2,1}^{(P_1^S)} = \alpha_2^G (1 - \frac{T_2^G}{T}) - \beta^G (1 - \frac{T_2^G}{T})^2 + \ln 1.01325 \quad (3.10)$$

$\alpha^G{}_2$ and $T^G{}_2$ are constants specific to the solute. β^G is a universal constant for simple gases.

Hayduk and Laudie (1973) and Hayduk and Buckley (1971) have investigated the temperature coefficient (at fixed partial pressures) of gas solubilities for regular solutions and for gases in polar solvents. They found a linear correlation between the solubility and the logarithm of the temperature for a number of gases dissolved in various solvents. From one known value of the solubility (at any temperature) of the gas in the particular solvent, the solvent solubility parameter and the critical temperature of the solvent, they were able to predict the solubility for this particular binary mixture at other temperatures.

The correlation line is a straight line for non-polar solvents such as propane, carbon tetrachloride, benzene and *cyclo*-hexane, where all the lines for a series of solutes dissolved in one single solvent, appear to approach a constant value as the solution temperature was increased towards the critical temperature of the solvent. The constant value corresponds to the solubility of that gas for which the entropy of solution or temperature coefficient in that particular solvent is zero. Figure 3.5 illustrates this tendency (from Fleury and Hayduk, 1975).

The polar solvents like water and chlorobenzene behave differently. Their correlation line is far from a straight line. Hayduk and Laudie (1973) developed a method for estimating the effect of hydrogen-bonding on gas solubilities, the so-called HB-factor based on the ideal gas solubilities and the solubilities in water. Using the estimated HB-factors, they were able to predict solubilities in solvents containing a carbonyl group or dihydroxy groups and other associated solvents.

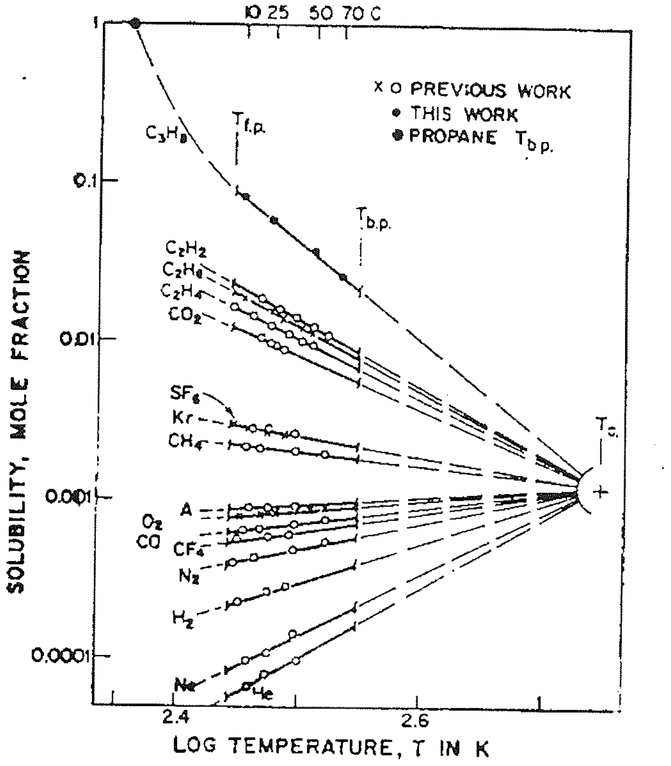


Figure 3.5. Solubilities of gases at 101.325 kPa partial pressure and at varying temperature in benzene.

3.3 Predictions of solubility of gases in liquids

As with prediction of other phase equilibria, the prediction of gas-solubilities with the help of equations of state can be divided into two different procedures

(A) This procedure employs fugacity coefficients for both the liquid and the gas phase.

(B) This procedure employs a fugacity coefficient for the gas phase only, whereas liquid phase non-idealities are described by activity coefficients.

The special problem of gas-liquid equilibria with determination of the standard fugacity arises because the conventional standard state, pure liquid at system temperature and pressure, does not exist for supercritical components.

Only a limited number of methods to predict the solubility of gases in liquids exist at the moment. Among them are group contribution methods using UNIFAC (Sander et al., 1983) and equations of state (Skjold-Jørgensen, 1984) and Hildebrand's regular solution method (Hildebrand et al., 1970, Hildebrand and Scott, 1964).

In the Department of Chemical Engineering & Applied Chemistry there are computer programs available to calculate the solubility of gases in liquids. Sitthiosoth (1987) wrote a number of computer programs (in FORTRAN) for calculating the solubility of gases in liquids at both high and low pressure. There is one program for low pressures, developed using the equations by Sander et al. (1983). The program calculating solubility of gases in liquids at high pressures, is written on the basis of the GC-EOS equations in Skjold-Jørgensen (1984).

At the moment, a number of methods to predict the solubility exist. Table 3-2 shows an overview of the methods, their basic theory and their authors.

METHOD	AUTHOR(s)	Basic theory
Regular solutions and UNIFAC		
regular solution theory	Guggenheim, 1952	
	Prausnitz and Shair, 1961	
	Hildebrand and Scott, 1964	
	Hildebrand et al., 1970	
	King et al., 1977	
ASOG	Tochigi and Kojima, 1982	group-contribution (ASOG)
UNIFAC (reference solvent)	Sander et al., 1983	group contribution (UNIFAC)
UNIWAALS	Gupte et al., 1986	UNIFAC group-contribution, van der Waal's EOS
UNIWAALS extended	Gani et al., 1989	UNIFAC group-contribution, van der Waal's EOS
MHV2	Dahl et al., 1991	modified Huron-Vidal (2), UNIFAC group-contribution
Perturbation methods		
	Wilhelm and Battino, 1971	
	Pierotti, 1976	
DDCL	Mollerup 1981, 1983 and 1985	density dependent local composition
	Mollerup and Clark, 1989	
DDCL truncated	Mathias and Copeman, 1983	density dependent local composition, Peng-Robinson EOS

Table 3-2. An overview of methods for prediction of solubility of gases in liquids (continued over).

METHOD	AUTHOR(s)	Basic theory
one fluid model	Sadus and Young, 1991	hard sphere EOS
perturbation theory	Triska and Boublik, 1992	Lorentz combining rules
Equations-of-state and Monte Carlo methods		
GC-EOS	Skjold-Jørgensen, 1984, 1988	group-contribution equation of state
	Wolff et al, 1992	
molecular thermodynamics	Hu et al., 1985	hard sphere perturbation theory
	Xu and Hu, 1986	
hard sphere model	Swope and Andersen, 1984	WCA-LL-GH, Lennard-Jones potential
	Shukla and Lucas, 1986	
molecular thermodynamics	O'Connell, 1980	density dependent local composition
	Mathias and O'Connell, 1981	
Monte-Carlo	Shing and Gubbins, 1983	Lennard-Jones potential, canonical ensemble
	Shing and Chung, 1987	Lennard-Jones potential, canonical ensemble
	Shing et al., 1988	Lennard-Jones potential, canonical ensemble

Table 3-2. An overview of methods for prediction of solubility of gases in liquids.

Solubility of gases in liquids is an equilibrium between the gas and the liquid (GLE). Fundamentally the equations for VLE and GLE are identical, but with two major differences. One is that the solubility of gases in liquids is very small, thus the solubility calculations are in general carried out at approximately infinite dilution, i.e., the state where one solute molecule's nearest neighbours are all solvent molecules (Guggenheim, 1952).

The other is that in vapour-liquid calculations, for given values of liquid composition x_i, temperature T and pressure P, we calculate the values of vapour composition y_i, but in solubility calculations, for given values of temperature T and pressure P the value of the liquid composition, x_i, is calculated.

In other words, the vapour composition is less important in solubility calculations due to the usually low concentration of the solute in the liquid phase, which, in the binary case, gives a vapour phase composition of $y_{\text{solvent}} \approx 0.0$ and $y_{\text{solute}} \approx 1.0$ (ideal vapour phase).

3.3.1 Reference solvent method

The reference solvent method is used in this thesis as a standard method with which to compare the results obtained from solubility calculations using the AGAPE method. The method was developed by Sander et al. (1983) and the name "reference solvent" method has been allocated in this work. The reference solvent method is one of the methods in Table 3-2 for predicting solubility of gases in liquids. The derivation of the reference solvent equations is briefly described in this section.

Using the definition of the general phase equilibrium equations (equations (2.19) and (2.20)) the following expression for Henry's constant can be obtained:

$$f_i^L = f_i^G = \varphi_i^L \, x_i \, P = H_{i,\,\text{solvent}} \, \gamma_i^* \, x_i = \gamma_i \, x_i \, f_i^0 \qquad (3.11)$$

where $H_{i,\,\text{solvent}}$ is Henry's constant for solute i dissolved in the solvent and γ_i and γ_i^* are the activity coefficients in the symmetric and the unsymmetric convention, respectively.

Using a method developed by Mathias and O'Connell (1981) Sander et al. (1983) reformulated the problem of finding a value for the reference fugacity f_i^0 in equation (3.11), necessary as this value for the gaseous component represents a property of a hypothetical pure liquid, whenever the temperature is greater then the critical temperature of the gas.

As suggested by Prausnitz et al. (1986) it is common to extrapolate subcritical liquid fugacities obtained from experimental data into the hypothetical region.

The extrapolation method is most uncertain in cases where the difference between T and the critical temperature of the gaseous component is great. In following the method developed by Mathias and O'Connell (1981) the problem of estimating the reference fugacity f_i^0 is changed into one of estimating Henry's constant for a reference solvent.

For this purpose, f_2^0 for a solute (2) dissolved in a solvent s can be expressed as:

$$f_2^0 = \frac{H_{2,\,s}}{\gamma_{2,\,s}^{\infty}} \tag{3.12}$$

by rewriting equation (3.11). In equation (3.12) s could as well be a reference solvent R. Introduction of the reference solvent R in equation (3.12) and then in equation (3.11) gives:

$$f_2^G = \frac{H_{2,\,R}\ x_2\ \gamma_2}{\gamma_{2,\,R}^{\infty}} \tag{3.13}$$

For given values of f_2^G and T, the solubility x_2 can be found from equation (3.13) by iteration.

In the reference solvent method, the activity coefficient γ_2 and $\gamma_{2,R}^{\infty}$ are calculated from UNIFAC. Sander et al. (1983) describes a method for the necessary estimation of the UNIFAC interaction parameters between gas molecules and solvent groups.

The reference Henry's constant is assumed to be a function of temperature as follows:

$$\ln H_{2,R} = A^R + \frac{B^R}{T} + C^R \ln T \tag{3.14}$$

where the coefficients A^R, B^R, and C^R are estimated from experimental solubility data for component 2 in the reference solvent by means of the equation

$$H_{2,R} = \frac{f_2^G}{x_{2,R}} \tag{3.15}$$

where it is assumed that $\gamma_{2,R} / \gamma_{2,R}^{\infty} = 1$.

In choosing a reference solvent for a given gas it is crucial to find a solvent for which reliable experimental solubility data for the gas are available. The data should preferably cover as broad a temperature range as possible, and the solubility should be small, because of the assumption that $\gamma_{2,R} / \gamma_{2,R}^{\infty} = 1$.

3.3.2 The regular-solution theory applied to solubility predictions

3.3.2.1 The Hildebrand-Scatchard theory applied to solubilities

The use of the regular-solution theory (developed by Hildebrand and Scatchard) and to predict the solubility of gases in liquids for non-polar mixtures has been discussed by Prausnitz et al. (1986) and by Hildebrand et al. (1970). The theory is an example of procedure B.

As mentioned earlier, the dissolution of a gas in a liquid is accompanied by a large decrease in volume. The regular-solution concept is based on no volume change and to apply this theory to the prediction of solubilities, it has been necessary to consider the dissolution process as a two-step process (Hildebrand et al., 1970). The process is to "condense" the gas to its partial molar volume in the liquid solvent ("liquid 2") followed by the step of dissolution of pure "liquid 2" in solvent 1 (assuming that the gas is component 2 and the liquid is component 1).

The Hildebrand equations for the activity coefficients in a binary mixture are (see section 2.10.3)

$$\begin{aligned} RT \ln \gamma_1 &= v_1 \, w_2^2 (\delta_1 - \delta_2)^2 \\ RT \ln \gamma_2 &= v_2 \, w_1^2 (\delta_1 - \delta_2)^2 \end{aligned} \tag{3.16}$$

This equation is the regular-solution equation and has, because of its approximate nature, not been used as successfully as in theoretical predictions of gas solubilities in liquids as in forming the basis of some semi-empirical correlations, as those of Prausnitz and Shair (1961) and Yen and McKetta (1962).

Yen and McKetta (1962) derived the following equation for systems consisting of a non-polar and a polar, non-associated liquid

$$RT \ln \gamma_2 = v_2 \, w_1^2 \left(\delta_1^2 + \delta_2^2 - 2\zeta\delta_2(\delta_2^2 + \eta)^{1/2} \right) \tag{3.17}$$

where ζ is a constant depending on the intermolecular distance and the potential function. η is a characteristic constant for polar, non-associated liquid and relates to the intermolecular distance and the angular dependence of the dipole-dipole interaction.

Prausnitz and Shair (1961) used the above mentioned assumption of the two-step process and derived a method for predicting the gas-solubilities. Their final equation, assuming the fugacity of component 2 in the gaseous phase is unity, is

$$- \ln x_2 = \ln f_2^L + \frac{v_2(\delta_1 - \delta_2)^2 w_1^2}{RT} \tag{3.18}$$

where f_2^L is the fugacity of pure "liquid 2" at temperature T and 101.325 kPa pressure. A figure of f_2^L as a function of ratio of the solution temperature to the solute's critical temperature can be found in, e.g. , Hildebrand et al. (1970). This equation can be used to calculate the solubility. The calculations are of the trial-and-error type, as w_1 depends on x_2 (see section 2.10.3). The equation for the fugacity of "liquid 2" at total pressure P is (Hildebrand et al., 1970)

$$f_2^L(P) = f_2^L(\text{graph}) \exp\left(\frac{v_2^L(P - 1.013)}{RT} \right) \tag{3.19}$$

provided that P is in bar (10^5 Pa).

The solubility at total pressure P is then given as

$$- \ln x_2 = \ln \frac{f_2^L(P)}{\varphi_2 y_2 P} + \frac{v_2(\delta_1 - \delta_2)^2 w_1^2}{RT} \qquad (3.20)$$

where y_2 is the mole fraction and φ_2 is the fugacity coefficient of component 2 in the gas phase. φ_2 can be calculated from an equation of state for the gas mixture.

The solubility parameters δ_1 and δ_2 can be calculated from either calorimetric heats of vaporization, from the vapour pressures, estimated from the Hildebrand rule or estimated from solubility data. Hildebrand and Scott (1962) show examples of the various ways of calculating the solubility parameters. The values for the solubility parameters are often estimated at 298.15 K, and therefore only for substances which have a critical temperature above 298.15 K.

The correlation technique of Prausnitz and Shair (1961) has been extended to predict solubilities of mixed solvents (Hildebrand et al, 1970). The solubility of a gas in a mixture of two or more solvents is given by

$$- \ln x_2 = \ln \frac{f_2^L(P)}{\varphi_2 y_2 P} + \frac{v_2(\delta_2 - \bar{\delta})^2}{RT} \qquad (3.21)$$

where

$$\bar{\delta} = \sum_i w_i \delta_i \quad (i = 1, 2, \ldots) \qquad (3.22)$$

is the average solubility parameter for the entire solution and the summation includes all the components, also the solute.

Prausnitz et al. (1986) show how two correlation curves can be used for the prediction. One of the curves is a plot of experimental solubilities at 298.15 K and 101.325 kPa partial gas pressure of 12 solutes as a function of the solubility parameter of the solvent (shown in Figure 4.1). The other shows a plot of experimental solubilities at the same conditions as a function of the Lennard-Jones energy parameters (described in section 2.7 and shown in Figure 4.2). From the two curves it is possible to predict the solubility at 298.15 K and 101.325 kPa partial pressure of a specific gas in a specific liquid, provided that they both are in the plots of Prausnitz et al. (1986) and that both the solute and solvent are non-polar.

3.3.2.2 The regular solution theory as used by Guggenheim

Guggenheim (1952) has developed expressions for the calculation of Henry's law based on the regular solution theory. The expressions involve the interchange energy (discussed in section 2.10.3.1). For dilute regular solutions, Guggenheim shows that the partial vapour pressures can be obtained as

$$\frac{p_1}{p_1^0} = (1 - x_2)$$

$$\frac{p_2}{p_2^0} = x_2 \exp\left(\frac{w'}{k_B T}\right)$$

where 1 is the solvent and 2 is the solute. Rearranging the expression for the solute, one obtains

$$p_2 = x_2\ p_2^0 \exp\left(\frac{w'}{k_B T}\right) = x_2\ H_{2,1} \qquad (3.23)$$

where Henry's constant, in this case, is

$$H_{2,1} = p_2^0 \exp\left(\frac{w'}{k_B T}\right) \qquad (3.24)$$

In the case of a gas pressure of 1 bar (10^5 Pa), the following equation can be derived

$$-\ln x_2 = \ln p_2^0 + w' / (k_B T) \qquad (3.25)$$

Equation (3.23) is entirely analogous to the standard equation

$$H_{2,1} = \gamma_2^\infty\ f_2^0$$

where the standard state fugacity of the solute is simply replaced by a hypothetical vapour pressure and where the activity coefficient at infinite dilution is seen to be a single function of the interchange energy analogous to the usual activity coefficient but independent of composition.

Prausnitz et al. (1986) has made use of the corresponding states principle to establish reference values of f^0_2 for gases at different temperatures. Guggenheim (1952) developed the following linear correlation between the pressure and the temperature (using the principle of corresponding states) for a pure component and with pressure units in bar (10^5 Pa))

$$\ln p = 5.3 + \ln P_C - \frac{5.3\ T_C}{T} \qquad (3.26)$$

If this equation is used above the critical point, it calculates an alternative value of a "pseudo" fugacity as opposed to the method described in Prausnitz et al. (1986).

3.3.2.3 The regular solution theory as used by King

King and co-workers (King et al., 1977b) have, from an extensive data analysis of solubility data of primarily carbon dioxide, but also hydrogen sulfide and to a lesser extent propane, dissolved in n-alkanes (C_6H_{14} to $C_{16}H_{34}$) used a modification of the regular solution theory to develop a prediction method for solubilities of the mentioned mixtures. The prediction results for carbon dioxide show excellent accuracy when compared with experimental data. The modification involves adding a Flory-Huggins entropy term because the molecular size ratio is far removed from unity in some of the systems examined. An interaction parameter that allows for deviations from the geometric mean mixing rule for the attractive potential between molecules 1 and 2, is introduced. The interaction parameter is assumed to have a constant value for all the investigated alkanes, and thus is only dependent on the solute. The actual value of the interaction parameter has been obtained by back-calculating from the experimental value.

3.3.3 The scaled-particle model

One of the methods for prediction solubility of gases in liquids is the scaled-particle model as used by Pierotti (1976). The model is based on a statistical-mechanical theory of dense fluids, developed by Reiss et al. (1960) and Helfand et al. (1960). This theory yields an approximate expression for the reversible work required to introduce a spherical particle of species into a dense fluid containing spherical particles of species 1.

A brief introduction of the theory (Prausnitz et al., 1986) follows here.

Consider a very dilute solution of non-polar solute 2 in non-polar solvent 1 at low pressure and at a temperature below the critical temperature of the solvent. In other words, at these conditions Henry's law applies. It is assumed that the dissolution process can be broken down into two steps. In the first step, a cavity is formed in the solvent (1) to allow introduction of a solute molecule. In the second step, the solute molecule (its cavity filled by molecule 2) interacts with the surrounding solvent.

Henry's constant can then be expressed as a sum of two terms, one for the cavity forming (subscript c) and one term for the interaction (subscript I)

$$\ln \frac{H_{2,1}^{(P_1^s)}\ v_1}{RT} = \frac{\overline{g_c}}{RT} + \frac{\overline{g_I}}{RT} \tag{3.27}$$

where v_i is the molar volume of the solvent, and $\overline{g}$ stands for the partial molar Gibbs energy for the solute.

If the pressure is low, the scaled-particle model gives for $\overline{g_c}$

$$\frac{\overline{g_c}}{RT} = \frac{6Y}{1 - Y}\left(2(r^{HS})^2 - r^{HS}\right) + \frac{18Y^2}{(1 - Y)^3}\left(r^{HS} - \frac{1}{2}\right)^2 - \ln(1 - Y) \tag{3.28}$$

where

$$\begin{aligned} r^{HS} &= \frac{a_1^{HS} + a_2^{HS}}{2(a_1^{HS})^2} \\ Y &= \frac{\pi\ (a_1^{HS})^3\ L}{6v_1} \end{aligned} \tag{3.29}$$

and a^{HS}_1 and a^{HS}_2 are the hard-sphere diameters for the solvent and for the solute, respectively.

To obtain an expression for the partial molar Gibbs energy for the interaction (for the solute), it is necessary to assume that all changes in entropy which result from the dissolution of a gas in a solvent are given by the cavity-formation calculation. Further, assuming a Lennard-Jones 6,12 potential as an expression for the potential energy function for the description of the intermolecular forces between solute and solvent as done by Wilhelm and Battino (1971), the partial molar Gibbs energy for the interaction becomes

$$\overline{g_I} = -\left(\frac{32\ \pi\ R}{9v_1}\right)\left(\frac{L\sigma_{12}^3\varepsilon_{12}}{k_B}\right) \tag{3.30}$$

where σ_{12} and ε_{12} are parameters in the Lennard-Jones potential, k_B is Boltzmann's constant, and R is the universal gas constant.

The scaled-particle model is a variation of the perturbation theory which has been applied to gas solubilities. The perturbation theory combines statistical mechanics with some physical model. The essence of the perturbation theory is, firstly, to focus the attention on the properties of some idealized dense fluid, and then, secondly, relate the properties of the real dense fluid to those of the idealized fluid. This procedure has been necessary due to the inadequate knowledge of fluid structure and intermolecular forces. When the perturbation theory is applied to mixtures of real fluids, it involves non-analytic calculations. Numerical integrations are required for every temperature, density and composition. It is also necessary to establish a useful reference system, and the intermolecular forces must be characterized by a credible potential function. However, due to increasingly efficient computers, perturbation theory has provided a powerful tool for molecular thermodynamics (Gubbins, 1989 and Gubbins and Street, 1981)

3.3.4 The GC-EOS model

The group-contribution equation-of-state (GC-EOS) was derived (Skjold-Jørgensen, 1984, 1988) from a van der Waals equation of state (see section 2.10.3) with mixing rules based on an NRTL-like expression (see section 2.10.3.4) for the total excess Helmholtz function. The aim was to develop a model with no limitation of low pressure or low concentration. The theory is an example of procedure A.

The model represents an example of a method based on statistical thermodynamics, a different approach to thermodynamics then the classical approach described in chapter 2. As the GC-EOS model is a group-contribution method, it relies on experimental data for the calculation of group interaction parameters.

It is beyond the scope of this work to set out the derivation of the equations of the GC-EOS model.

3.3.5 The MHV2 model

The MHV2 model (Dahl and Michelsen, 1990) was briefly described in section 2.10.3.10. The model has been used to predict solubilities with excellent results (Dahl et al., 1991). The model predicts fugacity coefficients for all components in both the liquid and the gas phase. The model has been used as an alternative method to predict solubilities of gases in liquids in this work (see section 4.6) at low pressure. The results obtained are not as good as the results obtained by Dahl et al. (1991). The MHV2 model seems to predict solubilities with best accuracy at moderate to high pressures.

3.3.6 The UNIFAC-FV model

The UNIFAC-FV model is a variation of the UNIFAC model including a term for the free volume and has been applied with success to calculate a Henry's constant for hydrocarbon gases and vapours in high-boiling hydrocarbon solvents. A brief description follows (Stelmachowski and Ledakowich, 1993).

We write Henry's constant as a product of the fugacity of a hypothetical liquid at the system temperature and pressure of 101.325 kPa and the symmetric infinite dilution activity coefficient for a gaseous solute in a given solvent, in other words as

$$H_i = \gamma_i^\infty f_i^L \tag{3.31}$$

The f_i^L is similar to that mentioned in the description of the regular-solution method applied to gas-solubilities. Chappelow and Prausnitz (1974) have extrapolated it as a function of reduced temperature, $T_{r,i} = T/T_{C,i}$ and the critical pressure $P_{C,i}$

$$\ln \frac{f_i^L}{P_{C,i}} = \text{function}(T_{r,i})$$

For certain hydrocarbons the extrapolation gives the alternative equation

$$\ln f_i^L = \text{function}(T)$$

The symmetric infinite dilution activity coefficient is considered a sum of two terms

$$\ln \gamma_i^\infty = \ln \gamma_i^{UNIFAC} + \ln \gamma_i^{FV} \tag{3.32}$$

where $\ln \gamma_i^{UNIFAC}$ is the activity coefficient found when using the modified UNIFAC equations (see section 2.10.3.9) and $\ln \gamma_i^{FV}$ accounts for the free volume.

Stelmachowski and Ledakowich (1993) have for mixtures of alkanes developed equations for the parameters in their expression for $\ln \gamma_i^{FV}$. The parameters (coefficients and exponents) were estimated in such a way to render Henry's constants which were close to empirical values. Despite the intuitive derivation of the parameters, Stelmachowski and Ledakowich (1993) obtained good results when predicting Henry's constant for alkanes employing the method mentioned above.

3.3.7 Gas solubilities from an equation of state

As mentioned earlier it is difficult to distinguish between solubility and vapour-liquid equilibrium. It is therefore not surprising that the equations of state (described in section 2.9.2) can be used to predict solubility as well as vapour-liquid equilibrium (Prausnitz et al., 1986). The essential requirement is that the equation of state must be valid for the solute-solvent mixture from zero density to the density of the liquid. Using an equation of state gives fugacity coefficients, and using the equation for Henry's constant

$$H_{2,1}^{(P_1^S)} = \varphi_2^{L,\infty} P \qquad (3.33)$$

where $\varphi_2^{L,\infty}$ is the fugacity of the solute in the liquid solvent at infinite dilution. Good results have been obtained applying an equation of state to predict solubilities (Prausnitz et al., 1986).

3.3.8 The UNIWAALS equation of state

As the name indicates, the UNIWAALS equation-of-state developed by Gupte et al. (1986) and further extended by Gani et al. (1989) combines the van der Waals equation of state with the modified UNIFAC group method (Larsen et al., 1987) to predict the solubility of gases in liquids.

The UNIWAALS equation of state (Gupte et al., 1986) requires a "liquid-like" root of the pure components at the pressure and temperature of the system and of the mixture at the temperature, pressure and composition of the phase (vapour or liquid) in question. As the system temperature approaches the critical temperature of a component or the mixture, the existence of "liquid-like" roots becomes uncertain. The modification by Gani et al. (1989) is applicable to mixtures containing non-condensable gases and to conditions of pressure and temperature approaching the mixture critical point.

The modified UNIWAALS equation-of-state (Gani et al., 1989) is

$$P = \frac{RT}{v - b} - \frac{a}{v^2} + \frac{d}{v} \qquad (3.34)$$

where d is defined as da/dv and both a and d are functions of (T, P, v and x_i). The energy size parameter a is expressed by Mathias and Copeman (1983) (see the description of the MHV2 method in section 2.10.3.10). The covolume parameter b is the same parameter as described in section 2.10.3.10.

It is then possible to derive an expression for the fugacity coefficient. Details of the derivation and the equation of the fugacity coefficient are in Gani et al. (1989).

The procedure for prediction of phase equilibria is described by Gani et al.(1989). One of the steps involves the estimation of the excess Gibbs energy, which in this case is calculated using the modified (Larsen et al., 1987) UNIFAC method. The results obtained by using the modified UNIWAALS equation of state to predict solubilities of gases in liquids fit very well with experimental data, especially at elevated pressures.

3.4 Database for solubilities of gases in liquids

A small database of gas solubilities was constructed mainly to evaluate potential predicted solubilities against experimental solubilities. It also formed a convenient way of presenting gas solubilities in chemical families, i.e., homologous series, in order to make quantitative observations on the solubility values.

3.4.1 The data

A series from IUPAC Solubility Data Series has been shown to be very useful as a source of solubility data. The volumes used in this work are: IUPAC Solubility Data Series (Clever, 1979 (vol. 1), Clever, 1980 (vol. 4), Young, 1981 (vol. 5/6), Battino, 1981 (vol. 7), Hayduk, 1982 (vol. 9), Battino, 1982 (vol. 10), Hayduk, 1986 (vol. 24), and Clever and Young, 1987 (vol. 27/28)). Another source with abundant solubility data is Fogg and Gerrard (1991).

The collected solubility data are given as Table A3-1 (Appendix 3).

The collected solubility data have been presented in graphs in Figures 3.6 and 3.7 and in Figures in Appendix 3.

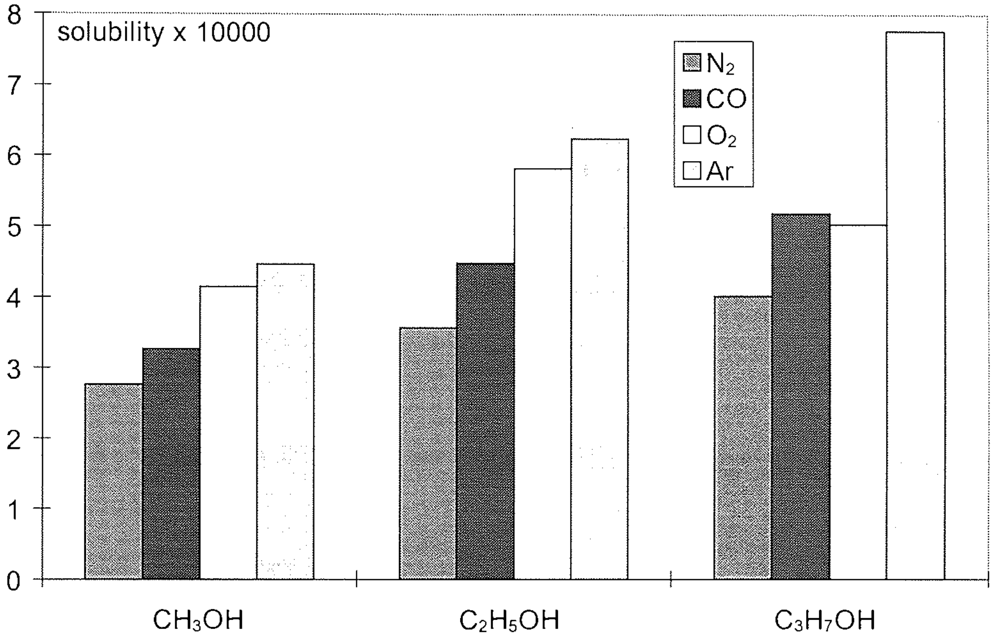


Figure 3.6. Solubilties of various solutes dissolved in various solvents.

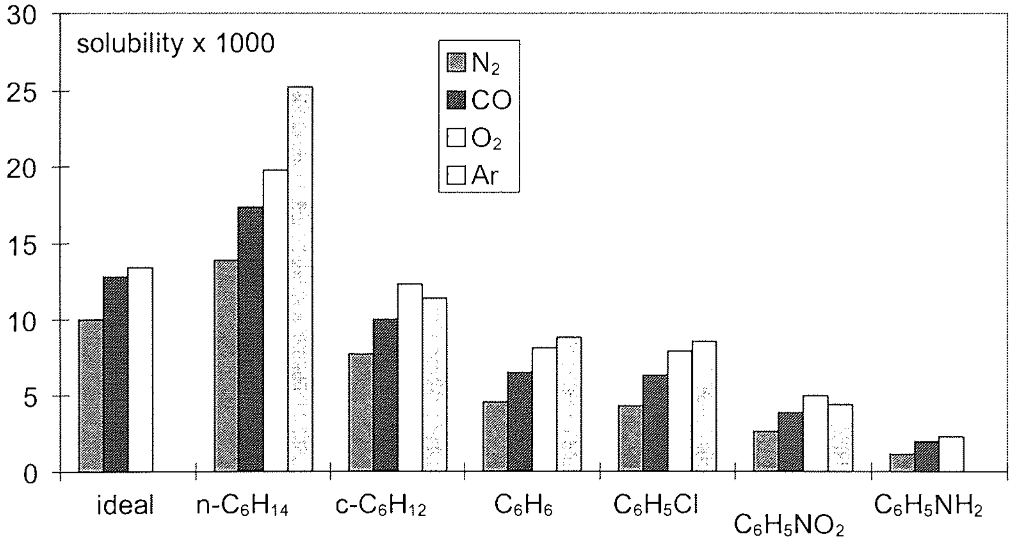


Figure 3.7. Solubilties of various solutes dissolved in various solvents.

3.4.2 Conclusion of the collected solubility data

The solubilities of light gases such as neon, hydrogen and nitrogen are very small in nearly all the solvents. The solubilities of the much heavier hydrocarbons n-propane and n-butane in various solvents are the largest of all the collected solubility data.

Water represents a special case. Nearly all solutes dissolved in water have very small solubilities, in fact the solubilities in water are the lowest values of the collected data. Surprisingly, the solubilities of n-propane and n-butane in water are of the same magnitude as methane, whereas the solubility of methane in other solvents is much less then the solubilities of n-propane and n-butane.

Except for water, as a general rule, the solubility in a certain solvent increases when the molecular weight of the solute increases. This is true for the homologous series alcohols and single chained hydrocarbons.

The solubilities of argon, oxygen and carbon monoxide in the same solvent all have very similar values.

3.4.3 Variation of solubilities with temperature

This investigation has mainly used solubility data at 298.15 K as they were plentiful. In gas-solubility studies, the solubility is unique at a single temperature. The solubility varies with temperature and some examples of the relationship between solubility and temperature are shown here.

Figures 3.8 to 3.9 show the variation of the solubility of ethane dissolved in various liquid solvents with temperature (figures are from Fogg and Gerrard, 1991).

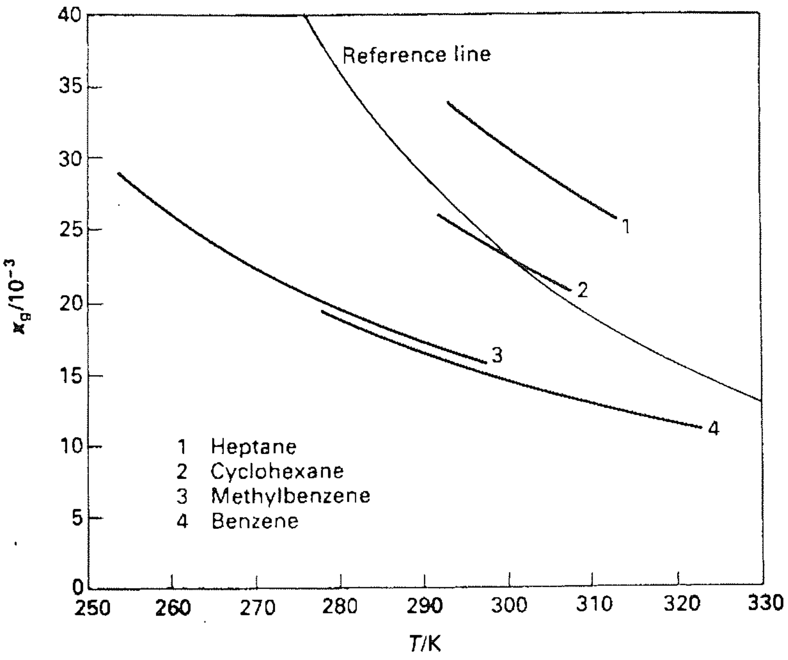


Figure 3.8. Mole fractions of solubilities of ethane as a function of temperature at a partial pressure of 101.325 kPa in hydrocarbons.

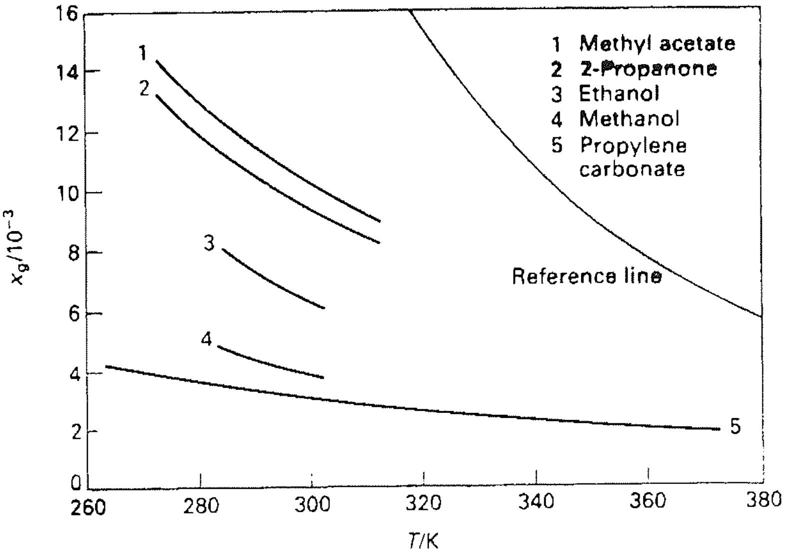


Figure 3.9. Mole fractions of solubilities of ethane as a function of temperature at a partial pressure of 101.325 kPa in solvents containing oxygen.

Chapter 4 - Results and Analysis

Throughout Chapter 4 the notation P will be equivalent to the pair potentials, Φ, used in the previous equations. P11, P22 will be used as equivalent to Φ_{11} and Φ_{22} (equation (2.79) for pairs i-i and j-j, respectively). P12 will be used as a notation for the unlike pair potentials for a binary mixture, Φ_{12}. P12-GLP indicates that the value is calculated using the London combining rule (equation (2.79)). P12-GM indicates that the value was derived by applying the geometric-mean combining rule (equation (2.82)). The equilibrium separation (often in the form of R1 or R2) is similar to the parameter R^A in the section 2.11 (equation (2.80)). R1 and R2 are, of course, the equilibrium separations for component 1 and component 2, respectively. For a binary mixture consisting of components 1 and 2, the equilibrium separation is (Mohammadi, 1986)

$$R^A_{mix} = (R^A_1 + R^A_2) / 2 \tag{2.95}$$

This notation has been used to indicate that the various values have been calculated by running the computer programs. The notation is also due to a limitation in the spreadsheet computer program used, that can only handle the ordinary alphabetic letters A-Z.

4.1 Relationship between solubility and intermolecular behaviour of the solute-solvent (interaction)

A linear relationship between the base 10 logarithm of the experimental solubility at 298.15 K and 101.325 kPa and a solubility characteristic has been shown by Hildebrand and Scott (1962) and referred to in Prausnitz et al. (1986). A similar relationship was found by Mohammadi (1986) and it was decided to continue this work, using the generalized unlike London pair potential as the solubility characteristic to see how far this relationship could be used to accommodate studies of the solubility of gases in liquids.

As briefly discussed in Chapter 3 the solubility of solutes in dilute solutions depends on properties of both the solute and the solvent. Hildebrand and Scott (1962) showed that the logarithm of the solubility (at 298.15 K and 101.325 kPa partial gas pressure) for non-polar non-reactive gas solutions *versus* the solubility parameter of the solvent,

$\delta_{solvent}$ (discussed in section 3.3.2) shows a fair regularity. The figure (from Hildebrand and Scott,1962) is shown as Figure 4.1. The solubility parameters, $\delta_{solvent}$ are derived at 298.15 K (from the square root of the cohesive energy densities).

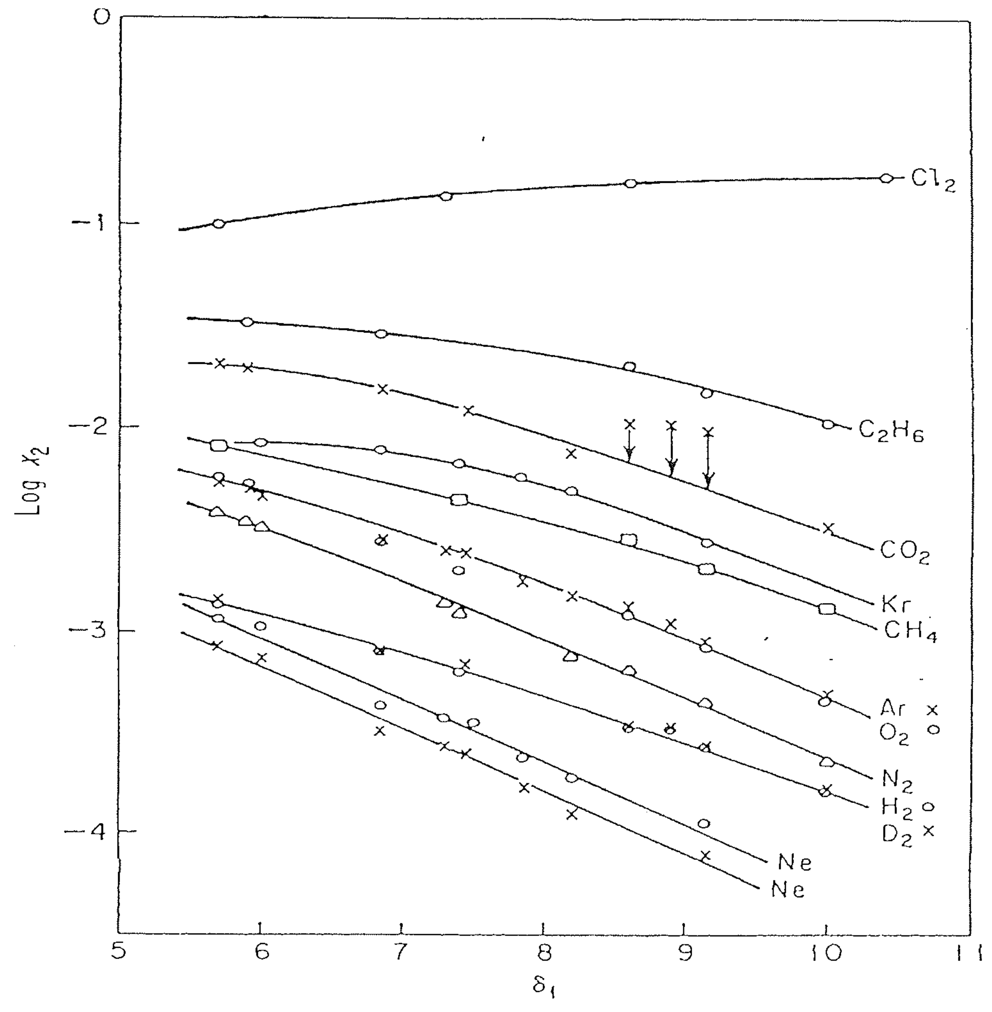


Figure 4.1. Gas solubility at 298.15 K and 101.325 kPa partial pressure versus the solubility parameter of the solvent $\delta_{solvent}$.

The solvents in Figure 4.1 are: C_7F_{16} (δ=5.8), $(C_4F_9)_3N$ (δ=5.9), $C_6F_{11}CF_3$ (δ=6.0), i-C_8H_{18} (δ=6.9), n-C_7H_{16} (δ=7.4), $(C_2H_5)_2O$ (δ=7.4), $C_6H_{11}CH_3$ (δ=7.8), c-C_6F_{12} (δ=8.2), CCl_4 (δ=8.6), $C_6H_5CH_3$ (δ=8.9), C_6H_6 (δ=9.2), and CS_2 (δ=10.0)

Further, Hildebrand and Scott (1962) showed that solutes in different solvents exhibit a regularity of behaviour which seems to be related to the Lennard-Jones intermolecular pair potential ε/k_B for the solute, derived from gas phase studies. The graph is shown as Figure 4.2. The graph also appears in Prausnitz et al. (1986). The intermolecular interaction parameter ε/k_B represents the negative minimum negative energy (ε) over Boltzmann's constant (k_B). This interaction parameter (force constant) is unique for one component, and the interaction parameters for the solutes are thus independent of the solvent. Another important feature of the interaction parameter is its independence of temperature.

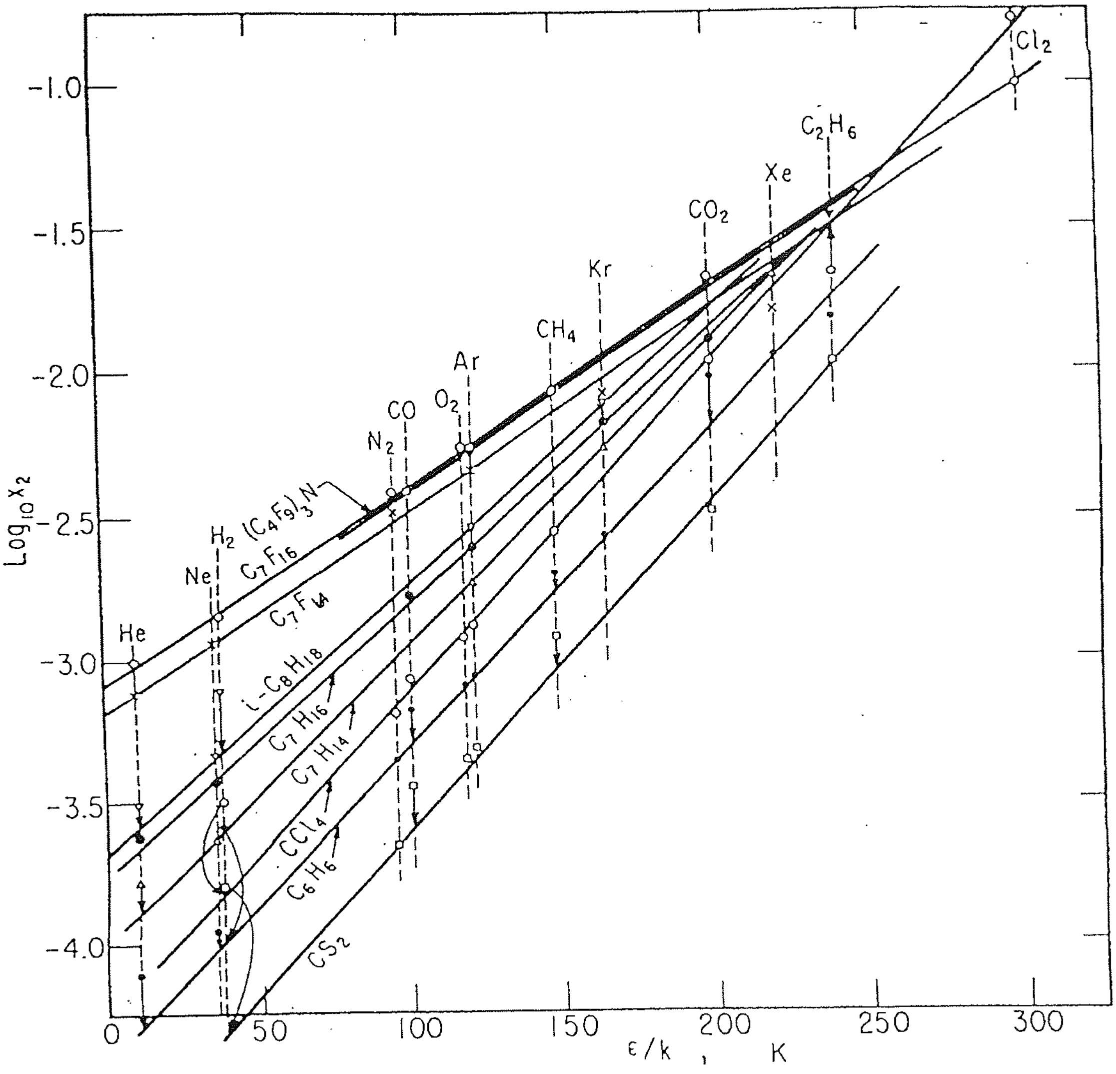


Figure 4.2. Solubilites of gases in liquids at 298.15 K and at a partial pressure of 101.325 kPa as a function of solute characteristic ε/k_B (Lennard-Jones 6-12 potential).

The position of the lines of the log x_{solute} *versus* ε/k_B depends, however, on the solvents and this positioning appears to relate to the Hildebrand solubility parameter for a limited group of non polar solvents as indicated by Figure 4.1.

Hildebrand and Scott (1962) conclude four characteristic features from Figures 4.1 and 4.2. Firstly, the experimental points fall upon two regular grids (with exceptions). The spacing of the lines in the region of low solubility is strictly in order. In Figure 4.1 in the order of the solubility parameters of the solvents and in Figure 4.2 in the order of the force constants of the solutes. It is therefore possible to predict the solubility of the missing cases (as discussed in section 3.3.2). Secondly, Figures 4.1 and 4.2 indicate cases of specific interactions such as the data points for carbon dioxide dissolved in benzene, toluene and carbon tetrachloride are above the line (Figure 4.1) indicating larger values of solubilities then predicted from results obtained in other solvents. The high solubility in aromatic hydrocarbons can probably be attributed to a Lewis acid-base interaction between acidic CO_2 and the basic aromatic. The specific chemical interaction between CO_2 and CCl_4 may be related to the quadrupole moment of CO_2. Thirdly, in Figure 4.2 the solubilities of the quantum gases (He, Ne and H_2) appear a little higher then expected. These anomalies are not fully understood but may be related to quantum effects. For the fourth, a gas whose force constant places it at the crossing of the lines of two solvents (Figure 4.2) is midway between these solvents in its molecular forces.

The regularity of the "grids" is in accord with the concept of regular solutions. Hildebrand and Scott (1962) conclude further that the entropy (except in a few specific cases) is the sum of two factors: dilution and expansion and that these factors are determined by the interrelations of intermolecular forces.

The relationship between the entropy and the solubility is shown in Figure 4.3 (from Prausnitz et al., 1986) where the entropy of solution (in the form of the partial molal entropy of the solute minus the partial molal entropy of the solute in the gaseous state) is plotted against solubility (in the form of -R ln x_{solute}).

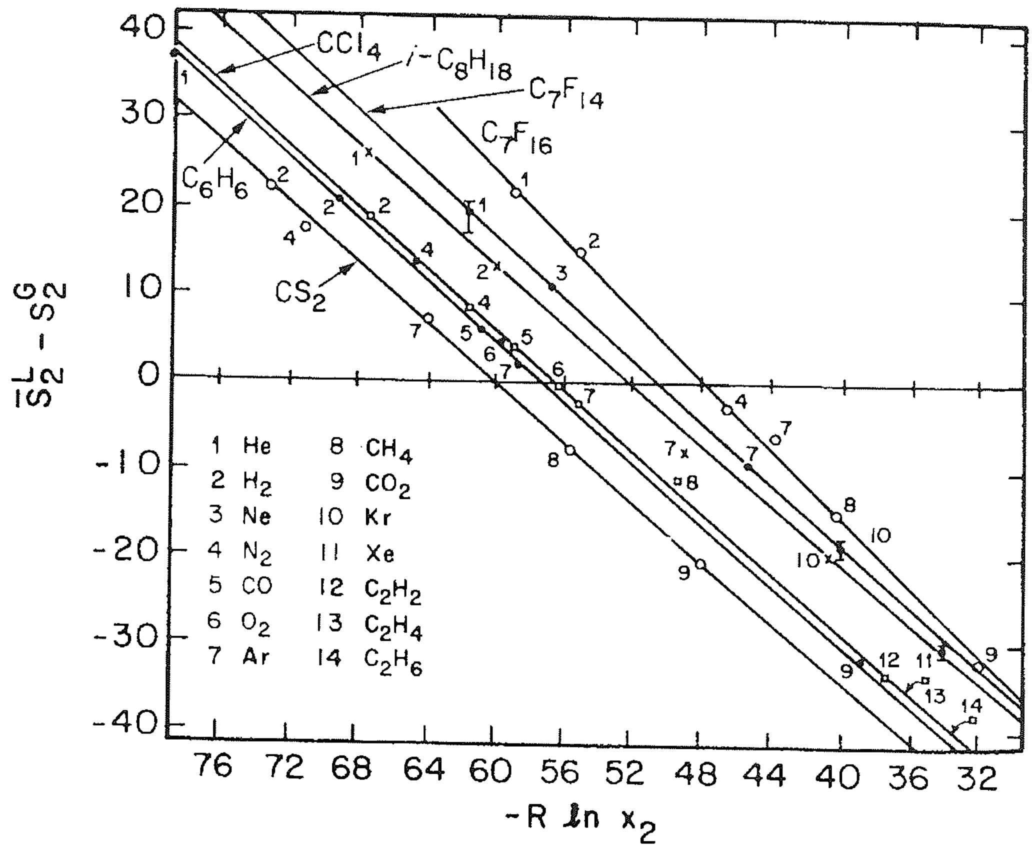


Figure 4.3. Entropy of solution of gases in liquids as a function of gas solubility (mole fraction) x_2 at 298.15 K and 101.325 kPa partial pressure.

The following features are noted. Firstly, a regular system of relationships exists between entropy and solubility. Secondly, it is possible to predict the temperature coefficient from a single value of solubility due to the fact that the dividing line between positive and negative temperature coefficients of solubility is at the 0.0 value of the entropy of solution. Thirdly, the entropy of solution becomes more negative in passing from less soluble to the more soluble gases. For the fourth, the entropy of solution increases much more rapidly than $-R \ln x_{solute}$.

Figure 4.2 is quite heavily weighted by large fluorocarbon solvents of higher molar volume. Because the use of the solubility parameters is rather limiting, excluding as it does water and alcohols, we sought a single parameter which might incorporate the behaviour of both solute and solvent in a simple model. This single parameter should depend on both the solute and the solvent, and the unlike pair potential (either London or the geometric mean) would be suitable.

As pointed out previously, the application of models to thermodynamic data requires both a properly-defined mixing rule and a properly-defined combining rule for the unlike interactions. It is therefore pointed out that by a more precise description of the combining rule as in the Generalized London Pair potential, we might have a sufficient encapsulation of the behaviour of both the solute and the solvent and so need a no more complex mixing rule.

The aim of this investigation is to see if the unlike pair potential (preferably the London potential but the geometric mean would also do) shows a similar regularity to that of the Lennard-Jones parameter in Figure 4.2. If this investigation leads to a "grid-like" plot where each unique solute-solvent mixture is represented by one point with the solutes and the solvents along separate lines, the solubility for other mixtures then that investigated could be predicted using the plots from the calculated value (known) of the unlike London potential.

Development of a new prediction method for predicting solubilities of gases in liquids using the unlike London pair potential was the aim of this investigation.

4.1.1 Mohammadi's (1986) work on solubility of gases in liquids

Mohammadi (1986) was able to show a linear relationship between the logarithm of the experimental solubility at 298.15 K and 101.325 kPa and a buffeting field. As an expression for the buffeting field, he used a modification of the original London pair potential for the mixture.

4.1.1.1 Buffeting field and gas solubilities

From the argument for real solutions (described in section 3.1.2) a pattern emerges for a quantitative discussion of solubility, namely, the assumption that if the solute and the solvent have similar intermolecular pair potentials in their pure states, then the solute will exert forces on the molecules of the solvent similar to those it exerts on the solute resulting in their mutual solubilities. Departures from similar forces lead to decreasing solubilities. This is the fundamental idea underlying the Hildebrand (Hildebrand and Scott, 1964) theory which leads to the concept of the solubility parameter.

There are other functions of the intermolecular pair potentials that may be used as a measure of the solubility of the solute in the solvent. For example, one is the gain in pair potential energy, ΔPE, on making one dissimilar pair "uv" from two isolated pairs "uU" and "vv" (Mohammadi, 1986)

$$\Delta PE = PE(uv) - \frac{1}{2}\left[PE(uu) + PE(vv)\right] \qquad (4.1)$$

where u and v indicate the solute and the solvent, respectively. This is related to the definition of the interchange energy, w', equation (2.59).

However, Gerrard (1980) contends that the tendency of a gas u to condense, characterised by PE(uu), is the driving factor to consider with respect to any liquid. A second factor may relate to the intermolecular structure of the solvent, PE(vv), as well as arising from the inevitable interaction between the solute and the solvent, PE(uv).

Mohammadi (1986) used a modified pair potential as an expression of PE(uv) in his work:

$$PE(uv) \propto - \Sigma_i \Sigma_j W_i W_j < m^2 >_i < m^2 >_j F^A (R^A)^{-6} \quad (4.2)$$

where the symbols are the same as used in section 2.11. As before, <> represents electronic time averaging and $<m^2> = 3\alpha v_0 \hbar/2$ is the bonded atom mean square moment. F^A is assigned to account for the molecular rotations. Their best Monte Carlo-derived expression for F^A is given in section 2.11. W_j is the number of structurally equivalent atoms j in the molecule and R^A is the equilibrium separation.

There are two things to note about equation (4.2). Firstly, the pair potential which Mohammadi (1986) used is different from the unlike London pair potential as described in section 2.11. The unlike London pair potential for mixtures is expressed as:

$$\Phi_{ij} = \Phi(\text{pair}) = -0.25\ (R^A)^{-6} \sum_i \sum_j (\alpha_i < m^2 >_j + \alpha_j < m^2 >_i) F^A\ W_i\ W_j \qquad (4.3)$$

In equation (4.2) the mean-square moments are multiplied as compared to the addition in equation (4.3). The other thing to note is that he used an equilibrium separation that is considered to be independent of temperature. The R^A in equation (4.2) is calculated from R^A-values for the pure component at their freezing points. In the cases where an experimental value for equilibrium separation for the pure component at its freezing point was not available, Mohammadi did however use any convenient temperature. This means that in some cases the R^A was calculated using values for the equilibrium separation for the pure compounds from non-consistent temperatures for the two fluids.

Here Mohammadi's original work has been used as a basis, and then investigated further. Initially, the original unlike London pair potential (equation (4.3)) was used in connection with Mohammadi's concept of a temperature independent equilibrium separation, but a temperature dependent equilibrium separation was also used in the calculations described in the following section. This work is described in sections 4.3 and 4.5.

4.1.1.2 PE(uv) versus the logarithm of the solubility

Mohammadi (1986) calculated the PE(uv) as in equation (4.2) for a series of solutes dissolved in each of three solvents. He used the experimental value for the molar volume at the melting (freezing) point to calculate the equilibrium separation from the equation

$$R^A = 2(0.17\ V^m)^{1/3} \tag{4.4}$$

where the R^A for the mixture is given as

$$R^A_{mix} = (R^A_1 + R^A_2)\ /\ 2 \tag{4.5}$$

A list of the solutes and the solvents is given in Table 4-1.

SOLUTES	freezing temperature (K)	molar volume at freezing point (cm^3/mol)	equilibrium separation R^A (Å)
helium	-	24.7	3.77
hydrogen	14.0	14.0	3.16
nitrogen	63.3	34.67	4.28
carbon monoxide	68.1	34.73	4.28
argon	83.8	24.12	3.76
oxygen	54.4	22.43	3.70
methane	90.7	30.94	4.17
carbon dioxide	216.6	28.20	3.99
sulphur dioxide	197.7	-	-
SOLVENTS	**freezing temperature (K)**	**molar volume at freezing point (cm^3/mol)**	**equilibrium separation, R^A (Å)**
water	273.15	19.82	2.82
benzene	278.7	77.28	6.18
carbon tetrachloride	250.0	87.90	5.90

Table 4-1. A list of the solutes and solvents as used by Mohammadi (1986).

The values of the molar volume and the equilibrium separations in Table 4-1 are from Mohammadi (1986) (a - indicates no value given by Mohammadi), the freezing points are from Reid et al. (1987). The modified unlike London pair potential (equation (4.2)) was then plotted versus the base 10 logarithm of the experimental solubility at 298.15 K and 101.325 kPa. Tables A4-1 to A4-3 and Figures A4.1 to A4.3 (all in Appendix 4) show the original results as obtained by Mohammadi (1986). From the graphs and the tables it can be concluded that the "universal" potential energy function expressed as PE(uv) for unlike pair interactions appears to fit the solubilities especially well for the solvents benzene and carbon tetrachloride. The fit for the solvent water is slightly worse since, although the PE(uv) values are large, the solubilities are very small.

No attempt has been made to recalculate Mohammadi's results. Firstly, he used a modification of the London pair potential and secondly, he did not use R^A-values at a consistent temperature for the binary mixtures he investigated. In Mohammadi's thesis (1986) there are a number of tables containing R^A-values, some are experimental values for the pure compound in the solid phase, other values are experimental values for the pure compounds at any convenient temperature and other values are obtained from an experimental molar volume, again at any convenient temperature.

The majority of the solutes in Table 4-1 (except carbon dioxide and sulphur dioxide) are low-boiling fluids with a critical temperature below 298.15 K, the temperature where all the experimental solubility data are measured.

4.2 Relationship between unlike pair potential and solubility-method VNUN

Mohammadi (1986) had obtained a linear relationship between the logarithm of the solubility and a modified unlike London pair potential for mixtures for different solutes dissolved in three solvents. Applying the generalized unlike London pair potential instead of the modified pair potential as developed by Mohammadi would show how far a relationship between the solubility and the unlike London pair potential could be used to accommodate studies of the solubility of gases in liquids.

4.2.1 Calculations of relationship - method VNUN

There are two ways of investigating the relationship. One way is for a series of solutes dissolved in one single solvent, as done by Mohammadi (1986) and Prausnitz et al. (1986). The results obtained by Prausnitz and workers show a similar linear relationship between a solubility characteristic and the solubility, so this was to be expected for one single solute dissolved in a series of solvents. The other way of investigating the relationship is to evaluate a single solute dissolved in a series of solvents and this way is also described.

The method described in this Section is named VNUN. This indicates that parameters for both the solvent (V) and the solute (U) are calculated as if they were independent of temperature (N). Later in this Chapter 4, other methods where the unlike London pair potential is calculated as a function of temperature will be described.

When employing the AGAPE method to predict vapour-liquid equilibria it involves the presumption that the like molecular potential Φ_{like} is defined by the relation (equation (2.81))

$$\Delta H_{vap} = -(60.24 \; L \; z \; \Phi_{like} \; / \; 2) + RT$$

Thus the value of Φ_{like} varies with the energy of vaporization and is therefore a temperature-dependent quantity. This definition of the like pair potential means that in the activity coefficients calculated by equations (2.93) and (2.94) the Φ_{like} is introduced at the operating temperature. This has the extensible merit of recognising that activity coefficients and excess functions are indeed temperature dependent.

When seeking to apply the AGAPE mixing rule to gas-liquid equilibria we should expect to construct a temperature-dependent parameter Φ_{like} for both the solute and the solvent. In the case of the solutes at operating temperatures above their critical temperatures this can not be done with reference to the heat of vaporization or the liquid molar volume since at these temperatures, no liquid phase truly exists for the pure solute. This is the reason for carrying out this investigation with temperature independent parameters, using individually "standard" temperatures instead of the operating temperature. The temperatures were not consistent, as the freezing point differs from one component to another but could be considered to be "corresponding" points.

Temperature-independent interaction parameters are used in the UNIFAC method and this limits the application of the method to between 275 and 425 K (see section 2.10.3.8). Some attempt to make the interaction parameters dependent on temperature has been made (Skjold-Jørgensen et al., 1980). Thus in relation to the UNIFAC method it makes sense to investigate how far a "standard" like pair potential can be used to accommodate solubility calculations.

Calculations of the unlike London pair potential, using the computer program PP mentioned in section 2.11.10, were carried out. The equilibrium separation for each pure compound at the freezing points was used to calculate the unlike London pair potential as given in equation (4.3). The option of screen inputting the values of equilibrium separations was used in this case. The equilibrium separations for the pure compounds at their freezing points were taken from Mohammadi (1986). Values are given in Table 4-4 together with the values of the like pair potential obtained from the computer program PP.

4.2.2 Results of relationship - method VNUN

4.2.2.1 A series of solutes dissolved in a single solvent

Method VNUN. The like London pair potentials for the pure compounds were derived from the equilibrium separation at freezing point temperatures or temperatures close to freezing point. The unlike London pair potential is then calculated at a pseudo-standard temperature and is therefore independent of temperature.

Mixtures of the following solvents and solutes have been tested.

SOLVENTS	**name**	**Freezing temp. (K)**	**Boiling temp. (K)**	**Critical temp. (K)**
C_6H_6	Benzene	278.7	353.2	562.2
$c\text{-}C_6H_{12}$	*cyclo*-hexane	279.6	353.8	553.5
CCl_4	carbon tetrachloride	250.0	349.9	556.4
CS_2	carbon disulfide	161.3	319.0	552.0
H_2O	water	273.2	373.2	647.3
$CHCl_3$	chloroform	209.6	334.3	536.4
CH_3OH	methanol	175.7	537.7	512.6
C_2H_5OH	ethanol	159.1	351.9	513.9
C_3H_7OH	1-propanol	146.9	370.3	563.8

Table 4-2. The selected solutes and solvents to be used in this investigation (continued over).

SOLUTES	**name**	**Freezing temp. (K)**	**Boiling temp. (K)**	**Critical temp. (K)**
CH_4	methane	90.7	90.7	111.6
Ar	argon	83.8	119.9	209.4
Ne	neon	24.5	27.1	44.4
H_2	hydrogen	14.0	20.3	33.0
N_2	nitrogen	63.3	77.4	126.2
O_2	oxygen	54.4	90.2	154.6
CO	carbon oxide	68.1	81.7	132.9
CO_2	carbon dioxide	216.6	(194.7) at pressure = 500 kPa	304.1
C_2H_4	ethylene	104.0	169.3	282.4
C_2H_6	ethane	89.9	184.6	305.4
n-C_3H_8	n-propane	85.5	231.1	369.8
n-C_4H_{10}	n-butane	134.8	272.7	425.2

Table 4-2. The selected solutes and solvents to be used in this investigation.

Nine of the solutes have critical temperatures below the experimental temperature of 298.15 K. Neither the molar volume nor the heat of vaporization has a value above the critical temperature, and it was therefore necessary to develop a method to overcome this problem. This method will be described in Section 4.4.

The PP computer program was used to calculate the results (see description in section 2.11.10). The relevant parameters were as follows:

INPUT

R1	- the equilibrium separation for component 1 independent of temperature, values from Table 4-4
R2	- the equilibrium separation for component 2 independent of temperature, values from Table 4-4

The chosen option for the calculation of the R1 and R2 values means, that the P11 and P22 values in this case were calculated from the following option

OUTPUT

P11, P22	- calculated at the freezing points

The unlike pair potential, P12 was calculated using the two options of combining the two like pair potentials

OUTPUT

P12-GLP	- calculated at the freezing points of the individual compounds from the London theory
P12-GM	- calculated at the freezing points of the individual compounds from the Berthelot theory (the geometric mean)

The number of nearest neighbours, z and the r value (the difference in sizes of volumes between molecule 1 and 2) are not used as parameters in the equations, when the equilibrium separations are screen inputs.

Methanol, ethanol, and 1-propanol

Calculations have been carried out for mixtures including the solvents ethanol, 1-propanol, and methanol. These solvents are both polar and contain hydrogen bondings. Including them in the calculations is a test of how far the GLP model can accommodate such compounds despite the limitations of the developed AGAPE theory.

n-Propane, n-butane, and carbon dioxide

The three mentioned solutes all have their critical temperatures above 298.15 K. Including them in the calculations is a test of whether the linear plot is unique for solubility calculations or also valid for VLE calculations and therefore providing a bridge to the use of the developed AGAPE equations.

Water

Water represents a special case. It is highly polar and contains hydrogen bonds. Including it in the calculations is a test of how far the GLP model can accommodate for this specific compound despite the limitations of the developed AGAPE theory. Water has, so far, not been tested in vapour-liquid equilibrium calculations, as no predictions have been carried out for mixtures including water. Using water in these calculations is also a test, whether water can be used in VLE predictions.

Equilibrium separations (R-values)

The equilibrium separations at freezing point for the majority of the compounds in Table 4-4 are from Mohammadi (1986) or from Homer and Mohammadi (1987b). A number of compounds are not included in Mohammadi's extensive work. These compounds are: the three alcohols, n-propane, and n-butane. For these five solutes/solvents the equilibrium separation at the freezing point have been calculated using the Yen-Woods method (1966) for calculating liquid densities. Extrapolating this method to calculate molar volumes (from densities) in the solid state, is not the intended way of using this method. A thorough analysis of this method and the extrapolation to the solid state is given in Appendix 14. The equilibrium separations at the freezing points as calculated by the extrapolation of the Yen-Woods method for most compounds are well within the values found in the literature. The equilibrium separations for the mentioned five compounds have therefore been calculated using the Yen-Woods method at freezing points. The molar volume option was chosen as it was the way the equilibrium distances originally had been calculated by Mohammadi (1986).

Values of the pair potentials

The values of the like pair potential in Table 4-4 have been calculated by running the computer program PP. They are not from Mohammadi's work, as no values of the like pair potential are given in his work. The values of the unlike pair potential (Tables A5-1 to A5-2) could not been compared with the values from Mohammadi (1986, and repeated in Appendix 4), as the values in Appendix 4 are obtained by employing equation (4.3).

Choosing among the options

Another point to notice is which options to chose. Here the options are the unlike pair of London pair potentials or the geometric mean pair potential. All options are calculated, though every option for all combinations of solute/solvent from Table 4-2 has not been covered. The unlike pair potential calculated by the London method has been tested in most detail. The other option of the geometric mean pair potential has only been tested in a number of cases. The chosen combination of options is shown in Table 4-3.

Combination	**equilibrium separation (mainly at freezing points)**	**unlike pair potential**	**Calculations**
1	from experimental data (mainly at the freezing points. For 5 compounds from molar volumes at their freezing points)	London	thoroughly
2	from experimental data (mainly at the freezing points. For 5 compounds from molar volumes at their freezing points)	geometric mean	a small number of cases

Table 4-3. A table of the different options and their combination.

Table 4-4 shows the relevant equilibrium separations (column 2, mainly from Mohammadi (1986)) that are used to calculate the like London pair potential (equation (4.3)), which is shown in column three.

	molar volume	
compound solutes	**R^A (Å)**	**$\Phi_{ii}*10^{19}$ (J)**
methane	4.17	-0.029110
argon	3.76	-0.018024
neon	3.16	-0.004063
hydrogen	3.78	-0.003681
nitrogen	4.28	-0.009564
oxygen	3.70	-0.010828
carbon dioxide	3.99	-0.046398
carbon monoxide	4.28	0.010828
ethylene	4.82	-0.03777
ethane	4.91	-0.043996
n-propane	5.246835	-0.094536
n-butane	5.65164	-0.1466552
compound solvents	**R^A (Å)**	**$\Phi_{ii}*10^{19}$ (J)**
benzene	6.18	-0.071373
cyclo-hexane	6.20	-0.114516
carbon tetrachloride	5.90	-0.093893
carbon disulfide	5.14	-0.109444
water	2.82	-0.141916
chloroform	5.67	-0.075520
methanol	4.275855	-0.071482
ethanol	4.783208	-0.253580
1-propanol	5.231429	-0.355660

Table 4-4. The equilibrium separations used in method VNUN and the calculated like pair potentials for the different solutes and solvents.

The results of the computer calculations carried out are shown in tables in Appendix 5. There are two ways to analyse the calculated results. The calculated values of the unlike London pair potential for the mixtures can be plotted versus the base 10 logarithm of the experimental solubilities (x_{solute}) at 298.15 K and 101.325 kPa for a series of solutes dissolved in a single solvent, or the other way is to consider a single solute dissolved in a series of solvents. The experimental solubilities were obtained from either the IUPAC Solubility Data Series (Clever, 1979 (vol. 1), Clever, 1980 (vol. 4), Young, 1981 (vol. 5/6), Battino, 1981 (vol. 7), Hayduk, 1982 (vol. 9), Battino, 1982 (vol. 10), Hayduk, 1986 (vol. 24), and Clever and Young, 1987 (vol. 27/28)) or Fogg and Gerrard (1991). The method of presenting the data was chosen such that the graphs could be compared with Figure 4.2 from Prausnitz et al. (1986).

Typical examples of both the types are shown below. Figure 4.4 for carbon disulfide and Figure 4.5 for methanol show the plots for a series of solutes dissolved in a single solvent. Figure 4.6 shows the plot for two solvents, carbon tetrachloride and benzene. Figure 4.7 for argon and methane represents a typical example of the plot for a single solute dissolved in a series of solvents.

The following Table 4-5 shows the results of the plots. The first column shows the name of the solvent, the second column the origin of the equilibrium separation for the solvent (the value is shown in Table 4-4), then follows the name of the solute and the origin of the equilibrium separation for the solute. The fourth column displays which combining rule is used to calculate the unlike pair potential, either the London combining rule or the geometric mean. The last column shows the figure number (A refers to Appendix) and the resulting linear correlation coefficient of the plot. The closer the linear regression correlation coefficient is to unity, the better the data points lie close to a straight line.

solvents	equilibrium separation (freezing point)	solutes	equilibrium separation (freezing point)	unlike pair potential	Figure no. and linear regression coefficient
Benzene	Mohammadi (1986)	Table 4-2	Mohammadi (1986)	London	Figure A5.1 0.8772
cyclo-hexane	Mohammadi (1986)	Table 4-2	Mohammadi (1986)	London	Figure A5.3 0.9772
carbon tetrachloride	Mohammadi (1986)	Table 4-2	Mohammadi (1986)	London	Figure A5.2 0.9751
carbon disulfide	Mohammadi (1986)	Table 4-2	Mohammadi (1986)	London	Figure 4.4 0.9637
water	Mohammadi (1986)	Table 4-2	Mohammadi (1986)	London	Figure A5.7 0.1159
chloroform	Mohammadi (1986)	Table 4-2	Mohammadi (1986)	London	Figure A5.4 0.9915
methanol	from molar volume	Table 4-2	Mohammadi (1986)	London	Figure 4.5 0.8553
ethanol	from molar volume	Table 4-2	Mohammadi (1986)	London	Figure A5.5 0.8822
1-propanol	from molar volume	Table 4-2	Mohammadi (1986)	London	Figure A5.6 0.9027
Table 4-2	Mohammadi (1986)	methane	Mohammadi (1986)	London	Figure A5.12 < 0.000001
Table 4-2	Mohammadi (1986)	argon	Mohammadi (1986)	London	Figure A5.11 0.0837
Table 4-2	Mohammadi (1986)	hydrogen	Mohammadi (1986)	London	Figure A5.15 0.0513
Table 4-2	Mohammadi (1986)	nitrogen	Mohammadi (1986)	London	Figure A5.16 0.0064
Table 4-2	Mohammadi (1986)	oxygen	Mohammadi (1986)	London	Figure A5.17 0.0541

Table 4-5. List of results, method VNUN including figure numbers (continued over).

solvents	**equilibrium separation (freezing point)**	**solutes**	**equilibrium separation (freezing point)**	**unlike pair potential**	**Figure no. and linear regression coefficient**
Table 4-2	Mohammadi (1986)	carbon monoxide	Mohammadi (1986)	London	Figure A5.18 0.0100
Table 4-2	Mohammadi (1986)	ethane	Mohammadi (1986)	London	Figure A5.19 0.0087
Table 4-2	Mohammadi (1986)	n-propane	Mohammadi (1986)	London	Figure A5.13 0.0116
Table 4-2	Mohammadi (1986)	carbon dioxide	Mohammadi (1986)	London	Figure A5.14 0.0127
methanol	from molar volume	Table 4-2	Mohammadi (1986)	geometric mean	Figure 4.5 0.8391
ethanol	from molar volume	Table 4-2	Mohammadi (1986)	geometric mean	Figure A5.5 0.9031
1-propanol	from molar volume	Table 4-2	Mohammadi (1986)	geometric mean	Figure A5.6 0.9308
carbon tetrachloride	Mohammadi (1986)	Table 4-2	Mohammadi (1986)	geometric mean	Figure A5.2 0.9567
benzene	Mohammadi (1986)	Table 4-2	Mohammadi (1986)	geometric mean	Figure A5.1 0.9286

Table 4-5. List of results, method VNUN including figure numbers.

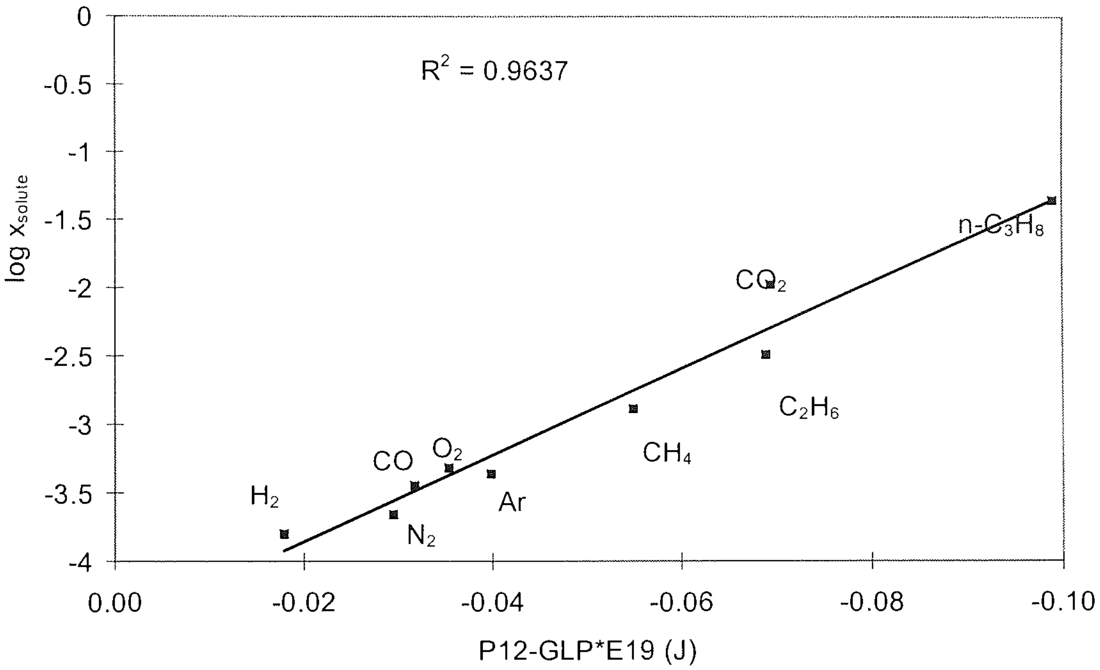


Figure 4.4. Solubilities of gases in **carbon disulfide** at 298.15 K, 101.325 kPa as a function of the generalized unlike London pair potential (P12-GLP) calculated by method VNUN.

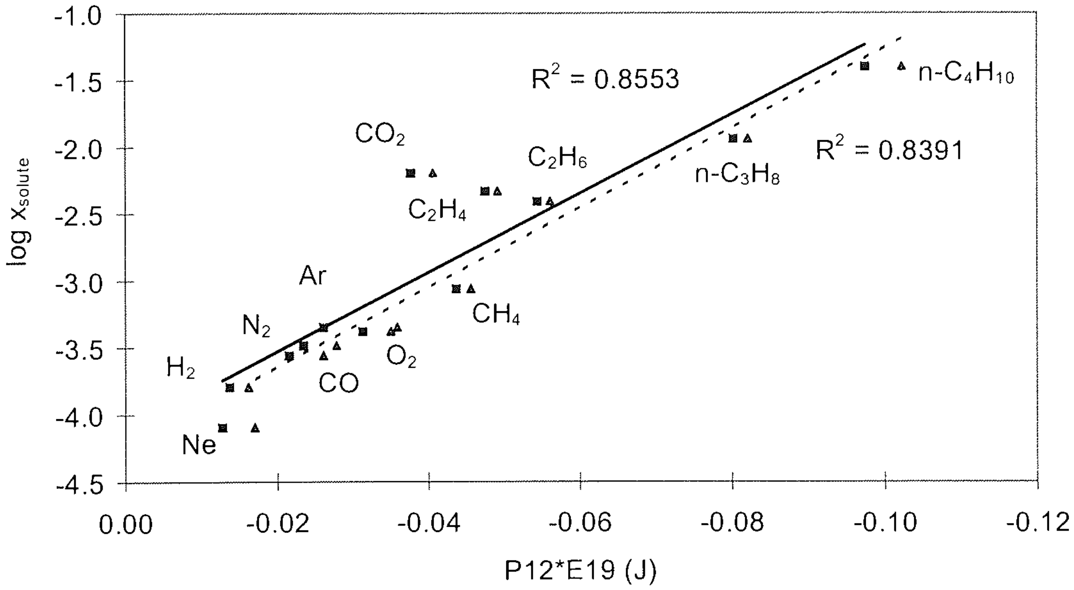


Figure 4.5. Solubilities of gases in **methanol** at 298.15 K, 101.325 kPa as a function of the generalized unlike London pair potential (P12-GLP, ■ points and – line) and the geometric mean unlike pair potential (P12-GM, ▲ points and -- line) calculated by method VNUN.

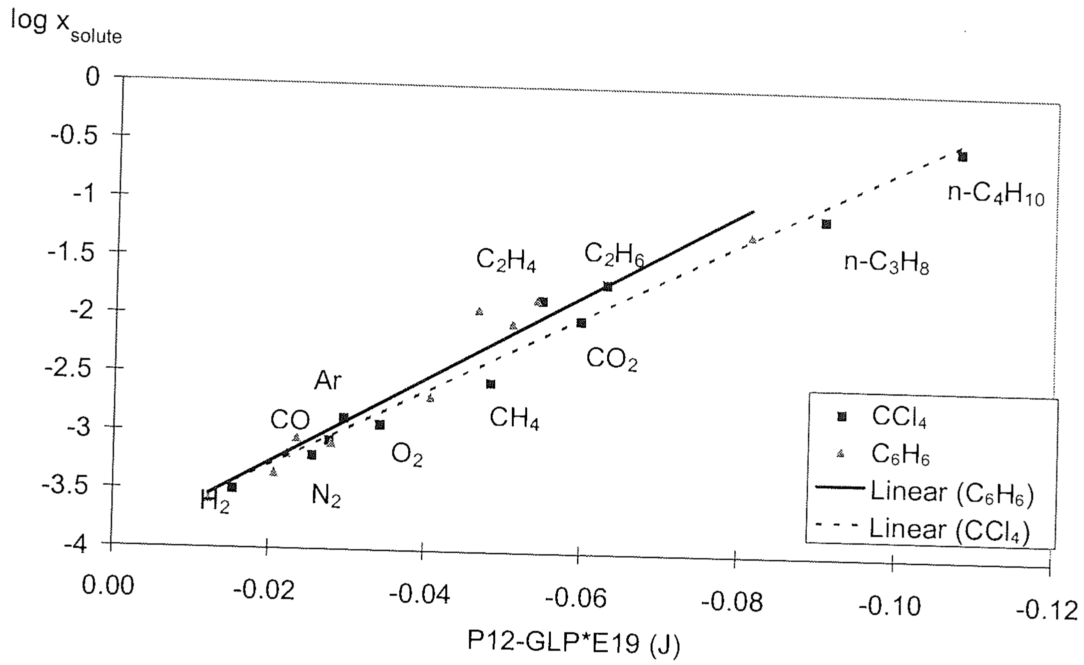


Figure 4.6. Solubilities of gases in **benzene** (▲ and —) and **carbon tetrachloride** (■ and --) at 298.15 K, 101.325 kPa as a function of the generalized unlike London pair potential (P12-GLP) calculated by method VNUN.

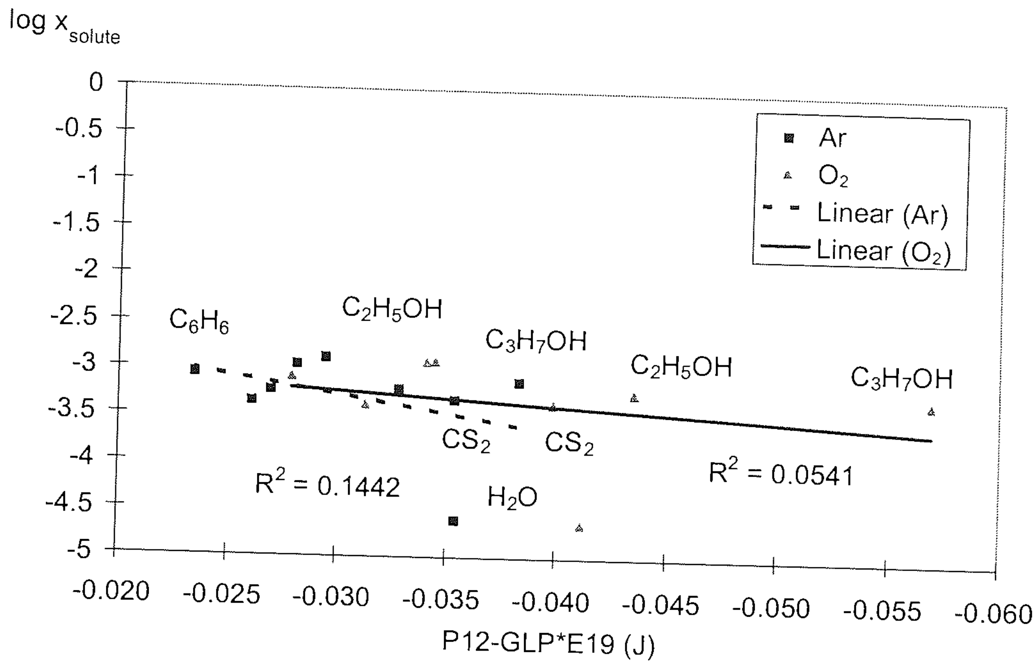


Figure 4.7. Solubilities of **oxygen** (▲ and —) and **argon** (■ and --) in solvents at 298.15 K, 101.325 kPa as a function of the generalized unlike London pair potential (P12-GLP) calculated by method VNUN.

Figure 4.6 is a combination of Figures A5.1 and A5.2 without the regression lines and Figure 4.7 is a combination of Figures A5.11 and A5.17, where all the solvents are named on the figures.

4.2.3 Discussion of relationship - method VNUN

4.2.3.1 A series of solutes dissolved in a single solvent

Sadly, the aim of developing a new gas-solubility prediction method was unsuccessful in the VNUN case. From the results of the linear regression coefficients in Table 4-5 it can be seen that the plots of a series of solutes dissolved in a single solvent show the same regularity as Figure 4.2. The plots of a single solute dissolved in a series of solvents show far from the same pattern of regularity. This indicates that it was not possible to produce the wanted "grid" pattern using the VNUN method.

Comparison to Figure 4.2

Figure 4.6 demonstrates the regularity of solutes dissolved in a single solvent very well. The solutes follows the same sequence with hydrogen first (lowest solubility of the examined solutes), nitrogen, carbon monoxide, argon, oxygen, methane, carbon dioxide, ethane, propane, and finally n-butane (with the highest solubility).

This is the same sequence as shown in Figure 4.2 and is not only due to the solubility, but the sequence of solutes is also influenced by the value of the (in Figure 4.6) unlike London pair potential.

The sequence of the solvents in Figure 4.6, where the carbon tetrachloride trendline lies below the trendline for benzene, is the opposite of the sequence in Figure 4.2. This is a very peculiar result and to investigate this, the carbon disulfide trendline has been added to the figure in Figure A5.10. The carbon disulfide lies as the lowest of the three lines, which is in agreement with Figure 4.2. The reason for the opposite tendency in Figure 4.2 compared to Figure 4.6 is that in Figure 4.2, the benzene and carbon tetrachloride lines are not trendlines for the best linear regression between all the data points, but the best regression lines where the data points for hydrogen have been excluded. The same goes for the propane and n-butane data points in Figure 4.6, two solutes which are not included in Figure 4.2.

In Figure 4.6 the two trendlines cross each other around -3 on the y-axis and then the difference between them increases with increasing value of the pair potentials. In Figure 4.2 the lines for benzene and carbon tetrachloride do not cross, but they become further and further apart, when the force constant increases.

Water and the alcohols

The solvent water was expected to give bad results as the compound is both polar and contains hydrogen bonding. As expected, the linear relationship was far the worst among the above mentioned solvents. The linear regression coefficient was around 0.1. As no other phase equilibrium predictions including water had been carried out at that time, these calculations were a test case for water. Compared to the alcohols: methanol, ethanol, and 1-propanol that are also polar and contain hydrogen bondings, water shows the worst linear relationship (taking the linear regression coefficient as an expression for how good the linear relationship is). The alcohols show surprisingly good linear relationship, surprisingly when their polarity and hydrogen bondings are taken into account. In fact, the alcohols show the same accuracy in their linear relationship as benzene.

Apart from water, the solvents included in this VNUN linear relationship investigation all show a relatively good agreement with a straight line.

Comparison to Mohammadi's results (1986)

One of the most distinctive result is the much better linear regression coefficients (i.e. the data points lie much closer along a straight line) obtained by Mohammadi (1986, repeated in Appendix 4) using the modified unlike potential (equation (4.2)). The linear regression coefficients are 0.9795, 0.9911 and 0.8837 for the solvents benzene, carbon tetrachloride and water, respectively compared to 0.8772, 0.9751 and 0.1159 as obtained in this investigation. The solvents included in his investigation and the solutes included in the VNUN investigation are the same, except for the heavier hydrocarbons n-propane and n-butane. The explanation for the much better linear regression coefficients lies in the modified potential Mohammadi used, and also in the equilibrium separation for the mixture, where he either used the arithmetic mean value or the biggest value of the two individual equilibrium separations. Throughout this investigation the arithmetic mean value has been used.

Water

In Appendix 5 are two plots for water, one without the data points for n-propane and n-butane (Figure A5.8) and the other similar but also excluded is the data point for ethylene (Figure A5.9). The linear regression coefficient for the first plot is 0.642, while that for the second plot is 0.7418. These plots compare better to the plot (Figure A4-3) by Mohammadi as they include the same solutes and consequently they show greater similarity to Figure A4-3. This shows that the solubilities for propane and n-butane in water are much lower then expected, a fact that can be seen by examining the tables and graphs in Appendix 3. The solubilities for propane and n-butane in water are in fact of the same order of magnitude as the solubility of methane. In most other solvents, the solubilities of propane and n-butane are much higher then the solubility of methane.

By omitting these three solutes, the results of Mohammadi and this investigation (VNUN) are more comparable and they are of the same order of magnitude but with a slightly higher linear regression coefficient obtained by Mohammadi.

Mohammadi could have obtained a higher linear regression coefficient because he used a modified potential (equation (4.2)).

4.2.3.2 One single solute dissolved in a series of solvents

As indicated by the linear regression coefficients in Table 4-5, the relationship between the unlike London pair potential and the logarithm of the solubility for one single solute dissolved in a series of solvents is far from a linear relationship.

Comparison to Figure 4.2

It was not the result hoped for. Figure 4.2 from Prausnitz et al. (1986), shows a relationship between the logarithm of the experimental solubility and the solute characteristic ε/k_B. The unlike London pair potential is dependent on both the solvent and the solute. If an investigation more alike to the one referred to in Prausnitz et al. (1986) had been carried out, the like pair potential for the solute should have been the variable instead of the unlike pair potential. This would have given a similar result as the one in Figure 4.2. This particular investigation was chosen differently with the aim of contributing to the knowledge of intermolecular forces and their dependence on both the solute and the solvent.

Despite this, Figure 4.7 demonstrates the lack of regularity of solvents very well. The solvents follow the same sequence with benzene first. It has the highest value of the unlike pair potential of the examined solvents. Then follows methanol and in both cases 1-butanol has the lowest value of the unlike pair potential. The data points for the solvents *cyclo*-hexane and carbon tetrachloride are in reversed sequence on the two solute curves, and this is also the case for the solvents carbon disulfide, ethanol and water where the sequence is different for the two solutes. The sequence is probably best seen in Figures A5.11 and A5.17.

Despite this irregularity, the pattern with the sequence of benzene, carbon tetrachloride and carbon disulfide is recognised from Figure 4.6.

Overall, the results seem to indicate that energetic or enthalpic terms may not be dominant in this case.

4.2.4 Conclusion of relationship - method VNUN

The aim with this investigation was to determine whether the linear relationship found between the solubilities of gases in liquids and the force constants of solutes (Figure 4.2) could be established, when replacing the force constant with a parameter related to the intermolecular forces, in this case the unlike potential. The force constant is independent on temperature, so in the first instance a temperature independent unlike potential was employed. As opposed to the force constant of the solute, the unlike potential depends on both the solute and the solvent and could probably provide more information about the intermolecular forces then the force constant for the solutes.

The result of the calculations carried out is that there is, indeed a linear relationship for a series of solutes dissolved in a single solvent. This applies even for polar solvents such as alcohols. The only exception is water, where there is no relationship to be found. This result does not surprise, as the solubility of various gases in water is generally very small and not consistent with the variation for a homologous series as seen for other solvents (discussed in Chapter 3).

The analysis of a single solute dissolved in a series of solvent showed that in this case, there was no linear relationship to be established.

The results obtained inspired new calculations, where the unlike pair potential was dependent on temperature.

4.3 Relationship between unlike pair potential and solubility- method VDUN

The method described in this section is named VDUN. This indicates that parameters for the solvent (V) are dependent on temperature (D) and those for the solute (U) are independent of temperature (N).

The majority of the solutes in Table 4-2 have critical temperatures well above the experimental temperature which in this case is 298.15 K. The problem of contriving "liquid" parameters for the hypothetical liquid above the critical temperature has been met by other authors, notably Prausnitz in his work on regular solution theory (Prausnitz and Shair, 1961).

Similar calculations as described under method VNUN were then carried out, but here the equilibrium separations for the solvents at 298.15 K were used.

To let the solvent be temperature dependent in solubility studies also reflects the fact, that for the vast majority of mixtures the solubilities are small. In most cases, the solvent is the dominant compound with the highest concentration in a binary solute-solvent mixture, and letting the solvent be temperature dependent and the solute independent of temperature makes sense.

4.3.1 Calculations of relationship - method VDUN

Calculations of the unlike London pair potential, using the computer program PP mentioned in section 2.11.10, were carried out. The equilibrium separation for each pure solute at their freezing points and the equilibrium separation for the solvents at 298.15 K were used to calculate the unlike London pair potential as given in equation (4.3). The option of screen inputting the values of equilibrium separations was used in this case. The equilibrium separations for the pure solutes at their freezing points were taken from Mohammadi (1986). The equilibrium separations for the pure solvents at 298.15 K were first calculated from the computer program PP. In this case (pure solvents at 298.15 K) the single component option, the molar volume option and the operating temperature were input to the program.

It should be noted, that in this case, the unlike London pair potential was intended to be calculated at different temperatures for the solute and the solvent.

The relevant parameters in the computer programs were as follows:
INPUT

R1 - the equilibrium separation for the solute independent of temperature, values from Table 4-4
R2 - the equilibrium separation for solvent calculated by program PP at 298.15 K from the molar volume option

The chosen option for the calculation of the R1 and R2 values means, that the P11 and P22 values in this case were calculated from the following option
OUTPUT

P11 - calculated at the freezing point for the solute
P22 - calculated at 298.15 K from the molar volume option

The unlike pair potential, P12 was calculated using the two options of combining the two like pair potentials
OUTPUT

P12-GLP - calculated at the inconsistent temperatures of the individual compounds from the London theory
P12-GM - calculated at the inconsistent temperatures of the individual compounds from the Berthelot theory (the geometric mean)

When the equilibrium separations are screen input, the parameters z (the number of nearest neighbours) and the r value (the difference in sizes of volumes between molecule 1 and 2) are not used in the equations.

Choosing among the options

A point to notice is which options to chose. The like pair potentials (in this case only the like pair potentials for the solvents) can be calculated from either the heat of vaporization or the molar volume. The other option is the unlike pair of London pair potentials or the geometric mean. All options are calculated, though calculations of every option for all combinations of solute/solvent from Table 4-2 have not been carried out. The option: equilibrium separation from the molar volume (at 298.15 K and only for the solvents) and the unlike pair potential calculated by the London method has been tested in most detail. The other options have only been tested in a number of cases. The chosen combination of options is shown in Table 4-6.

Combination	equilibrium separation		unlike pair potential	Calculations
	solvents (at 298.15 K)	solutes (at freezing points)		
1	from molar volume	from experimental data (mainly at the freezing points. For 5 compounds from molar volumes at their freezing points)	London	a small number of cases
2	from molar volume	from experimental data (mainly at the freezing points. For 5 compounds from molar volumes at their freezing points)	geometric mean	a small number of cases
3	from heat of vaporization	from experimental data (mainly at the freezing points. For 5 compounds from molar volumes at their freezing points)	London	no cases
4	from heat of vaporization	from experimental data (mainly at the freezing points. For 5 compounds from molar volumes at their freezing points)	geometric mean	no cases

Table 4-6. A table of the different options and their combination.

Combinations number 3 and 4 are considered inconsistent and therefore no calculations involving these combinations have been carried out.

	molar volume	
compound solutes	R^A (Å)	$\Phi_{ii}*10^{19}$ (J)
methane	4.17	-0.029110
argon	3.76	-0.018024
neon	3.16	-0.004063
hydrogen	3.78	-0.003681
nitrogen	4.28	-0.009564
oxygen	3.70	-0.010828
carbon dioxide	3.99	-0.046398
carbon monoxide	4.28	0.010828
ethylene	4.82	-0.03777
ethane	4.91	-0.043996
n-propane	5.246835	-0.094536
n-butane	5.65164	-0.1466552

	molar volume	
compound solvents	R^A (Å)	$\Phi_{ii}*10^{19}$ (J)
benzene	5.90631	-0.123816
cyclo-hexane	6.284148	-0.098488
carbon tetrachloride	6.04657	-0.075741
carbon disulfide	5.245798	-0.092490
water	3.427886	-0.030407
chloroform	5.900903	-0.053716
methanol	4.471602	-0.047341
ethanol	5.024571	-0.132554
1-propanol	5.497517	-0.204653

Table 4-7. The equilibrium separations used in method VDUN and the calculated like pair potentials for the different solutes and solvents.

Table 4-7 shows the relevant equilibrium separations that are used to calculate the like London pair potential (equation (4.3)), which is shown in column three and five depending on whether the equilibrium separation is derived from the molar volume option (column two) or the heat of vaporization option (column four).

The results of the computer calculations carried out are shown in Appendix 6. The calculated values of the unlike London pair potential for the mixtures were plotted versus the base 10 logarithm of the solubilities (x_{solute}) at 298.15 K and 101.325 kPa. Again the experimental solubilities were obtained from either IUPAC Solubility Data Series (Clever, 1979 (vol. 1), Clever, 1980 (vol. 4), Young, 1981 (vol. 5/6), Battino, 1981 (vol. 7), Hayduk, 1982 (vol. 9), Battino, 1982 (vol. 10), Hayduk, 1986 (vol. 24), and Clever and Young, 1987 (vol. 27/28)) or Fogg and Gerrard (1991). The plots are shown in Appendix 6.

The following Table 4-8 shows the results of the plots. The first column shows the name of the solvent, the second column the origin of the equilibrium separation for the solvent (the value is shown in Table 4-7), then follows the name of the solute and the origin of the equilibrium separation for the solute. The fourth column displays which combining rule is used to calculate the unlike pair potential, either the London combining rule or the geometric mean. The last column shows the figure number (A refers to Appendix) and the resulting linear correlation coefficient of the plot. The closer the linear regression correlation coefficient is to unity, the better the data points lie close to a straight line.

solvents	equilibrium separation (298.15 K)	solutes	equilibrium separation (freezing point)	unlike pair potential	Figure no. and linear regression coefficient
benzene	from molar volume	Table 4-2	Mohammadi (1986)	London	Figure A6.1 0.9370
carbon tetrachloride	from molar volume	Table 4-2	Mohammadi (1986)	London	Figure A6.2 0.9763
water	from molar volume	Table 4-2	Mohammadi (1986)	London	Figure A6.3 0.1315
methanol	from molar volume	Table 4-2	Mohammadi (1986)	London	Figure A6.4 0.8617
ethanol	from molar volume	Table 4-2	Mohammadi (1986)	London	Figure A6.5 0.8933
ethanol	from molar volume	Table 4-2	Mohammadi (1986)	geometric mean	Figure A6.5 0.9031
methanol	from molar volume	Table 4-2	Mohammadi (1986)	geometric mean	Figure A6.4 0.8391
benzene	from molar volume	Table 4-2	Mohammadi (1986)	geometric mean	Figure A6.1 0.8365
carbon tetrachloride	from molar volume	Table 4-2	Mohammadi (1986)	geometric mean	Figure A6.2 0.9567
Table 4-2	from molar volume	methane	Mohammadi (1986)	London	Figure A6.6 0.3448

Table 4-8. List of results, method VDUN including figure numbers.

4.3.2 Results of relationship - method VDUN

4.3.2.1 A series of solutes dissolved in a single solvent

Compared to the results obtained from the VNUN method, the VDUN method shows very small improvements, when using the linear regression coefficient as the values to be improved, e.g., the linear regression coefficient for the solvent water goes from 0.11 (method VNUN) to 0.13 (method VDUN).

This is probably due to the very small change in the equilibrium separations (for the solvents) used in method VNUN and method VDUN. Despite the fact that the like pair potential is very sensitive to the value of the equilibrium separation (see Appendices 7 and 8), these results seem to indicate that the unlike pair potential is less sensitive to a changed value of one of the like potentials.

The sequences of the solutes and the solvents have remained unchanged from the VNUN case.

4.3.2.2 One single solute dissolved in a series of solvents

The slight improvements resulting in larger values of the linear regression coefficients, when comparing method VDUN with method VNUN do not seem to justify carrying out this analysis to its full extent in this VDUN case. Considering the very small values of the linear regression coefficients that were obtained when using method VNUN analysing a single solute dissolved in a series of solvents, one case was examined, choosing methane as the solute.

The result was an extremely large improvement in the linear regression coefficient from less then 0.00001 to 0.3448. This was taken as an indication that the use of a temperature dependent pair potential which, right from the start, had been applied to calculate the vapour-liquid equilibria predictions was right.

The use of a temperature dependent like pair potential for the solvents gave an enormous increase in the linear regression coefficient, and it inspired to further calculations, where both the solute and the solvent were dependent on temperature. There is, however, a problem with the solutes, whose critical temperatures are below 298.15 K. They are regarded as hypothetical liquids at 298.15 K.

A number of different authors had overcome the problem of the hypothetical liquids in different ways, and they work was used as inspiration to the approach developed in this study. The approach is described in section 4.4.

4.3.3 Conclusion of relationship - method VDUN

The results of employing a temperature dependent pair potential for the solvents and use a like pair potential obtained at the compounds freezing points for the solutes gave a slight improvement in the linear regression coefficients when compared to the results of method VNUN for the analysis of a series of solutes dissolved in one single solvent. When analysing one single solute dissolved in a series of solvents, the results was an astonishing improvement of the linear regression coefficient.

The result confirmed the belief of using a temperature dependent unlike pair potential, which had been employed in the vapour-liquid predictions.

This particular result also initiated a search for a way of calculating the like pair potential, primarily at 298.15 K for solutes, whose critical temperatures are below 298.15 K.

4.4 The like pair potential for low-boiling pure gases above their critical temperatures

4.4.1 Introduction to the problem

The derivation of the AGAPE equations in section 2.11 shows that the unlike London pair potential for the mixture is derived from the like London pair potentials for the pure components. These like London pair potentials are, on the other hand, a function of a number of variables, among them is the equilibrium separation for the pure components. The equilibrium separation for the pure components is calculated as a function of temperature from either the molar volume or the heat of vaporization. The problem lies in the fact, that neither the molar volume nor the heat of vaporization has a value when the temperature exceeds the critical temperature of the components. This is the reason for the limitation of the operating temperature to be below the critical temperature of each of the components.

The limitation is not crucial for predictions of vapour-liquid equilibrium, but for calculations concerning the solubility of gases in liquids this is a serious limitation. Vapour-liquid equilibrium data are usually measured below the critical temperature of the lowest-boiling component, whereas gas-solubility measurements are made at temperatures above the critical temperature of the lowest boiling component. As explained in Chapter 3 this difference is sometimes used to distinguish between measurements of vapour-liquid equilibrium and of solubility of gases in liquids.

The results of the previous methods VNUN and VDUN also made it clear that it was necessary to develop a method that would make it possible to carry out various gas-solubility calculations at temperatures above the critical temperature of the components.

4.4.2 Calculations of the pair potential of pure gases as a function of temperature

A number of different approaches towards calculating the solubility of gases in liquids at temperatures above the critical temperature of the gas has been carried out.

Methane was chosen as a test case because its critical temperature is 190.4 K, and an extension to 298.15 K, a temperature where several experimental data could be found seemed to be a reasonable extension.

The heat of vaporization, the equilibrium separation from the heat of vaporization and the like London pair potential calculated from the heat of vaporization were calculated as a function of temperature for methane in the temperature interval 0 K to the critical temperature 190.4 K using one of the AGAPE computer programs. The heat of vaporization is calculated using Watson's correlation (Reid et. al, 1987). The heat of vaporization ($\Delta H_{vap,1}$) at the boiling point (T_1) is included in the AGAPE database. The program calculates the latent heat of vaporization ($\Delta H_{vap,2}$) at another temperature (T_2) using Watson's correlation.

$$\Delta H_{vap,2} = \Delta H_{vap,1} \left(\frac{1 - T_{r2}}{1 - T_{r1}} \right)^{0.38} \qquad (4.6)$$

where

$$\begin{aligned} T_{r1} &= T_1 / T_C \\ T_{r2} &= T_2 / T_C \end{aligned} \qquad (4.7)$$

The latent heat of vaporization is given by

$$\Delta H_{vap} = - \text{const} \frac{1}{2} L z U(\text{pair}) + T R \qquad (4.8)$$

where const is a constant to convert to the right units. The const is 60.24, if ΔH_{vap} is calculated in kJ/mole, and the units of R^A, α_i and $<m^2>$ are, respectively, Å, Å^3 and 10^{-36} erg cm^3.

Equation (4.8) is derived under the assumption that the major part of the cohesion energy is due to immediate interactions between nearest neighbours. To repeat, the pair potentials is given by

$$\Phi_{ij} = \Phi(\text{pair}) = -0.25(R^A)^{-6} \sum_i \sum_j (\alpha_i < m^2 >_j + \alpha_j < m^2 >_i) F^A W_i W_j \qquad (4.9)$$

From known heat of vaporization at a given temperature (calculated from Watson's correlation) the equilibrium separation R^A can be found by combining equation (4.8) and (4.9), and solving them for the equilibrium separation, R^A.

Similarly, the molar volume, the equilibrium separation from the molar volume and the like London pair potential calculated from the molar volume were calculated as a function of temperature for methane in the temperature interval 0 K to the critical temperature 190.4 K using the same AGAPE computer program.

The equilibrium separation is found from the molecular volume

$$R^A = 2(0.17 V^m)^{1/3} \qquad (4.10)$$

The molecular volume is related to the molar volume by L, Avogadro's number. The molar volume can be calculated as a function of temperature by a method from Yen and Woods (1966)

$$v = R Z_C T_C / (P_C \rho^S) \qquad (4.11)$$

where R is the gas constant. The saturated density ρ^S is calculated from the reduced saturated density ρ_r^S given by

$$\rho_r^S = \frac{\rho^S}{\rho_C} = 1 + A(1 - T_r)^{1/3} + B(1 - T_r)^{2/3} + C(1 - T_r)^{4/3} \qquad (4.12)$$

where A, B, and C are functions of the critical compressibility factor Z_C and given in Yen and Woods (1966).

It is worth mentioning that using the calculations in this way was not how they originally were intended to be used. When the GLP theory originally was derived (Homer and Mohammadi, 1987a) the basis for prediction of heats of vaporization was to evaluate the equilibrium separation R^A from the molar volume close to the freezing points (corresponding temperatures) and to use that value of R^A to find a value for the like potential and hence the interaction for all the atoms predicting the heat of vaporization at a temperature close to the boiling point (corresponding temperatures).

It was never envisaged that the heat of vaporization could be correlated with the molar volumes over a substantial temperature range. The relation between these two quantities is a complex one. The quotient $\Delta H_{vap} / v$ is related to the van der Waals factor a' which is known to be temperature dependent.

Only in the event that the heat of vaporization data is not being available, has it been found necessary to calculate R^A from the molar volume option for predicting vapour-liquid equilibrium.

In Appendix 13 the values of the heat of vaporization as calculated by the POT method (explained in Appendix 13) will be compared with other methods for prediction of the heat of vaporization. In Appendix 14 the molar volume values as calculated by the Yen-Woods method will be compared with experimental values of the molar volumes, mainly for the compounds in their solid state which is beyond the temperature limit of the Yen-Woods method.

The like pair potential calculations for methane are carried out using the following options in the computer programs:

Heat of vaporization:

INPUT	temperature and the component
OPTION	heat of vaporization
OUTPUT	heat of vaporization
	equilibrium separation from heat of vaporization
	London pair potential from heat of vaporization

Molar volume:

INPUT	temperature and the component
OPTION	molar volume
OUTPUT	molar volume
	equilibrium separation from molar volume
	London pair potential from molar volume

Table A7.1 (Appendix 7) shows the results obtained. Figure A7.1 shows the molar volume as a function of temperature and the best fit for the graph, which is a sixth-order polynomial expression. Figures A7.2 and A7.3 show the like London pair potential for methane as a function of temperature calculated from the molar volume and the heat of vaporization option, respectively. Also plotted on the figures are the best curve-fit expressions, which are fifth-order polynomial expressions for both curves. Figures A7.4 and A7.5 show the equilibrium separation as a function of temperature calculated from the molar volume and the heat of vaporization option, respectively. Also plotted on the figures are the best curve-fit expressions, which are fifth-order polynomial expressions for both curves.

Figure A7.6 shows the calculated heat of vaporization as a function of temperature and the experimental data for the heat of vaporization from Table A7-2.

4.4.3 Discussion of various methods

The first idea of extension was an extrapolation of the like London pair potential curves (from the heat of vaporization or the molar volume) up to the operating temperature, i.e. up to 298.15 K. The London pair potential curves were both fitted with a fifth-order polynomial expression which proved to be the best fit from using all the available options for curve fitting and comparing the curve fitting coefficient. It is obvious from Figures A7.9 and A7.10 that show the plots of the London pair potential for methane as a function of temperature extrapolated to 350 K that the London pair potential calculated in both cases is positive at a temperature at 298.15 K. In fact, the like London pair potential changes sign from negative to positive at the critical temperature of methane.

The like and the unlike London pair potentials are bound to be negative due to the common convention of expressing attractive forces as negative, and the dispersion forces account only for the attractive forces.

The next approach was to extrapolate the curves for the equilibrium separation from either the molar volume or the heat of vaporization beyond the critical temperature. Figures A7.11 and A7.12 show the fitted curves extrapolated to 350 K for the equilibrium separation calculated from the molar volume and the heat of vaporization, respectively. Values for the equilibrium separation for methane at 298.15 K were calculated from the expressions for the fitted curves. The values were approximately 55 and 135 from molar volume and heat of vaporization, respectively.

A new variation of the previously used AGAPE computer program was written. An extra option was included of inputting the equilibrium separation for the pure component (as an input) instead of using the default value calculated by the program. This program was then used to derive values of the London pair potential as follows.

INPUT	equilibrium separation and the component
OPTION	screen input
OUTPUT	heat of vaporization at that equilibrium separation London pair potential (at screen input equilibrium separation)

This computer program can be used for both a single component or a binary mixture. Using this version of the computer programs, the above values of R^A for methane of 55 and 135, respectively, were inputs to the program. In both cases, the program calculated a positive like pair potential.

It was not possible to obtain a value for the like pair potential of methane by extrapolating either the like pair potential as a function of temperature or the equilibrium separation as a function of temperature, because the like pair potential in both cases became positive, and another approach had to be developed.

One way is to force the pair potential for the pure gas to remain negative for all values of temperature. This could be done by curve fitting on selected values in a temperature range well above the triple point and well below the critical point.

4.4.4 The selected method

This idea of a selected temperature interval was investigated further. Various temperature intervals were suggested, but were rejected because of non-continuous properties, such as density. By focusing on a temperature interval where the density would be continuous, the temperature interval between the triple (freezing) point and the boiling point was chosen.

The triple point is characterised as the only point, at a fixed temperature and pressure, the triple point, where the three phases of a pure substance, solid, liquid and gas, can remain in mutual equilibrium. For a number of substances, the triple point temperature is equal to its freezing temperature (Rowlinson and Swinton, 1982).

Again, methane was used as the test case. The next question was: which parameter of either the equilibrium separation or the like London pair potential should be chosen for the extrapolation from the selected temperature interval to 298.15 K.

The like pair potential is a function of the equilibrium separation, which itself is a function of temperature. Both the equilibrium separation and the like pair potential were plotted as a function of temperature in the interval: the triple point to the boiling point. The graphs for the equilibrium separation for methane in the chosen temperature interval from a temperature a little below the triple point (90.7 K) to a temperature a little above the boiling point (111.6 K) from both the molar volume and the heat of vaporization option is shown as Figure 4.8. The similar graph for the like pair potential is Figure A7.13.

The lines are fitted with linear regression expressions, and all four line regression coefficients are larger then 0.95. This indicates that all four lines are very close to being straight lines.

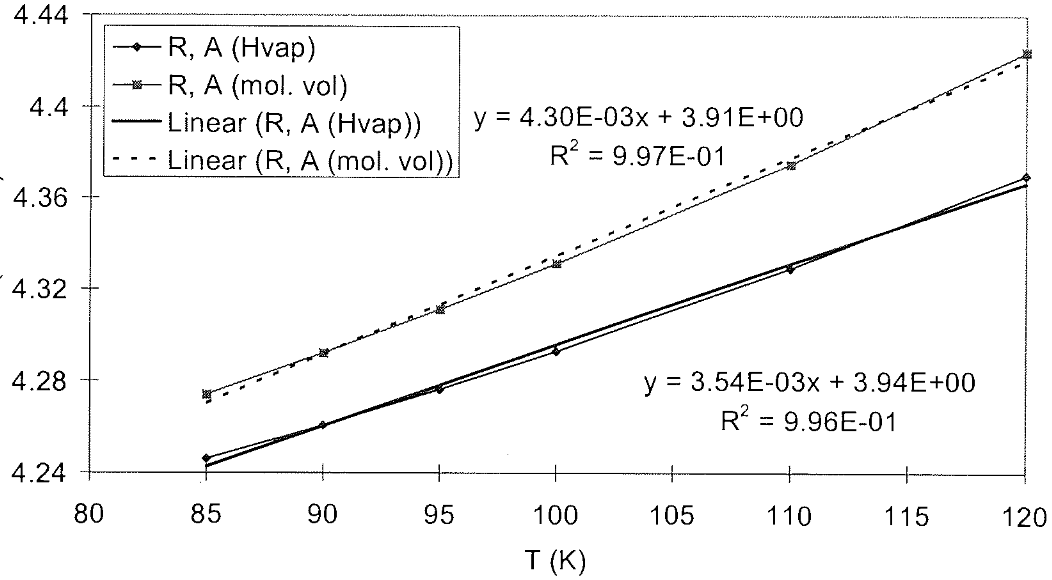


Figure 4.8. The equilibrium separations as a function of temperature in the interval: the triple point to the boiling point and the best fitting curves.

The four lines have all been extrapolated to 320 K. The results are shown as Figures 4.9 and A7.14, respectively. The graphs show that the extrapolated lines of the two lines for the like pair potential both give positive values of the extrapolated like pair potentials at 298.15 K. Extrapolation gives positive like pair potentials at app. 240 K and 270 K.

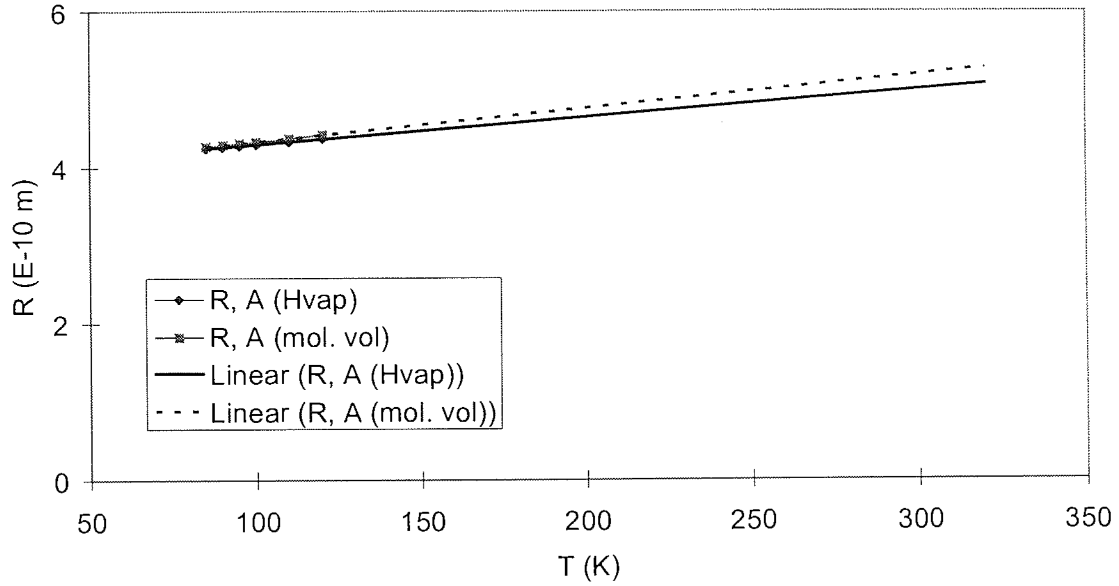


Figure 4.9. The equilibrium separations as a function of temperature and the best fitting curves extrapolated to 350 K.

The extrapolated values of the equilibrium distances at 298.15 K calculated from the fitted linear regression expression were both input parameters to two separate runs of a computer program to calculate the like or unlike pair potential. In both cases, the obtained like pair potential for methane were negative.

It was then decided to use the equilibrium distance rather then the like pair potential as the parameter to extrapolate to find a value for the like pair potentials (and unlike pair potential for mixtures) at higher temperature then the critical temperature for low-boiling gases.

The method was named the extrapolation method.

The values for the equilibrium separation at 298.15 K using the extrapolation method and the values for the like pair potentials are shown in Table 4-9.

Methane	heat of vaporization		molar volume	
	R, Å	$\Phi_{ii}*10^{19}$, J	R, Å	$\Phi_{ii}*10^{19}$, J
	4.99829	-0.008062	5.173	-0.006385

Table 4-9. Equilibrium separations and the like pair potentials for methane at 298.15 K calculated by the extrapolation method.

Comparison between the like pair potentials for methane as calculated by the two options: the molar volume and the heat of vaporization is shown as Figure A7.8.

One important to note about the extrapolation method, is the fact that the equilibrium separation is not unique at a certain temperature, but the same value of the equilibrium separation can be found at two different temperatures.

A reasonable question to ask at this point is: Why not use the calculations the opposite way round ? That is: from known solubility use the AGAPE equations (section 2.11.5) to calculate the like pair potential for methane that fits the known solubility at 298.15 K in a given solvent and then using this fitted pair potential in future calculations involving methane. This option was considered. In the AGAPE equations to calculate the vapour composition from known temperature and liquid composition, three pair potentials are involved, one like pair potential for each of the components and one unlike pair potential for the mixture. The unlike pair potential is a function of both like pair potentials. The problem was found to be the (in the case of solubility calculations) unknown vapour composition. Despite the known (in most cases) partial pressure of the solute and assuming that the partial pressure of the solvent was equal to its saturated vapour pressure, derivation of equations to calculate the like pair potential for the solute was not successful.

A fitting method is described in section 4.7. In this method, an approach to fit the like pair potential, again using methane as test case, to the given solubility is investigated using numerical analysis for the like pair potential rather then exact mathematical analysis.

4.4.5 Conclusion of the extrapolation method in the test case

A method to eliminate the limitation of temperatures below the critical temperature has been developed using methane as the test case. The method is called the extrapolation method and by extrapolating the equilibrium distance in the temperature interval: the triple point to the boiling point, a value for the equilibrium distance at 298.15 K has been found. This value was used as input to calculate a value of the like pair potential.

One satisfactory outcome of applying the extrapolation method to the test case: methane has been, that the like pair potential was negative as the pair potentials are supposed to be by the common convention of negative values of attractive forces.

4.4.6 Application of the extrapolation method to other pure gases

Because of the successful application of the extrapolation method to methane, the method was applied to other gases. The gases which all have boiling temperatures lower then 298.15 K are shown in Table 4-10. The triple point temperatures and the boiling points are from Reid et al. (1987).

SOLUTES	name	Triple point (K)	Boiling point (K)
CH_4	methane	90.7	111.6
Ar	argon	83.8	87.3
Ne	neon	24.5	27.1
H_2	hydrogen	14.0	20.3
N_2	nitrogen	63.3	77.4
O_2	oxygen	54.4	90.2
CO	carbon monoxide	68.1	81.7
C_2H_4	ethylene	104.0	169.3

Table 4-10. A list of solutes with boiling points below 298.15 K.

4.4.7 Results of application of the extrapolation method

The extrapolation method was thus applied to the gases in Table 4-10. Tables in Appendix 8 show the results of the equilibrium separation and the corresponding like pair potential below the gases critical temperatures. Figures A8.1 to A8.7 (Appendix 8) show the graphs for the equilibrium separation as a function of temperature in the chosen temperature interval (the triple point to the boiling point).

Table 4-11 shows the intermolecular distance results of applying the extrapolation method.

	heat of vaporization		molar volume	
compound	**R^A (Å)**	**$\Phi_{ii}*10^{19}$ (J)**	**R^A (Å)**	**$\Phi_{ii}*10^{19}$ (J)**
methane	4.99829	-0.008062	5.173	-0.006385
argon	4.784437	-0.004246	5.03754	-0.003117
neon	6.936966	-0.000036	6.101046	-0.000078
hydrogen	10.97063	-0.000006	7.81744	-0.000044
nitrogen	5.32727	-0.002478	5.76097	-0.001535
oxygen	4.423303	-0.005466	4.883527	-0.002930
carbon monoxide	5.222174	-0.003126	5.62584	-0.001974
ethylene	5.029482	-0.024069	5.187144	-0.018977

Table 4-11. Equilibrium separations and the like pair potentials for low-boiling gases at 298.15 K calculated by the extrapolation method.

It is worth noticing that even for neon and hydrogen which both have very low critical temperature, the like pair potentials are negative.

Table 4-11 also shows that there is a difference in the values obtained by the two different options. When employing the AGAPE equations to predict VLE data, the heat of vaporization method has been preferred. Appendix 13 describes calculations of the heat of vaporization for eight selected compounds by three different methods. Appendix 14 describes the result of employing the Yen-Woods method for calculating the molar volume beyond the designed temperature range.

The conclusion of the calculations in Appendices 13 and 14 will be made here, as this is relevant to show how well results of calculating the heat of vaporization and the molar volume fit with experimental data. If possible, the values in Table 4-11 calculated by the most accurate of the options will be chosen.

4.4.8 Conclusion of the heat of vaporization and the molar volumes calculations

4.4.8.1 Conclusion of the heat of vaporization calculations

The results (shown in Appendix 13) obtained by the three alternative methods for calculation of the heat of vaporization differ from each other. The results obtained by the method of Daubert and Danner (1984) and Watson's correlation show very little difference from the experimental values. It must be concluded from the figures, that the latent heat of vaporization calculated by the POT method differs significantly from the experimental values of the heat of vaporization and the calculated values obtained by the other two methods.

The difference is even greater than 100% in the worst case. This difference occurs, because the R^A is determined from a prediction method (molar volumes), and the R^A is used in the power of -6. This means the accuracy may be good for the molar volumes, which in fact it is (Yen and Woods, 1966), but the errors increase for the like pair potential, and therefore also for the heat of vaporization.

Homer and Mohammadi (1987b) obtained much better results in their calculations of the heat of vaporization. In the first place, this is because they used experimental molar volumes (at the freezing points) to calculate the latent heat of vaporization. In the second place, they calculated the heat of vaporization at a single temperature (the melting point). Thirdly, they omitted polar compounds and compounds containing hydrogen bondings from their selected compounds. They calculated the heat of vaporization for the compounds: carbon tetrachloride, nitrogen and oxygen, and obtained much better results then obtained here. Essentially, this is because they only calculated ΔH_{vap} at a single temperature, in fact at the temperature, where they had experimental values for R^A. Mohammadi (1986) also calculated the heat of vaporization for benzene at a single temperature, also with good accuracy compared to experimental data. But, for benzene he did not use the equilibrium separation calculated from the molar volume (equation (2.80)). He used a geometric mean separation, which gave a much better result for H_{vap}. Also, Homer and Mohammadi (1987b) presented their results differently. They plotted the calculated heat of vaporization against the experimental value, in which case a deviation is less significant. The conclusion is that the GLP theory does not calculate the latent heat of vaporization with as great accuracy as the other methods, especially not for the polar compounds and for the compounds containing hydrogen bonding.

As a result of the heat of vaporization calculations, it was decided not to include acetic acid in the AGAPE database, mainly because of its strong tendency to form a dimer. The polar and hydrogen bonding containing compounds methanol, ethanol, and acetone were included in the AGAPE database. In the long term, the inclusion of these three compounds together with water, 1-propanol, and 2-propanol is thought to determine a way of including such compounds i.e. by adding a term to take polarity and/or hydrogen bonding effect into account in the GLP theory.

4.4.8.2 Conclusion of the molar volume calculations

Figure A14.1 indicates that the equation for calculating liquid densities by Yen and Woods (1966) can be used to calculate molar volume for pure compounds in their solid state with good accuracy. Figure A14.2 indicates that the Yen-Wood method to calculate the equilibrium separation for the pure compounds in their solid state can be applied with good accuracy.

4.4.8.3 Which method predicts the most accurate results ?

The above conclusions show that each of the options (Watson's correlation for the heat of vaporization and Yen-Woods method for the molar volume) has its limitations, but that they both predict results that are reasonable accurate compared to experimental data. It seems not possible to choose one of the options as better to calculate the equilibrium separation then the other from the above conclusions, and the two options complement each other.

4.4.9 Conclusion of extrapolation method

A method for calculating the like pair potential for, primary, low-boiling gases above their critical temperature by extrapolating the equilibrium separation from the temperature interval, where the density is continuous has been developed. It has not been possible to compare the results with data from the literature, as such data to the best of knowledge are unavailable.

4.5 Relationship between unlike pair potential and solubility- method VDUD

The method described in this section is named VDUD. This indicates that both the solvent (V) and the solute (U) are dependent on temperature (D).

Similar calculations as described under method VNUN were then carried out, but here the equilibrium separations for both the solvents and the solutes at 298.15 K were used.

4.5.1 Calculations of relationship - method VDUD

Calculations of the unlike London pair potential, using the computer program PP mentioned in section 2.11.10, were carried out. The equilibrium separations for each pure solute and for each pure solvent at 298.15 K were used to calculate the unlike London pair potential as given in equation (4.3). The option of screen inputting the values of equilibrium separations was used in this case. The equilibrium separations for the pure solutes at 298.15 K were calculated applying the extrapolation method described in section 4.4. The equilibrium separations for the pure solvents at 298.15 K were calculated from the computer program PP. In this case (pure solvents at 298.15 K) the single component option, the molar volume option and the relevant temperature were input to the program.

Using the extrapolation method to calculate equilibrium separation for the solutes, whose critical temperatures are below the experimental temperature (298.15 K) is a way of testing the extrapolation method. A linear relationship has been found using methods VNUN and VDUN between the logarithm of the experimental solubility and the unlike London pair potential for a series of solutes dissolved in one solvent. If this linear relationship is not found using method VDUD then it could be an indication of failure of the extrapolation method.

It should be noted, that in this case, the unlike London pair potential was intended to be calculated at similar temperatures for the solute and the solvent.

The relevant parameters in the computer programs were as follows:

INPUT

R1	the equilibrium separation for the solute calculated at 298.15 K by applying the extrapolation method
R2	the equilibrium separation for solvent calculated at 298.15 K

The chosen option for the calculation of the R1 and R2 values means, that the P11 and P22 values in this case were calculated from the following option

OUTPUT

P11 - calculated at 298.15 K

P22 - calculated at 298.15 K

The unlike pair potential, P12, was calculated using the two options of combining the two like pair potentials

OUTPUT

P12-GLP - calculated at 298.15 K and using the London theory

P12-GM - calculated at 298.15 K using the Berthelot theory (the geometric mean)

Again, the two parameters: the nearest number of neighbours and the difference between the size in the molecules of component 1 and 2 are not used in this special case where the screen option for the equilibrium separation is chosen.

Choosing among the options

Again, the question is which options to chose. The like pair potential (in this case the like pair potential for either the pure solvents or for the pure solutes) can be calculated from either the heat of vaporization or the molar volume. The other option is choosing the unlike pair of London pair potentials or the geometric mean. All options are calculated, though every option for all combinations of solute/solvent from Table 4-2 has not been covered. The option: equilibrium separation from the molar volume (at 298.15 K) and the unlike pair potential calculated by the London method has been tested in most detail. The other options have only been tested in a number of cases. The chosen combination of option is shown in Table 4-12.

Combination	**equilibrium separation (all values at 298.15 K)**		**unlike pair potential**	**Calculations**
	solutes	solvents		
1	from molar volume	from molar volume	London	thoroughly
2	from heat of vaporization	from heat of vaporization	geometric mean	a small number of cases
3	from molar volume	from molar volume	London	a small number of cases
4	from heat of vaporization	from heat of vaporization	geometric mean	a small number of cases

Table 4-12. A table of the different options and their combination.

The four different combinations have been chosen, so there is consistency in the options.

	molar volume		**heat of vaporization**	
compound solutes	**R^A (Å)**	**$\Phi_{ii}*10^{19}$ (J)**	**R^A (Å)**	**$\Phi_{ii}*10^{19}$ (J)**
methane	5.173	-0.006385	4.998290	-0.008062
argon	5.0375	-0.003117	4.784437	-0.004246
neon	6.101046	-0.000078	6.936966	-0.000036
hydrogen	7.61744	-0.000044	10.97063	-0.000006
nitrogen	5.76097	-0.001535	5.32727	-0.002478
oxygen	4.88357	-0.002930	4.423303	-0.005466
carbon dioxide	5.182803	-0.007489	4.989505	-0.009652
carbon monoxide	5.62484	-0.001976	5.222174	-0.003126
ethylene	5.187144	-0.018977	5.029482	-0.024069
ethane	6.0558	-0.008562	6.138064	-0.007760
n-propane	5.926528	-0.029806	5.789507	-0.036630
n-butane	6.112082	-0.058990	6.146469	-0.055632
compound solvents	**R^A (Å)**	**$\Phi_{ii}*10^{19}$ (J)**	**R^A (Å)**	**$\Phi_{ii}*10^{19}$ (J)**
benzene	5.90631	-0.123816	6.036324	-0.0941
cyclo-hexane	6.284148	-0.098488	6.325035	-0.091765
carbon tetrachloride	6.04657	-0.075741	5.920835	-0.091008
carbon disulfide	5.245798	-0.092490	5.375406	-0.075917
water	3.427886	-0.030407	2.85615	-0.127049
chloroform	5.900903	-0.053716	5.571801	-0.088039
methanol	4.471602	-0.047341	4.103010	-0.107612
ethanol	5.024571	-0.132554	5.052042	-0.122746
1-propanol	5.497517	-0.204653	5.710862	-0.136980

Table 4-13. The equilibrium separations used and the calculated like pair potentials for the different solutes and solvents.

Table 4-13 shows the relevant equilibrium separations that are used to calculate the like London pair potential (equation (4.3)), which is shown in column three and five depending on whether the equilibrium separation is derived from the molar volume option (column two) or the heat of vaporization option (column four).

The results of the computer calculations carried out are shown in tables in Appendix 9. The two ways to analyse to calculated results have been employed. The calculated values of the unlike London pair potential for the mixtures can be plotted versus the base 10 logarithm of the experimental solubilities (x_{solute}) at 298.15 K and 101.325 kPa for a series of solutes dissolved in a single solvent, or the other way is to consider a single solute dissolved in a series of solvents. The experimental solubilities were obtained from either the IUPAC Solubility Data Series (Clever, 1979 (vol. 1), Clever, 1980 (vol. 4), Young, 1981 (vol. 5/6), Battino, 1981 (vol. 7), Hayduk, 1982 (vol. 9), Battino, 1982 (vol. 10), Hayduk, 1986 (vol. 24), and Clever and Young, 1987 (vol. 27/28)) or Fogg and Gerrard (1991).

Typical examples of both the types are shown below. Figure 4.10 for carbon disulfide (molar volume option) and Figure 4.11 for methanol (molar volume option) show the plots for a series of solutes dissolved in a single solvent. Figure 4.12 shows the plot for two solvents, carbon tetrachloride and benzene. Figure 4.13 for argon and methane represents a typical example of the plot for a single solute dissolved in a series of solvents.

The following Table 4-14 shows the results of the plots. The first column shows the name of the solvent, the second column the origin of the equilibrium separation for the solvent (the value is shown in Table 4-13), then follows the name of the solute and the origin of the equilibrium separation for the solute, the fourth column displays which combining rule is used to calculate the unlike pair potential, either the London combining rule or the geometric mean. The last column shows the figure number (A refers to appendix) and the resulting linear correlation coefficient of the plot. The closer the linear regression correlation coefficient is to unity, the better the points lie close to a straight line.

Solvents	**equilibrium separation (298.15 K)**	**solutes**	**equilibrium separation (298.15 K)**	**unlike pair potential**	**Figure no. and linear regression coefficient**
benzene	from molar volume	Table 4-2	from molar volume	London	Figure A9.1 0.8772
cyclo-hexane	from molar volume	Table 4-2	from molar volume	London	Figure A9.3 0.9233
carbon tetrachloride	from molar volume	Table 4-2	from molar volume	London	Figure A9.2 0.9319
carbon disulfide	from molar volume	Table 4-2	from molar volume	London	Figure 4.10 0.9105
water	from molar volume	Table 4-2	from molar volume	London	Figure A9.5 0.0491
chloroform	from molar volume	Table 4-2	from molar volume	London	Figure A9.4 0.9038
methanol	from molar volume	Table 4-2	from molar volume	London	Figure 4.11 0.8735
ethanol	from molar volume	Table 4-2	from molar volume	London	Figure A9.6 0.8690
1-propanol	from molar volume	Table 4-2	from molar volume	London	Figure A9.7 0.8138
methanol	from molar volume	Table 4-2	from molar volume	geometric mean	Figure 4.11 0.8818
ethanol	from molar volume	Table 4-2	from molar volume	geometric mean	Figure A9.6 0.9075
1-propanol	from molar volume	Table 4-2	from molar volume	geometric mean	Figure A9.7 0.7894
benzene	from molar volume	Table 4-2	from molar volume	geometric mean	Figure A9.1 0.8861
carbon tetrachloride	from molar volume	Table 4-2	from molar volume	geometric mean	Figure A9.2 0.9261

Table 4-14. List of results, method VDUD including figure numbers (continued over).

Solvents	equilibrium separation (298.15 K)	solutes	equilibrium separation (298.15 K)	unlike pair potential	Figure no. and linear regression coefficient
benzene	from heat of vaporization	Table 4-2	from heat of vaporization	London	Figure A9.10 0.8454
carbon tetrachloride	from heat of vaporization	Table 4-2	from heat of vaporization	London	Figure A9.11 0.8909
ethanol	from heat of vaporization	Table 4-2	from heat of vaporization	London	Figure A9.12 0.8943
benzene	from heat of vaporization	Table 4-2	from heat of vaporization	geometric mean	Figure A9.10 0.8414
carbon tetrachloride	from heat of vaporization	Table 4-2	from heat of vaporization	geometric mean	Figure A9.11 0.9
ethanol	from heat of vaporization	Table 4-2	from heat of vaporization	geometric mean	Figure A9.12 0.8742
Table 4-2	from molar volume	n-propane	from molar volume	London	Figure A9.15 0.7812
Table 4-2	from molar volume	hydrogen	from molar volume	London	Figure A9.17 0.4602
Table 4-2	from molar volume	argon	from molar volume	London	Figure A9.14 0.5002
Table 4-2	from molar volume	methane	from molar volume	London	Figure A9.13 0.6268
Table 4-2	from molar volume	carbon dioxide	from molar volume	London	Figure A9.16 0.0669
Table 4-2	from molar volume	nitrogen	from molar volume	London	Figure A9.18 0.5187
Table 4-2	from molar volume	oxygen	from molar volume	London	Figure A9.19 0.5382
Table 4-2	from molar volume	carbon monoxide	from molar volume	London	Figure A9.20 0.6302

Table 4-14. List of results, method VDUD including figure numbers (continued over).

Solvents	**equilibrium separation (298.15 K)**	**solutes**	**equilibrium separation (298.15 K)**	**unlike pair potential**	**Figure no. and linear regression coefficient**
Table 4-2	from molar volume	ethane	from molar volume	London	Figure A9.21 0.8094
Table 4-2	from molar volume	n-butane	from molar volume	London	Figure A9.22 0.6689
methanol	from molar volume	Table 4-2	from molar volume	interchange energy (London)	Figure A9.9 0.8934
ethanol	from molar volume	Table 4-2	from molar volume	interchange energy (London)	Figure A9.8 0.9186
Table 4-2	from molar volume	methane	from molar volume	interchange energy (London)	Figure 4.14 0.1998
Table 4-2	from molar volume	n-propane	from molar volume	interchange energy (London)	Figure 4.16 0.0843
Table 4-2	from molar volume	n-propane	from molar volume	interchange energy (geometric mean)	Figure 4.16 0.31116
Table 4-2	from heat of vaporization	n-propane	from heat of vaporization	interchange energy (London)	Figure 4.15 0.7928
Table 4-2	from heat of vaporization	n-propane	from molar volume	interchange energy (geometric mean)	Figure 4.15 0.5413

Table 4-14. List of results, method VDUD including figure numbers (continued over).

Solvents	**equilibrium separation (298.15 K)**	**solutes**	**equilibrium separation (298.15 K)**	**unlike pair potential**	**Figure no. and linear regression coefficient**
Table 4-2	from heat of vaporization	carbon dioxide	from heat of vaporization	interchange energy (London)	Figure 4.17 0.1402
Table 4-2	from heat of vaporization	carbon dioxide	from heat of vaporization	interchange energy (geometric mean)	Figure 4.17 0.1147

Table 4-14. List of results, method VDUD including figure numbers.

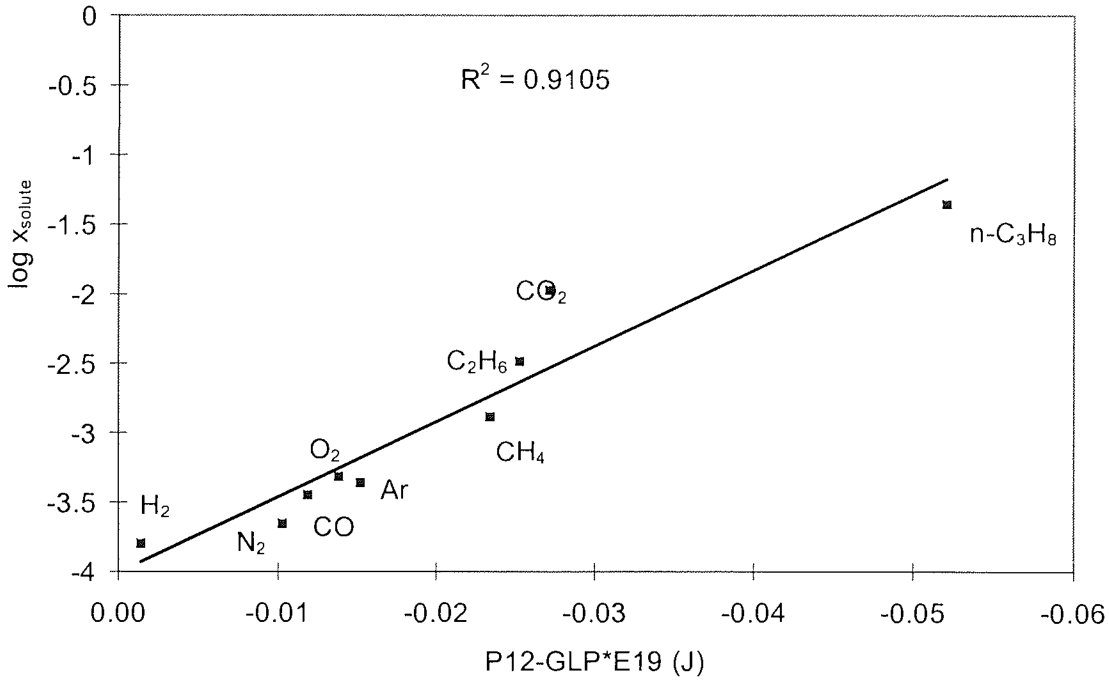


Figure 4.10. Solubilities of gases in **carbon disulfide** at 298.15 K, 101.325 kPa as a function of the generalized unlike London pair potential (P12-GLP) calculated by method VDUD.

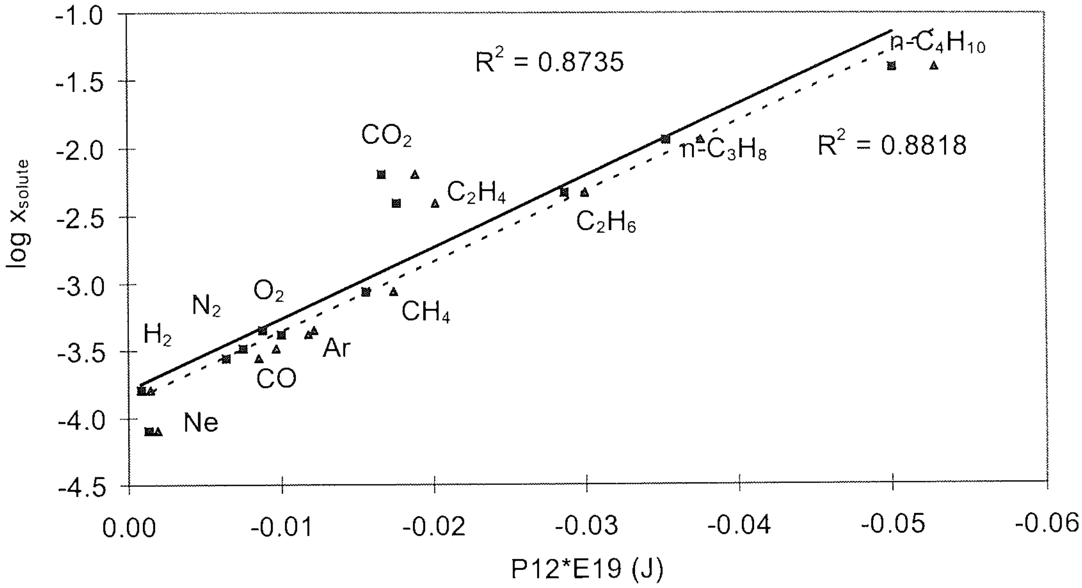


Figure 4.11. Solubilities of gases in **methanol** at 298.15 K, 101.325 kPa as a function of the generalized unlike London pair potential (P12-GLP, ■ points and – line) and the geometric mean unlike pair potential (P12-GM, ▲ points and -- line) calculated by method VDUD.

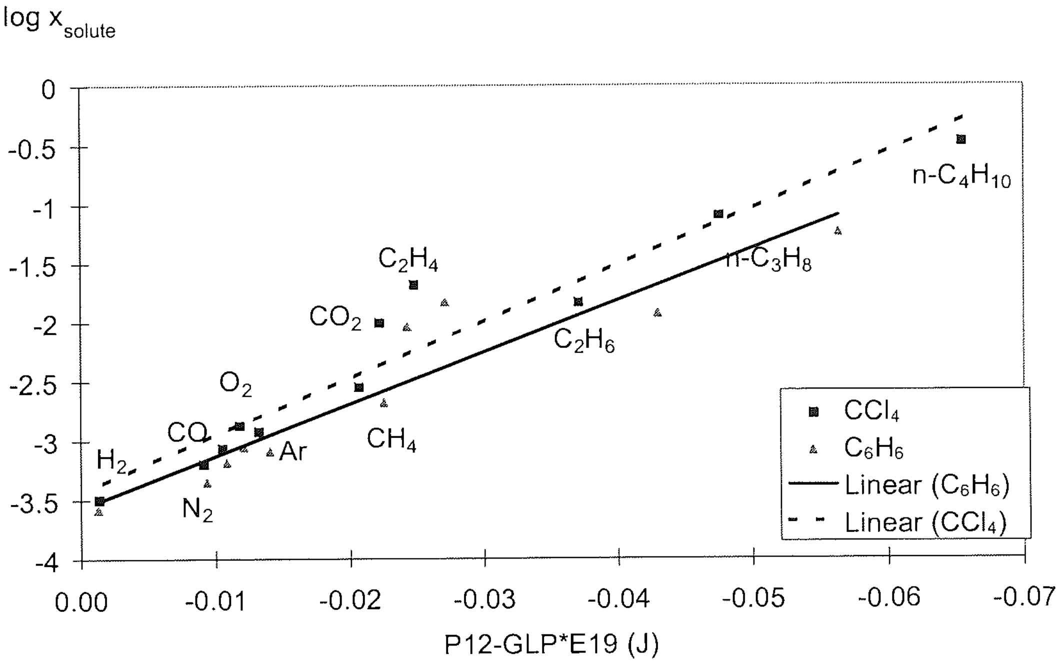


Figure 4.12. Solubilities of gases in **benzene** (▲points and – line) and **carbon tetrachloride** (■points and -- line) at 298.15 K, 101.325 kPa as a function of

the generalized unlike London pair potential (P12-GLP) calculated by method VDUD.

This Figure is a combination of Figures A9.1 and A9.2.

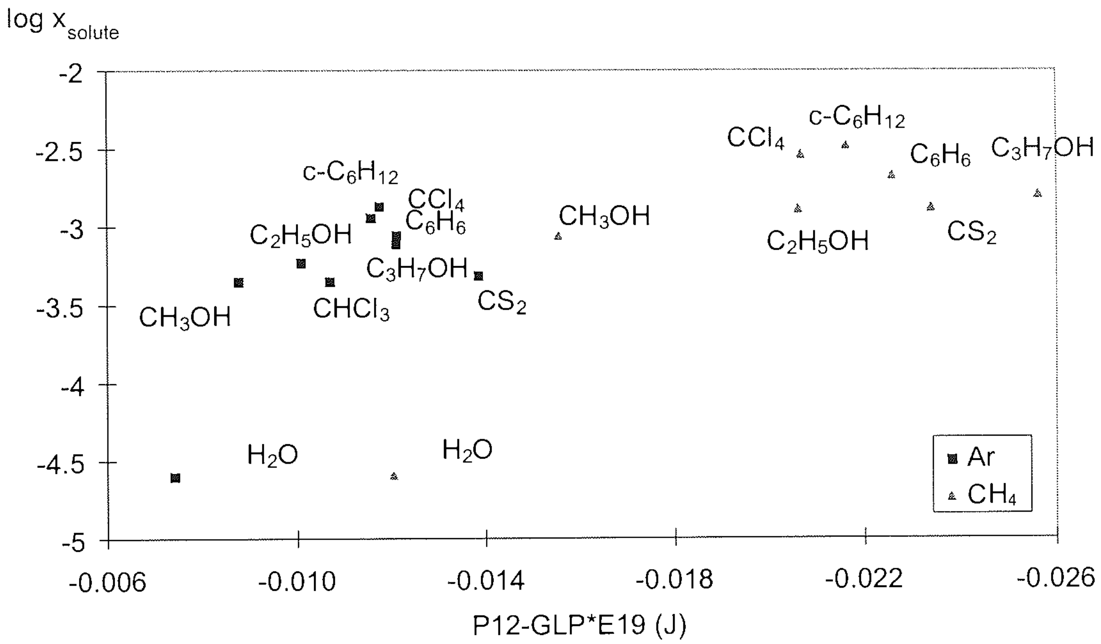


Figure 4.13. Solubilities of **methane** (▲) and **argon** (■) in solvents at 298.15 K, 101.325 kPa as a function of the generalized unlike London pair potential (P12-GLP) calculated by method VDUD.

This Figure is a combination of Figures A9.13 and A9.14.

4.5.2 Correlation between temperature and pair potential

There is no need to investigate the correlation between temperature and the pair potential for method VNUN, as all the pair potentials are calculated from one single temperature. As the method VDUN does not change very much of the overall results compared with method VNUN, it was not found informative enough to investigate a relationship between the temperature and the pair potential for this method.

The method VDUD described in this section gives quite different results from the previous mentioned methods, and it was found worthwhile to investigate how the unlike pair potential varies with temperature. For this investigation it was decided to use selected gases, with critical temperatures below 350 K and boiling point above 275 K. Three gases were selected:

carbon dioxide
n-propane and
n-butane.

A number of solvents from Table 4-2 was selected as well. The pair potentials were calculated using the PP program with the following parameters:

INPUT	temperature
	the components
	number of nearest neighbours, z = 11
OPTION	heat of vaporization
OUTPUT	London pair potential from heat of vaporization
	equilibrium separations from the heat of vaporization

The results of the calculations are shown in Appendix 10 and discussed in section 4.6.

4.5.3 Results of relationship - method VDUD

4.5.3.1 A series of solutes dissolved in a single solvent

Again the linear regression coefficients show a slight improvement resulting in larger values when comparing the results of the VDUD calculations with the outcome of the VDUN calculations, apart from the solvent water.

Figure 4.12 shows the solvents in same sequence as Figure 4.2 and the opposite of Figure 4.6. As the experimental solubilities are the same, this change is due to a significant change in the values of the unlike pair potentials. The sequence and the larger values of the linear regression coefficient indicate that the method VDUD produces the best relationship of the three methods. Thus there is reason to believe that the unlike pair potential must be dependent on temperature.

Water

The linear regression coefficient for water decreases considerably from 0.13 (method VDUN) to 0.05. If, as done in method VNUN the solutes n-propane and n-butane are excluded from the plot, the linear regression coefficient improves to a value of 0.3825 (see Figure A9.5). This value is further improved to 0.4112 when the solute ethylene is excluded from the plot (Figure A9.5). This value is considerably improved from 0.05 to 0.4112, but not nearly as much as the corresponding VNUN values (from 0.1159 to 0.7418). In fact, the results for water seem to indicate that the VDUN method gives the best linear relationship between the unlike pair potential and the logarithm of the solubility for water, when including all the selected solutes. When the solutes n-butane, propane, and ethylene are excluded from the plot, the VNUN method gives the best linear correlation.

4.5.3.2 One single solute dissolved in a series solvents

As opposed to the analysis (VDUD) of a series of solutes dissolved in one single solvent, the analysis of one single solute dissolved in a series of solvents (VDUD) shows remarkable improvements in the values of the linear regression coefficients. In fact, the linear regression coefficients increase so much in values that the results were rechecked twice, as such an improvement was hard to believe.

Figure 4.13 shows a very different sequence of the solvents compared to Figure 4.7. The solvent water is now the first solvent (the highest value of the unlike pair potentials), then follows methanol for both solutes (in this case argon and methane). The rest of the solvents appear in different sequence for the two solutes. Carbon disulfide has the lowest value of the unlike pair potential when looking at the solute argon, whereas, in the case of methane, the solvent with the lowest pair potential value is 1-propanol, the same solvent as in the VNUN case.

Compared to the sequence in Figure 4.2, the sequence in Figure 4.13 follows the same sequence for the three solvents: carbon disulfide, benzene, and carbon tetrachloride with the lowest values of the unlike pair potentials for the solvent carbon disulfide.

4.5.4 Interchange energy

The interchange energy, w′ was defined in the description of the lattice theory as

$$w' \equiv z\,[\Phi_{12} - \frac{1}{2}(\Phi_{11} + \Phi_{22})] \qquad (2.53)$$

and is therefore related to the London pair potential. Employing the regular solution theory as developed by Guggenheim (1952), Henry's constant is a function of the interchange energy (section 3.3.2.2).

For a number of mixtures, the interchange energy has been calculated. One of the figures is shown below (for methane).

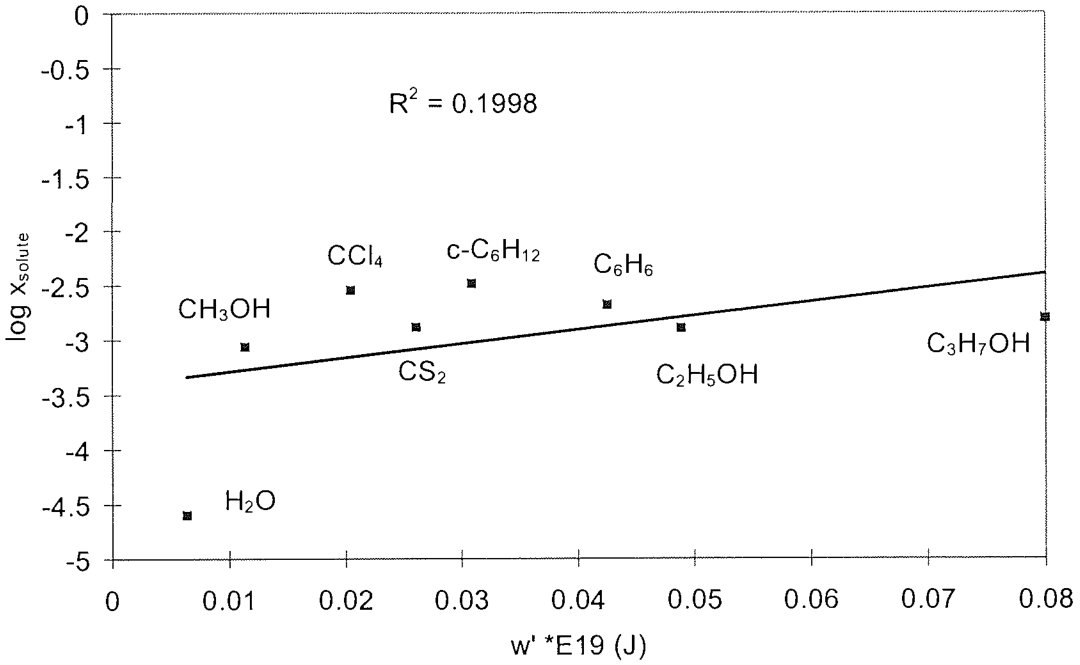


Figure 4.14. Solubilities of gases in **methane** at 298.15 K, 101.325 kPa as a function of the interchange energy (w′) calculated by method VDUD using the GLP.

When looking at the order of magnitude for the unlike pair potentials, the order is very small. The values of the unlike pair potential do not vary very much for the mixtures. By using the interchange energy instead of, it was hoped to obtain a larger order of magnitude. The aim was also to find out, whether the interchange energy could produce a regularity as shown in Figure 4.2 because of its relation to the pair potential. The objective was to use calculate Henry's constant from the interchange energy, in case of a regularity similar to Figure 4.2.

As can be seen from Figure 4.14, the order of magnitude has increased. Four interchange energy graphs have been produced: methanol and ethanol as examples of a series of solutes dissolved in a single solvent and propane and methane as examples of a single solute dissolved in a series of solvents.

The results for ethanol and methanol show an increased value of the linear regression coefficients. The value for ethanol goes from 0.9075 to 0.9186. The opposite is the case for methane and propane. The regression coefficient for methane falls from 0.6268 to 0.1998, whereas propane falls from 0.7812 down to 0.0843. These results are peculiar, especially seen in the light of the fact that the like pair potential for propane, whose critical temperature is above 298.15 K is calculated by the molar volume. The like pair potential for methane at 298.15 K is calculated by employing the extrapolation method.

The extrapolation method can be regarded as dubious, mainly because the equilibrium separation is not unique at a certain temperature, but the same value of the equilibrium separation can be found at two different temperatures. The above results seem to confirm the correctness in the extrapolation method.

Propane

The interchange energy result for propane initiated a more detailed investigation, where the interchange energy for propane was calculated using both options: the heat of vaporization and the molar volume for the equilibrium separation and both the geometric mean unlike pair potential as well as the generalized unlike London pair potential.

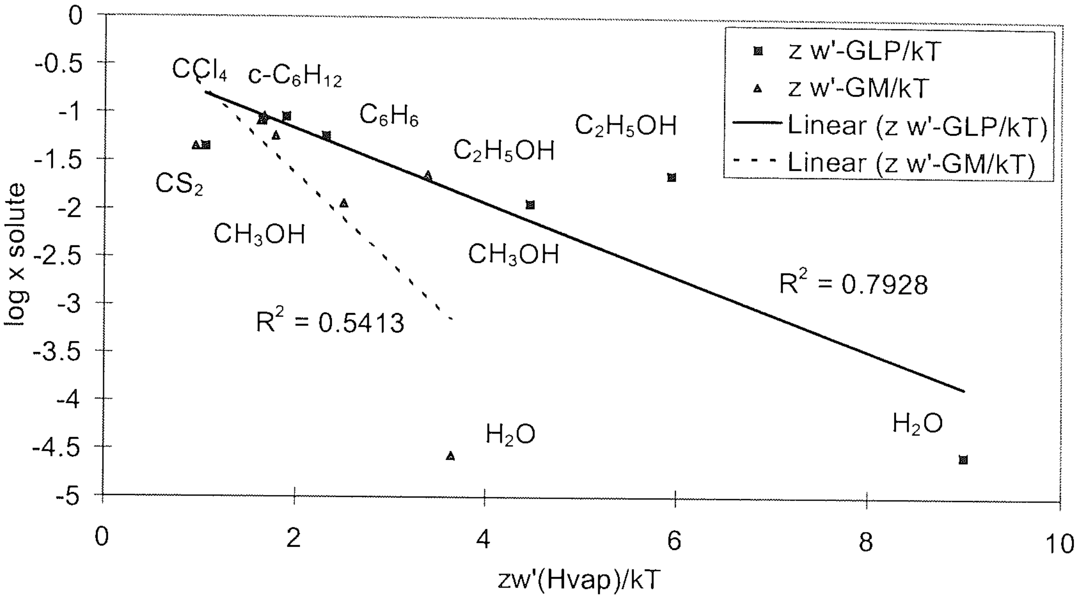


Figure 4.15 Solubilities of gases in **propane** at 298.15 K, 101.325 kPa as a function of the interchange energy (zw′/ k_BT) calculated by method VDUD using the GLP (■ for the points and — for the best fitted line though the points) and the GM (▲ for the points and -- for the best fitted line though the points) options. Both potentials are calculated using the H_{vap} option.

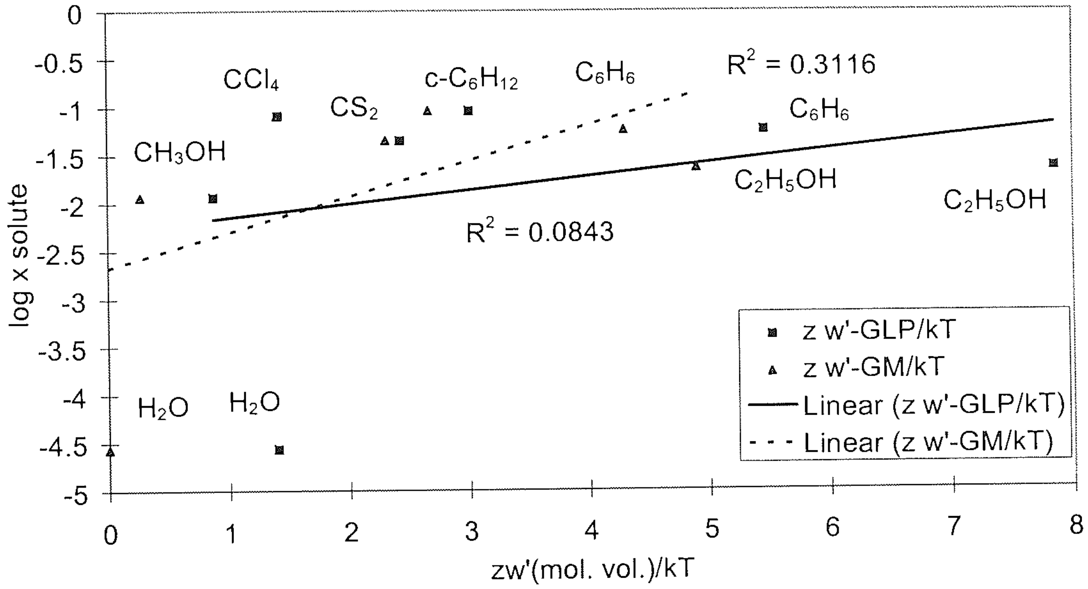


Figure 4.16. Solubilities of gases in **propane** at 298.15 K, 101.325 kPa as a function of the interchange energy (zw'/ k_BT) calculated by method VDUD using the GLP (■ for the points and — for the best fitted line though the points) and the GM (▲ for the points and -- for the best fitted line though the points) options. Both potentials are calculated using the molar volume option.

These results were so intriguing that a similar investigation was carried out for carbon dioxide. Figure 4.17 shows the result.

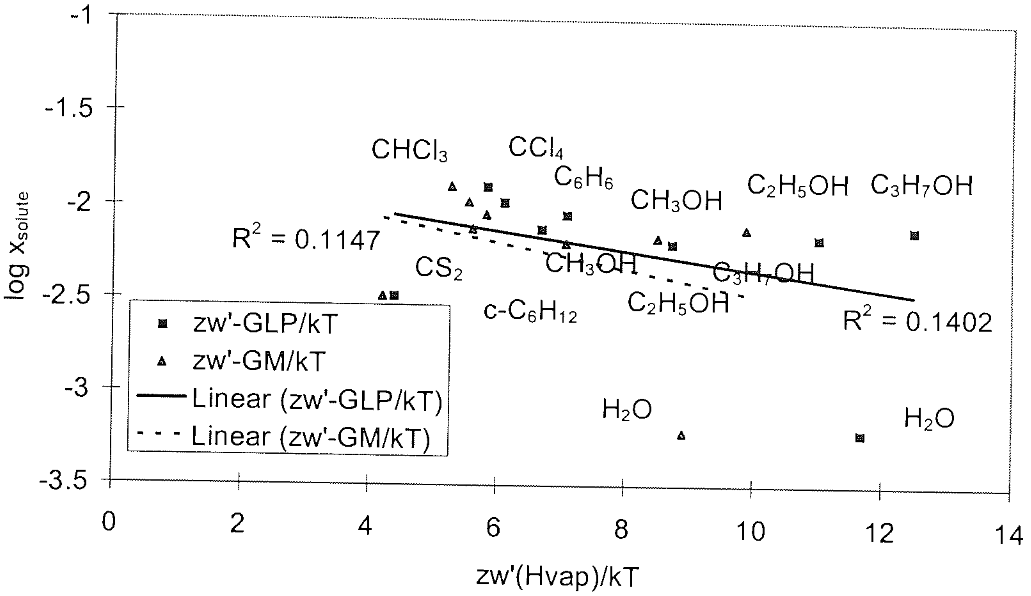


Figure 4.17. Solubilities of gases in **carbon dioxide** at 298.15 K, 101.325 kPa as a function of the interchange energy (zw′/ k_BT) calculated by method VDUD using the GLP (■ for the points and — for the best fitted line though the points) and the GM (▲ for the points and -- for the best fitted line though the points) options. Both potentials are calculated using the heat of vaporization option.

The result for carbon dioxide (where it is not necessary to employ the extrapolation method) shows that the interchange energy calculated from the heat of vaporization option, does not give a particularly good linear regression coefficient. It was only in the case of propane, where the heat of vaporization gave an extraordinary high value of the linear regression coefficient.

Overall, the results of the interchange energy calculation indicate that the interchange energy can not be used as a replacement for the force constant in Figure 4.2 to produce a plot from where it is possible to predict the solubility of gases in liquids.

4.5.5 Conclusion of relationship - method VDUD

Again, a slight improvement in the linear regression coefficients for a series of solutes dissolved in one single solvent was found when employing method VDUD compared to method VDUN.

For one single solute dissolved in a series of solvents, the VDUD method resulted in remarkable improvements of the linear regression coefficients. Still, the regularity of Figure 4.2 was not found. Use of the interchange energy instead of the unlike pair potential did not improve the overall result, but resulted in much decreased linear regression coefficients for the analysis of one single solute dissolved in a series of solvents.

The conclusion of the VDUD calculations is that there definitely is a dependency of the pair potential (whether it is the like or the unlike pair potential) on temperature, and that this dependency has to be taken into account, when calculating the pair potentials.

The results also indicated the correctness of the extrapolation method.

4.5.6 Final discussions of relationship

4.5.6.1 Generally

The aim of the quite detailed work done on the relationship calculations (described in sections 4.2., 4.3, and 4.5) was to be able to produce plots similar to Figures 4.1 to 4.3 (Hildebrand and Scott, 1962). From such plots it would hopefully be possible to determine the solubility of various gases in various liquids. This was not the outcome of the work done. Using the unlike pair of pair potential did give (in many cases) a relatively straight line, but the regularity of the grids in Figures 4.1. 4.2 and 4.3 were impossible to obtain. In the case of Figure 4.2, the force constant (expressed by the Lennard-Jones constants) is constant for a single solute. This is also the case in Figure 4.1 where the solubility parameter for the solvent is used in the plot. This is not the case for the unlike pair potential, as this depends on both the solute and the solvent.

The only way a constant value (independent of the solvents) could have been obtained would have been by using the like pair potential for solutes along the x-axis, instead of the unlike pair potential. This has not been investigated, as the information obtained from such an investigation would contribute very little to this project.

It seems that the majority of time and effort spent on this particular investigation of the relatively simple relationship between the logarithm and the unlike pair potential has given a somewhat disappointing outcome.

4.5.6.2 Temperature dependence

What has been the result of this detailed investigation is information on the temperature dependence of the pair potentials, whether they are like or unlike pair potentials. Mohammadi's (1986) early work on the pair potentials was independent of temperature. The AGAPE equations only take into account the temperature dependence by letting the pair potentials be a function of temperature. The conclusion of the relationship investigation is that there is a temperature dependence of the pair potentials and that the dependence can not be neglected, even in the case, where one of the compounds in a binary mixture is present in excessive amounts. This is opposed to the feature of the regular solution theory where the London dispersion forces are taken into account assuming the London pair potential is independent of temperature (Hildebrand and Scott, 1962).

The reason why the VNUN calculations were carried out was mainly to investigate this assumption of the regular solution theory and also because Mohammadi (1986) had been able to obtain a very accurate linear relationship by using a "standard" equilibrium separation at a "standard" temperature.

In the AGAPE equations, the equilibrium separations are dependent of temperature. The calculations carried out in sections 4.2, 4.3 and 4.5 more then verify that using temperature dependent values of the equilibrium separations is the correct thing to do.

Then there is the question of how to determine an accurate value for the equilibrium separation. As the results in section 4.4 (and Appendices 13 and 14) show there is quite a difference in the equilibrium separation values calculated from either the heat of vaporization or the molar volume. Despite these quite large differences, they seem to be less important when applied to potential calculations as can be concluded from the results of the (few) heat of vaporization calculations in sections 4.2, 4.3 and 4.5. The linear regression coefficient is significantly different from the linear regression coefficient in the molar volume cases. The above question cannot be answered with one of the methods, but both methods exist and provide a way of calculating this very important parameter (in the AGAPE theory).

4.5.6.3 Reflections on the VNUN, VDUN, and VDUD methods

For the solvents: benzene and carbon tetrachloride the results of the unlike pair potentials calculated by the methods: VNUN, VDUN, and VDUD have been plotted in one figure for each solvent. Figures 4.18 and 4.19 show the results.

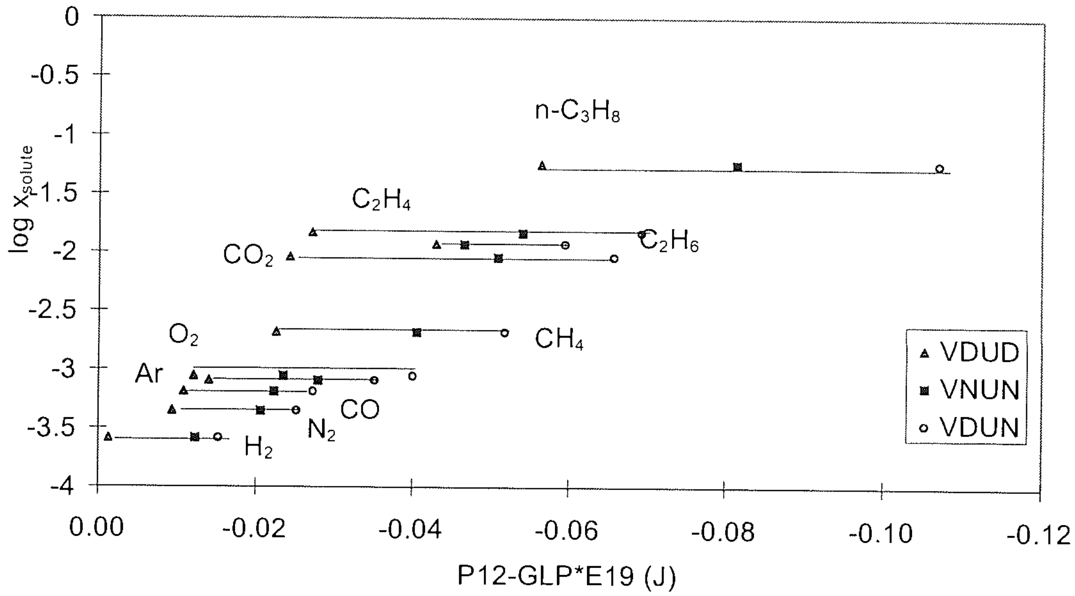


Figure 4.18. Results of calculation by the VNUN (the points marked ■), VDUN (the points marked ●), and VDUD (the points marked ▲) methods for **benzene**.

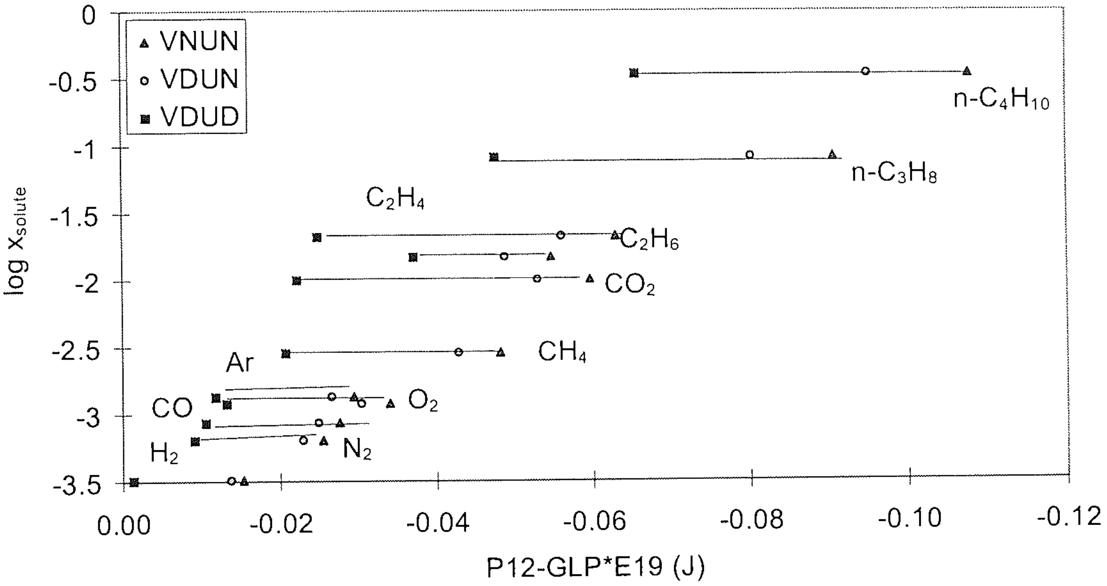


Figure 4.19. Results of calculation by the VNUN (the points marked ▲), VDUN (the points marked ●), and VDUD (the points marked ■) methods for **carbon tetrachloride**.

The figures show that for benzene, the results of method VDUN seem to lie approximately halfway between the results of the VNUN and VDUD methods. This is not the case for carbon tetrachloride, where the results of the VDUN method lie much closer to the results of the VNUN method. This has to do with the VNUN value of the equilibrium separation for benzene. This was taken to be 6.18 Å (Mohammadi, 1986) which is not the value at the freezing point, but the value that Mohammadi found to give the best representation of the ring structure in his calculations. Some mixtures show a much larger difference of the unlike pair potential for the methods VNUN and VDUD compared to other mixtures.

The same conclusions can be made for a single solute dissolved in a series of solvents. For the solute methane the results of the unlike pair potentials calculated by the methods: VNUN, VDUN, and VDUD have been plotted in one figure, Figure 4.20.

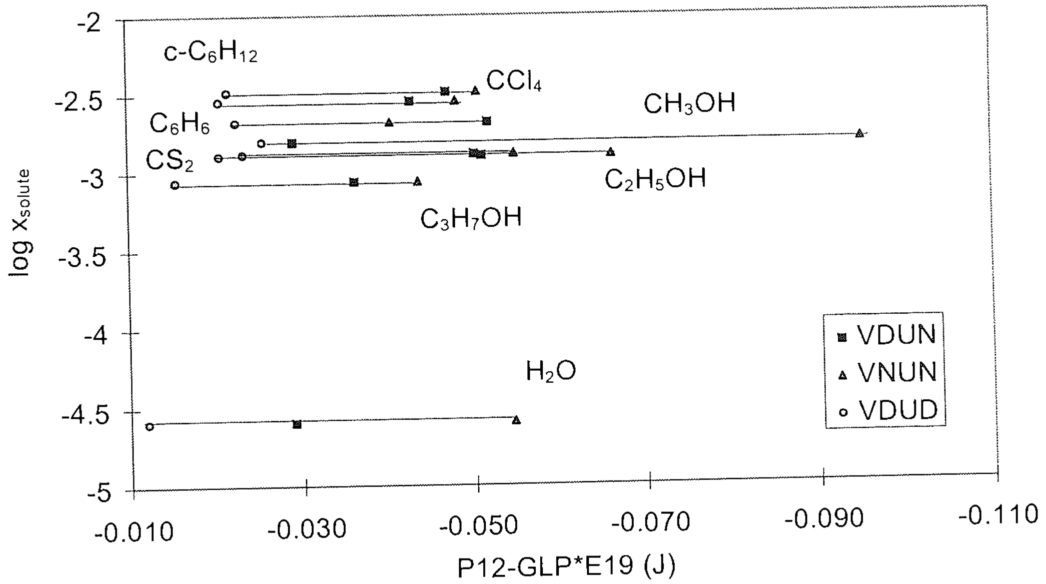


Figure 4.20. Results of calculation by the VNUN (the points marked ▲), VDUN (the points marked ■), and VDUD (the points marked ●) methods for **methane**.

4.5.7 Final conclusions of relationship

4.5.7.1 Generally

The majority of this work seems to have concentrated on this relatively simple relationship between the logarithm of the solubility and the unlike pair potential for the mixture despite the fact that a range of other factors might contribute to the solution process.

There seems to be a need for gaining information of the intermolecular forces. Despite the obvious importance of solubility in biology, medicine, chemistry and chemical engineering the fundamental understanding of gas-liquid equilibria is still in the rudimentary state (Prausnitz et al., 1986).

This investigation has revealed the very important dependence of the logarithm of the solubility not only of the solvent, but also of the solute despite the very low liquid-phase concentration of the solute (solubility) in the majority of the investigated mixtures.

It can be argued that the force constant (ε/k_B) is related to the ideal solubilities and that Figure 4.2 shows a re-statement of the extrapolated Raoult's law which lead to ideal solubility. The vapour pressures P^{sat} close to the critical temperatures are given as a function of the critical temperatures, $\ln(P^{sat}) = f(T/T_C)$ according to Guggenheim (1952). If this "equates" to fugacities above the critical point then the ideal solubilities are a function of the critical temperature and hence of the force constant.

The regular solution theory does not provide a better description of the differences in the solubilities with temperature or with the solvent then Raoult's law. The regular solution theory offers no clear molecular interpretation of the change from negative temperature dependence of solubility of the larger less volatile solutes to the positive dependence of light gases (see Prausnitz et al., 1986), even though the change is explained in thermodynamic terms.

One example of thermodynamic compensation can be found in the study of binary liquid-liquid mixtures, where the excess free energies are much closer to simple regular solution behaviour then the constituent enthalpy and entropy factors, making simple analysis of excess free energies possible.

In dilute solutions appropriate to the study of gas-liquid solubilities the solution process is dictated by the differential or the partial molar properties of the solute, since the solute is relatively unaffected by the solution process. Bell (1937) and Butler (1937) showed that for non-polar dilute solutions the solute enthalpy and entropy changes are related in a linear way. Butler (1946) has further suggested that there is a single relationship connecting the heats and entropies of vaporization from solutions and pure unassociated liquids at 298.15 K.

This indicates that it might be believed that gas solubilities do depend mainly upon the temperature dependent molecular potential energy terms which determine the differential enthalpy of solution. These terms involve the formation of a cavity in the solvent as well as equilibrium attraction. The cavity-forming enthalpy must involve a parameter of the solvent which could be related to its own potential energy coupled with that of solute molecules.

In the achievement of a precise definition of the unlike intermolecular pair potential Φ_{12} to offer a basis for establishing a simple correlation, perhaps an important step is setting up a perturbation or computer simulation analysis of solubility.

At present a number of more elaborate models have significant predictive short-coming arising from the inadequacies of their mixing rules or the limitations of their "interaction potentials" which lead to the need to ascribe large "combining rule" correlations for the geometric mean or Berthelot combining rule approximation in their explanation of solubility sequences in homologous series or in describing the influence of temperature on solubility (Sadus and Young, 1991). By employing a well structured combining rule, based on London's dispersion general principles, it might be possible to approach the problem from the other end. In fact, the detailed calculations carried out for molecules of quite different shapes such as nitrogen or argon and benzene or carbon tetrachloride showed that the unlike potential calculated from the GLP method (P_{12}-GLP) was significantly different from the unlike potential from the Berthelot equation (P_{12}-GM). However, it is possible that there may be an element of mathematical artifact in these calculations because the summed atom-atom potentials created from inert gas atomic structures may over represent the solid angle effects in a bonded structure, whereas the bonded atoms do not "see" the whole 360° (Walsh et al., 1991). This artifact can give smaller values for the unlike London pair potential then expected though it virtually disappears when larger molecules such as ethane or n-propane are involved in the calculations.

One significant finding of this study is that by adopting temperature dependent parameters for both the solute and the solvent (employing extrapolation techniques where necessary) a much better statistical correlation between the logarithm of the solubility and the unlike potential was obtained. This result is consistent with the basis of temperature dependent energy (potential) parameters which the AGAPE model has been developed in its main use in vapour-liquid equilibrium studies of binary liquid mixtures.

The collection of solubility data in Appendix 3 shows the large deviation between the high solubility of gases in hydrocarbons and their low solubility in water. Solubility of gases in perfluorinated hydrocarbons (see Figure 4.2) are of even higher values then in hydrocarbons. This large deviation would not be very sensitively reflected by the unlike pair potential values which change by a factor of not more then 2. Despite a good correlation of solubility for solutes and a broad correlation for solvents with the unlike pair potential, the quantitative links are not good enough for prediction. The relationship does however point the way to a progressive development (see final conclusions).

The treatment of introducing a "liquid-like" potential for gases like nitrogen, argon and hydrogen has been used before in the attempts of developing the methods of regular solution theory to provide more understanding of the solubility relations. Guggenheim's treatment (1952, see also section 3.3.2.2) is an example of that.

4.6 Use of activity coefficient (lattice) models to develop better mixing rules

One of the first approaches in the investigation of the AGAPE method and its application to solubility calculations was to employ the AGAPE equations without any change to predict solubility of gases in liquids. This section describes this approach.

4.6.1 Use of the AGAPE equations to predict solubility

In adapting the AGAPE method to predict the solubility of gases in liquids the AGAPE equations were used (equations (2.93) and (2.94)) without modifications to predict the solubility of gases in liquids. The aim of this approach was to see how far the existing AGAPE model could accommodate the solubility predictions.

4.6.2 Selection of mixtures

As explained in section 2.11, one of the limitations of the AGAPE model is that the temperature has to be below the critical temperature of each component, as neither the heat of vaporization nor the molar volume has a value above the critical temperature. The vast majority of experimental solubility data available in the literature is measured at 298.15 K. This meant that low-boiling gases like methane, argon and nitrogen could not be included in this calculation. The solutes to be used in this calculation were then selected from the following criteria. They should be present in the existing AGAPE database, they should have a boiling point at about 270 K and a critical temperature about 350 K. The existing AGAPE theory could then be applied directly to these gases.

Table 4-15 shows the gases that were selected.

GAS	**T boiling (K)**	**T critical (K)**
C_3H_8, propane	231.1	369.8
n-C_4H_{10}, n-butane	272.7	425.2
$C(CH_3)_4$, neopentane	282.6	433.8
CO_2, carbon dioxide	194.7 *	304.5

Table 4-15. The gases that were selected for this specific investigation.

The boiling point of carbon dioxide is at 520 kPa as indicated by the star.

It was not possible to find experimental data for binary mixtures containing neopentane, so this solute was actually not included in the calculations.

4.6.3 The selected mixtures

The next step was to choose some solvents. They were chosen from the availability of experimental solubility data at various temperatures. No experimental data for the vapour phase were available. The actual chosen solvents are all included in the present AGAPE database.

The solvents were: benzene
cyclo-hexane
n-hexane
methanol
ethanol
carbon tetrachloride

carbon disulphide.

4.6.4 AGAPE calculations

The computer program VLE (described in section 2.11.10) was chosen for the predictions of the solubility. This program is able to perform either isothermal or isobaric calculations. Both options were used in this work. The other parameters were as follows

ISOTHERMAL CASE. The input parameters were

INPUT	temperature
	the components
	the liquid mole fractions
	number of nearest neighbours, z = 11
	r as the molar volume ratio
OPTION	heat of vaporization
	isothermal calculations
	London potentials from heat of vaporization
OUTPUT	the vapour mole fractions
	the total pressure
	the activity coefficients
	the natural logarithm of the activity coefficients

ISOBARIC CASE. The input parameters were

INPUT	the total pressure
	the components
	the liquid mole fractions
	number of nearest neighbours, z = 11
	r as the molar volume ratio
OPTION	heat of vaporization
	isobaric calculations
	London potentials from heat of vaporization
OUTPUT	the vapour mole fractions
	the temperature

the activity coefficients
the natural logarithm of the activity coefficients

4.6.5 The results of the AGAPE calculations

The results of the employed calculations are shown in Tables A10-1 (isobaric case) and A10-2 (isothermal case) (both tables in Appendix 10) where the equilibrium separation and the pair potentials are included besides the predicted temperature (isobaric case) at the predicted total pressure (isothermal case). Tables A11-2 and A11-3 (Appendix 11) show the predicted temperature (isobaric case) or the total pressure (isothermal case) together with the other predicted data, e.g. activity coefficients and vapour mole fractions for both the solvent and the solute.

The experimental data were:

the components
the liquid phase mole fractions (solubility of the solute)
the temperature
the partial pressure of the solute

This illustrates the difference between vapour-liquid equilibrium and solubility of gases in liquids, which is a gas-liquid equilibrium. The vapour phase mole fractions and the activity coefficients are not important in measurements of solubility of gases in liquids. It also illustrates the difficulty in employing vapour-liquid phase predictions to predict solubilities of gases in liquids. The results of the predictions are difficult to compare with experimental data, as one is only able to compare ONE of the outputs with the experimental data. This is either the pressure (isothermal case) or the temperature (isobaric case). Even this causes problems in the isothermal case, because the predicted data is the total pressure, whereas the experimental data is the partial pressure of the solute. This is due to the way the measurements are carried out, where the solute is usually at atmospheric pressure, and very easily kept at this pressure throughout the measurements.

Comparing only one single value for one datapoint for each individual mixture out of 7 predicted results was not satisfying. To obtain more data to compare the AGAPE predicted results with, it was decided to employ other (mainly in-house) prediction methods to the same mixtures.

The missing experimental vapour phase data and the activity coefficients could be calculated under the assumption of infinite dilution interpreted as the activity coefficient of the solvent was equal to unity (assuming ideal behaviour, in other words obeying Raoult's law). This will be described later in this section.

4.6.6 Discussion of the AGAPE solubility predictions

4.6.6.1 Temperature dependence

The unlike London pair potential and the temperature were both plotted as a function of the logarithm of the solubility.

The graphs (Figures 4.21, A10.1 to A10.7) show that there is a linear relationship between the logarithm of the solubility and the temperature. The unlike pair of potentials do not show a similar linear relationship. If the unlike pair of potential was calculated by the method VNUN, it would have been a line parallel to the x-axis.

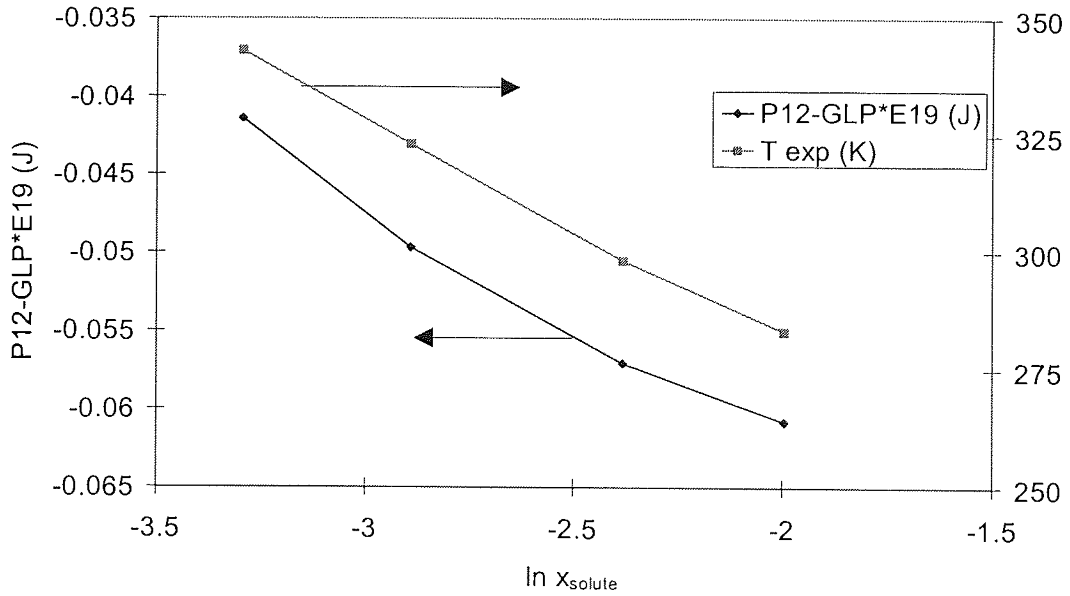


Figure 4.21. Temperature and unlike London pair potentials as a function of the natural logarithm of the solubility for n-propane (1) and *cyclo*-hexane (2).

The linear relationship between temperature and the logarithm of the solubility has been shown by Hayduk and co-workers (Hayduk and Laudie (1973), Hayduk and Buckley (1971), and Fleury and Hayduk (1975)) who found a linear correlation between the solubility and the logarithm of the temperature for a number of gases dissolved in various solvents. The linear relationship is a consequence of applying the regular solution theory since the slope of the logarithm mole fraction solubility versus logarithm absolute temperature is directly related to the entropy of solution (Hildebrand et al, 1970).

The following mixtures:

n-propane - *cyclo*-hexane
n-propane - benzene
n-propane - carbon disulphide
n-propane - carbon tetrachloride
carbon dioxide - n-hexane
carbon dioxide - carbon disulphide

can then be considered regular solutions.

Two mixtures do not show a linear relationship between temperature and logarithm of the solubility. Figure A10.1 for n-propane (1) and n-hexane (2) and Figure A10.5 for n-butane (1) and n-hexane (2) show irregular lines for these two mixtures. The fact that both mixtures contain n-hexane could indicate that mixtures including this particular solvent does not behave as regular solutions.

The unlike pair potential does not appear to be a linear function of the logarithm of the solubility for any of the selected mixtures. This eliminates the possibility of applying a similar method as Hayduk and co-workers to predict the solubility from a known value of the unlike pair potential.

4.6.6.2 Solubility predictions

The results of the isobaric and isothermal AGAPE predictions are show in Tables A11-1 and A11-2 together with the percentage error between the experimental value and the predicted value of either temperature or pressure. The predictions agree reasonably with the experimental values with some exemptions. Predictions for mixtures including the solute carbon dioxide show larger deviations from the experimental values then the two other solutes. Predictions of mixtures including the alcohols, methanol and ethanol, also seem to give poorer results then the other solvents.

Mixture	**liquid mole fraction, x_1**	**measured pressure (10^5Pa). All measurements at 298.2 K**	**calculated pressure (10^5Pa) GLP method**
$n\text{-}C_3H_8+CS_2$	0.0446	1.013	1.7043
$n\text{-}C_3H_8+c\text{-}C_6H_{12}$	0.0924	1.013	1.2586
$n\text{-}C_3H_8+CCl_4$	0.0813	1.013	1.1443
$n\text{-}C_4H_{10}+CCl4_4$	0.339	1.013	1.0673
$n\text{-}C_4H_{10}+C_2H_5OH$	0.0815	1.013	0.8247
$CO_2+c\text{-}C_6H_{12}$	0.0o759	1.013	1.5005
CO_2+CS_2	0.00328	1.013	1.555

Table 4-16. Experimental data and predicted results calculated by employing the AGAPE method.

Table 4-16 shows a representative selection of the predicted results.

The result for alcohols is not surprising as the basic London theory is applicable to non-polar compounds without hydrogen bonding. The alcohols are polar and do contain hydrogen bonding, so the result confirms that the London theory should not be applied to such compounds.

The predicted results for mixtures containing CO_2 also seem to be relatively inaccurate compared to experimental data. This is most likely due to the temperature, which in close to the critical temperature of CO_2. The fact that CO_2 forms a quadrupole no doubt also influences the inaccurate prediction results for CO_2.

4.6.7 Conclusion of the AGAPE solubility predictions

In order to examine the full AGAPE-GLP model as a means of calculating detailed solubilities at different temperatures, the straight-forward way was described above. This was employed for volatile solutes below their critical temperatures such as butane, propane, and carbon dioxide. For solutions of low boiling hydrocarbons and for carbon dioxide in various solvents, the results obtained with the programme VLE in hydrocarbon mixtures using the GLP potential values show quite good agreement is obtained, but for carbon dioxide agreement is poor. Thus predictions based on GLP do not seem to be practicable for a range of gases other then non-polar ones.

The logarithm of the solubility shows a linear relationship with the temperature as expected from investigations referred to in the literature. The unlike pair potential does not show an equivalent relationship and that eliminates the possibility of predicting the solubility from the unlike pair potential.

4.6.8 Supplementary calculations on fitting the unlike potential.

However, a systematic method might be possible using *a piori* size ratios and fitted interaction potentials. The use of the AGAPE program VLEF gives values for the unlike potential (Φ_{12}) which are parametric, but having no *ab initio* value, might still be reconciled in some physical model *post hoc.*

The procedure for the calculation is as follows (McCoubrey, 1996): The theoretical value of excess molar volume is used to give a fit parameter Φ_{12}^{FIT} which can be expressed as a multiple of its geometric mean value Φ_{12}-GM = $-(\Phi_{11}\ \Phi_{22})^{1/2}$. Also given are values of γ_{FIT}^{∞} derived with reference to the saturation vapour pressure of the solute. z was kept constant at a value of 11.0 throughout the calculations.

The fitting was not carried out employing the AGAPE-FIT model (described in section 2.11.13), because no values of the excess enthalpy or excess Gibbs free energy was available. The fitting procedure was carried out manually using a trial-and-error method. The criteria for stopping the procedure was that the total pressure was approximately 101.325 kPa, only taken into account the partial pressure of the gas and ignoring the (small) vapour saturation pressure of the solvent.

Inspection of Table 4-17 shows that a lattice model of this type can give a reasonable representation of solutions of propane in CS_2 or C_6H_6 and even a physically proper picture of the known weak interactions of SF_6 with hydrocarbons. It is interesting that that the use of a geometric mean combining rule however appears to give a more reasonable representations of the solutions of inert gases in hydrocarbons than the GLP procedure.

By contrast the solution of CO_2 in CS_2 or n-C_4H_{10} in CH_3OH may represent discrepancies in the combining rule but could equally well be due to inadequacies in the mixing rule for these “polar” molecules.

The reason why the geometric mean pair potential was chosen in this investigation and not the London pair potential is that the ratio of $\Phi_{12}^{FIT}/\Phi_{12}$-GLP for most mixtures was too far out. The calculations in sections 4.2, 4.3, and 4.5 show that indeed, the difference between the unlike pair potential calculated by the London method and the geometric mean unlike pair potential can be very different from each other.

In the evaluation of the manually employed fitted AGAPE model for the system CO_2 - CS_2 it became apparent that the values of Φ_{12} being thrown up for the CO_2 - CS_2 interaction were unreliable. The values were too near to the fast moving part of the heat of vaporization curve, close to the critical temperature (of CO_2). In order to avoid this artificiality a modification of the computer programme was introduced, where input values of Φ_{11} and Φ_{22} can be made manually to the programme.

Mixture solute - solvent	x_{solute}	T (K)	r = (V_{solute} / $V_{solvent}$)	ratio $\Phi_{12}^{FIT}/\Phi_{12}$-GM (at T)	ratio $\Phi_{12}^{FIT}/\Phi_{12}$-GLP	γ_{FIT}^{∞}
C_3H_8 - C_6H_6	0.0813	283.15	1.0	0.95		1.96
C_3H_8 - C_6H_6	0.0581	298.2	1.0	0.96		1.90
C_3H_8 - C_6H_6	0.037	323.15	1.0	1.0		-
C_3H_8 - CS_2	0.146	258.15	0.694	0.94	0.94	3.05
C_3H_8 - CS_2	0.0842	273.15	0.694	0.94		3.06
C_3H_8 - CS_2	0.0446	298.15	0.694	0.97		2.58
C_3H_8 - CS_2	0.0345	308.15	0.694	0.98	0.99	2.24
C_3H_8 - n-C_6H_{14}	0.116	298.2	1.42	1.01		0.91
C_3H_8 - CH_3OH	0.0115	298.2	0.43	0.87		10.0
C_3H_8 - C_2H_5OH	0.0228	298.2	0.61	0.87		5.3
n-C_4H_{10} -n-C_6H_{14}	0.386	298.2	1.30	0.99		1.06
n-C_4H_{10} - CH_3OH	0.0398	298.2	0.43	0.84		12
n-C_4H_{10} - CH_3OH	0.0192	308.2	0.43	0.83		15
n-C_4H_{10} - CH_3OH	0.008075	323.2	0.43	0.82		23
CO_2 - CS_2	0.003785	281.65	1.0416	0.83		6.6
CO_2 - CS_2	0.003538	289.7	1.0416	0.92		4.35
CO_2 - CS_2	0.00328	298.15	1.0416	1.05		3.4
CO_2 - n-C_6H_{14}	0.0126	293.2	2.13	0.93		13
SF_6 - C_6H_6	0.002638	298	0.83	0.82	0.86	12.1
SF_6 - c-C_6H_{12}	0.005419	298	1.0	0.87	0.9	5.4
Xe - CH_3OH	0.00325	270	0.58	1.0	1.68	7.2
Rn - n-C_6H_{14}	0.0737	298	2.0	1.0	1.6	0.81
Rn - C_6H_6	0.392	298	2.5	0.95	1.5	1.64

Table 4-17. Results of fitting the unlike pair potential to experimental data (McCoubrey, 1996)

By examining the relative sizes of the critical temperatures and other comparable references to intermolecular constants, a normalised value of Φ_{11} based on AGAPE for CS_2 - CS_2 was set at -0.08 10^{-19} J/mol and a value of Φ_{22} for CO_2 - CO_2 was chosen to be -0.04 10^{-19} J/mol. Using these values and assuming them to be independent of temperature (a reasonable assumption when the relatively small temperature interval is considered), the following fits were obtained (McCoubrey, 1996).

Mixture solute - solvent	x_{solute}	**T (K)**	$r = (V_{solute} / V_{solvent})$	**ratio** $\Phi_{12}^{FIT}/\Phi_{12}$-**GM(at T)**
CO_2 - CS_2	0.003785	281.65	1.0416	0.88
CO_2 - CS_2	0.003538	289.7	1.0416	0.90
CO_2 - CS_2	0.00328	298.15	1.0416	0.91

Table 4-18. Results of fitting the unlike pair potential for CO_2 - CS_2 to experimental data.

This suggests that the mixing rule is quite capable of dealing with this mixture and that the values of $\Phi_{12}^{FIT}/\Phi_{12}$-GM are indeed a realistic representation of the low values of unlike pair interaction relative to the Berthelot geometric combining rule probably due to the effect of the large quadrupole moment in CO_2.

Overall the AGAPE model does not appear to explain qualitatively the temperature dependency of solubility, a fact which probably means that its representation of energy changes is inadequate even though it takes into account the Flory-Huggins entropy as required by King et al. (1977a and 1977b).

4.6.9 Scaled particle model

A more comprehensive treatment is provided by the scaled particle treatment by Pierotti (1976). Calculations of the component partial molar free energies for cavity formation (usually taken to be the entropy effect) for propane dissolved in four solvents show the following results. All calculations are done manually using the equations in section 3.3.3 and carried out at 298.15 K (McCoubrey, 1996).

Mixture solute-solvent	solubility at 298.15 K and 101.325 kPa partial pressure	g^C (usually taken to be TS^C) (J/mol)
propane-n-hexane	0.116	-20770
propane-benzene	0.0581	-25560
propane-carbon disulphide	0.0446	-27240
propane-methanol	0.010	-29830

Table 4-19. The end-results of employing the scaled-particle method.

This table indicates that indeed enthalpy effects play a significant part. Experimental data for propane also show that for water in particular entropy effects can become dominant in deciding solubility as the following (manually calculated) small table shows (McCoubrey, 1996).

Mixture, solute - solvent	ΔH (J/mol)	$T\ \Delta S$ (J/mol)
propane - benzene	-16560	-23610
propane - water	-22000	-48000

Table 4-20. Calculated enthalpy and entropy for mixtures of propane dissolved in benzene and water, respectively.

This relatively simple analysis begins to point to the need in a successful model for the inclusion of effects which reflect non-rigid underlying structures which is tantamount to the inclusion of both "repulsive" and attractive effects.

This will be further discussed in the final discussions after a number of predictions of solubilities has been carried out using other prediction methods.

4.6.10 Other prediction methods

A number of methods to predict the solubility exist at the moment and some of them were described in section 3.3. From Sittiosoth's research work (Sittiosoth, 1987) two computer programs using the reference solvent method (section 3.3.1) and the GC-EOS method (section 3.3.5), respectively, were available. Computer programs using the MHV2 method (section 3.3.4) had been obtained from Denmark. To compare the prediction results obtained by using the AGAPE model, the same predictions were performed using the other models mentioned. It was presumed that by employing the reference solvent method developed by Sander et al. (1983) it could be used to investigate more of the basic London theory.

The computer programs were tested using the test examples in the original references. The reference solvent program and the MHV2 program both reproduced the same results as given in the references (Sander et al., 1983 and Dahl et al., 1991, respectively). When testing the GC-EOS program it was found to be impossible to reproduce the data given in Skjold-Jørgensen (1984), that describes the GC-EOS method. A lot of effort and time were spent investigating the problem, before the final conclusion was that the phase rule was not fulfilled. The program uses too many known input parameters. The number of chosen mixtures in Table A11-1, whose solubility could be predicted by the GC-EOS method was very limited, so the method was not employed in this investigation. An extension of compounds included in the GC-EOS database has recently been published (Wolff et al., 1992).

Table A11-1 shows the chosen mixtures, and which methods can be employed to predict solubilities. All the mentioned methods are available as executable programs.

Each method has its limitations. The reference method does not include interaction parameters for propane and n-butane, but was still included in this investigation because it was hoped this specific method could contribute valuable information to the further investigations of the AGAPE calculations. The MHV2 method uses some coefficients to fit the vapour pressure as a function of temperature, and these coefficients are not commercially available for all compounds, so MHV2-predictions of the solubility of gases in the solvents carbon tetrachloride, carbon disulphide and cyclo-hexane are not possible to calculate.

The difference between predictions of vapour-liquid equilibrium and solubility (gas-liquid equilibrium) was outlined in section 4.6.4. The MHV2-method predicts (as the AGAPE method) the vapour-phase composition and the total pressure. Only the reference solvent method predicts the liquid phase mole fractions.

4.6.11 Results of the solubility predictions

4.6.11.1 Calculations

The fact that the computer programs calculate the vapour-phase composition means that the calculations were used backwards. In case of the MHV2 and the AGAPE method the known parameters are the temperature and the liquid phase mole fractions, then the vapour phase mole fractions and the pressure are calculated (isothermal calculations). In the AGAPE program another option is an isobaric calculation, which was used as well. In a solubility prediction, the known parameters are usually temperature and pressure, and then the liquid mole fractions are calculated.

A modification was made to the MHV2 programs obtained, so the modified version calculates and prints the activity coefficients as well.

A spreadsheet with the calculated pressure, vapour mole fractions and activity coefficients was set up, so all the results obtained are in one spreadsheet making it possible to extract the wanted data and present them graphically. Tables A11-1 to A11-4 (in Appendix 11) show the results of the calculations performed.

4.6.11.2 Results

Mixture	liquid mole fraction, x_1	measured pressure (10^5Pa). All measurements at 298.2 K	calculated pressure (10^5Pa) GLP method	calculated pressure (10^5Pa) MHV2 method	calculated pressure (10^5Pa) reference solvent method
$n\text{-}C_3H_8+C_6H_6$	0.0581	1.013	1.0991	1.3618	-
$n\text{-}C_3H_8+n\text{-}C_6H_{14}$	0.116	1.013	1.8712	1.2757	-
$n\text{-}C_4H_{10}+n\text{-}C_6H_{14}$	0.386	1.013	1.0754	1.0801	-
$n\text{-}C_4H_{10}+CH_3OH$	0.0398	1.013	0.7246	1.6009	-
$CO_2+n\text{-}C_6H_{14}$	0.0119	1.013	2.0575	1.1855	1.0846
$CO_2+C_6H_6$	0.00912	1.013	2.7258	1.3415	1.0252

Table 4-21. Experimental data and predicted results from three different methods.

Table 4-21 shows a representative selection of the predicted results.

Figure 4.22 shows the experimental pressure as a function of temperature for the mixture n-propane - benzene. The third variable is the solubility that also varies for each individual T, P data point. The calculated pressures from both the AGAPE method and the MHV2 method are also plotted.

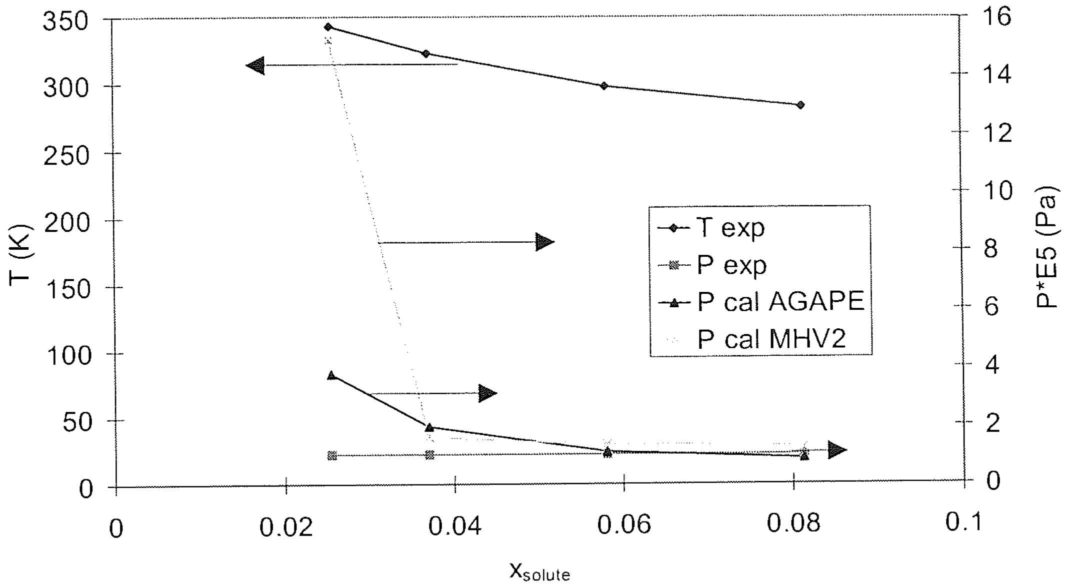


Figure 4.22. The experimental temperature (left y-axis) and experimental pressure and pressures predicted by the AGAPE and MHV2 methods (right y-axis) as a function of the solubility for n-propane (1) and benzene (2).

Figures A11.1 to A11.3 show exactly the same but for the mixture n-propane (1) and n-hexane (2), the mixture n-propane (1) and *cyclo*-hexane (2), and the mixture carbon dioxide (1) and n-hexane (2), respectively.

As it can be seen from the Figures 4.22, A11.1, A11.2, and A11.3 both methods predict a pressure that is very inaccurate compared with the experimental pressure.

Tables A11-2 and A11-4 show that there is a great difference in both the calculated vapour mole fractions and the calculated activity coefficients obtained from the two methods.

4.6.11.3 Experimental results to compare with and assumptions

The first assumption that has been done when comparing the experimental data and the predicted results is assuming that the partial pressure of the solute is equal to the total pressure of the mixture. This assumption is not true, as the partial pressure of the solvent then is assumed to be zero. The total pressure P is equal to the sum of the two components partial pressures

$$P = p_{solute} + p_{solvent}$$

Inserting the vapour mole fractions instead of, the total pressure is equal to

$$P = y_{solute} P + y_{solvent} P$$

Usually, solubility is defined as liquid mole fractions of the solute below 0.1 even though no fixed limit exists (see introduction in Chapter 3). A characteristic of solubility as opposed to vapour-liquid equilibrium is then that the vapour phase mole faction of the solute is assumed to be unity and therefore the total pressure is assumed to be equal to the partial pressure of the solute.

The results in Tables A11-2 to A11-5 show that this is not always the case. However, the need to gain more information from the experimental data made it necessary to make the above (and the following) assumptions. These assumptions are generally accepted as being the solubility assumptions necessary to carry out any work on solubility.

The calculations described above all give the mole fractions of the vapour phase (y-values) as the results of the calculations. These values were not among the experimental data given in the various references. In order to compare the predicted results with experimental data, the activity coefficient of the solvent was assumed to be unity. With this assumption it was then possible to calculate the vapour mole fractions and the activity coefficient for the solute from the experimental values of temperature, pressure, and liquid mole fractions.

Using one of the key equations for vapour-liquid equilibrium, equation (2.25)

$$y_i P = x_i P_i^S \gamma_i \tag{4.13}$$

for the solvent (component 1), it becomes

$$y_1 P = x_1 P_1^S \gamma_1 \tag{4.14}$$

Assuming that the activity coefficient is equal to 1.0, equation (4.14) becomes

$$y_1 P = x_1 P_1^S \tag{4.15}$$

The total pressure P (assumed to be equal to the partial pressure of the solute) and the mole fraction x_1 are known from the experimental data. The saturation vapour pressure P_1^S of the solvent can be calculated, as in the AGAPE computer programs, by an extended Antoine-equation (Reid et al., 1987)

$$\ln\left(\frac{P^S}{P_C}\right) = \left(\frac{1}{1 - \frac{T}{T_C}}\right)\left[A\left(1 - \frac{T}{T_C}\right) + B\left(1 - \frac{T}{T_C}\right)^{1.5}\right] + \left(\frac{1}{1 - \frac{T}{T_C}}\right)\left[C\left(1 - \frac{T}{T_C}\right)^{3} + D\left(1 - \frac{T}{T_C}\right)^{6}\right] \tag{4.16}$$

where the coefficients A, B, C, and D are given in Reid et al. (1987) for the components in the AGAPE database. Equation (4.16) is valid for a single component.

The mole fraction y_1 can then be calculated. The mole fraction of the solute (component 2) in the gas phase is then calculated as

$$y_2 = 1.0 - y_1 \tag{4.17}$$

The activity coefficient of the solute is calculated from

$$\gamma_2 = \frac{y_2 P}{x_2 P_2^S} \tag{4.18}$$

Again, the mole fractions and the total pressure are known, and the saturation pressure is calculated from equation (4.16).

The prediction of solubilities was carried out by employing the AGAPE method, the MHV2 method, and the reference solvent method. These calculations by the AGAPE method can be used as VDUD calculations.

4.6.12 Discussion of the solubility predictions

The results of the AGAPE predictions were showing a reasonable good agreement with the experimental results except for mixtures containing alcohols and carbon dioxide, which compounds are polar and contain hydrogen bonding and therefore are outside the range of the basic London theory.

The MHV2 is reported to give highly accurate prediction results (Dahl et al., 1991), a result which is not obtained in this investigation. The overall results of the MHV2 predictions are in the same order magnitude of accuracy as the AGAPE predictions.

Especially the mixtures of propane(1) and benzene(2) and n-butane(1) and methanol(2) show large deviations from the experimental data.

The MHV2 method combines the UNIFAC group-contribution activity coefficient method with an equation of state. The dominant features stem from the equation of state, a prediction method that research has shown to be more accurate at high pressures (Reid et al., 1987) then at low pressures. In this investigation a compromise has to be made, because neither the reference solvent method nor the AGAPE method is designed to predict phase equilibrium at high pressures as neither method takes vapour phase non-ideality into account.

The experimental pressures are all equal to or below 101.325 kPa. The MHV2 method is not developed to give accurate prediction results at these low pressures as it accounts for vapour phase non-ideality.

The best prediction results appear to be predicted by the reference solvent method. The results for the few mixtures which were included in the database for the reference solvent method show very good agreement with the experimental data. The sparcity of the prediction results make it difficult to conclude that the reference solvent method is the best. For the examined mixtures, the reference solvent method gives the most accurate prediction results, but it must be remembered that the predictions by the reference solvent method are very sparse compared to the AGAPE and the MHV2 methods.

4.6.13 Conclusion of solubility predictions

The prediction results of three different prediction methods of a number of selected mixtures were examined and compared with experimental data. The results show more about the limitations of each method then an overall picture of the best prediction method.

The AGAPE method should not be applied to polar compounds and/or compounds containing hydrogen bonding. When applied to mixtures containing these compounds, the prediction results are, of course, inaccurate compared to the experimental results. For mixtures not containing the above mentioned compounds, the prediction results are in reasonable agreement with the experimental data.

In this work, the MHV2 method is employed to low pressures, where the method is not intended to be employed, so the prediction results are slightly better compared to the AGAPE prediction results, but still only within reasonable accuracy compared to the experimental data.

From this limited investigation, the best prediction method seems to be the reference solvent method, but this could be due to the very limited number of the selected mixtures that this method is able to handle.

The overall conclusion is that from this limited examination where the MHV2 and the AGAPE methods have been employed beyond their limitations, the reference solvent method predicts phase equilibrium data with a good accuracy compared to experimental data.

4.7 Solubility Parameter

4.7.1 Relationship between the solubility parameter and a GLP parameter

The aim of this investigation was to find out whether it was possible to find a relationship between the solubility parameter (δ) as defined by Hildebrand (see section 2.10.3) and a GLP parameter.

This investigation is carried out for mixtures at 298.15 K and at a partial pressure of solute of 101.325 kPa.

The solubility parameter for the solutes and the solvents in Table 4-22 were found in two sources. Most of the solubility parameters (marked 2) were found in Prausnitz et al. (1986). The solubility parameters (marked 3) for the solutes: ethane, propane, and butane and the solvents: water, methanol, ethanol, and 1-propanol are from the DIPPR database (Daubert and Danner, 1994). The Handbook of Physics and Chemistry (1975-1976) warns against the use of the solubility parameter for water and the three alcohols as these compounds are polar and contain hydrogen-bonds, exactly the compounds for which the theory of regular solutions is not valid. Neither Prausnitz et al. (1986) nor Hildebrand and Scott (1962) contain any solubility parameter for these four compounds. Both Daubert and Danner and The Handbook state, that they are calculated using the definition of the solubility parameter given in equation (2.49). The solubility parameter for chloroform (marked 4) was found in Hildebrand and Scott (1962).

It must be remembered that the solubility parameters are calculated from experimental data (Prausnitz and Shair, 1961) and that reliable solubility data for the very light gas: neon are scarce, so no solubility parameter for this solute has been calculated. The solubility parameter for hydrogen is from Prausnitz and Shair (1961) (marked 1).

The following Table 4-22 shows the solubility parameters and the equilibrium separations and the like pair potential calculated at 298.15 K from the two options: the heat of vaporization and the molar volume. The four last columns are identical to Table 4-13.

		molar volume		**heat of vaporization**	
compound solutes	**solubility parameter, δ (J/cm^3)$^{0.5}$**	**R^A (Å)**	**Φ_{ii}*10^{19} (J)**	**R^A (Å)**	**Φ_{ii}*10^{19} (J)**
neon	1)	6.101046	-0.000078	6.936966	-0.000036
hydrogen	6.65$^{1)}$	7.61744	-0.000044	10.97063	-0.000006
methane	11.6$^{2)}$	5.173	-0.006385	4.998290	-0.008062
argon	10.9$^{2)}$	5.0375	-0.003117	4.784437	-0.004246
nitrogen	5.30$^{2)}$	5.76097	-0.001535	5.32727	-0.002478
oxygen	8.18$^{2)}$	4.88357	-0.002930	4.423303	-0.005466
carbon dioxide	12.3$^{2)}$	5.182803	-0.007489	4.989505	-0.009652
carbon monoxide	6.40$^{2)}$	5.62484	-0.001976	5.222174	-0.003126
ethylene	13.5$^{2)}$	5.187144	-0.018977	5.029482	-0.024069
ethane	13.5$^{2)}$	6.0558	-0.008562	6.138064	-0.007760
n-propane	13.1$^{3)}$	5.926528	-0.029806	5.789507	-0.036630
n-butane	13.7$^{3)}$	6.112082	-0.058990	6.146469	-0.055632
compound solvents	**solubility parameter, δ (J/cm^3)$^{0.5}$**	**R^A (Å)**	**Φ_{ii}*10^{19} (J)**	**R^A (Å)**	**Φ_{ii}*10^{19} (J)**
benzene	18.8$^{2)}$	5.90631	-0.123816	6.036324	-0.0941
cyclo-hexane	16.8$^{2)}$	6.284148	-0.098488	6.325035	-0.091765
carbon tetrachloride	17.6$^{2)}$	6.04657	-0.075741	5.920835	-0.091008
carbon disulfide	20.5$^{2)}$	5.245798	-0.092490	5.375406	-0.075917
chloroform	18.8$^{4)}$	5.900903	-0.053716	5.571801	-0.088039
perfluoro-n-heptane	12.3$^{2)}$				
water	47.813$^{3)}$	3.427886	-0.030407	2.85615	-0.127049
methanol	29.523$^{3)}$	4.471602	-0.047341	4.103010	-0.107612
ethanol	26.421$^{3)}$	5.024571	-0.132554	5.052042	-0.122746
1-propanol	24.557$^{3)}$	5.497517	-0.204653	5.710862	-0.136980

Table 4-22. The solubility parameters and the solutes and the solvents for this enquiry.

A number of plots were produced. The equilibrium separations and the like pair potentials were plotted, each as a function of the solubility parameter for the solutes and the solvents, respectively. The solvents excluded water and the three alcohols. Plots were made for the values from each of the options: the heat of vaporization and the molar volume.

The plot of the equilibrium separation as a function of the solubility parameter for the five solvents using the molar volume option showed to lie very close to a straight line. Figure 4.23 shows the plot.

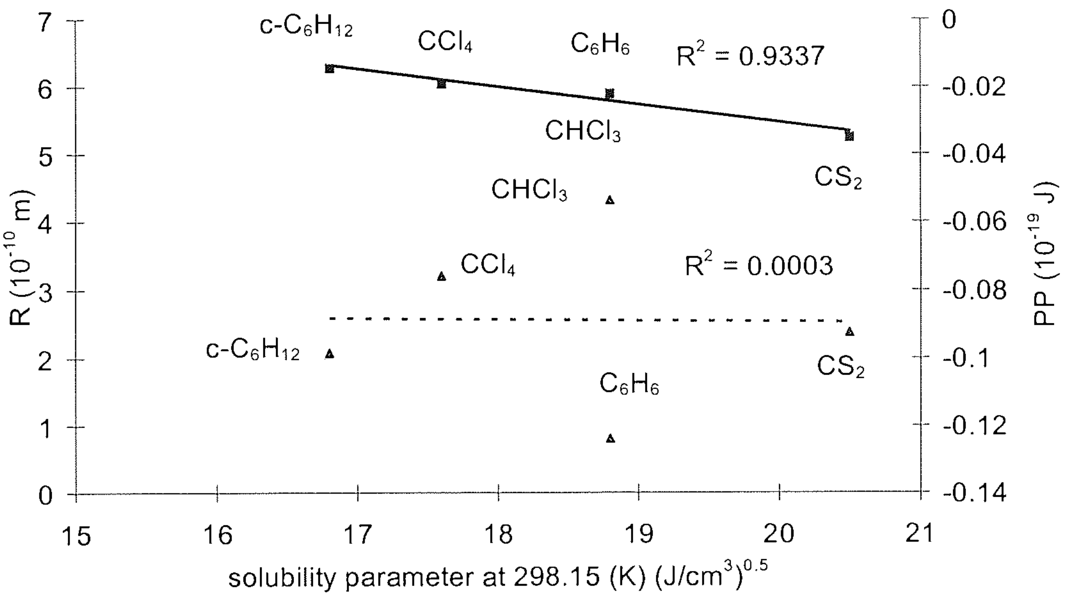


Figure 4.23. The equilibrium separations and the like pair potentials each as a function of the solubility parameter for the solvents excluding water and the three alcohols.

In Figure 4.23 the points ■ represent the R^A value (left y-axis) and the continuous line (—) is the best linear fitted line between the points. The points ▲ represent the PP-values (right y-axis) and the dashed line (- -) is the best linear fitted line between the points.

4.7.2 New solubility parameters for water and the three alcohols

This curve was then used to provide calculation of new values of the solubility parameters from the values of the equilibrium separation for water and the three alcohols. The values are shown in Table 4-23. The same procedure was applied to perfluoro-n-heptane. This solvent was included as a representative for the fluorocarbons which present a problem of their own in solubility predictions because the solubility of all solutes dissolved in fluorocarbons are very high, whereas the solubility in water for all solutes is very low.

solvents	**literature solubility parameter, δ $(J/cm^3)^{0.5}$ 1)**	**extrapolated solubility parameter, δ $(J/cm^3)^{0.5}$ 2)**
methanol	29.523	23.44379855
ethanol	26.421	21.49825579
1-propanol	24.557	19.83426258
water	47.813	27.1159648
perfluoro-n-heptane	12.3 3)	7.528676078

Table 4-23. The solubility parameters from: 1) the DIPPR database (Daubert and Danner, 1994) and 2) extrapolated from the curvefit in Figure 4.22 and 3) from Prausnitz et al. (1986).

It should be noticed that the equilibrium distance calculated from the molar volume in itself is an expression of the molar volume, and that the above curvefit could as well have been carried out using the molar volume instead of the equilibrium separation.

These extrapolated values of the solubility parameters were then used in the equation of the solubility derived from the regular solutions theory which is equation (3.18) repeated below

$$-\ln x_2 = \ln f_2^L + \frac{v_2(\delta_1 - \delta_2)^2 w_1^2}{RT} \qquad (3.18)$$

provided that the fugacity of solute (component 2) is unity which is assumed in our case as all the calculations are carried out at a partial pressure of the solute at 101.325

kPa. The volume fraction of the solvent, w_1, is a function of the mole fractions and this makes solving of equation (3.18) a trial-and-error process. In the calculations carried out here, it is assumed that $w_1 = 1.0$ due to the very low mole fraction of the solute. The same assumption is made in Prausnitz and Shair (1961).

Equation (3.18) involves the fugacity of the hypothetical liquid (f^L_2). This is plotted in Prausnitz and Shair (1961) as a function of the reduced temperature (for the solute). No expression for the curvefit is given, nor is one presented in Yen and McKetta (1962) whose curve for the fugacity of the hypothetical liquid differs slightly from the curve in Prausnitz and Shair (1961). Values taken from the curve in Prausnitz and Shair (1961) have been plotted and a similar curve has been produced. Various curvefitting options have been employed, and the best (in the very limited interval of a reduced temperature from 0.6 to 3) showed to be a fifth order polynomial expression. The graph is shown as Figure A11.4.

The expression for the curvefit is then used to calculate the fugacity of the hypothetical liquid at the actual reduced temperature. A Table of the data used in the application of equation (3.18) is given as Table A11-6 (Appendix 11).

The results of the prediction of the solubilities of gases in liquids using the regular solution theory (equation (3.18)) are shown in the following Table 4-24. The solubility predictions in column 3 are calculated by using the extrapolated solubility parameters for the solutes from Table 4-23, and Table 4-22 for the solvents. The solubility predictions in column 5 are calculated using the literature solubility parameters from Table 4-22 for both the solutes and the solvents. Columns 4 and 6 show the percentage error between the predicted solubility and the experimental solubilities (column 2 from Table A3-1 and (marked 1) from Hildebrand and Scott, 1962).

Mixture solute-solvent	x_1-obs (experimental)	x_1-calculated (extrapolated solubility parameter)	error %	x_1-calculated (literature solubility parameter)	error %
O_2-CH_3OH	0.000415	0.000154597	62.74772625	7.48409E-06	98.19660492
O_2-C_2H_5OH	0.0005825	0.000329461	43.4401286	3.97871E-05	93.16959315
O_2-C_3H_7OH	0.000503	0.000579911	15.29037918	9.57325E-05	80.96770371
O_2-H_2O	0.0000229	2.7994E-05	22.24459222	1.92202E-12	99.99999161
O_2-n-C_7F_{16}	0.00553 1)	0.003659903	33.81729836	0.003543637	35.91977379
C_2H_4- CH_3OH	0.0047	0.001686118	64.12514622	2.45185E-05	99.47832956
C_2H_4-H_2O	0.00008582	0.000165915	93.32895083	4.71593E-16	100
CH_4- CH_3OH	0.000871	0.000285124	67.26479731	5.88857E-06	99.32393031
CH_4- C_2H_5OH	0.00128	0.000706183	44.82942353	5.19772E-05	95.93928055
CH_4- C_3H_7OH	0.00156	0.001348567	13.5533753	0.000157744	89.8881759
CH_4-H_2O	0.00002548	3.30746E-05	29.8059403	3.54886E-15	99.99999999
CH_4- n-C_7F_{16}	0.008262 1)	0.004044688	51.04468792	0.005710438	30.88309802
CO- CH_3OH	0.000327	8.99E-05	72.50765681	3.54945E-06	98.91454031
CO- C_2H_5OH	0.000449	0.00020569	54.18926637	2.08667E-05	95.35263169
CO- C_3H_7OH	0.0005193	0.000385589	25.74836396	5.35198E-05	89.69385801
CO-H_2O	0.0000172	1.43456E-05	16.5953685	5.82426E-13	99.99999661
CO- n-C_7F_{16}	0.00388 1)	0.004132631	6.511105409	0.002651281	31.66801934
CO_2- CH_3OH	0.00639	0.001377787	78.43838462	2.75911E-05	99.5682151
CO_2- C_2H_5OH	0.00689	0.003380373	50.93798794	0.000250245	96.36799616
CO_2- C_3H_7OH	0.00772	0.006356014	17.66821571	0.000763169	90.11438761
CO_2-H_2O	0.0006116	0.0001586	74.06803325	8.73211E-15	100
CO_2- n-C_7F_{16}	0.02088 1)	0.013741764	34.18695546	0.023028061	10.2876492
Ar- CH_3OH	0.000447	9.13335E-05	79.56744805	1.05517E-06	99.76394457
Ar- C_2H_5OH	0.0006257	0.00026363	57.86631155	1.27729E-05	97.95861472
Ar- C_3H_7OH	0.000777	0.000566664	27.07022639	4.59623E-05	94.08464047

Table 4-24. Predicted and observed solubilities for some mixtures using the extrapolated values of the solubility parameter and the literature values of the solubility parameters (continued over).

Mixture solute-solvent	x_1-obs (experimen-tal)	x_1-calculated (extrapolated solubility parameter)	error %	x_1-calculated (literature solubility parameter)	error %
Ar-H_2O	0.00008582	7.59923E-06	91.14515523	4.3383E-17	100
Ar- n-C_7F_{16}	0.0054 1)	0.002839719	47.41261642	0.003543637	34.37710168
C_3H_8- CH_3OH	0.0115	0.001967331	82.89277605	4.04593E-06	99.96481804
C_3H_8- C_2H_5OH	0.0228	0.00786983	65.48319986	0.000135058	99.40764034
C_3H_8-H_2O	0.00002732	6.55873E-05	100	1.45759E-21	100

Table 4-24. Predicted and observed solubilities for some mixtures using the extrapolated values of the solubility parameter and the literature values of the solubility parameters.

4.7.3 Discussion of the prediction results

The prediction of the solubilities of several mixtures with water, the three alcohols, and perfluoro-n-heptane as solvents using the solubility parameter found by extrapolating the molar volume curve show a more accurately predicted solubility then when using the literature solubility parameters for the five solvents.

The use of the extrapolated solubility parameter predicts solubilities much closer to the experimental solubility. The relationship between the solubility parameter and the molar volume (or the equilibrium separation which is an expression of the molar volume) is essentially the same as only taking the van der Waals forces into account. Using a value of the solubility parameter extrapolated from the molar volume of five non-polar solvents corresponds to pretending that water and the three alcohols only take van der Waals forces into account. This means that if the heat of vaporization is written as a product of an energy accounting for the dispersion interaction multiplied by an energy accounting for all the other interactions, then only the dispersion interaction term is taken into account when using extrapolated solubility parameters for water and the three alcohols. This is a way of assuming that water and three alcohols behave like the regular solutes, where only interaction with the dispersion part of the interaction forces counts.

The predicted results using the literature values of the solubility parameters are not surprising as the regular solution theory is developed for regular solutions, that is, non-polar compounds. The regular solution theory should not be applied to polar compounds or hydrogen bonding compounds and that is why, applying the regular solution theory (using the solubility parameter as calculated by the definition) gives very inaccurate prediction results.

Despite this, when actually employing the regular solution theory with alternative solubility parameters for polar compounds and compounds containing hydrogen bonding, the predicted solubilities show a surprisingly good accuracy.

In most of the mixtures examined, the predicted solubility (calculated using the extrapolated solubility parameters) of the solutes dissolved in water and 1-propanol are the most accurate. The percentage error is 10 to 30 % and in all cases much more accurate then the results when using the solubility parameters from Daubert and Danner (1994).

The solvents methanol and ethanol show a much higher diversity of accuracy. The solubility for some mixtures are more accurate then for others.

The solvent perfluoro-n-heptane shows the same tendency. For the majority of the mixtures, the predicted solubilities using the literature solubility parameter are more accurate then the predictions where the extrapolated solubility parameter is employed. Perfluoro-n-heptane is non-polar and contain no hydrogen bonding, so in fact, the regular solution theory is applicable to this solvent and with the solubility parameter as found in the literature. Perfluoro-n-heptane was included in this investigation to examine whether an alternative solubility parameter could be employed to accommodate for the large solubilities of the fluorocarbons. From this investigation it can be concluded that using the extrapolated value of the solubility parameter gives prediction results with slightly larger errors.

It should be noticed that employing the regular solution theory to predict solubilities of gases in liquids in itself contains several parameters which are all determined with large uncertainties. As the solubility values are small, another value of one of the parameters can give an enormously different solubility. The regular solution theory should be used to give the order of magnitude of the solubility rather then be expected to predict the solubility within 5-10 % accuracy.

4.7.4 Discussion of the prediction results in a broader perspective

A classic problem in the solubility of gases and vapours in non-aqueous solvents relates to the differences in behaviour of hydrocarbons and perfluorocarbons in this field. Mixtures of hydrocarbons and fluorocarbons liquids exhibit large positive deviations from Raoult's law which are attributed to unusually small unlike pair interactions between the "peripheral" fluorocarbons and the more "central" hydrocarbons in which the carbon atoms rather then the hydrogen atoms dominate the intermolecular forces. Liquid mixtures of carbon tetrachloride with inert gases also show small unlike interactions.

Fluorocarbons by virtue of their large molar volumes and energies of vaporization which are little different from those of hydrocarbons have solubility parameters which are quite small. It is thus not very surprising that their ability to dissolve inert gases or nitrogen or oxygen is greater then that of hydrocarbons using the classic Hildebrand arguments (Hildebrand and Scott, 1962).

What is more surprising is that, although the solubility of CF_4 or SF_6 in hydrocarbons is substantially less then predicted from their vapour pressure (fugacity), the solubility of methane or ethane in perfluorocarbons does not seem to show such negative effects, but is more closely in line with the higher solubilities of argon, oxygen etc.

When we examine the GLP potentials of interaction between freely rotating CH_4 and CF_4 we find, surprisingly, that they are very close to the geometric mean value of the pair potential (see Table 4-25 where all the values are calculated at 110.0 K using the heat of vaporization option in the computer program PP) indicating that the weak forces are perhaps not due to van der Waals effect but to an affect such as a quadrupole interaction which may be strong in the fluorocarbon-fluorocarbon case but less favoured in the unsymmetrical interaction CF_4/CH_4. Another interaction, however, is that interaction of hydrogen in hydrocarbons could be smaller then specified in the generalized London potential.

Mixture	Φ_{11}*10^{19} (J)	Φ_{22}*10^{19} (J)	Φ_{12}-GLP*10^{19} (J)	Φ_{12}-GM*10^{19} (J)
CH_4 - CF_4	-0.022119	-0.038564	-0.028908	-0.029206
Ar - CF_4	-0.013893	-0.038564	-0.01745	-0.023146
Xe - CF_4	-0.042333	-0.038564	-0.030714	-0.040405

Table 4-25. Pair of potential values for CF_4 mixtures at 110.0 K.

When we calculate the GLP cross term interactions for freely rotating CF_4 and Ar or Xe, we find that indeed, Φ_{12}-GLP is smaller then the geometric mean potential by 20-30 % (Table 4-25). This suggests that the solubility of such gases in perfluorocarbons would be smaller rather then larger using the ideas of interchange energies.

If however, the dilute solute gas is freely rotating in solution but the solvents molecules are not, then a different picture might emerge in which the unlike pair interactions were a quite different average of the atom-atom interaction with an inert gas interacting with effectively more fluorine atoms and less carbon atoms to give Φ_{12} larger then the geometric mean, thus making the interchange energy much smaller.

If such an effect was responsible then we might detect a change in the shape of the excess Gibbs energy versus the solubility curve at low values of the solubility, say for CF_4/Xe.

When the hydrocarbon solvents dissolve fluorocarbons it appears that no change occurs in the unlike pair interaction on passing from, say equimolar to very dilute solution suggesting that no change occurs in the relative rotation of species. The fluorocarbon has thus either lost its favourable self complexation (quadrupole) at all dilutions, or, the naturally low (e.g. CH_4-CF_4) potential is simply maintained in a freely rotating fluorocarbon which takes little account of the hydrogen atom interaction whether they are rotating or not.

This points to an area for future development which is to expand the generalized London potential to include variable rates of relative rotation of the unlike molecules.

4.7.5 Conclusion of solubility predictions using regular solutions theory

The work which evaluates the so-called interchange energy in a lattice model of activity is normally constructed on the mathematical assumption that the entropy of mixing is close to that of a random or an ideal mixture. Additions to this are usually made, e.g., in UNIFAC, by reference to the positional entropy factors outlined by Flory (1941) and Huggins (1941), sometimes called combinatorial terms. Simple calculations show, however, that these Flory-Huggins terms are small for solutes dissolved in solvents which are no more then twice their size (molar volume). Yet in real mixtures entropies of mixing are seldom small and this means that lattice models in their mathematics subsume non-random entropy effects associated with their key energy parameters.

Guggenheim (1952) recognised this even for model lattices of hydrocarbons and drew attention to the fact that w′ (the interchange energy) as applied in practice is not a parameter of U^E (total excess energy) but a parameter of A^E (excess Helmholtz energy) which can be taken to be nearly equal to G^E in most cases.

When we come to the theory of dilute solutions as interpreted by lattice type models, where

$$H_{\text{solute, solvent}} = \gamma^{\infty}_{\text{solute}}\, f_{\text{solute}}^{0}$$

when $\gamma^{\infty}_{\text{solute}}$ can be described by combining equations (3.23), (3.24), and (3.25)

$$\ln \gamma^{\infty}_{\text{solute}} = \ln (p^0_{\text{solute}} / f^0_{\text{solute}}) + w' / RT$$

then w′ is a parameter which although it is ostensibly defined by reference to the configurational energy of pure compounds and of unlike pair interactions (Φ_{12} - 0.5 ($\Phi_{11} + \Phi_{22}$)) is reflecting not total energy but free energy changes in the mixture.

Several factors then become important in the definition of Φ_{12} because the way in which unlike forces are compounded from like forces relates to the configuration of free energy in the mixture. Constructing Φ_{12} from simple averaged Φ_{11} and Φ_{22} by use of $(\Phi_{11}\Phi_{22})^{0.5}$ appears to be moderately satisfactory for molecules of similar size and construction, but is progressively less so when $\Delta U^{vap} = 1/2\ Lz\ \Phi_{ii}$ contains a large term of non-dispersion energy (multipoles or hydrogen bonding). For these hydroxyl molecules, Φ_{ii} effective for solutes can either be assumed to be smaller or to be more accurately represented by a distribution of force close to that of the GLP form.

This line of argument can be applied again to use of solubility parameters in the Hildebrand theory.

Again the equations can best be construed to predict not the total energy, but the whole configurational free energy of mixing (i.e. minus Flory-Huggins effects) so that the effects of configurational entropy changes are encapsulated with those differences which lead to enthalpy changes on mixing.

Once more this appears to suggest that non-dispersion forces play little part in the determination of unlike terms for, if the solubility parameter for water or the alcohols is constructed by reference to an extrapolated plot of the solubility parameter *versus* molar volumes then using the standard molar volumes for methanol, ethanol, 1-propanol, and water, the solubility parameters become the values as shown in the third column of Table 4-23 which can be compared to the conventional values (second column in Table 4-23). Use of these modified values of the solubility parameters which are lower then the conventional values, give good semi-quantitative predictions of solubility of solutes in water or alcohols which are more commonly explained by ascribing their low solubility to anomalous entropy effects.

4.8 Fitting of the like London pair potential.

4.8.1 Introduction to fitting of the like London pair potential

The investigation in applying the AGAPE method to predict the solubility (described in section 4.6) concluded that in principle, the AGAPE method could be used to predict the vapour phase composition of solute-solvent mixtures. One disadvantage is that the vapour phase composition is not the main priority in solubility calculations. The other disadvantage is that the original AGAPE method cannot cope with temperatures above the critical temperatures of each of the pure compounds.

The recently developed variant of the AGAPE method, the AGAPE-FIT method uses one single experimental data point (of one excess property) to determine a value for an unlike pair potential (Φ_{12}) for the binary mixtures and the difference in the volumes (r). The two fitted parameters are then used to predict the vapour composition of the mixture at various liquid compositions. The unlike pair potential is not calculated by the London method (described in chapter 2.11), and despite a detailed investigation (McCoubrey et al., 1993) it has not been possible to derive a relationship between the fitted unlike pair potential and the unlike London pair potential, calculated in the usual way. Nor has a relationship between the geometric mean unlike pair potential and the fitted pair potential been established.

This section describes a similar approach in the solubility investigations. Values for the unlike pair potential and the like pair potential for the solute (the experimental temperature was above the critical temperature of the solute) were calculated to fit the given solubility.

The aim was mainly to derive a value of the like pair potential for the solute above its critical temperature that fitted the experimental data. This value could then be used to predict solubilities (from known values of the two like potentials) of this specific solute dissolved in various solvents (provided that the critical temperatures of the solvents were above the experimental temperature).

The AGAPE-fit method was not employed in this investigation because the results of the fitting procedure (Φ_{12}-fit and r-fit) are temperature dependent and therefore only employable to calculate x-y values at this specific temperature. In gas-solubility studies, the solubility is unique at a single temperature, the solubility varies with the temperature and there is no need to be able to predict concentration profiles at this single temperature.

4.8.2 Calculations of the fitted like pair potential

4.8.2.1 Procedure

The actual method employed was a trial-and-error analytical method to find the values of both the unlike London pair potential for the mixture and the like pair potential for the solute that fit the given experimental solubility.

The extrapolation of the like pair potential for compounds whose critical temperatures are below 298.15 K was described in section 4.4. The calculated information for the equilibrium separation as a function of temperature in the interval from the triple point to the boiling point was extrapolated beyond the critical temperature. The curve appears to fit well with an expression for a straight line. The interval was chosen because the density is continuous in this temperature interval.

The value for the equilibrium separation obtained this way was used as an input in an AGAPE computer program. The program uses the equilibrium separations for both methane and benzene to calculate the unlike London pair potential for the mixture at the chosen temperature. The temperature 298.15 K was chosen, as experimental data for the solubility of methane in benzene at this temperature were available. Again, methane was chosen as the test case together with benzene because of the plentiful experimental solubility data for this binary mixture.

Another computer program uses the calculated unlike London pair potential for the mixture to calculate the solubility of methane in benzene. This computer program is a recently developed variant of the VLE computer program (see description in section 2.11.10). From the input to the program, it calculates the composition of the vapour phase.

The new version of the computer program uses the following input (calculates for binary mixtures only)

INPUT	the components the experimental temperature the unlike London pair potential for the binary mixture both the like London pair potentials for the pure components

	the partial pressure of the solute
	the experimental mole fractions in the liquid phase
OPTION	heat of vaporization
OUTPUT	the activity coefficients
	the vapour phase composition

The program is based on the assumption that the partial pressure of the solvent is equal to its saturation pressure. This assumption basically means that for the solvent

$$x_{\text{solvent}}\ \gamma_{\text{solvent}} = 1.0 \qquad (4.19)$$

As the characteristic feature of solubilities in most cases is that the liquid mole fraction of the solvent is very close to one, the above assumption seems acceptable.

In order to gather more information about the vapour phase mole fractions and because the original program only calculated the vapour pressure up to the critical temperature, the vapour pressure of methane has been extended above its critical point. To do this, a new function for methane's vapour pressure as a function of temperature has been developed. The function is valid down to a reduced temperature of 0.5. A plot of the vapour pressure of methane as a function of temperature is shown in Figure A12.1. and the corresponding table in Table A12-1. The vapour pressure below the critical temperature was calculated using equation (4.16) (from Reid et al., 1987). Equation (4.16) is valid for a single component.

The best linear fit gives the equation

$$\ln\left(\frac{P^S}{P_C}\right) = -5.3983\left(\frac{T_C}{T}\right) + 5.3831 \qquad (4.20)$$

where P^S is in 10^5Pa and T is in K.

Using this equation, the saturated vapour pressure of methane at 298.15 K is obtained to be 318.742 10^5 Pa. Using equation (4.20) to calculate the vapour pressure, it is possible to estimate a value for the activity coefficient for the solute.

The chosen test mixture (methane-benzene) was chosen because it fulfilled the criteria

experimental temperature > critical temperature of the solute

experimental temperature < boiling temperature of the solvent
experimental temperature > boiling temperature of the solute, and
experimental pressure < 500 kPa.

This choice has one disadvantage. Methane and benzene are far from being of similar size. A mixture of methane-ethane, where the components are of similar size has been suggested. This has not been chosen, as the mixture does not fulfil the above mentioned criteria.

The employed procedure was as follows:
Initially, the unlike pair potentials for methane at 298.15 K (the experimental temperature) was calculated from the extrapolated curve as described in section 4.4. The like pair potential for benzene at the same temperature was calculated by running the program PP using the heat of vaporization option (see section 2.11.10). The unlike London pair potential and the unlike geometric mean pair potential were calculated running the same computer program PP with the equilibrium separations as input values.

Then from given values of:

x_{solute}, the solubility
T, the temperature
P_{solute}, the partial pressure of the solute
$\Phi_{liq,liq}$, the London pair potential for the pure solvent

$\Phi_{gas, gas}$, the London pair potential for the pure solute (initially, this was the value obtained from the extrapolated curve and it became the parameter that was changed)

$\Phi_{liq,gas}$-GM, the geometric mean pair potential for the mixture interaction was derived from the values of the two like pair potentials.

$\Phi_{liq,gas}$-GLP, the London pair potential for the mixture interaction was derived from the value of the geometric mean pair potential minus a difference.

The calculation gave values of:

y_{solute}
$y_{solvent}$
γ_{solute}
$\gamma_{solvent}$.

The sum of the values of the vapour composition has to be unity (mass-balance criterion for any equilibrium). When this criterion was fulfilled, the calculations were stopped, and a fitted value for the like pair potential for the solute and the unlike pair potential for the mixture were the end results of the trial-and-error calculations.

Initially, the value of the like pair potential for the solute was the extrapolated value. The results reveal that the first initial values gave vapour composition results whose sum was not unity.

The second step in the manual iteration procedure was to change the value for the like pair potential for the solute to another value of the trial-and-error kind. From this (not quite arbitrarily) chosen value, the matching value of the equilibrium separation, employing the extrapolation method where necessary, was found. Again, the unlike pair potential was derived running the program PP. The like pair potential for the solvent did not change value during the whole procedure; nor were the other changeable parameters in the AGAPE equations changed. In all calculations, the number of nearest neighbours (z) was set to 11.0 and the difference in size (r) was in all calculations set to the option of van der Waals volumes. This particular option was chosen because the liquid molar volume for the solute has no value, as the solute is above its critical temperature and therefore in a hypothetical state.

From the given values of the input parameters (as in the initial run), the vapour mole fractions were calculated. Step two was repeated until the vapour phase fulfilled the mass-balance criterion. As most of the experimental data include only the solubility, the temperature and the partial pressure of the gas, but not the mole fractions of the gas phase, the y-value calculated for the solvent had to be taken as it stood.

4.8.2.2 Assumptions

The underlying assumption of doing this is that the AGAPE predicted value of the vapour phase composition of the solvent is as it stands. Even though the predictions for VLE were very accurate compared with experimental data for the majority of mixtures (see section 2.11.15 and Appendix 2), a few mixtures show more or less diversity from the experimental data. Taking the GLP calculated $y_{solvent}$ as it stands is probably correct for many mixtures, but incorrect for a few mixtures.

The other assumption that was made during the calculations is in fact not necessary at all, that is, the assumption of a temperature independent, constant difference between the unlike geometric mean pair potential and the unlike London pair potential. From the values of the two like pair potentials for the solvent and the solute, respectively the unlike geometric mean pair potential is calculated using equation (2.89). Both the unlike pair potentials (the geometric mean and the London) have been calculated using the computer program PP in a certain temperature interval with temperatures below the critical temperature of the solute. A nearly constant difference between the two unlike pair potentials had been found for all mixtures involved in these calculations. The difference was assumed to be the same at the actual (experimental) temperature. It was then possible to derive a value for a *pseudo* unlike London pair potential at the experimental temperature, as the unlike geometric mean pair potential was known.

This assumption is in fact, unnecessary to make. The fitted unlike pair potential is not necessarily related to the London pair potential, but is the value of some potential that fits the experimental data. The assumption was done because it was estimated that a potential calculated as described above, would be if not exactly, then close to the value of the "real" London potential.

The critical temperature of propane was in these calculations above the experimental temperatures. Mixtures of propane were chosen after some of the calculations involving methane had failed to succeed. The calculations for the two mixtures including propane as the solute were successful. The results of these calculations are then a fitted like pair potential for propane and indirectly a fitted unlike pair potential for the mixture as opposed to the AGAPE-FIT method, where a fitted unlike pair potential is the result. Fitting the like pair potential for propane could show how far this value is from the (default) value calculated using the AGAPE standard methods (either the heat of vaporization or the molar volume).

Despite these assumptions, the procedure described above was employed.

When taken the y-value for the solvent as it stands, the calculations concentrated on finding the value for the like London pair potential for the pure solute, that fitted the solubility, or rather that gave a y-value for the solute, that made the sum of the y-values 1.0.

4.8.3 Results of the fitted like pair potential calculations

Initially, the procedure was employed the mixture methane-benzene. Table A12-3 shows the results of the trial-and-error calculations.

To obtain more information about the fitted values, similar calculations were performed for the mixtures:

1. methane - benzene	(Table A12-3)
2. methane - *cyclo*-hexane	(Table A12-4)
3. methane - carbon tetrachloride	(Table A12-8)
4. methane - n-hexane	(Table A12-5)
5. methane - n-butane	(Table A12-6)
6. methane - propane	(Table A12-12)
7. methane - carbon disulphide	(Table A12-7)
8. ethane - *cyclo*-hexane	(Table A12-11)
9. propane - benzene	(Table A12-10)
10. propane - *cyclo*-hexane.	(Table A12-9)

These mixtures were chosen on the basis of the availability of experimental data and also to perform the calculations using components, whose sizes are similar. Including propane as the solute is a test of how well the AGAPE pair potentials fit the actual vapour composition, as the critical temperature of propane in this case is higher then the experimental temperature.

In all the calculations performed for the mixtures mentioned above, the equation for the gas's vapour pressure as a function of temperature was applied as described previously. This enabled the program to calculate the vapour pressure of the pure gas at temperatures above the critical temperature. Figure A12.1 shows the graph for methane and equation A12.1 is the equation that was used at temperatures beyond the critical temperature for methane. A similar graph for ethane as for methane has been drawn and is shown in Figure A12.2 together with the equation A12.2 for ethane. The critical temperature of propane is above 298.15 K, so there was no need to extend the vapour pressure graph for propane.

Tables A12-3 to A12-11 (Appendix 12) show the results of the trial-and-error calculations.

The results obtained from the calculations showed a high degree of inconsistency.

4.8.4 Discussion of the fitted like pair potential calculations

Tables A12-3 to A12-11 show that, firstly, it was possible to carry out the calculations for five of the above mixtures. The calculations were successful for the mixtures:

1. methane - benzene
2. methane - *cyclo*-hexane
3. methane - carbon tetrachloride
9. propane - benzene
10. propane - *cyclo*-hexane.

The like pair potential for the pure compound is defined in such a way that it is only a function of intermolecular parameters, such as the equilibrium separation. The separation is a function of temperature. For the same temperature, one would have expected an equal value for the like pair potential for the pure component. For the two solutes dissolved in different solvents the results of the trial-and-error calculations were a different pure solute pair potential for each of the five mixtures. The three pair potentials for methane in three different solvents were very far apart as Table 4-26 shows. The same result was obtained for propane.

mixture	the fitted like pair potential for the solute (E19 J)
methane - benzene	-0.006
methane - *cyclo*-hexane	-0.01
methane - carbon tetrachloride	-0.053
propane - benzene	-0.020
propane - *cyclo*-hexane	-0.025

Table 4-26. The fitted like pair potential for the solute.

The results for methane is plotted in Figure 4.24 on the graph for the equilibrium separation as a function of temperature.

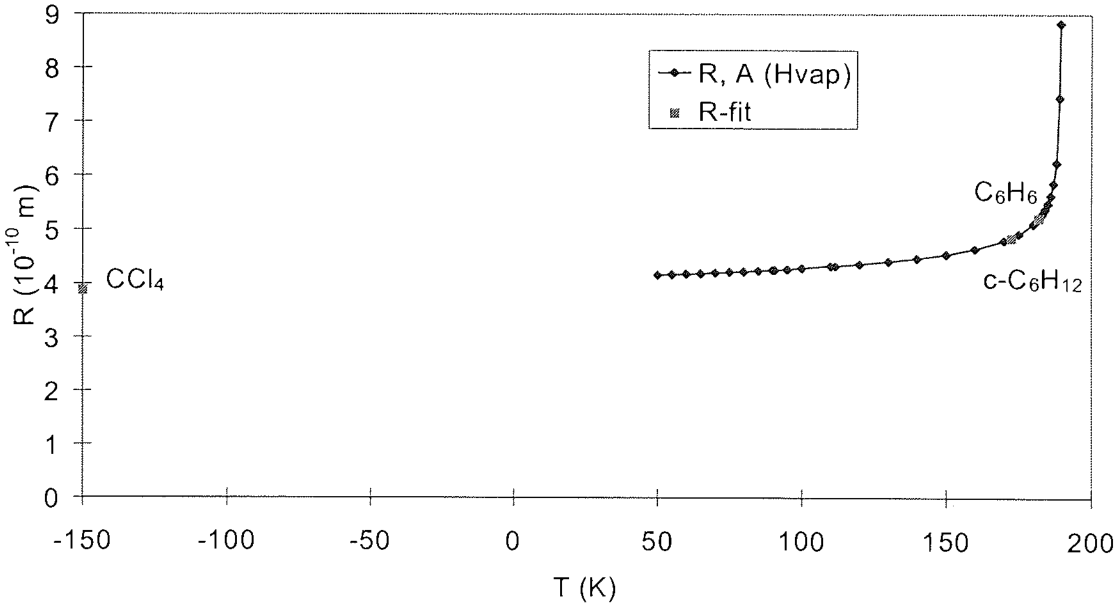


Figure 4.24. Equilibrium distance for methane as a function of temperature with three inserted values for the fitted R.

Secondly, it was not possible to obtain a London pair potential for the solutes for these mixtures:

4. methane - n-hexane
5. methane - n-butane
6. methane - propane
7. methane - carbon disulphide
8. ethane - *cyclo*-hexane

There are possible explanations for this. Either, one of the other intermolecular parameters has to be changed (e.g. the ratio between the molecular sizes) for these special mixtures, or the assumption of taking $y_{solvent}$ as it stands is wrong.

Another explanation could be the lack of repulsive forces in the AGAPE model. The repulsive forces are thought to cancel out at temperatures below the critical temperature of the gas. At temperatures above the critical temperature for the gas, the repulsive forces maybe have greater influence due to solvent-solute interactions. This could explain the results obtained from the trial-and-error calculations.

As mentioned previously, the idea of using propane as a solute was to compare the fitted like pair potential with the default like pair potential. The like pair potentials (in 10^{19} J) for propane as calculated by the computer program PP (option heat of vaporization) are

298.15 K	-0.033103
310.93 K	-0.036630

The fitted like pair potentials are -0.020 and -0.025, respectively. The difference is quite large, about 30 and 40 % error. This gives thoughts about the reliability of calculating the equilibrium separation from the heat of vaporization or the molar volume. As mentioned earlier (section 2.11) this matter was investigated in detail by Mohammadi (1986) with the result that equation (2.80) is the most accurate equation for deriving R^A values.

4.8.5 Conclusion of the fitted like pair potential calculations

This section describes an attempt to fit the like pair potential for the solute to the experimental value of the solubility. Ten mixtures were analysed, of them eight mixtures contained the solutes methane and ethane, whose critical temperatures are below the temperature of the experimental data. Two mixtures contained propane, whose critical temperature is above the experimental temperature.

The results of this investigation show that the aim of deriving a single value for the like pair potential for the solute above its critical temperature was not fulfilled. Several values for the same solute were derived.

The calculations were carried out using two assumptions. One assumes a constant difference between the unlike geometric mean pair potential and the unlike London pair potential, and the other assumes that the AGAPE predicted value of the solvent vapour phase mole fraction is as it stands. These two assumptions are debatable and the end results of this fitting attempt illustrate the uncertain nature of this approach.

The results of the calculations are a fitted like pair potential for 5 of the mixtures, whereas it proved impossible to fit the like pair potential for the other 5 mixtures. The like pair potential for the solute should be dependent of the temperature, but be the same value independent of the solvent. The three values of the like pair potential for methane at 298.15 K that were the results of the calculations showed to be far from equal. Two of them (in solvents *cyclo*-hexane and benzene) were close to each other, whereas the like pair potential for methane dissolved in carbon tetrachloride was very far from the other two values. The two values for n-propane were, compared to the values obtained for methane, quite close.

The results showed such a degree of inconsistency that, in the end, it was decided not to continue this specific approach to fit the like pair potential for the solute. A probably much better approach would have been to carry out calculations using the, at that time, just developed AGAPE-FIT method. In the AGAPE-FIT method an unlike pair potential (neither the geometric mean pair potential nor the London pair potential) and the size parameter (r) are calculated to fit with experimental values of phase equilibrium and one (experimental) data point for one of the excess thermodynamic properties. Results stemming from applying the AGAPE-FIT method to vapour-liquid equilibrium showed a discrepancy between the fitted unlike pair potential and both the London pair potential and the geometric mean pair potential (McCoubrey et al., 1993). Despite numerous efforts it has not been possible to derived a relationship between the fitted pair potential and either the London pair potential or the geometric mean pair potential. The AGAPE-FIT method works very well, and indeed gives more accurate predictions of phase equilibrium for certain mixtures then the AGAPE method (Kakhu and Homer, 1996a). The fact that it has not been possible to relate the fitted unlike pair potential to any of the two pair potentials unfortunately places the AGAPE-FIT method in the same category of prediction methods as e.g. the UNIFAC method. There are two major differences though. The UNIFAC method demands a vast number of experimental data to derive the values of the interaction parameters as opposed to the AGAPE-FIT method where one single value of an excess thermodynamic property is enough (of course, besides the mole fractions at that specific data point). The second difference is that the UNIFAC interaction parameters have little or no relation to a meaningful physical variable. In the AGAPE-FIT method the fitted unlike pair potential is a meaningful physical variable. It is just not related to any of the two pair potentials usually used in the AGAPE model.

Due to the inconsistent results obtained in this analysis and the lack of relationship between the fitted pair potential obtained from employing the AGAPE-FIT method to VLE predictions and either the unlike London pair potential nor the geometric mean pair potential, it was decided not to pursue this specific attempt any further.

4.9 Activity coefficients at infinite dilutions

4.9.1 Activity coefficients at infinite dilution calculated by the AGAPE method

Values for the activity coefficient for both the solute and the solvent at infinite dilution were determined by carrying out calculations where the x_{solute} was getting smaller and smaller. The x-values did not match any experimental data, which did not matter in this case, as the main result of the calculations was the activity coefficient for the solute.

The calculations were carried out using the a modification of the computer program VLE (see section 2.11 for a brief description of VLE).

The new version of the computer program used the following input (calculates for binary mixtures only)

INPUT	the components the temperature equilibrium separations of the components the liquid phase composition
OPTION	heat of vaporization
OUTPUT	the activity coefficients the vapour phase composition
INTERMEDIATE RESULTS	the like London pair potentials and the unlike London pair potential from heat of vaporization.

In this case the liquid phase composition was chosen with the x_{solute} values to be: 0.1, 0.01, 0.001, and 0.0001. At least the last two calculations gave activity coefficients for the solute, that were very little different. The sum of the liquid phase compositions did not equal 1.0 or any experimental results found in the literature, but this was not thought to be important, as the emphasis in these calculations was the activity coefficient for the solute at infinite dilution.

After an extensive literature research, the conclusion was, that there were no data for the activity coefficient for the solute at infinite dilution at temperatures above the critical temperatures to compare the results obtained with.

4.9.2 Application of MOSCED parameter and the like pair potential

The aim of applying the MOSCED parameter and the like pair potential was an attempt to calculate the activity coefficient at infinite dilutions using the MOSCED method but substituting the dispersion parameter with an expression using the like pair potentials instead.

The MOSCED and the SPACE methods for calculating the activity coefficients at infinite dilutions have been discussed in section 2.10.3.16. Of particular interest is the dispersion parameter, λ. In Thomas and Eckert (1984) it is a function of the refractive index n_D

$$
\begin{aligned}
f(n_D) &= \left(\frac{n_D^2 - 1}{n_D^2 + 2}\right) \\
\lambda_{\text{non-aromatic}} &= 20.3f(n_D) + 3.02 \qquad (4.21) \\
\lambda_{\text{aromatic}} &= 19.5f(n_D) + 2.79
\end{aligned}
$$

An attempt to evaluate a possible relation between the MOSCED dispersion parameter and the London pair potential will be described in this section.

4.9.3 Results of MOSCED calculations

It was investigated if a relationship exists between λ, the parameter presenting the dispersion forces in the MOSCED method (Thomas and Eckert, 1984 and further developed in the SPACE method by Hait et al., 1993) and the like pair potentials for the pure compounds. These methods predict the activity coefficients of infinite dilution at various temperatures from a number of pure component parameters.

The like pair potentials (Φ_{ii}) and the equilibrium separation (R^A) for a number of relatively high-boiling liquids were calculated using the computer program PP (described in section 2.11.10) and both options: heat of vaporization and molar volume. The temperature in all calculations was fixed to 298.15 K, as this is the temperature, for which values of the dispersion parameter, λ were given in Thomas and Eckert (1984).

The results have been plotted in various ways and represented in Appendix 15. The equilibrium separation and the like pair potential (AGAPE) as a function of natural logarithm of the dispersion parameter (MOSCED) are shown in Figure 4.25. For the other option (heat of vaporization), the dispersion parameter was plotted against the equilibrium separation (AGAPE, left y-axis) and the like pair potentials (right y-axis) as shown in Figure A15.1.

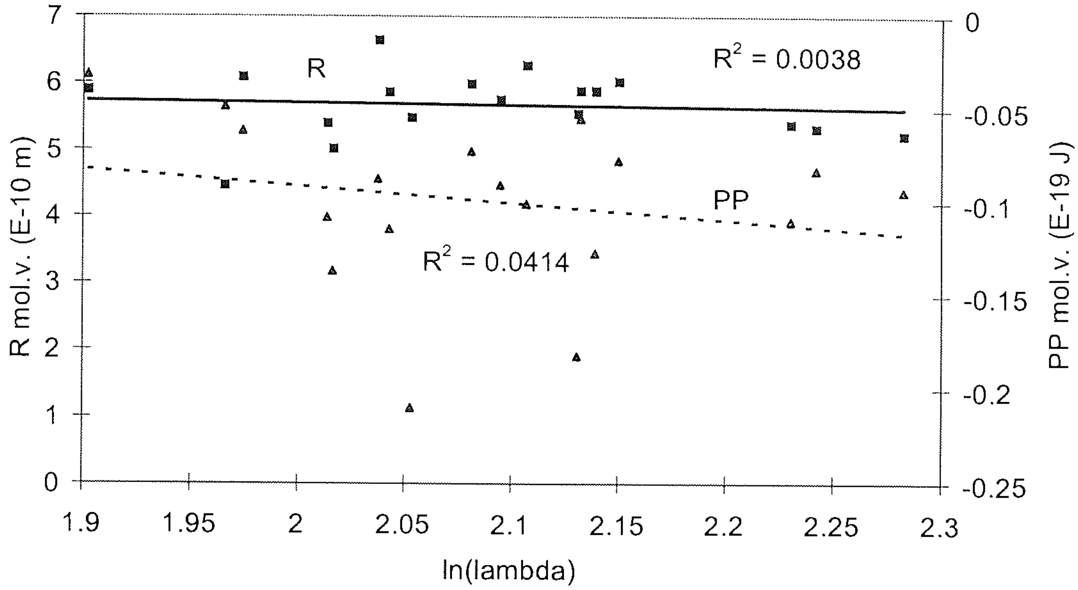


Figure 4.25 The equilibrium separation (■, left y-axis and – line) and the like pair potential (points ▲, right y-axis and -- line), both obtained from the molar volume option as a function of the natural logarithm of λ and the best fitted straight lines.

An attempt to combine the MOSCED-parameter and the like London pair potential for the pure compound was carried out with very limited success. Even though, both linear and logarithmic scale were used, there was no correlation between the MOSCED-parameter and the like London pair potential.

The molar volume of the compounds at 298.15 K is another parameter in the MOSCED method. The molar volume is a very important parameter in the AGAPE calculations, as the majority of section 4 shows. As the computer program PP calculates the molar volume for the pure compounds, it would be interesting to compare the two molar volumes with each other. The results are shown in Table A15-1 and the AGAPE molar volume (calculated using the Yen-Woods (1966) equation, see Appendix 14) is plotted as a function of the MOSCED molar volume in Figure A15.2.

4.9.4 Discussion of MOSCED calculations

An attempt to investigate the correlation between the MOSCED dispersion parameter and the GLP parameters in a different way was carried out. Selecting the components in homologous series like alcohols and alkanes and then carry out the same plots as described above, one of the plots showed an excellent linear regression line.

Two series were chosen. One consisting of methanol. ethanol, and 1-propanol and the other consisting of n-propane, n-butane, and n-hexane. For each of the series the like pair potentials (calculated from the molar volume option) was plotted as a function of the dispersion parameter. Figure 4.26 shows the graphs. As the trendlines show, there is an excellent linear relationship between the two parameters.

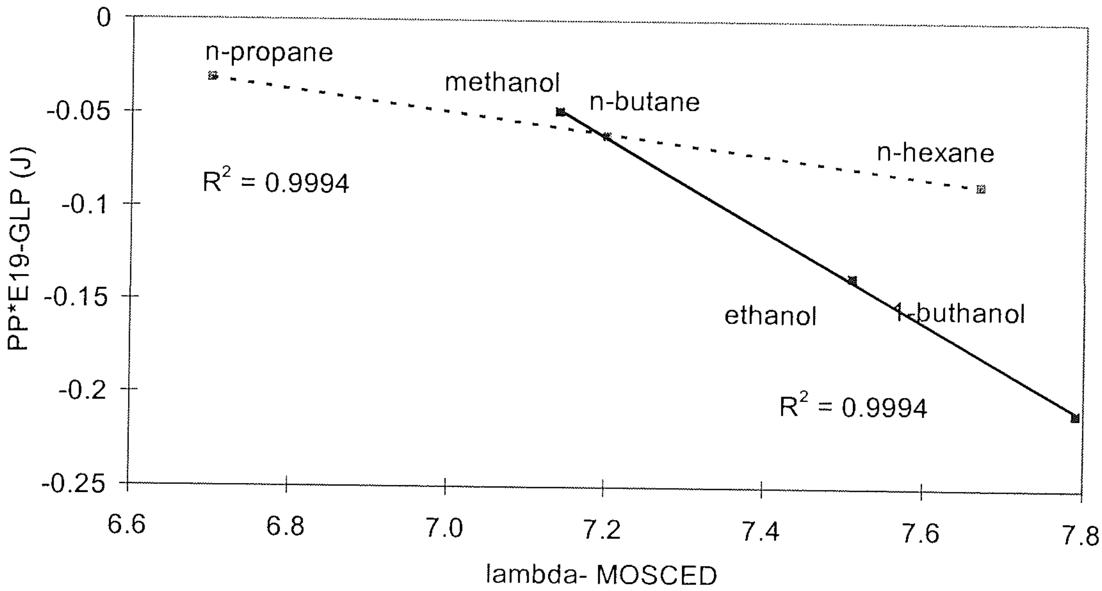


Figure 4.26. The like pair potentials for three alkanes and three alcohols as a function of λ.

4.9.5 Conclusion of MOSCED calculations

A linear relationship between the MOSCED dispersion parameter and the like London pair potential was shown for two homologous series consisting of three compounds each. This work was not investigated further, because of lack of homologous series in both the MOSCED database and the AGAPE database. Overall there was no easy detectable relationship between the two parameters mentioned. It should be kept in mind that the MOSCED parameter was only available for compounds which are solvents at a temperature of 298.15 K.

Chapter 5 - Compiled discussions

5.1 Results in context to general solubility considerations

As already mentioned in section 4.6, the total analysis of all the investigations carried out seems to point to the need in a successful molecular thermodynamic model for the inclusion of effects which reflect a non-rigid underlying structure which is tantamount to the inclusion of both “repulsive” and attractive effects as is done in an equation of state.

Successful simple treatments of solubility which include cavity formation (Pierotti, 1976) or use the rigid sphere model plus an attractive term (Snider and Herrington, 1967) generate an equation of state, albeit one in which considerable approximations about molecular sizes and attractive energies are introduced and with individual data being required for each individual calculation.

In the early 1980's the limitations of the original UNIFAC procedures began to be recognised but by this time a mass of valuable data had been generated and codified, mainly for VLE (excess Gibbs function and activity coefficients) on a molecular group basis. The tables had achieved world-wide use and the project was restructured to improve the versatility of the parameters in the UNIFAC model. The use of semi empirical means permitted not only VLE data but also enthalpy and liquid-liquid data to be codified via the systemisation of activity coefficients at infinite dilution, γ^{∞}. Extensive computer based packages were generated.

By this time also much work had been done by chemical engineers using cubic equations of state with increasing sophistication to codify higher pressure and high temperature phase equilibria, and methods for calculating fugacities had also been computerised.

The end-equation of the reference solvent method (derivation in section 3.3.1) is as follows

$$f_2^G = \frac{H_{2,R}\ x_2\ \gamma_2}{\gamma_{2,R}^{\infty}} \qquad (3.13)$$

If γ_2 is tabulated as a function of x_2 in different solvents by UNIFAC and $\gamma^{\infty}_{2,R}$ can also be found from UNIFAC, then, for known values of f^G_2, approximately 101.325 kPa, say, x_2 can be calculated by iteration. Section 4.6 shows the success of this practical method. Thus although ideas from both systems (activity coefficients and equation of state) are introduced, by providing group contribution tables for hydrogen, nitrogen, oxygen, etc., UNIFAC permits for low pressure gas solubilities (where the gas fugacity f^G_2 can be replaced by pressure) a direct calculation without use of an equation of state and this is possible as long as reference solvents are known of close proximity to the working solvent.

The simplest illustration of the direct use of an equation-of-state method arises from the thermodynamic equation

$$\gamma_i x_i (\varphi_i^S P_i^S) = \varphi_i^V y_i P \qquad (5.1)$$

where

$$f_i^0 = \varphi_i^S P_i^S \qquad (5.2)$$

with φ as the fugacity coefficient. Here φ_2^V is evaluated from the virial equation. If the vapour phase is ideal this becomes

$$\varphi_i^L x_i = \varphi_i^V y_i \qquad (5.3)$$

which is equation (2.20), where φ_i^L and φ_i^V are evaluated from an equation of state in the standard expressions of P, V, and T.

Cubic equations of state are all modifications of the van der Waals equation of state and the variables remain a' and b'. The relationship between mixing rules in these equations of state and excess free energy models was first introduced by Huron-Vidal (1979) as

$$a' / b' = \sum x_i \, a_i' / b_i' - G^E_{\infty} / \ln 2 \qquad (5.4)$$

where this expression is derived to accompany with the Redlich-Kwong equation of state, they took the infinite pressure limit of the excess Gibbs free energy in the Redlich-Kwong model, where $v = b'$ and also assuming $b' = \sum x_i \, b'_i$.

By matching the parameters with G^E at zero or low pressure instead it becomes possible to use the massive UNIFAC system of G^E values to determine the a' and b' parameters for use in equations of state. Equations for fugacity can be obtained in terms of a′ and b′ which are variously normalised to the excess Gibbs energies of the UNIFAC model. Procedures of this kind appear to be the way forward, but are not without problems. Such problems have recently been highlighted by Michelsen and Heidemann (1996), where they state that many of the newly developed mixing rules mainly effect the liquid behaviour and have little effect on the vapour phase. This leads to liquid excess free energies only partly obtained from the activity coefficient model, with other significant terms arising from elsewhere in the equation of state. A recently developed method by Novenario et al. (1996) takes another route. To obtain the mixture parameter a for a cubic equation of state, the excess free energy of the solution model is matched to that of the equation of state at a molar volume equal to a fixed multiple of the excluded volume b such that all of the mixed liquids are at a low pressure. They have been able to predict VLE for highly non-ideal mixtures, such as acetone and *cyclo* hexane. Their results appear to predict very well even for a binary mixture of acetone and water.

For the purposes of calculating or predicting Henry's law constants, these procedures may be used in any hybrid systems. For this γ^∞ can be obtained directly from the revised UNIFAC methods well fitted to infinite dilution activity coefficients and the relation

$$H_i = \gamma^\infty_i f^L_i \tag{5.5}$$

used. f^L_i is the fugacity of a hypothetical liquid at the system temperature and pressure.

UNIFAC has now fitted tables to include “gases” like nitrogen, oxygen, or argon.

5.2 An intuitive approach to gas-liquid solubility

Breman et al. (1994) presented measured solubilities of a number of common gases and vapours over a range of temperatures in several solvents including hexadecane and 1-hexadecanol in an interesting, recent paper. The data show very little difference between the solubilities in these two solvents suggesting that the effect of the alcohol (OH) group is overwhelmed by the long chain group.

This observation may be related to a system for correlating gas-liquid solubilities as a function of solvent structure which was introduced by Abraham and Nasehzadeh

(1981) and re-established recently by Thomas and Eckert (1984). In this the activity coefficients at infinite dilution were analysed as a function of functional groups exercising "dipole" or "hydrogen bonding" effects on top of the basic dispersion force "solubilities". It has been shown that an additivity equation can be constructed in which the solubility in hexadecane is taken as an "ideal" dispersion force norm to which perturbations may be added by structures.

Calculations of ideal Raoult's law solubilities for gases even such as hydrogen sulfide or hydrogen chloride show these to be very close to the measured solubilities in hexadecane and nearer still to the measured solubilities in heptane. Thus this norm actually corresponds to a Raoult's law norm or activity coefficients approximately equal to unity on the symmetrical convention. Calculations for permanent gases like nitrogen, oxygen or argon suggest that this is true also using extrapolated saturated vapour pressures or fugacity estimates.

The fact that a framework of solubility perturbations may be constructed from this norm makes for a simpler way of incorporating many organic compounds. It probably does not embrace water which because of its very small molecular size exerts unique effects not easily captured in such an analysis. Indeed, there seems little doubt that it is the very small size rather then the hydrogen bond effect which dictates the solvent power of water (Ben-Amotz and Herschback, 1990).

Examination of the data of Battino and Clever (1966) and of Breman et al. (1994) shows that solubilities increase by a factor of about 3 on passing from methanol to undecanol. Experimental data for the activity coefficient at infinite dilution of heptane in a series of alcohols shows that in octanol γ^{∞} is approximately unity whereas in methanol it is close to 3. This indicates that the strong hydrogen bond effect of methanol is almost completely diluted by the time the OH group has 8 carbon atoms attached.

By contrast the solubility of propane changes very slowly on passing from C_6 hydrocarbon to C_{24} hydrocarbon. Indeed the solubility of other non-polar gases behave similarly (IUPAC Solubility Data Series (Clever, 1979 (vol. 1), Clever, 1980 (vol. 4), Young, 1981 (vol. 5/6), Battino, 1981 (vol. 7), Hayduk, 1982 (vol. 9), Battino, 1982 (vol. 10), Hayduk, 1986 (vol. 24), and Clever and Young, 1987 (vol. 27/28)).

It seems probably therefore that most progress in understanding the solubility of gases and vapours at ambient temperature will come from a study of simple functional matrices along the lines of the linear free energy relationships set out by Abraham and Nasehzadeh (1981).

For temperature dependence of solubility we probably need to look to the scaled-particle method for computing the partial entropy of solution. In an "ideal" solution the partial molar entropy equals -R ln x which will change with temperature as x changes with p/p^{T}_{0}. For most systems, even those behaving ideally at ambient temperatures, the vapour pressure will have to be estimated above the critical point and the accuracy of the estimates of the fugacity with temperature become questionable.

Bo et al. (1993) have shown that scaled-particle calculations gave good estimates of Henry's constant even for alcohols and there seems every reason to believe that entropy terms thus calculated would predict solubilities for 50-100 K from the reference point.

For the light gases (H_2, N_2 or He) it seems clear that in hydrocarbon solvents the temperature change of enthalpy is very small and in oxygenated solvents the solubility goes up with temperature (rather than down as for most solutes, a phenomena mentioned in Chapter 3) due to positive entropy changes since no residual attractive energies remain.

5.3 The solubility of solutes in hydrocarbons and the concept of near ideal solubility

An observation of solubility of volatiles in normal hydrocarbons of moderate chain length suggests these to be close to their ideal solubility. Prausnitz et al. (1986) shows that for hydrogen dissolved in n-heptane the solubility at 298.15 K is 0.0007 moles compared to 0.0008 ideal and carbon dioxide to be 0.0122 moles compared to ideal of

0.0160. Published data for the solubility of propane in hydrocarbon C_6 to C_{16} at 298.15 K shows values of 0.115 moles to 0.133 in the longer chain compound (IUPAC Solubility Data Series Hayduk, 1986 (vol. 24)). A calculation based on published vapour pressures for propane gives the saturated vapour pressure to be 899.9 kPa at 298 K which gives for a 101.324 kPa saturated solution an ideal solubility of 0.113 moles.

Recently published data for hydrogen sulfide show a surprising conformity to the pattern. Values for Henry's constant given by Yokoyama et al. (1993) are given in Table 5-1 together with solubility of hydrogen sulfide in n-dodecane from Feng and Mather (1993) and Hu et al. (1985).

Mixture (solute - solvent)	**T (K)**	**H experimental (MPa)**	**Vapour pressure of solute (MPa)**	**H (ideal) calculated (MPa)**
propane - n-hexane	298	8.6	8.4	
propane - n-hexadecane	300	8.4	8.4	
butane - n-hexane	323	2.4	2.4	
butane - n-hexadecane	300	2.1	2.4	
hydrogen sulfide - n-dodecane	313	2.61	2.958	2.95
hydrogen sulfide - n-dodecane	352	4.52	6.26	6.98

Table 5-1. Values of Henry's constant for mixture at two different temperatures.

A calculation of saturated vapour pressure from data in Daubert and Danner (1994) (see Table 5.1) gives an ideal solubility of 0.0343 for hydrogen sulfide. The calculations are limited because of the critical temperature of hydrogen sulfide of 373 K. Even though, the calculations show that the simple concept of ideal solubility in hydrocarbons can go quite far in reasonable practical estimates for oil industry purposes.

During 1960^s to 1990^s a number of authors (Preston et al., 1971, Gunn et al., 1966, Yorizane and Miyano, 1978) achieved corresponding states graphical correlations of Henry's law constants making some use of lattice or equation of state ideas usually requiring a knowledge of the critical pressure and the critical temperature and possibly the acentric factor. Such correlations go a long way as a first order prediction of gas solubility in most common organic liquids.

Second order predictions can well be achieved by the use of methods by Sander et al. (1983) based on UNIFAC procedures. With the advent of the modified UNIFAC groups which include volatile substances like argon, oxygen and nitrogen and the continuous availability of more experimental data for potential "reference" solvents, like those from the Zavagoza laboratories (Gibanel et al., 1993) or those from Hayduk and co-workers (1971, 1973 and 1975), Battino and Clever (1966). Such calculations can be extended to quite high molecular weight species (up to C_{20}) with success.

The creation of a ubiquitous molecular model which rationalise and give good predictions for solvents which may range from the high solubility perfluorocarbons to the specially low solubility of non-ionic materials in water may have to wait some time. The treatment of non-ionic solutions in water with its specialised structure and large entropic effect poses a major problem in itself. Although, as this study has shown, there is no broadly sensible energetic reason why water with its high enthalpy of vaporization should show correlated low solubilities. The changes from different solutes and temperatures will remain a complex function. For liquid water, the changes will probably only be calculable using pure water as the reference fluid.

An alternative is to develop an equation of state designed for water, as has been done recently by Müller and Gubbins (1995). Their equation of state takes into account repulsive, dispersive, multipolar and association interactions. At this stage, their model needs some improvements, but its prospects look promising.

To expect to create a single model which would embrace the complexity of liquid water and take account of the homologous organic liquids is very demanding. The behaviour of both Henry's law constants and activity coefficients at infinite dilution probably becomes more and more determined by Flory-Huggins type entropy considerations, as the solvents have chain lengths in excess of 10 carbon atoms (Parcher et al., 1975). Even sophisticated equations of state, particularly the conventional cubic equations of state, however normalised, have problems with mixtures where the size differences of solutes and solvents are great.

The case of fluorocarbon fluids which show anomalously low un-like pair interactions with hydrocarbons yet appear to have high dissolving power for inert gases can not be rationalised by unlike pair potential parameters alone since the heat of vaporization is not very different from hydrocarbons. It is, however, the case that the orientation of these chain fluids is somewhat more randomised than that of hydrocarbons and certainly their high densities give them low values of internal pressure and solubility parameters, again suggesting that specific structural effects may have significant influence on the solution behaviour.

It seems as though this dependence of gas solubility on specific structural nature of solvents makes the rationalisation of quantitative behaviour so structure (entropy) sensitive that the usual mean field theories of intermolecular interaction (even those of the GLP method which does assume rapid rotation and overall spherical shapes) can not be expected to cope over the wide spectrum.

The orientational averaging of any one thermodynamic parameter like the heat of vaporization can not necessarily reflect the corresponding averaging of even a similar property like solubility across the fields of polarity and anisotropy. Perhaps models and computer simulation procedures will be able to overcome this in the future.

5.4 Final discussions

The objective of this work was to employ the concept of the AGAPE model (and indirectly the generalized London potential theory) to predict solubilities of gases in liquids. The AGAPE model is able to predict the solubility of gases in liquids with reasonable accuracy within the limitations of the AGAPE model, mainly at conditions below the critical conditions of the solute. As with any other activity coefficient model, the difficulty lies in the fact that what is predicted, when applying an activity coefficient model to solubilities, are the activity coefficients, and the end results are the vapour mole fractions. To predict solubility, the liquid phase mole fractions should be the end results, and not the input values.

This is where most models experience difficulties, because, ideally, a model developed to predict solubility of gases in liquids should be able to predict the liquid phase mole fractions from the known variables: temperature and (total) pressure. This should be theoretically possible according to the phase rule. As it can be seen from the thermodynamic background in Chapter 2, the majority of the thermodynamic relations and equations combine the vapour phase mole fractions in some way or another to the liquid phase mole fractions. It is thus practically difficult to develop a model in terms of independent parameters: temperature and pressure.

It was hoped to achieve a first stage to a prediction model, if it had been possible to produce a similar graph as in Figure 4.2 by replacing the solvent independent force constant with the solvent and solute dependent unlike pair potential. Common mixtures, which have been examined in the literature were chosen. The unlike pair potential was calculated by as many means as possible: dependent on temperature, at a "standard" temperature, the geometric and the London pair potential were examined, the interchange energy was employed, mixtures with water were included and excluded, and the two options of deriving a value for the equilibrium distance were employed. All these results were analysed in various ways of which the most important was distinguishing between the analysis of a single solute dissolved in a number of solvents, or analysing a number of solutes dissolved in a single solvent.

The result of these analyses is that there is indeed a linear relationship similar to that in Figure 4.2 between the unlike pair potential and the logarithm of the solubility. The closest linear relationship and thus the first stage of a prediction model, where some unlike pair potential is used to predict solubility, is at different options for each individual mixture. In other words, there is no clear indication of how to choose the parameters for an arbitrary mixture to calculate the unlike pair potential (also in the variant of the interchange energy) that will enable a reasonable accurate prediction of the solubility.

However, overall the analysis eliminates some of the options. It is clear from the results that the pair potential (whether like or unlike) is definitely a function of temperature. There is a tendency for the potentials calculated using the heat of vaporization option to give better results then when using the molar volume option. No such tendency was observed when employing the unlike London pair potential as opposed to the geometric mean unlike potential.

The analysis could only be carried out as a result of the development of the extrapolation method, where the equilibrium distance is extrapolated beyond the critical temperature of the "permanent" gases in order to obtain a value for the like pair potential for the gas in its supercritical state. This method was successfully applied in this study.

In this work a number of polar compounds and compounds containing hydrogen bonding have been included despite that the basic London theory excludes compounds like that. The results show that the alcohols: methanol. ethanol. and 1-propanol can be included as they are in the London theory and be expected to give reasonable accurate results. Water represents a bigger problem, and the overall conclusion is not to expect accurate results for mixtures where water is included.

The solubility prediction results using extrapolated values of the solubility parameter gave much better prediction results then when employing the literature values of the solubility parameters, even though the regular solution calculations of the solubility contain a number of parameters which are determined with large uncertainties. From this minor investigation it seems that taking the van der Waals forces to be the dominant forces both in the polar compounds and compounds containing hydrogen bonding achieves better solubility predictions.

Chapter 6 - Final conclusions and suggestions for future work

6.1 Final conclusions in relationship to solubility

This work began from an optimistic belief that the provision of an improved molecular combining rule for the attractions between unlike non-polar polyatomic molecules would enable the construction of a "simple" theory of dilute solutions of non-polar compounds including supercritical gases.

It has long been known that solubility of gases and vapours in common solvents at room temperature can be rationalised in terms of a grid of interaction effects made up from the like molecule interactions on the one hand and solubility parameter differences on the other. The search for a well defined unlike pair potential which would represent a dominant term in the mixing rule appropriate to dilute solutions has therefore been the main theme in this work.

Much of the work here has tended to show that the behaviour of dilute solutions of vapours is a good pointer to the behaviour of that of gases and that actually both can be embraced in one theory. In both cases however, since solubility is dictated by a free energy (Gibbs energy), one might expect both entropy and enthalpy terms to pay an independent part in its make up. In practice, it appears that for a variety of solvents either the entropy of solution is nearly constant, or it is sufficiently correlated with the enthalpy of solution to demonstrate a **broad** correlation between solubility and an intermolecular energy parameter at a standard temperature such as 298.15 K.

By contrast, the search for a **detailed** mixing rule which might be used to explain structure dependence or temperature dependence of solubility more closely, reveals the great sensitivity of activity coefficient models such as AGAPE to the assumptions made about both the like-pair and unlike-pair molecular interaction potentials. This suggests that, rather as in the successful UNIFAC treatment of excess free energies of more concentrated solutions, the energy parameters fit subsume a substantial entropy term, and the comparative success of the geometric mean combining rule (Berthelot's rule) may be somewhat of an artefact of the algebra of the models rather than a demonstration of the molecular interactions of the London type.

Correlations making use of corresponding states principles have been useful for broad understanding and interpretation by comparison to those models which are more properly defined as equation-of-state type which appear to deal more sensitively with both effects. Although in any cubic equation of state the parameters "a" and "b" are open to some ambiguity, may be temperature dependent or even correlated, they do provide a reasonable way of representing the principally energetic effect through "a" and the more geometrical repulsive or entropy related forces *via* "b". Even here, though however, it seems that model predictions may draw some benefit from the phenomenological compensations which actually occur in balancing enthalpic and entropic effects. This is probably demonstrated in the difficulty all models experience in extending their predictions to aqueous solutions. In the case of water as a solvent, entropic terms are very large and explicit and do not seem to be easily embraced in the scaled particle model or cavity procedure used for prediction.

Even for non-aqueous solvents the behaviour of both Henry's law constants and infinite dilution activity coefficients become more and more determined by Flory-Huggins combinational entropy considerations as the solvents have chain lengths in excess to 10 carbon atoms (Parcher et al., 1975). Despite their sophistication, even modern equations of state, particularly conventional cubic equations, however normalised, have problems with mixtures where the size difference of solutes and solvents are great.

By comparison, systems which "buy into" the vast base of phase equilibrium data contained in UNIFAC, by interfacing with it have much to offer for detailed prediction. Another fruitful area would appear to be a detailed study of linear free energy relationships using a common sense analysis of groupings instead of those dictated by UNIFAC.

Prospects of extending solubility models which work for non-aqueous solvents to water are mixed. Computer simulation procedures allow perturbation treatments to predict behaviour of different systems in water but to find a coherent and simple model which will embrace all solvents including water is difficult.

Finally, the clearest single message of this work is to point to the need to embrace some repulsive forces in models for solubility.

6.2 Final conclusions of work

The conclusions of this investigation can be described as:

A linear relationship between the logarithm of the solubility and the solute characteristic (ε/k_B) has been proven by Hildebrand and Scott (1962). Such a relationship has been further investigated in this work using the unlike pair potential instead of the solute characteristic. Three methods have been employed, one where the unlike potential is considered independent of temperature, one where the like potential for the solvent is a function of temperature and finally the method where both like potentials are functions of temperature. The options: unlike London pair potential, unlike geometric mean potential and the like potentials calculated from either the heat of vaporization or the molar volume have been examined.

A very reasonable linear relationship was achieved for the analysis of various solutes dissolved in a single solvent, except for water. The relationship improved when the unlike pair potential was a function of temperature. When analysing a single solute dissolved in a series of solvents, the linear relationship improved dramatically for the case, where the unlike pair potential was a function of temperature.

The conclusion of the linear relationship investigation is that the linear relationship closest to a straight line is obtained when both like potentials for the solute and solvent are functions of temperature. This result is consistent with the previous use of the AGAPE equations for predicting vapour-liquid equilibrium.

A number of mixtures has been investigated, i.e., water and n-butane. The solubilities of various solutes dissolved in water are much lower then the solubilities in n-butane. This leads to the conclusion that it is doubtful whether a solubility prediction model, based on a lattice model will be able to handle the full range of solubility values.

The previous investigations involved a number of low-boiling gases such as argon, nitrogen, hydrogen, and oxygen. For these gases it was necessary to develop a method to obtain a pseudo "liquid-like" like pair potential at temperatures above their critical temperatures. Such a method (the extrapolation method) was developed and applied successfully in this work.

The total pressure and the temperature were predicted, respectively for a number of mixtures which fall within the limitations of the AGAPE theory using the experimental solubility as a known parameter. Reasonable accurate values compared to both the measured pressure and the measured temperature, respectively were obtained. The accuracy was in the same order of magnitude as the results obtained from employing three other prediction methods.

The prediction of solubilities for mixtures including water and three alcohols (solvents) gave more accurate values compared to the experimental solubilities, when employing the regular solution theory using extrapolated values of the solubility parameter (pretending that the van der Waals forces dominate) then when using the literature values of the solubility parameter (where the forces also include dispersion forces).

A linear relationship between the MOSCED dispersion parameter and the like London pair potential was achieved for two homologous series consisting of three alcohols and three linear hydrocarbons, respectively. For the majority of the compounds included in the AGAPE database there were no easy detectable relationship between the two parameters mentioned. It should be kept in mind that the MOSCED parameter was only available for compounds which are solvents at a temperature of 298.15 K.

6.3 Suggestions for future work

6.3.1 Improvements in the basic London theory

There are a number of ways that the basic London theory could be improved.

London's dispersion forces only account for the attractive forces (and short-range repulsive forces) and one suggestion for future work would be to incorporate the long-range repulsive forces in the calculation of the pair potentials. The Lennard-Jones potential takes into account both the attractive and the repulsive forces, but application of the Lennard-Jones potential to predict phase equilibrium has not been as successful as the use of the London forces. Development of a new theory based on London's intermolecular forces and including a term to account for the repulsive forces could lead to improved phase equilibria predictions.

The basic London theory was developed for non-polar compounds and for compounds containing no hydrogen bonding. Research in the past has shown this approach to be quite successful, when a Flory-Huggins-like term is added to incorporate the compounds containing hydrogen bonding. Similarly, an added term could account for the polar components. This would extend the concept of the London theory to include many more components. Some compounds which are polar and contain hydrogen bonding, e.g., methanol, ethanol, and 1-propanol have already been successfully included in the AGAPE database without added terms for the polarizability or the hydrogen bonding. Predictions involving acetic acid which also forms a dimer, and therefore needs special focus, are shown to be less accurate. The same was the case for water which also forms a dimer and higher. Including terms to account for polar compounds and compounds containing hydrogen bonding would result in better prediction results for compounds such as acetic acid and water.

In all the calculations carried out in the work, the equilibrium separation for the mixture is calculated as the arithmetic mean values of the two equilibrium separations. This agrees with the very reasonable VLE predictions published by Kakhu and co-workers (Homer et al., 1991, Kakhu and Homer, 1996a, Kakhu and Homer, 1996b, and Kakhu et al., 1995), where the arithmetic mean value has been used, too. However, in cases where the difference in the sizes of the two compounds was large, Mohammadi (1986) used the maximum of the equilibrium separations as the equilibrium separation for the mixture.

To investigate this concept and incorporate it in the AGAPE theory, is another suggestion for improving the London theory.

A way of include larger molecules such as hydrocarbons with 6 to 12 carbon atoms in the London theory is by imaging that a small molecule like argon or methane does not "see" the whole of a large molecule with 6 to 12 carbon atoms, but just the ends of the larger molecule. This would agree very well with the London theory, where the molecules are assumed to be spherical. If, in the first instance, the hydrocarbons containing 6 to 12 carbon atoms could be symbolised with a "pseudo" ethane or propane molecule, this would open up the way for a whole range of larger compounds to be included in the AGAPE predictions.

Recently, attention has been paid to some inconsistency in the distribution of the C-H moment for hydrocarbons. This has initiated some work on a different distribution of charge, where the polarizability for the carbon atoms is lower then the values used in this work (where the same values as used throughout the published prediction results by Kakhu and co-workers have been used to make ensure compatibility), while the polarizability of the hydrogen atoms is larger. The work is in an early stage, but also here the preliminary results for a mixture of methane and carbon tetrafluoride indicates a much better prediction for the energy then the results previously obtained for this mixture.

The generalized London potential accounts for rotation between two unlike molecules by using an averaged value. Closer examination of especially the hydrocarbon-fluorocarbon interactions suggests that instead of using an average, the London potential between unlike molecules ought to account for variable rates of relative rotation.

6.3.2 The AGAPE theory

The MHV2 methods shows that it is possible to combine an equation of state with an activity coefficient model, and then apply the activity coefficient model to high pressures. The AGAPE model which is limited to low pressure due to the assumption of vapour phase ideality could be treated the same way. The combination of the AGAPE activity coefficient model with an equation of state has, in fact, started in this Department. The chosen equation of state is a modification of the van der Waals equation of state. The work is at an early stage, but very preliminary results are promising.

6.3.3 Improvements of solubility calculations in the future

Attempt to understand the anomalously high solubility of gases in perfluoro compounds as well as the unusually low solubility of gases in water by detailed reference to specific structure effects would seem to be a future way forward to improve solubility calculations.

Nomenclature

a	Redlich-Kwong constant
aa	a correction exponent (calculated from solute properties)
ac	acidity in the MOSCED model
a_i	activity of component i
a'_{ij}	van der Waals constant for molecular pairs i-j
a_i^0	activity of component i at standard state
a^A	parameter in the AGAPE equation
a^E	molar excess Helmholtz energy
a^{HS}_1, a^{HS}_2	hard-sphere diameters for the solvent and the solute, respectively
$a^U_{ij}{}^{(0)}$, $a^U_{ij}{}^{(1)}$, $a^U_{ij}{}^{(2)}$	temperature parameters (modified UNIFAC equations)
a^U_{mn}	UNIFAC group interaction parameter for compound m and n
a'	van der Waals constant
$\overline{A}_i$	parameter in the UNIWAALS equation
A_M	Margules constant
A_W	van der Waals surface area
A_{Wi}	van der Waals surface area of component i
A'_{VL}	van Laar constant
A^D, B^D, C^D, D^D, E^D, e^D	parameters in the Daubert and Danner heat of vaporization equation
A^E	excess Helmholtz energy
A^R	parameter in the reference solvent equation
A^S	parameter in a fitting equation for the normalised activity coefficient
A^{UW}	parameter in the UNIWAALS equation
A, B, C, D, and E	parameters in a fitting equation
b	Redlich-Kwong constant
bc	basicity in the MOSCED model
b^A_1, b^A_2	parameters in the AGAPE equations
b'	van der Waals constant
B	second virial coefficient

B_{mix}	second virial coefficient of the mixture
B_{11}	second virial coefficient of the pure component 1
B_{22}	second virial coefficient of the pure component 2
B_{12}	second virial coefficient corresponding to the 1-2 interaction
B^R	parameter in the reference solvent equation
B^S	parameter in a fitting equation for the normalised activity coefficient
B^{UW}	parameter in the UNIWAALS equation
$B^{UW}{}_i$	parameter for component i in the UNIWAALS equation
B'	variant of the second virial coefficient, depending on temperature
B'_{VL}	van Laar constant
c	cohesive-energy density
const	a constant to convert to the right units, equals 60.24 in this work
C	third virial coefficient
C_{mix}	third virial coefficient of the mixture
C_P	heat capacity
C_{111}	third virial coefficient of the pure component 1
C_{112}	third virial coefficient of the molecules 1-1-2 interaction
C_{122}	third virial coefficient of the molecules 1-2-2 interaction
C_{211}	third virial coefficient of the molecules 2-1-1 interaction
C_{221}	third virial coefficient of the molecules 2-2-1 interaction
C_{222}	third virial coefficient of the pure component 2
$C^A{}_i$	multicomponent AGAPE equation parameter
C^R	parameter in the reference solvent equation
C'	variant of the third virial coefficient, depending on temperature
d	parameter in the UNIWAALS equation
d_i	equilibrium separation of one atom i from the centre of mass
D	fourth virial coefficient

D'	variant of the fourth virial coefficient, depending on temperature
e_i	electric charges
$< \overline{E}^2 >$	mean-square value of the dispersion field
f_i	fugacity of component i
f_i^0	fugacity of component i at standard state
f_i^C	fugacity of component i in the compressed phase
f_i^G	fugacity of component i in the gaseous phase
f_i^L	fugacity of component i in the liquid phase
f_i^S	saturated vapour fugacity of component i
f_i^V	fugacity of component i in the vapour phase
f_i^α	fugacity of component i in phase α
f_i^β	fugacity of component i in phase β
F	numbers of degrees of freedom
F	force
F^A	a factor, assigned to account for the molecular rotations
$\overline{g}_i$	partial molar Gibbs energy for component i
$\overline{g}_i^E$	partial excess molar Gibbs energy for component i
$\overline{g}_c$	partial molar Gibbs energy for the solute, cavity forming term in the scaled-particle model equation
$\overline{g}_I$	partial molar Gibbs energy for the solute, interaction term in the scaled-particle model equation
g^E	excess molar Gibbs energy
G	Gibbs energy
G^E	excess Gibbs energy
G^E_∞	excess Gibbs energy at infinite pressure
h	molar enthalpy
h_2^G	molar enthalpy for the pure gas (2)
h_2^L	molar enthalpy of the hypothetical pure liquid (2) at the temperature of the solution
$\overline{h}_2^L$	partial molar enthalpy of the hypothetical pure liquid (2) at the temperature of the solution

$\Delta h_{i,vap}$	molar enthalpy of vaporization for component i
h^E	excess molar enthalpy
H	enthalpy
H	Henry's constant
H_{ij}	Henry's constant for solute i in solvent j
$H_{i,\,solvent}^{(P')}$	Henry's constant taken at some arbitrary reference pressure P′
H_{iR}	Henry's constant for solute i in reference solvent R
ΔH_{vap}	latent heat (enthalpy) of vaporization
H^E	excess enthalpy
I_i	first ionization potential
j	repulsion constant in the Lennard-Jones potential
J	calculated separately for each contribution due to dipole, induction, and dispersion effect
k	attraction constant in the Lennard-Jones potential
k_B	Boltzmann′s constant ($=1.38084\cdot10^{-23}$ J/K)
k_{ij}	characteristic binary constant, represents the deviation from the geometric mean
K_i	equilibrium constant
l	intermolecular distance
L	Avogadro′s number of molecules in a mole ($=6.023\cdot10^{23}$ mol^{-1})
m	number of components
m_i	dipole moment of component i
$m^W{}_2$	number of whole molecular contacts that a central molecule 1 makes with molecules of type 2 in its coordination shell
$m^W{}_1$	corresponding number that same central molecule 1 makes with molecules of type 1 in its coordination shell
$<m^2>$	bonded atom mean square moment ($3\alpha v_0 \hbar/2$)
n_i	number of moles of compound i
n_D	refractive index
n_T	total number of moles
N_1	molecules of type 1
N_{11}	number of nearest neighbours of type 1-1

N_{12}	number of nearest neighbours of type 1-2
N_2	molecules of type 2
N_{22}	number of nearest neighbours of type 2-2
p	partial pressure
p_g	partial pressure of the dissolved gas
p_i	partial pressure of component i in the gas phase
p_i^0	partial pressure of component i at standard state
P	total pressure
ΔPE	difference in potential energy
PE	potential energy
P^0	standard state pressure
P_i^S	saturated vapour pressure of component i
P_r	reduced pressure
P_C	critical pressure
P_{Ci}, $P_{C,i}$	critical pressure of component i
P'	some arbitrary reference pressure
q	relative contact surface areas of two molecules
q_i	multicomponent AGAPE parameter
$q^{HV}{}_1$, $q^{HV}{}_2$	fitting parameters in the MHV2 mixing rule
$q^U{}_i$	UNIFAC parameter
$q^*{}_i$	external surface area of molecule i
$Q^U{}_k$	UNIFAC surface area parameter for group k
r	difference in sizes of the molecular volumes between two molecules
r_i	multicomponent AGAPE parameter
r_{ij}	distance between atoms in two rotating molecules i and j
$\{r_{ij}^{-6}\}$	averaging of the inverse sixth power of r_{ij}
r^{HS}	a radii parameter in the hard-sphere equation
$r^U{}_i$	UNIFAC parameter
R	universal gas constant (=8.31439 J/(mol K))
R^A	equilibrium intermolecular separation for pure liquid
$R^A{}_i$	equilibrium intermolecular separation for pure liquid component i

R^{A}_{mix}	equilibrium intermolecular separation for a mixture
R^{U}_{k}	UNIFAC volume parameter for group k
s_2^{G}	molar entropy for the pure gas (2)
s_2^{L}	molar entropy of the hypothetical pure liquid at the temperature of the solution
$\bar{s}_2^{L}$	partial molar entropy of the hypothetical pure liquid (2) at the temperature of the solution
s^{E}	molar excess entropy
S	entropy
S^{E}	excess entropy
t^{W}_{2}	number of whole molecular contacts that a central molecule 1 makes with molecules of type 2 in its coordination shell
t^{W}_{1}	corresponding number that same central molecule 1 makes with molecules of type 1 in its coordination shell
T	absolute temperature
T_r	reduced temperature
T_{ri}, $T_{r,i}$	reduced temperature of component i
T_C	critical temperature
T_{Ci}, $T_{C,i}$	critical temperature of component i
T_0	reference temperature
T^{G}_{2}	constant specific to the solute
Δu_{ij}	parameter used in the UNIQUAC equations
Δu_{vap}	energy of complete vaporization
u^{E}	excess molar energy
U	potential energy
U_t	total potential energy
ΔU	change in total molar energy due to mixing
ΔU_{11}, ΔU_{22}	AGAPE parameters
U^{E}	excess energy
v	molar volume
v_i	molar volume of component i
v_{mix}	molar volume for the mixture
v_i^{C}	molar volume of component i in the compressed phase

$\overline{V}_i$	partial molar volume of component i (in the liquid phase)
$\overline{V}_i^{\infty}$	partial molar volume of component i (in the liquid phase) at infinite dilution
v^E	excess molar volume
v^L	molar volume of the pure liquid
V	volume
V_i	partial volume of component i
V_C	critical volume
V^m	molecular volume
V^m_i	molecular volume of component i
V^E	excess volume
x_g	mole fraction of the dissolved gas
x_i	mole fraction of component i in the liquid phase
$x_{2,R}$	solubility of component 2 in a reference solvent R
X_{12}, X_{11}	fractions of the total number of molecules around the central molecule 1 that are of type 2 or 1
X^U_m	parameter in the UNIFAC equations
y_i	mole fraction of component i in the vapour phase
Y	scaled-particle parameter
w_i	volume fractions of component i
w^m_i	molecular volume fraction of component i
w'	interchange energy
W_j	number of structurally equivalent atoms j in the molecule
z	number of nearest neighbours (coordination number)
z_i	(vapour or liquid) phase composition of component i
Z	compressibility
Z_{mix}	compressibility of the mixture
Z_C	critical compressibility
Z_{RK}	compressibility as expressed by Redlich-Kwong equation of state
Z_{VW}	compressibility as expressed by van der Waals equation of state

$\overline{Z}_i$	parameter in the UNIWAALS equation
$<>$	electronic time averaging

GREEK

α_i	polarizability for molecule i
α_{ij}	relative volatility
$\alpha^G{}_2$	constant specific to the solute
α^{HV}	Huron-Vidal parameter used in the MHV2 model
$\alpha^{HV}{}_{ij}$	Huron-Vidal parameter used in the MHV2 model for the molecules i-j
$\alpha^{HV}{}_{mix}$	Huron-Vidal parameter used in the MHV2 model for the mixture
α, β	phases
β^G	universal constant for simple gases
γ_i	activity coefficient of component i in the liquid phase
$\gamma_{k(i)}$	residual activity coefficient of group k in a reference solution containing only molecules of type i
$\gamma_{2,R}{}^{\infty}$	activity coefficient of component 2 in the gaseous phase in a reference solvent R at infinite dilution
γ_i^{∞}	activity coefficient of component i in the liquid phase at infinite dilution
$\gamma^{*}{}_{i}$	activity coefficient of component i in the unsymmetric convention
Γ	parameter in the UNIFAC equation
δ_i	solubility parameter of component i
$\overline{\delta}$	average solubility parameter for the entire solution
ε	negative minimum energy
ζ	constant depending on the intermolecular distance and the potential function
η	constant for polar, non-associated liquid
θ	parameter in the UNIFAC equation

θ^{A}_{i}	multicomponent AGAPE parameter
θ^{*}_{i}	UNIQUAC parameter, surface fraction of component i
Θ	parameter in the UNIFAC equation
Θ^{*}	parameter in the UNIQUAC equation
κ	parameter in Kohler's calculation of the interchange energy
λ	dispersion parameter in the MOSCED equations
λ^{A}_{i}	parameter in the multicomponent AGAPE equations
λ'_{21}, λ'_{11}	Boltzman parameter factor (used in the Wilson equations) related to potential energies of a 1-2 pair and a 1-1 pair, respectively
μ_i	chemical potential of component i
μ_i^0	chemical potential of component i at standard state
ν_{ki}	number of groups of type k in molecule i
ν_{0i}	frequency for molecule i in its unexcited state
ξ'_{i}	local volume fraction for component i
o	parameter in the MOSCED equation
π	number of phases
ρ	density
ρ^{S}_{r}	reduced, saturated density
ρ^{S}	saturated density
σ	intermolecular distance when $\Phi = 0$ (distance parameter in the Lennard-Jones potential)
σ_i'	hard-sphere diameter for component i
σ'	hard-sphere diameter
τ^{A}_{ij}	parameter in the multicomponent AGAPE equations
φ_i	fugacity coefficient of component i
φ_i^L	liquid fugacity coefficient of component i
φ_i^S	saturated vapour fugacity coefficient of component i
φ_i^V	vapour fugacity coefficient of component i
φ_i^0	fugacity coefficient of component i at standard state

$\varphi_2^{L,\infty}$	liquid fugacity coefficient of the solute (component 2) in the liquid solvent at infinite dilution
Φ	potential energy
Φ_{ii}	net potential energy between two molecules i and i
Φ_{ij}	net potential energy between two molecules i and j
Φ_{min}	minimum potential energy
$\overline{\Phi}_{ij}$	average potential energy between two dipoles i and j
χ	parameter in the MOSCED equation
Ψ_{km}	binary parameter for Wilson equation in the UNIFAC equations
ω	Pitzer's acentric factor
ω^U_i	UNIFAC parameter
$\hbar$	Planck´s constant ($=6.6242\cdot10^{-34}$ Js)

SUPERSCRIPTS

m	molecular
combinatorial	
residual	
A	AGAPE
C	compressed phase
E	excess
FV	free volume
G	group
HS	hard-sphere
L	liquid phase
S	saturated phase
U	UNIFAC
UW	UNIWAALS
V	vapour phase

0	standard state
∞	infinite

SUBSCRIPTS

c	cavity
g	dissolved gas phase
i	component
i	an atom i in a molecule
ideal	ideal state
mix	mixture
pair	
r	reduced
s	solvent
vap	vaporization
v_i^P	vapour pressure (of component i)
C	critical
D	Daubert and Danner
I	interaction
M	Margules
R	reference solvent
RK	Redlich-Kwong
VL	van der Laar
VW	van der Waals

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