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Synthesis gas solubility in Fischer-Tropsch slurry: Final report

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on
Synthesis Gas Solubility in
Fischer-Tropsch Slurry

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SUMMARY AND CONCLUSION

The objective of this research is to investigate the phase equilibrium behavior of synthesis gases and products in a Fischer-Tropsch slurry reactor. A semi-flow apparatus has been designed and constructed for this purpose. The apparatus provides contact for a flowing gas stream with a stationary liquid and is suitable for the determination of gas solubility in a molten wax of high melting point. The new apparatus has been tested with a mixture of carbon dioxide and toluene to verify attainment of equilibrium. The test data agree well with experimental results of Ng and Robinson from a static apparatus.

Measurements have been made for each of six gases (hydrogen, carbon monoxide, methane, ethane, ethylene, and carbon dioxide) in a heavy n-paraffin at temperatures from 100 to 300 °C and pressures 10 to 50 atm. Three n-paraffin waxes: n-eicosane (n-C₂₀), n-octacosane (n-C₂₈), and n-hexatriacontane (n-C₃₆), were studied in this work to model the industrial wax. Solubility of synthesis gas mixtures of H₂ and CO in n-C₂₈ was also determined at two temperatures (200 and 300 °C) for each of three gas compositions (40.01, 50.01, and 66.64 mol % of hydrogen). The measurements were extended to investigate the gas solubility in two industrial Fischer-Tropsch waxes: Mobil wax and SASOL wax.

The observed solubility increases in the order: H₂, CO, CH₄, CO₂, C₂H₄, C₂H₆, at a given temperature pressure, and in the same solvent, as shown by some typical result in the following table:

Solubilities in $n\text{-C}_{36}\text{H}_{74}$
at 200°C and 20 atm

	H_2	CO	CH_4	CO_2	C_2H_4	C_2H_6
x, mole fraction	0.0476	0.0614	0.118	0.155	0.204	0.234

In mole fractions the solubility of a gas increases slightly with the molecular weight of the wax at the same temperatures and pressure. The increase is not as much as in proportions to the molecular weight with the result that the solubility in mass fractions slightly decreases with the molecular weight of the wax as shown by some typical result in the following table:

Solubility of H_2 in Various Waxes
at 200°C and 20 atm

Solvent wax	$n\text{C}_{20}$	$n\text{C}_{28}$	$n\text{C}_{36}$	Mobil wax ($n\text{C}_{61}$)
x, mole fraction	0.0362	0.0402	0.0476	0.0661
w, mass fraction $\times 10^3$	0.268	0.214	0.199	0.166

Solubility increases with increasing pressure for all the gases studied. At the temperatures of this investigation the lighter gases H_2 and CO show increased solubility with increasing temperature, while the heavier gases CO_2 , ethane, and ethylene show decreased solubility with increasing temperature. The solubility of methane, the intermediate gas, changes little with temperature, and shows a shallow minimum at about 200°C or somewhat above. The observed variation with temperature agrees with the general pattern of the solubility of a gas to show a minimum, and for the temperature of minimum solubility to increase with the boiling point of the gas.

Henry's constant and partial molal volume of the gas solute at infinite dilution are determined from the gas solubility data.

A correlation is developed from the experimental data in the form of an equation of state. The Soave equation of state is modified to fit the vapor pressure of the n-paraffins up to n-C₁₀₀. The Huron-Vidal mixing rule is introduced into the modified Soave equation to extend the equation to mixtures. The correlation is useful for the calculation of solubility of the gases (H₂, CO, CH₄, CO₂, C₂H₄, and C₂H₆) in n-paraffins and industrial paraffin waxes. Calculations of the solubility of gas components in gas mixtures have been found to be as good as for the pure gases.

A computer program has been prepared to implement the correlation. Use of the program, list of the codes, input, output, and an example solubility calculation are described in the Appendix.

Solubility of the gases in solvents other than n-paraffins is of interest since some olefins, and oxygenates can also be present in Fischer-Tropsch waxes. Solubility can be a factor in the selection of solvent for slurry reactors of the future. Solubility data on gases of interest in solvents other than n-paraffins are scanty and must be measured to meet the needs.

Chapter 1. INTRODUCTION

Continued development of Fischer-Tropsch synthesis in a slurry reactor has created a need for information on gas solubility in the slurry media. Satterfield and co-workers (Satterfield et al., 1982; Satterfield and Stenger, 1985; Stenger and Satterfield, 1985), Stern et al. (1983), and Albal et al. (1984) have studied the effect of liquid composition on the rate of reaction and selectivity of Fischer-Tropsch synthesis in a slurry reactor, and concluded that the solubility of synthesis gases in the slurry was needed for interpretation of the synthesis reaction. The solubility information is also needed for the design and operation of synthesis processes.

Previous studies on the solubility of synthesis and product gases in heavy wax at conditions of temperature and pressure of the Fischer-Tropsch processes are limited. Albal and co-workers (1984) reported solubility data of synthesis gases (H_2, CO) in Gulf wax at temperatures of 348-523K. Matsumoto and Satterfield (1985) investigated the solubility of hydrogen and carbon monoxide in three selected liquids (n-octacosane, phenanthrene, and fomblin YR), which they used in their Fischer-Tropsch synthesis studies. High temperature gas solubility in paraffin wax was measured by Peter and Weinert (1955).

In this work we designed and constructed a new apparatus for measurement of vapor-liquid equilibrium (VLE) for gas + slurry mixtures at conditions of Fischer-Tropsch synthesis in slurry reactors. The apparatus, of semi-flow type, provides contact for a flowing gas stream with a stationary liquid and is suitable for the determination of gas solubility in a molten wax of high melting point.

Measurements have been completed for 18 binary mixtures: hydrogen, carbon monoxide, methane, ethane, ethylene, and carbon dioxide in $n\text{-C}_{20}$, $n\text{-C}_{28}$, and in $n\text{-C}_{36}$ at reactor conditions of Fischer-Tropsch synthesis, and for synthesis gas mixtures of H_2 and CO in $n\text{-C}_{28}$ at three feed gas compositions (40.01, 50.01, and 66.64 mol % of H_2). Gas solubility has also been determined in Mobil wax and SASOL wax at temperatures of 200-300 °C and pressures 10-50 atm.

Henry's constant and partial molar volume at infinite dilution of the dissolved gas in n -paraffin solvent are determined from the solubility data. A correlation of synthesis and product gas solubility in n -paraffins and industrial paraffin waxes has been developed from a modified Soave equation of state incorporating Huron-Vidal mixing rules.

Chapter 2. EXPERIMENTAL APPARATUS AND PROCEDURE

Figure 1 shows the scheme of the semi-flow apparatus, which consists of two main sections: the equilibration section and the sampling section. All parts exposed to high temperature and pressure are constructed of 316 stainless steel.

The heart of the equilibration section is the thermostated nitrogen bath in which two stainless steel cells are placed in series. The first cell serves as a presaturator, and the second, the equilibrium cell. The bath is a well insulated and regulated oven of 2.1 ft³ internal volume. Nitrogen gas fills the bath in the course of experiments. Circulation of nitrogen in the bath is maintained by an electric fan mounted at the back of the bath. Two heating wires insulated in ceramic beads and controlled by rheostats are placed at the fan outlet to heat the bath. A secondary heater is connected to a temperature controller (Halikainen Instrument Model 1053). The temperature sensor of the thermotrol is located in the vicinity of the equilibrium cell. The temperature uniformity in the bath was found to be within 0.5°C in the vicinity of the cells at bath temperature 100°C, and 1°C at 300°C. The uniformity should be improved when the apparatus is in operation with a gas stream flowing through the cells.

The temperature of the equilibrium cell is measured by a type K chromel-alumel thermocouple inserted into the cell and calibrated to an accuracy of $\pm 0.1^\circ\text{C}$. To ensure isothermal condition in the bath, a second thermocouple is placed outside the cell. Heating of the bath is controlled so that both thermocouples give the same reading within their accuracy in the course of an experiment. A model CMM 0-750 psi Heise gauge is used to read the pressure with an accuracy of $\pm 0.1\%$ of the

maximum range.

Both cells are loaded at the beginning of a series of runs with about 500 cm³ of solvent. The bath is heated to the desired temperature before introducing the gas. Gas is supplied continuously to the system from the gas cylinder to maintain the pressure of interest and to promote mixing. The cells are packed with raschig rings, and the gas is sparged through the solvent in the cells. Equilibration requires about 20-40 minutes at the end of which the liquid composition attains a constant steady value. The gas flow rate is varied to test for constancy of gas composition when the gas composition is of interest.

Sampling Procedure

Liquid-phase effluent from the equilibrium cell is reduced in pressure and temperature before entering a trap for sampling. The heavy paraffin is condensed and retained as a solid in the trap at ambient conditions and later weighed with an analytical balance. The liberated gas from the condensate is determined volumetrically in a buret. For test mixtures of CO₂ + toluene, toluene condensate is retained as liquid in the trap at ambient condition. Minor corrections for the quantities of CO₂ dissolved in toluene and toluene vaporized into CO₂ were made to the directly observed sample weight and gas volume. No such corrections are needed for the paraffin solubility experiments.

To prevent the entrainment of gas bubbles in the liquid samples and to maintain the system at constant pressure in the course of liquid-phase sampling, the gas stream from the presaturator is switched from the bottom of the equilibrium cell to a bypass at the top of the cell.

The sampling system and procedure for determination of the content of volatilized wax in the vapor phase, when the volatility is appreciable, are similar to those described above for the liquid sample, except that a wet test meter was used in place of a buret to measure the gas as the gas volume is substantial.

In experiment for the solubility of synthesis gas mixtures ($H_2 + CO$) in $n-C_{28}$, the weight of solidified wax in the trap and the volume of liberated gas were determined by the same procedure described above for binary mixtures. The gas composition was determined with a Carle analytical gas chromatograph (GC) Model 111, equipped with a palladium tube for hydrogen transfer. The GC was calibrated with Matheson Primary Standard gas mixtures of H_2 and CO .

Materials

The sources and purities of chemicals used in this work are as follows:

Chemical	Supplier	Purity
H_2	Airco	99.8 ⁺ mole %
CO	Matheson	99.5 ⁺ mole %
CH_4	Matheson	99 ⁺ mole %
C_2H_6	Matheson	99 ⁺ mole %
C_2H_4	Matheson	99.5 ⁺ mole %
CO_2	Matheson	99.8 ⁺ mole %
Toluene	Malinckrodt	99 wt %
$n-C_{20}$	Aldrich	99 wt %
$n-C_{28}$	Alfa	99 wt %
$n-C_{36}$	Alfa	99 wt %

The synthesis gas mixtures of H_2 and CO were purchased from Matheson Gas Products (Primary Standard gas mixtures) at specified compositions. Mobil wax was supplied by Mobil Research and Development Corporation at Paulsboro, New

Jersey. The wax was obtained from Run CT-256-7 of a two-stage Bench-Scale Unit. FIMS analysis gives a molar average molecular weight of 857 and weight average 1189. Detailed results of the analysis were reported by Kuo (1985). The characterization of the SASOL (commercial Arge) wax was performed by UOP Inc. under DOE Contract No. DE-AC22-85PC80017. The carbon number range of the SASOL (Arge) wax, determined by GPC (Gel Permeation Chromatography), is from C_{10} to C_{250} with an average carbon number of 43 from GPC, and 47 from NMR analysis (UOP, 1986).

Possible thermal degradation of the n-paraffin in the experiments was examined by GC analysis of the collected paraffin sample and by comparing the repeated data points at the same conditions of temperature and pressure. No decomposed products were detected from GC at any of the experimental conditions of this work. The solubility data were reproducible within the experimental errors regardless of the age of n-paraffin wax in operation.

Chapter 3. EXPERIMENTAL RESULTS

The apparatus has been tested with mixtures of carbon dioxide and toluene at 353K to verify attainment of equilibrium. As shown in Figures 2 and 3, the new data agree well with the experimental results of Ng and Robinson (1978) from a static apparatus. Further tests for the attainment of equilibrium have periodically been made by varying the gas flowrate over a factor of approximately 1.5. All of the results reported in this work were found to be independent of the flowrate.

Gas solubility measurements have been completed for 18 binary mixtures: hydrogen, carbon monoxide, methane, ethane, ethylene, and carbon dioxide in *n*-C₂₀, *n*-C₂₈, and in *n*-C₃₆ at three temperatures (100, 200, and 300°C). Along each isotherm, five pressures (10, 20, 30, 40, and 50 atm) were investigated for each system, except ethane binaries for which only four pressures (10-40 atm) were determined. The measurements at one temperature were made in the sequence of 10 atm, 30 atm, 50 atm, 40 atm, and 20 atm, to reveal any possible super or under saturation effects. No such effects have been observed for all the data reported in this work.

Tables 1-18 summarize the experimental results for each of the six gases in each of the three *n*-paraffins. At least four replicate samples were taken at an experimental condition of temperature and pressure. The multiple samples are generally reproducible to within 1.5% in the mol fraction of the gas component. The compositions reported in the tables are the average values of replicate samples. Figures 4-21 show the experimental solubility data, respectively, for 18 binary mixtures as a function of pressure at different temperatures. Individual sample

compositions are shown in the figures as separate points when they can be distinguished. In Figure 19 we include the results of Gasem and Robinson (1985) at 50 and 100°C for $\text{CO}_2 + n\text{-C}_{20}$ mixtures. The agreement of their data and ours is reasonable with a maximum deviation of about 2.5%, our data at higher pressures being consistently lower. Similarly, in Figures 20 and 21, we show the data of Gasem and Robinson (1985) at 100°C for CO_2 in $n\text{-C}_{28}$ and in $n\text{-C}_{36}$, respectively. The agreement of their work and ours is excellent.

Gas solubility always increases with pressure at the conditions of this study. Hydrogen and carbon monoxide were found to be significantly more soluble at higher temperatures. The observed solubilities of carbon dioxide, ethane, and ethylene, on the other hand, decrease with increased temperature. The solubility of the intermediate gas, methane, in $n\text{-C}_{20}$ and in $n\text{-C}_{28}$ shows a shallow minimum in the range of 100-300°C, but this transition is not observed in $n\text{-C}_{36}$, in which the methane solubility decreases with increase in temperature. The observed variation with temperature agrees with the general pattern of the solubility of a gas to show a minimum, and for the temperature of minimal solubility to increase with the boiling point of the gas. The decreasing solubility with increasing temperature at the lower temperatures is an indication of the dominant effect of the attractive forces between the solute and solvent molecules. However at the higher temperatures molecular collisions become more energetic and the repulsive forces between molecules dominate, resulting in increased solubility with increasing temperature, just like theoretically calculated solubility of hard core molecules.

The compositions of the saturated vapor phase have been determined for H_2 ,

CH_4 , C_2H_6 , and CO_2 in $n\text{-C}_{20}$ and in $n\text{-C}_{28}$ at higher temperatures. The experimental results are presented in the tables, while Figure 22 illustrates the results for each of the four gases in $n\text{-C}_{20}$ at 300°C . The gas compositions in the saturated vapor phase increase with pressure but decrease with temperature at the experimental conditions of this study. The concentrations of $n\text{-C}_{20}$ and $n\text{-C}_{28}$ in the equilibrium gas are extremely low at the lower temperatures and are not explicitly reported in the tables. The equilibrium gas was found to be almost pure in the vapor phase at any of the states studied with $n\text{-C}_{36}$.

K-values of the dissolved gas are reported in the tables at the conditions where the vapor-phase compositions have been measured. The K-values ($K \equiv y/x$) were calculated from the experimental mole fractions in the liquid (x) and mole fractions in the vapor (y).

Equilibrium gas composition was not measured for CO and C_2H_4 in any of the n -paraffins. Only the solubility data are reported in the tables for these two gases.

Solubility of synthesis gas mixtures of $\text{H}_2 + \text{CO}$ in $n\text{-C}_{28}$ was determined at three feed gas compositions: 40.01, 50.01, and 66.64 mol % of H_2 , which are also the compositions of the equilibrium gas on a solvent-free basis. For each feed mixture, measurements were made at two temperatures, 200 and 300°C , over the pressure range of 20-50 atm. The experimental results are reported in Table 19 and shown in Figures 23 and 24 for hydrogen solubility at different pressures. Figures 25 and 26 show K-values of H_2 and CO , respectively, as a function of mol fraction of hydrogen y_{H_2} in the gas mixture at 200°C . The terminal points at $y_{\text{H}_2} = 0$ and

$y_{H_2} = 1$ shown in the figures are taken from Tables 2 and 5. The K-values appear to be independent of gas composition within the experimental uncertainty. Similar results were found at 300°C, as shown in Figures 27 and 28.

The measurements are extended to solubility in industrial Fischer-Tropsch waxes. Two waxes were studied: a Mobil wax and a SASOL wax. Tables 20-24 present the experimental solubility data for each of five gases (H_2 , CO, CH_4 , C_2H_6 , and CO_2) in the Mobil wax. Figures 29-33 show the data as a function of pressure at different temperatures. Individual sample compositions at each condition of temperature and pressure are shown in the figures as separate points when they can be distinguished.

The Mobil wax contains a small amount of materials of relatively low molecular weight (Kuo, 1985). To minimize vaporization of these materials from the wax and the consequent alteration of its composition, we reduced the flowrate of the gas through the equilibrium cell to the minimum that could sustain the pressure. The solubility of the gases was observed to gradually decrease with the age of the wax to the extent of 3-5%. The solubility data in Table IV are subject to an uncertainty of this magnitude.

The SASOL wax was found to change composition upon being kept in the solubility apparatus for a prolonged period during initial measurement at 300°C. The lighter components of the wax vaporized, altering the composition of the wax, and the measured gas solubility changed up to 8% with time. Data that were observed to change were discarded. Only reproducible data are reported here. These were determined with fresh wax with gas flowing at a minimal rate to reduce

vaporization loss of the lighter material from the wax.

Tables 25-30 reports the solubility data for each of six gases in the SASOL wax. Figures 34-39 show the data with respect to pressure at three temperatures. Only two temperatures were measured for CO_2 and C_2H_4 in this wax. The solubility of the gases was again observed to gradually decrease with the age of the wax in operation.

Chapter 4. CORRELATION WITH KRICHEVSKY-KASARNOVSKY EQUATION

Krichevsky-Kasarnovsky (K-K) equation (1935) is useful for representing solubilities of sparingly soluble gases up to moderate pressures. The equation is

$$\ln(f_i/x_i) = \ln H_i + \bar{v}_i^\infty (p - p_j^s)/RT \quad (1)$$

where f_i stands for fugacity of solute i ; x_i , mole fraction of i in the liquid; H_i , Henry's constant of i ; $\bar{v}_i^\infty$, the partial molar volume of the solute at infinite dilution; p , pressure; p_j^s , vapor pressure of the solvent; R , gas constant; and T , temperature. According to eq. 1 a linear relation should be obtained between $\ln (f_i/x_i)$ and p for a given gas and solvent at a constant temperature. In Figures 40-48 experimental data of this work are presented to show $\ln (f_i/x_i)$ as a function of p . The solute fugacity f was calculated from the equilibrium gas data with the Lee and Kesler (1975) correlation of fugacity coefficients. For hydrogen the fugacity coefficient is assumed to be unity and $f_i = y_i p$. Straight lines are obtained in all the figures. The intercepts at $p = p_j^s$ of these plots give the Henry's constants according to the definition

$$H_i = \lim_{x_i \rightarrow 0} (f_i/x_i) \quad (2)$$

Henry's constant is useful for calculating gas solubility at low pressures. The slopes of the lines in Figures 40-48 determine the partial molar volumes of the dissolved gas in the liquid phase. The values of the Henry's constant and the partial molar volume at infinite dilution so determined are reported in Table 31. Henry's constant is subject to an uncertainty of about 3%, while the partial molar volume is less accurate with an uncertainty of about 10%. No values of $\bar{v}_i^\infty$ are reported for

hydrogen mixtures at 100°C as they are too small to be determined with any reasonable accuracy. The estimated standard deviations are listed in Table 31 for both H and $\bar{v}^x$ at each condition. Figures 49-51 show the results of the Henry's constant as a function of temperature. Included in the figures are also the data available in the literature for comparison. Excellent agreement with the data of Gasem and Robinson is obtained for CO_2 mixtures. However, our results for CH_4 and C_2H_6 in $n\text{-C}_{20}$ are different by about 5% from those of Chappelow and Prausnitz (1974). Poor agreement of our results with the data of Matsumoto and Satterfield is observed for H_2 and CO in $n\text{-C}_{28}$.

Chapter 5. CORRELATION WITH EQUATION OF STATE

Experimental gas solubility data in the model n-paraffin solvents were used to develop a correlation method in order to describe the solubility of the gases in n-paraffins of a wide range of molecular weights. Several equations of state including the Soave, the Peng-Robinson, and the Cubic Chain-of-Rotators equations with different mixing rules have been examined. We report here the calculations from a modified Soave equation with new mixing rules.

Soave Equation of State. The Soave equation (1972) has been in wide use for engineering calculations. The equation is

$$p = \frac{RT}{v - b} - \frac{\alpha a}{v(v+b)} \quad (3)$$

where

$$a = 0.42747 R^2 T_c^2 / p_c \quad (4)$$

$$b = 0.08664 RT_c / p_c \quad (5)$$

Soave expressed α in terms of reduced temperature T_r and acentric factor ω . The original α expression was found to be inadequate for the heavy n-paraffins of interest in this work. A new expression was developed as follows,

$$\alpha^n = 1 + m(1 - T_r^n) \quad (6)$$

where

$$n = 0.5 \quad \text{for } 142 < M \leq 268$$

$$= 0.5685 - 2.552 \times 10^{-4} M \quad \text{for } M > 268 \quad (7)$$

The factor m in eq. 6 is correlated with the molecular weight M of a n-paraffin in

the following form:

$$m = \sum_i B_i M^i \quad \text{for } i = 0 \text{ to } 4 \quad (8)$$

The coefficients of eq. 8 are

$$B_0 = 0.47135$$

$$B_1 = 0.63325 \times 10^{-2}$$

$$B_2 = -0.78307 \times 10^{-5}$$

$$B_3 = 0.44238 \times 10^{-8}$$

$$B_4 = -0.97365 \times 10^{-12}$$

We use M to replace ω for the convenient characterization of a n -paraffin. The critical temperature T_c and critical pressure p_c are also required in the equation. Literature values are available only up to n - C_{20} . A number of correlations proposed for T_c and p_c of n -paraffins can be used for extrapolation to heavier n -paraffins. As a result of a careful examination, we use in this work the Gasem and Robinson's method (1986), which requires the normal boiling point T_b and carbon number CN according to

$$Y = \left[\frac{C_1}{C_4} - \left(\frac{C_1}{C_4} - C_3^{1-C_2} \right) \exp \left\{ -C_4(CN - 1)(1 - C_2) \right\} \right]^{\frac{1}{1-C_2}} \quad (9)$$

where Y represents either p_c or T_b/T_c . The constants C_1 to C_4 are as follows:

	p_c , bar	T_b/T_c
C_1	8.0936	0.036175
C_2	0.99288	-0.47775
C_3	54.555	0.58524
C_4	8.0034	0.043358

The values of T_b reported in API-44 Tables up to $n-C_{100}$ are used in our calculations. The calculated values of T_c and p_c for some of the heavy n -paraffins and the waxes studied in this work are given in Table 32.

The modified Soave equation of eq. 3-8 represents vapor pressures of n -paraffins from $n-C_{10}$ to $n-C_{100}$ with an average absolute deviation (AAD) of 1.8%. The vapor pressure values were taken from API-44 Tables.

Mixing Rules. Mixing rules for the equation parameters a and b in eq. 3 are needed in order for the equation to apply to mixtures. The classical van de Waals one-fluid mixing rules have been extensively used. We have found those simple rules to describe quite well the gas solubilities in a particular heavy n -paraffin. However, the values of interaction parameter k_{aij} can not be correlated in any form useful for general calculations. We have therefore developed a mixing rule from the Flory-Huggins expression for the excess Gibbs energy of polymer solutions.

Huron and Vidal (1979) obtained an expression for the excess Gibbs energy at infinite pressure, g_x^E , in terms of the equation parameters in the Soave equation:

$$g_x^E = - \left[\frac{a}{b} - \sum_i \frac{a_i}{b_i} x_i \right] \ln 2 \quad (10)$$

The parameters a and b of a fluid mixture are related to the pure component a_i and b_i by the solution model that describes the g_E of the mixture.

The Flory-Huggins model,

$$\frac{g^E}{RT} = \frac{1}{2} \left(\sum_i x_i V_i \right) \left(\sum_i \sum_j A_{ij} \phi_i \phi_j \right) + \sum_i x_i \ln (\phi_i / x_i) \quad (11)$$

expresses the excess Gibbs energy of solutions in which the molecular sizes are significantly different. Solution of light gases in heavy paraffins is such a solution.

A_{ij} is the interaction parameter between species i and j . $A_{ii} = 0$ for $i = j$ and $A_{ij} = A_{ji}$ for $i \neq j$. Substituting eq. 11 into eq. 10, we obtain

$$\frac{a}{b} = \sum_i \frac{a_i}{b_i} x_i - \frac{RT}{\ln 2} \left[\frac{1}{2} (\sum_i x_i V_i) (\sum_i \sum_j A_{ij} \phi_i \phi_j) + \sum_i x_i \ln (\phi_i/x_i) \right] \quad (12)$$

Since

$$b = \sum_i x_i b_i \quad (13)$$

both a and b of the mixture are obtained. In eq. 11, V_i is the hard-core volume of the molecule i , and ϕ_i is defined as

$$\phi_i = \frac{x_i V_i}{\sum_j x_j V_j} \quad (14)$$

The values of hard-core volume are calculated in this work from Bondi's method (Bondi, 1968) and reported in Table 32 for all the substances studied in this work. The adjustable parameter A_{ij} in eq. 11 is determined from fitting experimental solubility data.

Tables 33-35 present the values of A_{ij} thus obtained for all the gases in $n-C_{20}$, $n-C_{28}$, and in $n-C_{36}$, respectively. The fitting of the experimental bubble pressure with these A_{ij} values is good to about 3-6% in average absolute deviation (AAD). The values of A_{ij} were correlated in terms of molecular weight M of n -paraffin:

$$A_{ij} = A_{ij}^{\infty} [1 - \exp(-M/M_0)] \quad (15)$$

The coefficients of M_0 and A_{ij}^{∞} are given in Table 36.

The solubilities calculated with the correlated A_{ij} are in general comparable with the results from the optimal A_{ij} as reported in Tables 35-37. Figures 52 and

53 show the A_{ij} values for the n-paraffins as a function of molecular weight. The A_{ij} value at a constant temperature increases with molecular weight to approach an asymptotic value for the very heavy paraffins. We approximate this asymptotic value with that for n-C₃₆ for the purpose of simplification in calculations. All the calculations in this work for Mobil wax and the Sasol wax were consequently based on the A_{ij} values for n-C₃₆.

Figures 54-57 compare the calculated gas solubility with the experimental data for hydrogen mixtures and CO mixtures at 200 and 300°C. Predicted solubilities for paraffins higher than those studied are shown in the figures to indicate the trend of variation of solubility with molecular weight. Figure 58 shows the comparison of the predicted CO₂ solubility in n-C₄₄ with the data of Gasem and Robinson at 100°C. Our data of CO₂ in n-C₂₀, n-C₂₈, and in n-C₃₆ are also included. The agreement is reasonable.

Figures 59-62 show the calculated results in comparison with experimental data for synthesis gas mixtures of H₂ and CO in n-octacosane at 200 and 300°C. The interaction parameters A_{ij} for H₂/n-C₂₈ and CO/n-C₂₈ are taken from Table 34, while A_{ij} for H₂/CO is assumed to be zero. The calculations are of a predictive nature. No experimental data on the synthesis gases were used in any way for adjustment of the equation. The predicted results appear to agree well with the data with a grand AAd of 2.8% in both x_{H_2} and x_{CO} . Detailed comparison for each data point is reported in Table 37. Comparable results were obtained with the correlated A_{ij} of eq. 15.

Extension to Wax. Kuo (1985) reported a molar average molecular weight of 857, corresponding to a $n\text{-C}_{61}$ paraffin, for the Mobil wax of this study. In the calculations here the wax is treated as a C_{61} n -paraffin. The values of T_c , p_c , and V required in the modified Soave equation are calculated by the methods described in the last section and the values are reported in Table 32. The interaction parameters A_{ij} for gas/wax at 200°C and 300°C are the same as gas/ $n\text{-C}_{36}$. The A_{ij} values used in the calculations at 270°C are estimated by interpolation. The calculations are of a predictive nature. Experimental solubility data are not used for adjustment of the equation constants. The predicted results are compared with the data in Table 38. The agreement is reasonable.

Figures 63-66 illustrate the calculated results for H_2 and for CO in several waxes at 200 and 300°C . Experimental data from this work and from Peter and Weinert (1955) are shown in the figures for comparison.

Table 39 compares the calculated results with experimental data for the SASOL wax. The average carbon number was reported by UOP Inc. to be 43 from GPC analysis and 47 from NMR. The SASOL wax was accordingly calculated as a C_{43} n -paraffin ($M = 605$) in the modified Soave equation described above. The A_{ij} values used are again taken from those of gas/ $n\text{-C}_{36}$. The comparison shows the prediction in reasonable agreement with the experimental data. We conclude that the modified Soave equation with the Huron-Vidal mixing rules is adequate for the calculations of gas solubilities in both Mobil and SASOL waxes.

Table 1. Hydrogen (H) + n-Eicosane VLE DATA

t, °C	p, atm	x_H	y_H	K_H
100.2	9.96	0.0113	-	-
	19.87	0.0229	-	-
	30.04	0.0348	-	-
	40.24	0.0464	-	-
	50.15	0.0563	-	-
200.4	9.89	0.0182	0.9985	54.9
	19.90	0.0362	0.9992	27.6
	30.04	0.0539	0.9994	18.5
	39.83	0.0715	0.9995	14.0
	49.69	0.0866	0.9996	11.5
300.1	9.81	0.0241	0.9617	39.8
	19.89	0.0501	0.9815	19.6
	29.93	0.0742	0.9878	13.3
	40.04	0.0965	0.9911	10.3
	49.99	0.117	0.9926	8.49

Table 2. Hydrogen (H) + n-Octacosane VLE Data

t, °C	p, atm	x_H	y_H	K_H
100.1	9.73	0.0149	-	-
	19.87	0.0296	-	-
	30.05	0.0428	-	-
	40.29	0.0597	-	-
	49.88	0.0715	-	-
200.1	10.01	0.0206	-	-
	19.75	0.0402	-	-
	30.01	0.0608	-	-
	39.97	0.0807	-	-
	50.01	0.0993	-	-
300.0	10.04	0.0288	0.9965	34.6
	19.83	0.0577	0.9982	17.3
	30.08	0.0850	0.9988	11.8
	40.03	0.110	0.9991	9.05
	50.04	0.136	0.9993	7.36

Table 3. Hydrogen (H) + n-Hexatriacontane VLE Data

t, °C	p, atm	x _H	y _H	K _H
100.0	10.09	0.0154	-	-
	20.02	0.0323	-	-
	30.04	0.0487	-	-
	40.00	0.0641	-	-
	50.00	0.0809	-	-
199.9	10.17	0.0227	-	-
	20.10	0.0476	-	-
	30.01	0.0704	-	-
	40.14	0.0926	-	-
	50.00	0.116	-	-
300.0	10.09	0.0314	-	-
	20.12	0.0636	-	-
	30.10	0.0946	-	-
	40.04	0.123	-	-
	50.00	0.150	-	-

Table 4. Carbon Monoxide + n-Eicosane VLE Data

t, °C	p, atm	x _{CO}	y _{CO}	K _{CO}
100.2	10.07	0.0187	-	-
	19.77	0.0380	-	-
	30.07	0.0571	-	-
	40.28	0.0761	-	-
	49.97	0.0922	-	-
200.3	9.89	0.0230	-	-
	19.78	0.0469	-	-
	29.91	0.0708	-	-
	40.16	0.0949	-	-
	49.90	0.117	-	-
300.0	9.94	0.0289	-	-
	19.84	0.0586	-	-
	29.89	0.0891	-	-
	40.25	0.117	-	-
	49.71	0.139	-	-

Table 5. Carbon Monoxide + n-Octacosane VLE Data

t, °C	p, atm	x _{CO}	y _{CO}	K _{CO}
100.3	9.95	0.0227	-	-
	19.73	0.0452	-	-
	29.98	0.0696	-	-
	40.21	0.0916	-	-
	50.03	0.112	-	-
200.0	10.07	0.0275	-	-
	19.65	0.0555	-	-
	30.14	0.0830	-	-
	39.92	0.109	-	-
	49.96	0.131	-	-
300.3	9.94	0.0336	-	-
	19.74	0.0669	-	-
	30.02	0.0993	-	-
	40.18	0.131	-	-
	50.06	0.156	-	-

Table 6. Carbon Monoxide + n-Hexatriacontane VLE Data

t, °C	p, atm	x _{CO}	y _{CO}	K _{CO}
100.0	10.02	0.0257	-	-
	20.06	0.0514	-	-
	30.01	0.0764	-	-
	40.00	0.101	-	-
	49.91	0.123	-	-
199.9	10.13	0.0307	-	-
	20.05	0.0614	-	-
	29.99	0.0917	-	-
	40.08	0.119	-	-
	50.14	0.146	-	-
299.8	10.07	0.0382	-	-
	20.11	0.0754	-	-
	30.02	0.110	-	-
	40.03	0.144	-	-
	50.04	0.173	-	-

Table 7. Methane (M) + n-Eicosane VLE Data

t, °C	p, atm	x_M	y_M	K_M
100.2	9.95	0.0472	-	-
	19.73	0.0903	-	-
	29.78	0.132	-	-
	39.84	0.172	-	-
	49.85	0.209	-	-
200.3	9.93	0.0427	0.9984	23.4
	19.69	0.0845	0.9990	11.8
	30.00	0.125	0.9992	7.97
	39.86	0.159	0.9993	6.27
	49.86	0.194	0.9993	5.16
300.0	9.96	0.0440	0.9595	21.8
	19.89	0.0869	0.9772	11.2
	29.84	0.127	0.9830	7.76
	39.96	0.165	0.9858	5.98
	49.74	0.203	0.9876	4.86

Table 8. Methane (M) + n-Octacosane VLE Data

t, °C	p, atm	x_M	y_M	K_M
100.1	9.77	0.0566	-	-
	19.90	0.113	-	-
	30.04	0.163	-	-
	40.19	0.204	-	-
	49.97	0.244	-	-
200.2	9.78	0.0496	-	-
	19.81	0.100	-	-
	29.88	0.143	-	-
	40.36	0.189	-	-
	49.95	0.224	-	-
300.1	9.48	0.0493	0.9962	20.2
	19.74	0.102	0.9979	9.78
	30.21	0.152	0.9985	6.57
	40.17	0.195	0.9986	5.12
	50.11	0.230	0.9986	4.34

Table 9. Methane (M) + n-Hexatriacontane VLE Data

t, °C	p, atm	x_M	y_M	K_M
100.0	10.11	0.0673	-	-
	20.07	0.130	-	-
	30.03	0.182	-	-
	40.06	0.230	-	-
	49.94	0.271	-	-
200.0	10.06	0.0605	-	-
	20.02	0.118	-	-
	30.06	0.171	-	-
	39.93	0.211	-	-
	49.93	0.255	-	-
300.0	10.08	0.0587	-	-
	20.12	0.114	-	-
	30.03	0.166	-	-
	40.08	0.212	-	-
	50.05	0.250	-	-

Table 10. Ethane (E) + n-Eicosane VLE Data

t, °C	p, atm	x_E	y_E	K_E
100.6	9.69	0.159	-	-
	19.91	0.284	-	-
	29.90	0.387	-	-
	39.91	0.463	-	-
200.5	9.83	0.0960	0.9978	10.4
	19.86	0.175	0.9986	5.69
	29.99	0.251	0.9988	3.97
	40.18	0.314	0.9988	3.18
299.7	9.83	0.0731	0.9499	13.0
	19.64	0.139	0.9682	6.97
	29.90	0.206	0.9768	4.75
	39.85	0.262	0.9810	3.74

Table 11. Ethane (E) + n-Octacosane VLE Data

t, °C	p, atm	x _E	y _E	K _E
100.1	9.76	0.180	-	-
	19.90	0.322	-	-
	28.82	0.425	-	-
	40.18	0.504	-	-
200.1	9.82	0.113	-	-
	19.87	0.207	-	-
	29.81	0.287	-	-
	37.46	0.335	-	-
300.0	9.62	0.0840	0.9957	11.9
	19.76	0.166	0.9973	6.00
	29.83	0.236	0.9976	4.24
	39.87	0.297	0.9977	3.36

Table 12. Ethane (E) + n-Hexatriacontane VLE Data

t, °C	p, atm	x _E	y _E	K _E
100.0	10.07	0.212	-	-
	20.01	0.362	-	-
	30.00	0.466	-	-
	39.80	0.532	-	-
199.9	10.01	0.126	-	-
	20.04	0.234	-	-
	29.98	0.321	-	-
	39.96	0.390	-	-
299.9	10.06	0.101	-	-
	20.07	0.190	-	-
	30.00	0.263	-	-
	39.99	0.327	-	-

Table 13. Ethylene Solubility in n-Eicosane

t, °C	p, atm	$x_{C_2H_4}$
100.1	10.10	0.122
	20.06	0.227
	29.94	0.319
	40.04	0.394
	49.95	0.454
200.0	10.18	0.0816
	20.03	0.154
	29.91	0.220
	39.96	0.280
	49.91	0.334
300.0	10.12	0.0656
	20.06	0.131
	29.95	0.190
	39.98	0.244
	49.93	0.295

Table 14. Ethylene Solubility in n-Octacosane

t, °C	p, atm	$x_{C_2H_4}$
99.9	10.04	0.145
	20.06	0.254
	30.02	0.343
	39.98	0.421
	49.94	0.487
199.9	10.03	0.0974
	20.00	0.180
	29.97	0.250
	39.99	0.310
	49.89	0.368
299.9	9.99	0.0799
	20.07	0.150
	30.01	0.213
	40.00	0.272
	49.98	0.320

Table 15. Ethylene Solubility in n-Hexatriacontane

t, °C	p, atm	$x_{C_2H_4}$
100.1	10.13	0.172
	19.99	0.291
	29.97	0.392
	39.97	0.466
	49.93	0.526
199.9	10.09	0.112
	20.06	0.204
	29.95	0.279
	40.01	0.350
	49.97	0.402
300.1	10.10	0.0932
	20.07	0.176
	29.99	0.241
	39.97	0.305
	50.01	0.360

Table 16. Carbon Dioxide (CD) + n-Eicosane VLE Data

t, °C	p, atm	x _{CD}	y _{CD}	K _{CD}
50.1	9.79	0.114	-	-
	19.89	0.217	-	-
	30.21	0.305	-	-
	39.97	0.379	-	-
	49.48	0.446	-	-
100.3	10.04	0.0842	-	-
	19.83	0.157	-	-
	30.02	0.228	-	-
	39.63	0.286	-	-
	49.90	0.342	-	-
200.0	9.85	0.0593	0.9979	16.8
	19.71	0.114	0.9989	8.75
	30.24	0.170	0.9991	5.88
	40.12	0.216	0.9992	4.62
	49.50	0.259	0.9992	3.86
300.2	9.76	0.0528	0.9563	18.11
	19.93	0.104	0.9748	9.33
	29.64	0.151	0.9812	6.52
	40.64	0.201	0.9846	4.91
	49.97	0.237	0.9861	4.17

Table 17. Carbon Dioxide (CD) + n-Octacosane VLE Data

t, °C	p, atm	x _{CD}	y _{CD}	K _{CD}
100.2	10.05	0.102	-	-
	20.14	0.184	-	-
	30.01	0.254	-	-
	40.15	0.324	-	-
	49.90	0.379	-	-
200.3	9.87	0.0688	-	-
	20.04	0.135	-	-
	30.18	0.194	-	-
	39.89	0.247	-	-
	49.95	0.293	-	-
300.3	9.81	0.0596	0.9957	16.7
	20.06	0.122	0.9975	8.16
	30.08	0.176	0.9981	5.69
	39.92	0.226	0.9983	4.42
	49.91	0.270	0.9983	3.69

Table 18. Carbon Dioxide (CD) + n-Hexatriacontane VLE Data

t, °C	p, atm	x _{CD}	y _{CD}	K _{CD}
100.0	10.08	0.110	-	-
	20.10	0.209	-	-
	29.97	0.289	-	-
	39.99	0.357	-	-
	49.99	0.415	-	-
200.2	10.09	0.0803	-	-
	19.75	0.155	-	-
	29.95	0.220	-	-
	39.90	0.274	-	-
	49.92	0.324	-	-
300.1	10.06	0.0706	-	-
	19.94	0.138	-	-
	29.97	0.198	-	-
	40.03	0.250	-	-
	50.00	0.297	-	-

Table 19. Solubility Data of Synthesis Gas Mixtures in n-C₂₈

t, °C	p, atm	x _H	x _{CO}	K _H	K _{CO}
Equilibrium Gas Composition: 40.01 mol % H ₂ , 59.99 mol % CO					
200.1	19.74	0.0164	0.0326	24.5	18.4
	29.98	0.0247	0.0495	16.2	12.1
	40.23	0.0330	0.0657	12.1	9.14
	49.89	0.0401	0.0791	9.97	7.59
299.8	19.94	0.0227	0.0417	17.6	14.4
	30.01	0.0336	0.0618	11.9	9.71
	40.18	0.0442	0.0811	9.06	7.39
	49.81	0.0525	0.0964	7.63	6.23
Equilibrium Gas Composition: 50.01 mol % H ₂ , 49.99 mol % CO					
199.7	19.70	0.0201	0.0275	24.9	18.2
	29.94	0.0303	0.0407	16.5	12.3
	39.99	0.0415	0.0544	12.0	9.20
	49.90	0.0494	0.0653	10.1	7.66
300.0	19.79	0.0281	0.0340	17.8	14.7
	29.87	0.0412	0.0506	12.1	9.88
	40.17	0.0552	0.0661	9.06	7.56
	49.78	0.0656	0.0785	7.63	6.37
Equilibrium Gas Composition: 66.64 mol % H ₂ , 33.36 mol % CO					
200.1	19.94	0.0275	0.0181	24.2	18.4
	30.14	0.0417	0.0276	16.0	12.1
	40.17	0.0543	0.0359	12.3	9.29
	49.91	0.0657	0.0434	10.1	7.69
299.9	19.93	0.0378	0.0228	17.6	14.6
	30.07	0.0562	0.0340	11.8	9.83
	40.22	0.0743	0.0448	8.97	7.44
	49.80	0.0887	0.0535	7.51	6.23

Table 20. Hydrogen Solubility in Mobil Wax

t, °C	p, atm	Solubility, mole/Kg wax
200.1	10.23	0.0397
	20.12	0.0826
	30.05	0.129
	39.96	0.172
	50.09	0.219
270.1	17.02	0.0931
	27.26	0.152
	37.49	0.208
	47.67	0.269
300.0	10.11	0.0519
	20.16	0.111
	30.05	0.170
	40.09	0.231
	50.04	0.289

Table 21. Carbon Monoxide Solubility in Mobil Wax

t, °C	p, atm	Solubility, mole/Kg wax
200.0	10.06	0.0522
	20.06	0.108
	29.98	0.165
	39.99	0.222
	49.94	0.285
270.0	17.06	0.111
	27.31	0.179
	37.39	0.248
	47.57	0.316
300.2	10.05	0.0619
	20.11	0.130
	29.99	0.197
	39.96	0.268
	49.63	0.336

Table 22. Methane Solubility in Mobil Wax

t, °C	p, atm	Solubility, mole/Kg wax
200.1	9.97	0.105
	20.12	0.226
	30.00	0.349
	40.04	0.475
	50.00	0.596
270.0	17.08	0.183
	27.15	0.304
	37.47	0.423
300.0	10.08	0.0954
	20.06	0.208
	29.99	0.317
	40.12	0.429
	50.00	0.550

Table 23. Ethane Solubility in Mobil Wax

t, °C	p, atm	Solubility, mole/Kg wax
200.0	10.00	0.223
	20.04	0.503
	29.93	0.774
	40.00	1.060
270.1	17.00	0.325
	27.09	0.548
	37.40	0.789
300.1	10.07	0.154
	20.13	0.350
	30.02	0.556
	39.95	0.760

Table 24. Carbon Dioxide Solubility in Mobil Wax

t, °C	p, atm	Solubility, mole/Kg wax
200.1	10.15	0.142
	20.03	0.309
	30.00	0.486
	39.95	0.657
	49.92	0.829
270.0	16.92	0.232
	27.10	0.386
	37.22	0.556
300.1	9.97	0.122
	20.11	0.271
	29.91	0.415
	39.95	0.553
	50.02	0.711

Table 25. Hydrogen Solubility in SASOL Wax

t, °C	p, atm	Solubility mole/Kg wax
200.0	10.02	0.0432
	19.98	0.0923
	29.96	0.141
	40.01	0.191
	49.95	0.241
260.1	10.04	0.0585
	20.02	0.119
	29.96	0.179
	39.98	0.240
	49.93	0.299
300	10.07	0.0644
	19.99	0.0130
	29.94	0.202
	39.94	0.269
	49.96	0.334

Table 26. Carbon Monoxide Solubility in SASOL Wax

t, °C	p, atm	Solubility mole/Kg wax
199.9	10.05	0.0701
	20.08	0.135
	29.95	0.198
	39.98	0.261
	50.00	0.322
260.0	10.07	0.0774
	20.04	0.146
	30.05	0.225
	39.96	0.300
	49.96	0.373
299.9	10.02	0.0810
	20.03	0.161
	30.03	0.242
	39.98	0.320
	50.01	0.400

Table 27. Methane Solubility in SASOL Wax

t, °C	p, atm	Solubility, mole/Kg wax
200.0	10.00	0.122
	20.02	0.246
	29.96	0.372
	39.94	0.497
	49.95	0.619
259.9	10.02	0.119
	20.05	0.242
	29.99	0.364
	39.99	0.491
	50.02	0.613
300.2	9.99	0.122
	20.03	0.247
	29.95	0.369
	39.94	0.497
	50.00	0.621

Table 28. Ethane Solubility in SASOL Wax

t, °C	p, atm	Solubility mole/Kg wax
200.1	10.06	0.281
	20.06	0.553
	29.95	0.861
	39.97	1.17
260.0	10.10	0.232
	20.05	0.470
	29.99	0.713
	40.00	0.985
300.0	10.04	0.203
	20.03	0.409
	29.96	0.610
	39.97	0.874

Table 29. Ethylene Solubility in SASOL Wax

t, °C	p, atm	Solubility, mole/Kg wax
200.0	10.03	0.237
	20.12	0.488
	29.99	0.742
	39.97	1.01
	49.90	1.25
259.9	10.04	0.199
	20.12	0.415
	30.90	0.630
	40.04	0.848
	50.95	1.07

Table 30. Carbon Dioxide Solubility in SASOL Wax

t, °C	p, atm	Solubility mole/Kg wax
260.1	20.06	0.305
	29.96	0.466
	39.99	0.626
	49.95	0.793
300.2	19.97	0.305
	29.95	0.460
	39.95	0.625
	49.97	0.777

Table 31. Henry's Constants (H) and Partial Molar Volumes at Infinite Dilution ($\bar{v}^\infty$) of Gases in n-C₂₀, n-C₂₈, and n-C₃₆

Solvent	100°C		200°C		300°C	
	H atm	$\bar{v}^\infty$, mL/mole	H, atm	$\bar{v}^\infty$, mL/mole	H, atm	$\bar{v}^\infty$, mL/mole
hydrogen						
n-C ₂₀	868(12)*	**	536(4)	33(9)	377(5)	103(19)
n-C ₂₈	653(15)	**	482(2)	32(5)	337(5)	80(19)
n-C ₃₆	619(6)	**	432(5)	34(11)	313(5)	47(21)
carbon monoxide						
n-C ₂₀	526(11)	15(9)	425(4)	34(6)	334(7)	63(23)
n-C ₂₈	431(6)	21(9)	354(8)	62(22)	286(4)	116(15)
n-C ₃₆	383(3)	35(8)	321(5)	88(13)	256(2)	124(14)
methane						
n-C ₂₀	205(1)	75(3)	223(3)	119(16)	212(2)	139(11)
n-C ₂₈	163(2)	125(13)	189(2)	141(14)	183(3)	152(24)
n-C ₃₆	141(2)	142(9)	157(3)	166(19)	164(2)	180(19)
carbon dioxide						
n-C ₂₀	114(1)	82(5)	160(1)	104(4)	171(1)	167(9)
n-C ₂₈	94(2)	115(6)	137(1)	133(8)	156(2)	169(10)
n-C ₃₆	84(1)	143(7)	117(2)	175(20)	134(2)	189(20)
ethane						
n-C ₂₀	55(1)	237(28)	96(2)	228(25)	123(2)	215(21)
n-C ₂₈	48(1)	274(22)	80(1)	289(15)	107(1)	261(19)
n-C ₃₆	41(1)	348(8)	73(1)	306(19)	93(1)	298(13)
ethylene						
n-C ₂₀	77(1)	129(6)	119(1)	139(3)	143(1)	144(2)
n-C ₂₈	64(1)	207(19)	96(1)	236(10)	119(1)	236(8)
n-C ₃₆	53(1)	274(13)	84(1)	271(10)	101(1)	282(16)

* Numbers in parentheses are standard deviations.

** too small to be determined with any reasonable accuracy.

Table 32. Physical Properties and van der Waal's Volumes of Substances

Substance	T_c , K	p_c , atm	V_i , mL/mole	ω
He	5.19	2.24	4.80	-0.387
H ₂	33.2	12.8	10.51	-0.22
CO	132.9	34.5	13.01	0.049
CO ₂	304.2	72.8	19.68	0.225
CH ₄	190.6	45.4	17.09	0.008
C ₂ H ₄	282.4	49.7	23.88	0.085
C ₂ H ₆	305.4	48.2	27.34	0.098
n-C ₁₀	617.1	20.7	109.18	-
n-C ₁₆	719.8	13.6	170.56	-
n-C ₂₀	768.8	11.0	211.48	-
n-C ₂₈	843.7	8.15	293.32	-
n-C ₃₆	900.8	6.73	375.16	-
n-C ₄₃	941.5	6.03	446.77	-
n-C ₄₄	946.7	5.96	457.00	-
n-C ₆₀	1016.6	5.25	620.68	-
n-C ₆₁	1020.3	5.23	630.91	-
n-C ₁₀₀	1116.8	4.87	1029.88	-

Table 33. Comparison of the Modified Soave Equation Calculated Gas Solubilities in n-Eicosane with Experimental Data

Gas	t, °C	Data Pts	Optimal A_{ij}				Correlated A_{ij}			
			A_{ij} mole/ml	Deviations in p, %			A_{ij} mole/ml	Deviations in p, %		
				RMS	AAD	BIAS		RMS	AAD	BIAS
H ₂	100	5	0.238	3.3	2.9	-0.2	0.235	4.9	3.8	-3.8
	200	5	0.217	3.0	2.7	-0.2	0.219	3.7	3.0	2.0
	300	5	0.216	3.4	2.8	-0.3	0.214	3.6	2.6	-1.6
CO	100	5	0.160	4.3	3.3	-0.9	0.160	4.3	3.3	-0.9
	200	5	0.148	5.3	4.4	-0.5	0.149	5.4	4.7	0.9
	300	5	0.150	5.4	4.7	-0.6	0.148	5.8	4.2	-2.8
CH ₄	100	5	0.0879	3.2	2.8	-0.2	0.0882	3.2	2.7	0.3
	200	5	0.0863	2.8	2.4	0.0	0.0863	2.8	2.4	0.0
	300	5	0.0900	3.2	2.7	-0.2	0.0898	3.2	2.8	-0.7
CO ₂	100	5	0.0969	3.9	3.4	-0.3	0.0978	4.4	3.9	1.6
	200	5	0.0838	3.0	2.7	-0.2	0.0848	3.5	3.1	1.5
	300	5	0.0806	2.0	1.9	-0.1	0.0806	2.0	1.9	-0.1
C ₂ H ₆	100	4	0.0385	0.8	0.8	0.0	0.0392	2.0	1.8	1.8
	200	4	0.0388	1.1	0.9	0.0	0.0386	1.1	0.7	-0.3
	300	4	0.0419	1.3	1.2	0.0	0.0410	2.4	2.0	-2.0
C ₂ H ₄	100	5	0.0475	4.1	3.7	-0.2	0.0491	5.6	4.9	3.5
	200	5	0.0474	3.3	2.7	-0.2	0.0482	3.7	3.2	1.5
	300	5	0.0520	4.7	3.8	-0.2	0.0509	5.2	3.8	-2.5

Table 34. Comparison of the Modified Soave Equation Calculated Gas Solubilities in n-Octacosane with Experimental Data

Gas	t, °C	Data Pts	Optimal A_{ij}				Correlated A_{ij}			
			A_{ij} mole/ml	Deviations in p, %			A_{ij} mole/ml	Deviations in p, %		
				RMS	AAD	BIAS		RMS	AAD	BIAS
H ₂	100	5	0.246	2.9	2.7	-0.1	0.251	6.6	5.8	5.8
	200	5	0.235	4.1	3.7	-0.6	0.235	4.1	3.7	-0.6
	300	5	0.228	4.7	3.7	-0.4	0.230	5.2	4.3	1.9
CO	100	5	0.171	4.8	4.3	-0.4	0.173	5.6	5.1	2.6
	200	5	0.160	4.6	3.6	-0.3	0.162	4.9	4.3	1.6
	300	5	0.160	4.4	3.8	0.0	0.160	4.4	3.8	0.0
CH ₄	100	5	0.0956	2.9	2.3	-0.2	0.0962	3.1	2.7	0.8
	200	5	0.0950	3.9	3.2	-0.3	0.0941	4.0	3.4	-1.5
	300	5	0.0965	4.5	3.9	-0.1	0.0979	5.1	4.5	2.1
CO ₂	100	5	0.106	3.8	3.6	0.0	0.106	3.8	3.6	0.0
	200	5	0.0919	4.1	3.5	-0.3	0.0917	4.1	3.4	-0.8
	300	5	0.0873	5.2	4.2	-0.4	0.0872	5.2	4.2	-0.6
C ₂ H ₆	100	4	0.0446	2.7	2.2	-0.1	0.0443	2.8	2.5	-0.9
	200	4	0.0438	0.8	0.7	0.0	0.0436	0.9	0.9	-0.5
	300	4	0.0460	2.9	2.3	-0.1	0.0463	2.9	2.5	0.4
C ₂ H ₄	100	5	0.0557	3.3	3.0	-0.3	0.0544	4.6	4.1	-3.4
	200	5	0.0538	2.0	1.5	0.0	0.0535	2.1	1.8	-0.7
	300	5	0.0566	2.6	2.4	-0.1	0.0565	2.6	2.4	-0.3

Table 35. Comparison of the Modified Soave Equation Calculated Gas Solubilities in n-Hexatriacontane with Experimental Data

Gas	t, °C	Data Pts	Optimal A_{ij}				Correlated A_{ij}			
			A_{ij} mole/ml	Deviations in p, %			A_{ij} mole/ml	Deviations in p, %		
				RMS	AAD	BIAS		RMS	AAD	BIAS
H ₂	100	5	0.260	6.1	4.9	-0.4	0.258	6.3	4.7	-2.0
	200	5	0.243	7.0	5.3	-0.8	0.241	6.9	5.2	-2.4
	300	5	0.237	6.2	5.2	-0.7	0.236	6.2	5.1	-1.4
CO	100	5	0.181	4.6	3.9	-0.2	0.179	4.8	4.0	-2.0
	200	5	0.170	5.0	4.3	-0.4	0.168	5.6	4.1	-3.0
	300	5	0.166	4.7	4.1	-0.4	0.166	4.7	4.1	-0.4
CH ₄	100	5	0.101	3.1	2.4	-0.2	0.100	3.5	2.5	-1.9
	200	5	0.0981	3.6	2.9	-0.2	0.0978	3.5	2.7	-0.6
	300	5	0.102	4.6	4.0	-0.6	0.102	4.6	4.0	-0.6
CO ₂	100	5	0.110	5.7	4.7	-0.6	0.109	6.1	4.8	-2.7
	200	5	0.0960	4.7	3.6	-0.3	0.0947	4.9	3.5	-2.6
	300	5	0.0908	4.9	4.1	-0.4	0.0901	5.0	3.8	-1.7
C ₂ H ₆	100	4	0.0475	2.0	1.9	-0.1	0.0470	2.4	1.8	-1.5
	200	4	0.0468	3.4	2.8	-0.2	0.0463	3.7	2.8	-1.2
	300	4	0.0483	2.8	2.2	-0.1	0.0492	3.6	3.3	2.2
C ₂ H ₄	100	5	0.0577	2.6	2.4	0.0	0.0571	2.9	2.3	-1.5
	200	5	0.0568	2.9	2.7	-0.1	0.0561	3.3	2.9	-1.8
	300	5	0.0579	3.4	2.9	-0.2	0.0593	4.6	4.0	2.9

Table 36. Correlation of A_{ij} by Molecular Weight of n-Paraffins

Solute	M_0	A_{ij}^∞ , mole/ML		
		100°C	200°C	300°C
H_2	127.30	0.2632	0.2456	0.2406
CO	140.75	0.1842	0.1723	0.1707
CH_4	146.06	0.1032	0.1009	0.1050
C_2H_6	188.16	0.05046	0.04967	0.05277
CO_2	137.02	0.1121	0.09710	0.09240
C_2H_4	164.89	0.05991	0.05884	0.06214

Table 37. Comparison of Calculated Gas Solubilities of Synthesis Gas Mixtures in n-Octacosane with Experimental Data

p, atm	-Experimental-		-Optimal A_{ij} -		-Correlated A_{ij} -	
	x_H	x_{CO}	x_H	x_{CO}	x_H	x_{CO}
Equilibrium Gas Composition: 40.01 % H ₂ + 59.99 % CO						
200.1°C						
19.74	0.0164	0.0326	0.0166	0.0339	0.0167	0.0333
29.98	0.0247	0.0495	0.0243	0.0495	0.0244	0.0487
40.23	0.0330	0.0657	0.0314	0.0640	0.0316	0.0629
49.89	0.0401	0.0791	0.0376	0.0766	0.0379	0.0753
		AAD %	3.4	2.4	3.1	3.2
299.8°C						
19.94	0.0227	0.0417	0.0237	0.0415	0.0232	0.0411
30.01	0.0336	0.0618	0.0339	0.0595	0.0332	0.0590
40.18	0.0442	0.0811	0.0434	0.0761	0.0425	0.0754
49.81	0.0525	0.0964	0.0516	0.0904	0.0505	0.0897
		AAD %	2.2	4.1	2.7	4.9
Equilibrium Gas Composition: 50.01 % H ₂ + 49.99 % CO						
199.7°C						
19.70	0.0201	0.0275	0.0207	0.0282	0.0208	0.0277
29.94	0.0303	0.0407	0.0303	0.0412	0.0305	0.0405
39.99	0.0415	0.0544	0.0390	0.0531	0.0393	0.0522
49.90	0.0494	0.0653	0.0471	0.0639	0.0474	0.0628
		AAD %	3.4	2.0	3.3	2.2
300.0°C						
19.79	0.0281	0.0340	0.0294	0.0344	0.0288	0.0341
29.87	0.0412	0.0506	0.0423	0.0494	0.0414	0.0490
40.17	0.0552	0.0661	0.0543	0.0634	0.0532	0.0629
49.78	0.0656	0.0785	0.0645	0.0754	0.0632	0.0748
		AAD %	2.6	2.9	2.5	3.2
Equilibrium Gas Composition: 66.64 % H ₂ + 33.36 % CO						
200.1°C						
19.94	0.0275	0.0181	0.0279	0.0192	0.0281	0.0187
30.14	0.0417	0.0276	0.0407	0.0279	0.0410	0.0273
40.17	0.0543	0.0359	0.0524	0.0359	0.0527	0.0350
49.91	0.0657	0.0434	0.0629	0.0431	0.0634	0.0421
		AAD %	2.9	1.9	2.5	2.4
299.9°C						
19.93	0.0378	0.0228	0.0394	0.0232	0.0386	0.0229
30.07	0.0562	0.0340	0.0567	0.0334	0.0556	0.0329
40.22	0.0743	0.0448	0.0724	0.0427	0.0710	0.0421
49.80	0.0887	0.0535	0.0860	0.0507	0.0843	0.0500
		AAD %	2.6	3.3	3.1	4.0

Table 38. Comparison of the Modified Soave Equation Calculated Gas Solubilities in Mobil Wax with Experimental Data

Gas	t, °C	Data Pts	A_{ij}^* mole/mL	Deviations in p, %		
				RMS	AAD	BIAS
H ₂	200	5	0.243	6.6	5.0	-2.8
	270	4	0.239	6.2	5.2	5.2
	300	5	0.237	7.8	5.8	-4.6
CO	200	5	0.170	6.5	5.4	-4.3
	270	4	0.167	3.1	2.7	1.5
	300	5	0.166	7.8	6.2	-6.0
CH ₄	200	5	0.0981	6.0	4.9	-1.1
	270	3	0.101	3.1	2.8	-0.1
	300	5	0.102	8.6	6.7	-6.0
CO ₂	200	5	0.0960	7.5	6.1	-1.5
	270	3	0.0924	4.8	4.1	1.7
	300	5	0.0908	6.4	4.7	-1.6
C ₂ H ₆	200	4	0.0468	7.7	5.3	-4.3
	270	3	0.0478	4.9	4.5	2.1
	300	4	0.0483	13.2	10.8	-10.8

* A_{ij} values are taken from those of n-C₃₆.

Table 39. Comparison of the Modified Soave Equation Calculated Gas Solubilities in SASOL Wax with Experimental Data

Gas	t, °C	Data pts	A_{ij}^* mole/mL	Deviations in p, %		
				RMS	AAD	BIAS
H ₂	200	5	0.243	6.5	5.0	-3.1
	260	5	0.239	5.4	4.7	3.9
	300	5	0.237	5.1	4.8	1.6
CO	200	5	0.170	5.6	5.5	5.5
	260	5	0.168	6.4	5.8	5.8
	300	5	0.166	3.9	3.2	3.2
CH ₄	200	5	0.0981	4.4	4.0	-4.0
	260	5	0.100	3.3	2.5	-2.1
	300	5	0.102	2.1	1.9	-0.6
CO ₂	260	4	0.0929	2.7	2.1	-1.1
	300	4	0.0908	1.8	1.7	0.4
C ₂ H ₆	200	4	0.0468	3.6	2.9	-2.9
	260	4	0.0477	2.8	2.5	-1.3
	300	4	0.0483	7.2	6.6	-6.6
C ₂ H ₄	200	5	0.0568	2.8	2.2	-1.2
	260	5	0.0575	4.6	3.9	-3.9

* A_{ij} values are taken from those of n-C₃₆.

Figure 1. Vapor-Liquid Equilibrium Apparatus

Figure 2. Mole Fraction of CO₂ in Saturated Vapor in CO₂ + Toluene Mixtures at 80°C

Figure 3. Solubility of CO_2 in Toluene at 80°C

Figure 4. Solubility of Hydrogen in n-Eicosane

Figure 5. Solubility of Hydrogen in n-Octacosane

Figure 6. Solubility of Hydrogen in n-Hexatriacontane

Figure 7. Solubility of Carbon Monoxide in n-Eicosane

Figure 8. Solubility of Carbon Monoxide in n-Octacosane

Figure 9. Solubility of Carbon Monoxide in n-Hexatriacontane

Figure 10. Solubility of Methane in n-Eicosane

Figure 11. Solubility of Methane in n-Octacosane

Figure 12. Solubility of Methane in n-Hexatriacontane

Figure 13. Solubility of Ethane in n-Eicosane

Figure 14. Solubility of Ethane in n-Octacosane

Figure 15. Solubility of Ethane in n-Hexatriacontane

Figure 16. Solubility of Ethylene in n-Eicosane

Figure 17. Solubility of Ethylene in n-Octacosane

Figure 18. Solubility of Ethylene in n-Hexatriacontane

Figure 19. Solubility of Carbon Dioxide in n-Eicosane

Figure 20. Solubility of Carbon Dioxide in n-Octacosane

Figure 21. Solubility of Carbon Dioxide in n-Hexatriacontane

Figure 22. Equilibrium Vapor Composition of Gas in Mixtures with n-Eicosane at 300°C

Figure 23. Solubility of H₂ in Synthesis Gas Mixtures of H₂ + CO in n-Octacosane at 200°C

Figure 24. Solubility of H₂ in Synthesis Gas Mixtures of H₂ + CO in n-Octacosane at 300°C

Figure 25. K-values of H₂ in H₂ + CO Mixtures in n-Octacosane at 200°C

Figure 26. K-values of CO in H₂ + CO Mixtures in n-Octacosane at 200°C

Figure 27. K-values of H₂ in H₂ + CO Mixtures in n-Octacosane at 300°C

Figure 28. K-values of CO in H_2 + CO Mixtures in n-Octacosane at 300°C

Figure 29. Solubility of Hydrogen in Mobil Wax

Figure 30. Solubility of Carbon Monoxide in Mobil Wax

Figure 31. Solubility of Methane in Mobil Wax

Figure 32. Solubility of Ethane in Mobil Wax

Figure 33. Solubility of Carbon Dioxide in Mobil Wax

Figure 34. Solubility of Hydrogen in SASOL Wax

Figure 35. Solubility of Carbon Monoxide in SASOL Wax

Figure 36. Solubility of Methane in SASOL Wax

Figure 37. Solubility of Ethane in SASOL Wax

Figure 38. Solubility of Ethylene in SASOL Wax

Figure 39. Solubility of Carbon Dioxide in SASOL Wax

Figure 40. Correlation with Krichevsky-Kasarnovsky Equation for n-Eicosane mixtures at 100°C

Figure 41. Correlation with Krichevsky-Kasarnovsky Equation for n-Eicosane mixtures at 200°C

Figure 42. Correlation with Krichevsky-Kasarnovsky Equation for n-Eicosane mixtures at 300°C

Figure 43. Correlation with Krichevsky-Kasarnovsky Equation for n-Octacosane mixtures at 100°C

Figure 44. Correlation with Krichevsky-Kasarnovsky Equation for n-Octacosane mixtures at 200°C

Figure 45. Correlation with Krichevsky-Kasarnovsky Equation for n-Octacosane mixtures at 300°C

Figure 46. Correlation with Krichevsky-Kasarnovsky Equation for n-Hexatriacotane at 100°C

Figure 47. Correlation with Krichevsky-Kasarnovsky Equation for n-Hexatriacotane at 200°C

Figure 48. Correlation with Krichevsky-Kasarnovsky Equation for n-Hexatriacotane at 300°C

Figure 49. Henry's Constants in n-Eicosane

Figure 50. Henry's Constants in n-Octacosane

Figure 51. Henry's Constants in n-Hexatriacotane

Figure 52. Plot of A_{ij} vs Molecular Weight of n-Paraffins

Figure 53. Plot of A_{ij} vs Molecular Weight of n-Paraffins

Figure 54. Calculated Hydrogen Solubilities in n-Paraffins at 200°C

Figure 55. Calculated Hydrogen Solubilities in n-Paraffins at 300°C

Figure 56. Calculated Carbon Monoxide Solubilities in n-Paraffins at 200°C

Figure 57. Calculated Carbon Monoxide Solubilities in n-Paraffins at 300°C

Figure 58. Calculated Carbon Dioxide Solubilities in n-Paraffins at 100°C

Figure 59. Comparison of Calculated H₂ Solubilities in Synthesis Gas Mixtures in n-Octacosane with Experimental Data at 200°C

Figure 60. Comparison of Calculated H_2 Solubilities in Synthesis Gas Mixtures in n-Octacosane with Experimental Data at $300^\circ C$

Figure 61. Comparison of Calculated CO Solubilities in Synthesis Gas Mixtures in n-Octacosane with Experimental Data at 200°C

Figure 62. Comparison of Calculated CO Solubilities in Synthesis Gas Mixtures in n-Octacosane with Experimental Data at 300°C

Figure 63. Prediction of Hydrogen Solubilities in Waxes at 200°C

Figure 64. Prediction of Hydrogen Solubilities in Waxes at 300°C

Figure 65. Prediction of Carbon Monoxide Solubilities in Waxes at 200°C

Figure 66. Prediction of Carbon Monoxide Solubilities in Waxes at 300°C

NOTATION

a	constant of Soave equation, eq. 4
AAD	average absolute deviation
A_{ij}	parameter in eq. 11
A_{ij}^{∞}	asymptotical value of A_{ij} , eq. 15
B	coefficients in eq. 8
b	constant of Soave equation, eq. 5
C	constant in eq. 9
CN	carbon number
f	fugacity
g^E	excess Gibbs energy
H	Henry's constant
K	vaporization equilibrium ratio = $\frac{y}{x}$
M	molecular weight
M_o	reference molecular weight, eq. 15
m	constant, eq. 6
p	pressure
R	universal gas constant
RMS	root mean square deviation
t	temperature, °C
T	absolute temperature, K
v	molar volume
$\bar{v}^{\infty}$	partial molar volume at infinite dilution
V	hard-core volume
x	liquid-phase mole fraction
y	vapor-phase mole fraction

Greek Letters

α	equation constant, eq. 3
ϕ	volume fraction, eq. 14

ω Pitzer's acentric factor

Superscripts

n constant, eq. 6

s saturated property

Subscripts

c critical state

CD carbon dioxide

E ethane

H hydrogen

i component i

j component j

r reduced property

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Appendix A Computer Program for the Calculation of Gas Solubility

A computer program has been prepared to calculate gas solubility in a *n*-paraffin wax based on the correlation of this work. Solubilities are calculated for any one of the gases H_2 , CO, CH_4 , CO_2 , C_2H_4 , C_2H_6 or their mixtures at a specified temperature, pressure, and wax-free mole fractions of the gases in the gas phase. The molecular weight of the wax is specified. The calculation gives the solubilities in mols per kg of wax and in mole fractions in the liquid. The equilibrium mole fraction of wax in the vapor is also calculated. The program is in FORTRAN.

The input for the program is illustrated below.

Card no.	Format	Variables
1	2F10.3	T in K and P in atm of the system
2	I1	number of solutes in the system
3	F10.3	molecular weight of the wax
4 and after	I1,f10.3	gas identification and vapor phase composition on wax-free basis

Gas identification is an interger, which represents a gas species studied in this work.

Gas Identification	Gas species
1	hydrogen
2	carbon monoxide
3	methane
4	carbon dioxide
5	ethane

The output lists the calculated liquid phase composition of each solute and the wax mol fraction in the vapor phase.

Program List

35005,b2u,t80,ll,pr

mnfftn(t,u)

#eor

program gas(input,output,tape5=input,
&tape6=output)

dimension x(5),f(5)

common t,p,y(5),ngas,ncomt,vcal(2),

&r,rmw,rn,tc(6),pc(6),omeg(6),

&a(6),b(6),am,bm,alpha(6),

&phi(6),chi(6,6),q(6)

common con(2,6),xx(6)

common /was/ ywax

c

c t: temperature, K

c p: pressure, atm

c ngas: number of gas species

c ncomt: number of total species including wax

c vcal: calculated gas or liquid volume

c x: liquid composition

c y: vapor composition

c r: gas constant

c rmw: molecular weight of the wax

c rn: equivalent carbon number of the wax

c a,b, alpha: RKS equation parameters

c tc,pc,omeg: physical properties of species

c phi: volume fraction of a species

c chi: adjustable parameter Aij

c q: van der Waal's volume of a species

c parm,xjac,xjtj,work,con: working variables

c

r=82.06

read(5,2)t,p

2 format(2f9.3)

read(5,3)ngas

3 format(i1)

ncomt=ngas+1

read(5,12)rmw

12 format(f10.3)

call wax

write(6,14)t,p

14 format(1x,'system temperature in k=',f10.2,/,

&8x,'pressure in atm =',f10.2,/))

write(6,15)rmw

15 format(1x,'wax molecular weight=',f10.2,/))

c

c read in the the gas id, and its vapor-

c phase composition

c

```

do 20 n1=1,ncomt
do 20 n2=1,ncomt
20 chi(n1,n2)=0.0
write(6,22)
22 format(/,1x,'species no.',5x,'species',12x,
&'y on wax-free basis')
do 39 j1=1,ngas
read(5,25)id,y(j1)
25 format(i1,2f10.4)
x(j1)=y(j1)/10.
call gprop(id,j1)
39 continue
ywax=0.0
write(6,49)ncomt,ywax
49 format(4x,i1,12x,'wax ',12x,f12.4)
do 50 n1=1,ncomt
50 chi(ncomt,n1)=chi(n1,ncomt)

```

c

c call subroutine to find the liquid composition.

c

```

do 100 icont=1,10
call obj(x,f)
grad=0.0
do 60 n1=1,ngas
60 grad=grad+abs(f(n1)/x(n1)-1.0)
if(grad-5.0e-5)110,90,90
90 do 95 n1=1,ngas
95 x(n1)=f(n1)
100 continue
110 write(6,118)
118 format(/,'species no.',5x,'calc. y',5x,
&'calc. x',7x,'solubility',/,
&42x,'(mol per kg wax)',/)
dumx=0.0
dumy=0.0
do 150 j1=1,ngas
sol=x(j1)/(1.0-x(j1))/rmw*1000.0
dumx=dumx+con(1,j1)
dumy=dumy+con(2,j1)
write(6,120)j1,con(2,j1),x(j1),sol
120 format(1x,i3,4x,f12.4,3x,e12.3,4x,e12.3)
150 continue
dumx=dumx+con(1,ncomt)
dumy=dumy+con(2,ncomt)
write(6,130)ncomt,con(2,ncomt),con(1,ncomt)
130 format(1x,i3,4x,f12.4,3x,e12.3,12x,'-')

```

```

      write(6,140)dumy,dumx
140 format(/,1x,'total',3x,f12.4,1x,f12.4,/)
      stop
      end

```

```

      subroutine obj(x,f)

```

```

c
c this subroutine set the objective function to be
c minimized by the levenberg-marquardt algorithm
c

```

```

      dimension coef(4),fu(2,6),x(5),f(5)
      common t,p,y(5),ngas,ncomt,vcal(2),
&r,rmw,rn,tc(6),pc(6),omeg(6),
&a(6),b(6),am,bm,alpha(6),
&phi(6),chi(6,6),q(6)
      common con(2,6),xx(6)
      common /was/ ywax
      complex z(3)
      con(1,ncomt)=1.0
      con(2,ncomt)=ywax
      do 10 i0=1,ngas
      con(1,i0)=x(i0)
      con(2,i0)=(1.0-ywax)*y(i0)
      con(1,ncomt)=con(1,ncomt)-con(1,i0)
10 continue
      con(1,ncomt)=abs(con(1,ncomt))
      do 50 j1=1,ncomt
      tr=t/tc(j1)
      call calal(j1,tr)
      a(j1)=0.42747*alpha(j1)*r*r*tc(j1)*tc(j1)/pc(j1)
      b(j1)=0.08664*r*tc(j1)/pc(j1)
50 continue
      do 90 i1=1,2
      call mix(i1)
      call mixb(i1)
      call mixa(i1)
      rtop=r*t/p
      coef(1)=1.0
      coef(2)=-rtop
      coef(3)=-bm*rtop-bm*bm+am/p
      coef(4)=-bm*am/p
      call zrpoly(coef,3,z,ier)
      vcal(1)=real(z(1))
      vcal(2)=real(z(3))
      do 90 j1=1,ncomt
      call rabrn(i1,j1,dadxi,dbdxi)
      call fugac(fu,vcal(i1),i1,j1,dadxi,dbdxi)

```

```

90 continue
  do 100 i1=1,ngas
    f(i1)=con(2,i1)/(fu(1,i1)/fu(2,i1))
100 continue
  xwax=1.0
  do 110 n1=1,ngas
110 xwax=xwax-f(n1)
    ywax=fu(1,ncomt)/fu(2,ncomt)*xwax
  return
end

```

subroutine wax

```

c
c given the molecular weight of the wax, this
c subroutine generates the necessary wax
c information for further calculations
c

```

```

  dimension coef(4,4)
  common t,p,y(5),ngas,ncomt,vcal(2),
&r,rmw,rn,tc(6),pc(6),omeg(6),
&a(6),b(6),am,bm,alpha(6),
&phi(6),chi(6,6),q(6)
  common con(2,6),xx(6)
  rn=(rmw-2.0158)/14.0268
  q(ncomt)=13.67*2.0+(rn-2.0)*10.23
  coef(1,1)=0.31391e04
  coef(2,1)=-0.76229e00
  coef(3,1)=0.11165e03
  coef(4,1)=0.16693e-01
  coef(1,2)=0.36175e-01
  coef(2,2)=-0.47775e00
  coef(3,2)=0.58524e00
  coef(4,2)=0.43358e-01
  coef(1,3)=0.80936e01
  coef(2,3)=0.99288e00
  coef(3,3)=0.54555e02
  coef(4,3)=0.80034e01
  coef(1,4)=0.73697e-01
  coef(2,4)=0.14880e00
  coef(3,4)=0.57077e-1
  coef(4,4)=0.44621e-1
  do 10 i=1,4
    c1=coef(1,i)
    c2=coef(2,i)
    c3=coef(3,i)
    c4=coef(4,i)
    dum1=c1/c4

```

```

dum2=1.0-c2
term2=dum1-c3**dum2
term3=exp(-c4*(rn-1.0)*dum2)
dum=(dum1-term2*term3)**(1.0/dum2)
goto (3,4,6,8),i
3 haha=3.03191-0.049901*rn**(2.0/3.0)
tb=1078.-10.0**haha
goto 10
4 tc(ncomt)=tb/dum
goto 10
6 pc(ncomt)=dum
goto 10
8 omeg(ncomt)=dum
10 continue
return
end

```

```

subroutine gprop(id,j1)
common t,p,y(5),ngas,ncomt,vcal(2),
&r,rmw,rn,tc(6),pc(6),omeg(6),
&a(6),b(6),am,bm,alpha(6),
&phi(6),chi(6,6),q(6)
common con(2,6),xx(6)

```

c
c this subroutine generates the gas information needed
c for calculations

c

```

goto (10,20,30,40,50),id
10 write(6,11)j1,y(j1)
11 format(4x,i1,12x,'hydrogen ',9x,f12.4)
tc(j1)=33.2
pc(j1)=12.8
omeg(j1)=-0.22
q(j1)=10.51
a1=0.2456
a2=0.2406
rmw0=127.30
goto 100
20 write(6,21)j1,y(j1)
21 format(4x,i1,12x,'carbon monoxide',3x,f12.4)
tc(j1)=132.9
pc(j1)=34.5
omeg(j1)=0.049
q(j1)=13.01
a1=0.1723
a2=0.1707
rmw0=140.75

```

```

      goto 100
30 write(6,31)j1,y(j1)
31 format(4x,i1,12x,'methane ',9x,f12.4)
      tc(j1)=190.6
      pc(j1)=45.4
      omeg(j1)=0.008
      q(j1)=17.09
      a1=0.1009
      a2=0.1050
      rmw0=146.06
      goto 100
40 write(6,41)j1,y(j1)
41 format(4x,i1,12x,'carbon dioxide ',3x,f12.4)
      tc(j1)=304.2
      pc(j1)=72.8
      omeg(j1)=0.225
      q(j1)=19.68
      a1=0.09710
      a2=0.09240
      rmw0=137.02
      goto 100
50 write(6,51)j1,y(j1)
51 format(4x,i1,12x,'ethane ',9x,f12.4)
      tc(j1)=305.4
      pc(j1)=48.2
      omeg(j1)=0.098
      q(j1)=27.34
      a1=0.04967
      a2=0.05277
      rmw0=188.16
100 factor=1.0-exp(-rmw/rmw0)
      chi(j1,ncomt)=(a1+(a2-a1)*(t-473.2)/100.0)*factor
      return
      end

```

```

      subroutine calal(j1,tr)

```

```

c
c   this subroutine calculates equation parameter
c   alpha for each species
c
      common t,p,y(5),ngas,ncomt,vcal(2),
&r,rmw,rn,tc(6),pc(6),omeg(6),
&a(6),b(6),am,bm,alpha(6),
&phi(6),chi(6,6),q(6)
      common con(2,6),xx(6)
      if(tc(j1)-550.)10,10,40
10 dum=omeg(j1)

```

```

      haha=0.480+1.574*dum-0.176*dum*dum
      haha=1.0+haha*(1.0-sqrt(tr))
      alpha(j1)=haha*haha
      goto 120
40  if(rmw-268.529)50,50,60
50  power=0.5
      goto 70
60  power=0.5685-2.552e-4*rmw
70  dum=rmw
      ff=0.47135+0.63325e-2*dum-0.78307e-5*dum*dum
      &+0.44238e-8*dum**3-0.97365e-12*dum**4
      alpha(j1)=(1.0+ff*(1.0-tr**power))**(1.0/power)
120 return
      end

```

```

      subroutine mix(i1)

```

```

c
c  this subroutine sets the parameters needed
c  for executing the mixing rules.

```

```

c
      common t,p,y(5),ngas,ncomt,vcal(2),
      &r,rmw,rn,tc(6),pc(6),omeg(6),
      &a(6),b(6),am,bm,alpha(6),
      &phi(6),chi(6,6),q(6)
      common con(2,6),xx(6)
      dum=0.0
      do 10 n1=1,ncomt
10  dum=dum+con(i1,n1)*q(n1)
      do 20 n1=1,ncomt
20  phi(n1)=con(i1,n1)*q(n1)/dum
      dum1=0.0
      do 30 n1=1,ncomt
30  dum1=dum1+con(i1,n1)
      do 40 n1=1,ncomt
40  xx(n1)=dum1*q(n1)/dum
      return
      end

```

```

      subroutine mixa(i1)

```

```

c
c  this subroutine executes the mixing rule
c  for a

```

```

c
      common t,p,y(5),ngas,ncomt,vcal(2),
      &r,rmw,rn,tc(6),pc(6),omeg(6),
      &a(6),b(6),am,bm,alpha(6),
      &phi(6),chi(6,6),q(6)

```

```

common con(2,6),xx(6)
rlam = alog(2.0)
sum1 = 0.0
do 100 n1 = 1, ncomt
100 sum1 = sum1 + con(i1,n1)*q(n1)
sum0 = 0.0
do 150 n1 = 1, ncomt
do 150 n2 = 1, ncomt
150 sum0 = sum0 + chi(n1,n2)*phi(n1)*phi(n2)
sum1 = 0.5*sum1*sum0
sum2 = 0.0
do 200 n1 = 1, ncomt
200 sum2 = sum2 + con(i1,n1)*alog(xx(n1))
ge = (sum1 + sum2)*r*t
sum3 = 0.0
do 400 n1 = 1, ncomt
400 sum3 = sum3 + con(i1,n1)*a(n1)/b(n1)
am = bm*(sum3 - ge/rlam)
return
end

```

```

subroutine mixb(i1)

```

```

c
c this subroutine executes mixing rule
c for b
c
common t,p,y(5),ngas,ncomt,vcal(2),
&r,rmw,rn,tc(6),pc(6),omeg(6),
&a(6),b(6),am,bm,alpha(6),
&phi(6),chi(6,6),q(6)
common con(2,6),xx(6)
bm = 0.0
do 100 n1 = 1, ncomt
bm = bm + con(i1,n1)*b(n1)
100 continue
return
end

```

```

subroutine rabrn(i1,j1,dadxi,dbdxi)

```

```

c
c this subroutines calculates the partial
c derivatives for a and b
c
common t,p,y(5),ngas,ncomt,vcal(2),
&r,rmw,rn,tc(6),pc(6),omeg(6),
&a(6),b(6),am,bm,alpha(6),
&phi(6),chi(6,6),q(6)

```



```

      common con(2,6),xx(6)
c
c   calculate partial b
c
      dbdxi=b(j1)
c
c   calculate prtial a
c
      rlam=alog(2.0)
      sum0=0.0
      do 100 n1=1,ncomt
100 sum0=sum0+con(i1,n1)*q(n1)
      sum1=0.0
      do 150 n1=1,ncomt
      do 150 n2=1,ncomt
150 sum1=sum1+chi(n1,n2)*phi(n1)*phi(n2)
      tum1=0.5*sum0*sum1
      sum2=0.0
      do 200 n1=1,ncomt
200 sum2=sum2+con(i1,n1)*alog(xx(n1))
      tum2=sum2
      ge=(tum1+tum2)*r*t
      sum3=0.0
      do 400 n1=1,ncomt
400 sum3=sum3+con(i1,n1)*a(n1)/b(n1)
      term1=b(j1)*(sum3-ge/rlam)
      term21=0.5*sum1*q(j1)
      sum4=0.0
      do 450 n1=1,ncomt
450 sum4=sum4+chi(n1,j1)*xx(j1)*phi(n1)
      sum5=0.0
      do 470 n1=1,ncomt
      do 470 n2=1,ncomt
470 sum5=sum5+chi(n1,n2)*phi(n1)*phi(n2)*xx(j1)
      term22=sum0*(sum4-sum5)
      term23=alog(xx(j1))
      sum6=0.0
      do 490 n1=1,ncomt
490 sum6=sum6+con(i1,n1)*xx(j1)
      term24=1.0-sum6
      dum2=term21+term22+term23+term24
      term2=bm*(a(j1)/b(j1)-r*t/rlam*dum2)
      dadxi=term1+term2
      return
      end

      subroutine fugac(fu,v,i1,j1,dadxi,dbdxi)

```

```

dimension fu(2,6)
c
c this subroutine calculates the fugacities
c
common t,p,y(5),ngas,ncomt,vcal(2),
&r,rmw,rn,tc(6),pc(6),omeg(6),
&a(6),b(6),am,bm,alpha(6),
&phi(6),chi(6,6),q(6)
common con(2,6),xx(6)
z=abs(p*v/r/t)
vdum=abs(v)
vpb=abs(v+bm)
vmb=abs(v-bm)
term1=log(vdum/vmb)
term2=(dadxi/bm-am*dbdxi/bm/bm)*log(vdum/vpb)/r/t
term3=dbdxi/vmb
term4=am/bm*dbdxi/vpb/r/t
philn=term1+term2+term3-term4-log(z)
fu(i1,j1)=exp(philn)
return
end

```

```
#eor
```

```
-----Sample Input-----
```

```

573.2   20.00  t(K) and p(atm) of the system; 2f10.3
5                               number of gases; i1
394.77                               molecular weight of wax;f10.3
1  0.3000                               gas id. and y in mol fraction;i1,2f10.3
2  0.3000
3  0.0500
4  0.3000
5  0.0500
#eof

```

```
----- Sample Output -----
```

```

system temperature in k= 573.20
pressure in atm = 20.00

```

```
wax molecular weight= 394.77
```

```

species 1 gas id= 1
species 2 gas id= 2
species 3 gas id= 3
species 4 gas id= 4
species 5 gas id= 5

```

species	y	calc. x	solubility (mol per kg wax)
---------	---	---------	--------------------------------

1	.3000	.173e-01	.445e-01
2	.3000	.204e-01	.527e-01
3	.0500	.520e-02	.132e-01
4	.3000	.380e-01	.100e+00
5	.0500	.870e-02	.222e-01

wax mole fraction in vapor phase= .165e-02