

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-C₂₀, n-C₂₈, and in n-C₃₆ at reactor conditions of Fischer-Tropsch synthesis, and for synthesis gas mixtures of H₂ and CO in n-C₂₈ at three feed gas compositions (40.01, 50.01, and 66.64 mol % of H₂). 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 thermostat 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 CO₂ + n-C₂₀ 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 CO₂ in n-C₂₈ and in n-C₃₆, 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-C₂₀ and in n-C₂₈ shows a shallow minimum in the range of 100-300°C, but this transition is not observed in n-C₃₆, 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 H₂,

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^∞ , 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^∞ 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}^{∞} 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 $i = j$

$A_{ij} = A_{ji}$ for $i \neq j$. Substituting eq. 11 into eq. 10, we obtain

$$\frac{a}{b} = \sum_i \frac{a_i}{b_i} x_i - \frac{RT}{4n^2} \left[\frac{1}{2} (\sum_i x_i V_i) (\sum_i \sum_j A_{ij} \phi_i \phi_j) + \sum_i x_i \ln (\phi_i/x_i) \right] \quad (12)$$

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-C₆₁ paraffin, for the Mobil wax of this study. In the calculations here the wax is treated as a C₆₁ 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-C₃₆. 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 H₂ 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 C₄₃ n-paraffin ($M = 605$) in the modified Soave equation described above. The A_{ij} values used are again taken from those of gas/n-C₃₆. 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.