L°_B = molar heat of vaporization for pure water, kcal./kg.-mole water
L_B = molar heat of vaporization for water out of ammonium nitrate solutions, kcal./kg.-mole water
m = slope of an isostere on a logarithmic partial-pressure plot
H = enthalpy, kcal./kg-mole (except if otherwise noted)
P = partial pressure of water above ammonium nitrate solutions, mm. Hg abs.
P° = vapor pressure of pure water, mm. Hg abs.
Q = integral heat of solution for solid ammonium nitrate, kcal./kg.-mole
q = integral heat of dilution, kcal./kg.-mole
t = temperature, °C.
T = absolute temperature, °K.
x = mole fraction
Z = abbreviation for the integral of Equation (7)

Subscripts

A = ammonium nitrate
B = water
s = solution
TR = transition
∞ = infinite dilution
1 = concentration where integral heat of solution Q is known
2 = any concentration

Superscripts

— = partial quantity
′ = infinite dilution
• = solid state
° = pure compound

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Hydrocarbon Vapor-Liquid Equilibria and Solubility Parameter

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Hydrocarbon vapor-liquid equilibria are expressed in terms of K values, which are functions of composition, as well as pressure and temperature. The composition effect in the liquid phase is calculated by the Hildebrand-Scatchard equation for regular solutions. The parameters in this equation, called *solubility parameters*, can be calculated simply from heat of vaporization for the heavier hydrocarbons, but an indirect method of calculation must be used for the lighter components. Solubility parameters for hydrogen, methane, ethane, and propane were computed from gas-solubility data in several hydrocarbon solvents at various temperatures and pressures. This computation also yielded simultaneously the fugacities of the hypothetical liquid-standard states.

The results presented are not complete for practical applications, owing to the scarcity of suitable solubility data, especially at high temperatures and pressures. However solubility parameters appear to give the right liquid-phase corrections in the correlation and prediction of hydrocarbon phase equilibria. Calculated K values for light hydrocarbons in paraffinic, naphthenic, and aromatic absorption oils are compared with experimental results. The average deviation for the forty-two values tested is 13%.

The composition dependence of the vaporization equilibrium ratio in hydrocarbon systems has been frequently neglected in practical applications. While the composition-independent K values are approximately applicable to mixtures composed entirely of one class of hydrocarbons, like the aliphatics, large deviations are encountered for mixtures composed of different classes of hydrocarbons, notably those containing aromatics and, to a lesser extent, naphthenes.

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The composition-independent K values follow from the assumption of Raoult's law for the liquid phase and Dalton's law for the vapor phase. Lewis's fugacity rule leads, likewise, to composition-independent K values. Ideal K-value charts, such as those prepared by Lewis and Kay (*15*) and by Souders, Selheimer, and Brown (*28*), were derived therefrom.

Benedict, Webb, and Rubin developed composition-dependent K values from their equation of state (*1, 2*). Their results were simplified and correlated in reduced variables by Edmister and Ruby (*5*) for more convenient application. The B.W.R. equation of state K values are valuable at conditions of extreme temperature and pressure for aliphatic systems. An equation-of-state approach such as this, however, is limited by the rules of combination of the constants. The validity of these rules was established for hydrocarbon mixtures composed entirely of one class of compounds, specifically the aliphatics. Behavior of mixtures of different classes of compounds, such as mixtures of hydrocarbons and carbon dioxide, was shown not to follow these combination rules (*3, 21*).

The widely used Natural Gasoline Association of America K charts (*31*) seek to correlate composition effect on K values by the convergence pressure of the system. These K values apply only to aliphatic mixtures. Again their use in aromatic-containing systems may lead to large deviations.

The present work proposes to answer the need for correct K values of light hydrocarbons in different solvents. The following developments and results are for conditions where deviation from ideal solution arises mainly in the liquid phase. The liquid-phase nonideality is treated with the Hildebrand-Scatchard equation for regular solutions.

The K values for a component i are computed by the rigorous thermodynamic relationship

$$K_i \equiv \frac{y_i}{x_i} = \frac{\gamma_i \nu_i}{\phi_i} \qquad (1)$$

REGULAR SOLUTIONS

Much has been written on regular solutions (*7*), and only a few features pertinent to the problem under consideration will be mentioned here. A regular solution is one in which the nonideality is due entirely to the heat of mixing. Its entropy of solution is equal to that of an ideal solution. While no solutions are exactly regular, the properties of solutions of nonpolar fluids, such as the hydrocarbons, are approximated by the regular-solution equations. It was shown by Hildebrand and Scott (*7*) and by Scatchard (*25, 26*) that the activity coefficient of a component i in a regular liquid solution containing n components is given by

$$\ln\gamma_i = \frac{V_i(\delta_i - \bar{\delta})^2}{RT} \qquad (2)$$

The solubility parameter is the square root of an energy density. For a liquid it is defined by

$$\delta = \left(\frac{\Delta E}{V}\right)^{1/2} \qquad (3)$$

At temperatures well below the critical this energy is essentially the enthalpy of vaporization minus RT.

In general, values of solubility parameters of the aromatic hydrocarbons are higher than those of the naphthenes; the latter are in turn higher than those of the paraffins. Among the normal paraffins the solubility parameter increases rapidly with molecular weight starting from methane but tends to level off for compounds heavier than n-pentane. Thus the difference in solubility parameters between a light and a heavy paraffin is less than that between the same light paraffin and an aromatic hydrocarbon. This explains the high K values of the light paraffins in aromatics.

It follows from Equation (3) that the solubility parameter decreases with temperature, but it is practically independent of pressure at a given temperature. The variation of solubility parameter with temperature was given by Hildebrand and Scott (*7*) to be approximately

$$\frac{d\ln\delta}{dT} \cong -1.25\,\alpha \qquad (4)$$

Over a moderate range of temperature where α may be taken to be approximately constant, Equation (4) states that log δ varies linearly with temperature. The solubility parameters of several common hydrocarbons are shown in Figure 1. The lines are based on δ and its slope $(d\ln\delta)/dT$ at a temperature of 25°C. Determination of the lines for the light gases methane, ethane, propane, and hydrogen is discussed in the next section. Solubility parameters of a number of other hydrocarbons have been given (*7*) at 25°C.

Dependence of K values on solubility parameter is illustrated in Figure 2 for methane at 100°F. and 500 lb./sq. in. abs. The solubility-parameter equation accounts for the variation of K over a wide range because of the nature of the solvent and various dissolved quantities of other light hydrocarbons (ethylene and isobutane). Figure 2 also bears out the linear relationship demanded by Equations (1) and (2). This linearity holds rigorously, barring significant variations in ϕ. Actually ϕ does not vary more than 3.3% for methane in these mixtures.

GASEOUS COMPONENTS

Since Equation (2) was derived for solutions of liquids mixing with no volume change, it does not in its present form have rigorous theoretical basis for solutions containing one component above its critical temperature. It was shown earlier (*20*) that Equation (2) can be modified to be theoretically applicable to gas-liquid solutions, but for the purpose of this paper it is more convenient to consider Equation (2) as a semiempirical relation with adjustable parameters suitable for all liquid-phase hydrocarbon solutions, including those containing both gaseous and liquid components.

For a gaseous solute in liquid solution the liquid molal volume is replaced by the partial molal volume of the dissolved gas, which can be estimated with fair accuracy from Watson's expansion factor, (*30*):

$$V = (V_1\omega_1)\left(5.7 + 3.0\frac{T}{T_c}\right) \qquad (5)$$

For a gaseous component i in a binary mixture Equation (*1*) is rewritten as

$$\nu_i = \frac{K_i\phi_i}{\gamma_i} \qquad (1a)$$

There are two adjustable parameters for a component: the hypothetical liquid-phase fugacity, which is a function of temperature and pressure, and the solubility parameter, which at moderate pressures is a function of temperature only. By fitting Equation (1a) to the solubility data of a gas in at least two solvents at the same temperature and pressure, one can solve for the parameters f^L (or ν) and δ for the gaseous component.

The calculations for a given gas at a fixed temperature and pressure were of the trial-and-error type, with solubility data used in at least two solvents. To obtain sensitivity in the calculations, it was always necessary to choose solvents of different chemical nature; usually one solvent was a paraffin, the second an aromatic hydrocarbon, and so on. To start the calculation, a first estimate of δ was substituted into Equations (2) and (1a), one value of ν being obtained from each solution. The difference between them is designated by $\Delta\nu$. The calculation was repeated with new estimates of δ used until $\Delta\nu$ vanished. This then gave the correct values for ν and δ. This procedure is

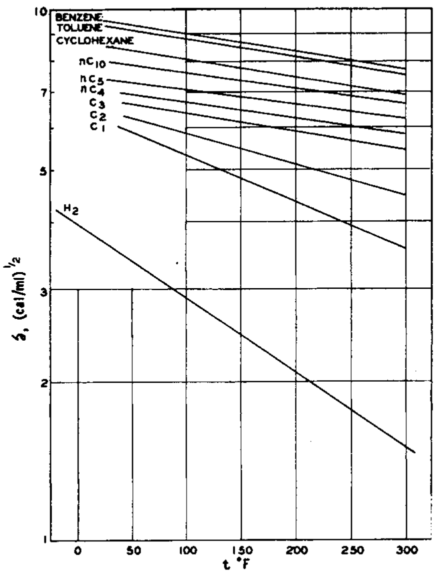

Fig. 1. Solubility parameters.

illustrated in Figure 3 for solutions of ethane in heptane and benzene at 110°F. and 400 lb./sq. in. abs. The fugacity coefficient in the vapor mixture was calculated from the Redlich and Kwong equation of state for this instance, as well as for all mixtures studied in this work. Discussions on vapor-phase correction are deferred to the next section.

Where solubility data for the same gas in more than two solvents are available, calculated ν's are directly plotted against assumed values of δ, resulting in a group of curves, one for each solution. A single point of intersection is to be expected if the equations are exactly applicable and the data are perfectly precise. Figure 4 illustrates the result of calculation for H_2 at $-25°C$. and atmospheric pressure. The curves display a tendency toward convergence, except for solution of H_2 in perfluoronormal heptane. The chosen point of convergence is marked with a large circle.

TABLE 1. SOURCES OF SOLUBILITY DATA

Solute	Solvent	Reference
Hydrogen	Benzene	*9*
	Toluene	*9*
	Cyclohexane	*9*
	n-Hexane	*18*
	n-Heptane	*4*
	n-Octane	*4*
	iso-Octane	*4*
	Perfluoro-*n*-heptane	*4*
	Benzene	*4*
	Toluene	*4*
	Carbon disulfide	*4*
	Carbon tetrachloride	*4*
Methane	Trimethylbutane	*24*
	n-Nonane	*24*
	Cyclohexane	*24*
	Benzene	*24*
	Toluene	*24*
Ethane	*n*-Heptane	*10*
	Benzene	*11*
Propane	*iso*-Pentane	*29*
	Benzene	*6*

Some arbitrariness was unavoidable in the selection of this convergence point as shown in Figure 4. However the determined δ and ν, when applied consistently, will lead to K values correct to the extent indicated by the scattering of the ν curves at the chosen δ. Thus for the systems at the conditions shown the K values of H_2 will be reproduced to within 10% (except in perfluoronormal heptane), even though the K values vary by as much as 570% in different solvents.

Solubility parameters determined in this manner for methane, ethane, propane, and hydrogen are shown in Figure 1.

Values of ν for the three lightest paraffins and hydrogen are shown in Figures 5 to 8, respectively. Computed values of ν from solubility data correspond to conditions of high reduced temperature. At conditions of low reduced temperatures, where the pure substance exists as an actual liquid, values of ν were obtained from generalized correlations prepared by Lydersen, Greenkorn, and Hougen (*16*). The combination of computed and generalized values in the preparation of these ν charts is illustrated in Figure 9 for propane.

Sources of solubility data that were used in this work are recorded in Table 1.

Extension of ν to lower pressures is facilitated by the relation that ν tends to be inversely proportional to pressure when the pressure is sufficiently reduced. From the thermodynamic relation

$$\left(\frac{\partial \ln \nu}{\partial \ln P}\right)_T = \frac{PV^L}{RT} - 1 \qquad (6)$$

it follows that

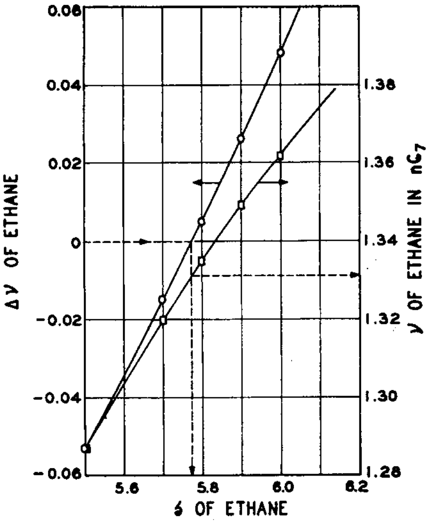

Fig. 3. ν from equilibrium data on ethane systems at 570°R. and 400 lb./sq. in. abs.

$$\lim_{P \to 0} \left(\frac{\partial \ln \nu}{\partial \ln P}\right)_T = -1 \qquad (7)$$

since V^L changes but slightly with pressure. This situation apparently holds even when the liquid state is hypothetical, as illustrated in Figure 10 for propane. The points shown are taken from the curves in Figure 9.

The constants $V_1\omega_1$ in Equation (4) have been given (*30*) for the normal paraffins. Constants for methane and ethane were slightly adjusted to give better agreement with observed data on partial volumes in dilute hydrocarbon solutions (*7*). A plot of $V_1\omega_1$ against number of carbon atoms was connected smoothly from methane and ethane to the higher paraffins, resulting in slight adjustment for propane. The constants for the other normal paraffins were not changed. In Table 2 the constants for other hydrocarbons were evaluated to fit densities given in A.P.I. Project 44. For hydrogen, partial volumes in hydrocarbon solutions (*8*, *13*,

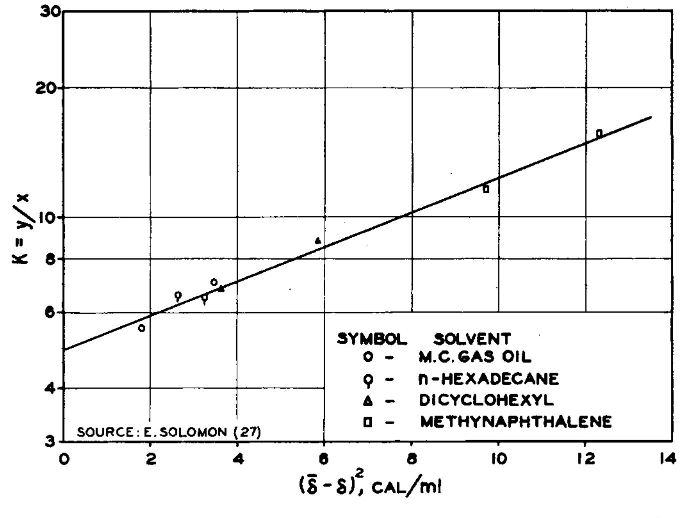

Fig. 2. Effect of solubility parameter on K value of methane at 100°F. and 500 lb./sq. in. abs.

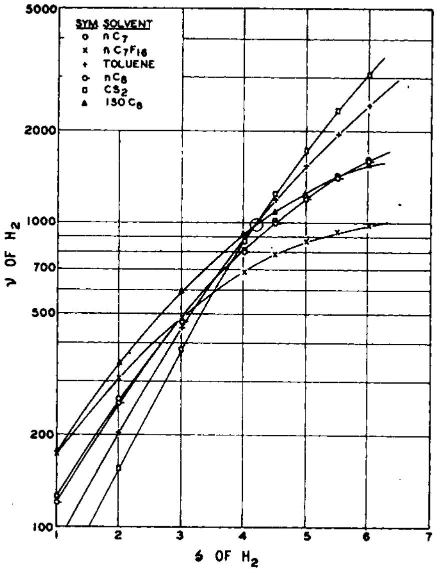

Fig. 4. Hydrogen systems at —25°C., 14.7 lb./sq. in. abs.

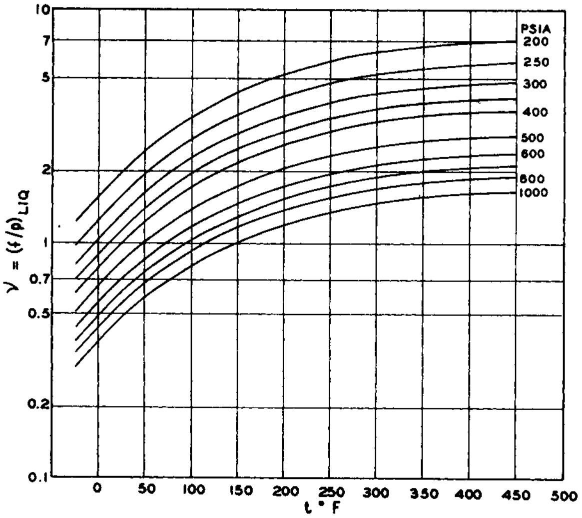

Fig. 6. Liquid fugacity for ethane.

14) under moderate pressures were the basis of the constant in Table 2.

VAPOR-PHASE CORRECTION

The fugacity coefficient in the vapor phase is, generally speaking, just as important as the liquid-phase activity coefficient in the determination of *K* values. There is however a point of distinction in emphasis, depending on the component. In systems composed of both light and heavy components the liquid activity coefficient is usually important for the light component but not for the heavy one, and the vapor fugacity coefficient is usually important for the heavy component but not for the light one.

The emphasis of this work is on liquid-phase correction and consequently on the *K* values of the light components. The vapor-phase fugacity coefficients for them are adequately given by the relatively simple Redlich and Kwong's equation of state (*22*) under the conditions investigated here. The characteristic constants in this equation are directly related to the critical temperature and pressure of the components. Other method for computing vapor-phase fugacity coefficients have been presented recently (*19*).

APPLICATIONS

Illustration 1

Application of the method outlined here to be the calculation of vapor-liquid equilibria in heavy-oil–absorption systems requires determination of the solubility parameter of the absorber oils. Strictly speaking, these oils should be broken down into narrow boiling cuts, the solubility parameter of the cuts evaluated according to Equation (3), and the over-all solubility parameter of the oil synthesized from that of the cuts as the volume-averaged mean value. This procedure is tedious, and the necessary information is often not available on the individual cuts, but it appears, fortunately, that sufficient accuracy is obtained by taking such oil as a single compound characterized by its average boiling point, A.P.I. gravity, and average molecular weight. These properties are included in standard inspections.

The solubility parameter is calculated at 25°C. of the hydroformer still bottoms used by Solomon in experimental studies of vaporization equilibrium ratios (*27*). The characteristics of this absorber oil are

Gravity, °A.P.I.	4.8
Mole average boiling point, °F.	634
Molecular weight	209

Solution: Density at 60°F. = 1.038 g./ml., from given °A.P.I.

Density correction factor to 25°C. (77°F.) = 0.993 (*17*)

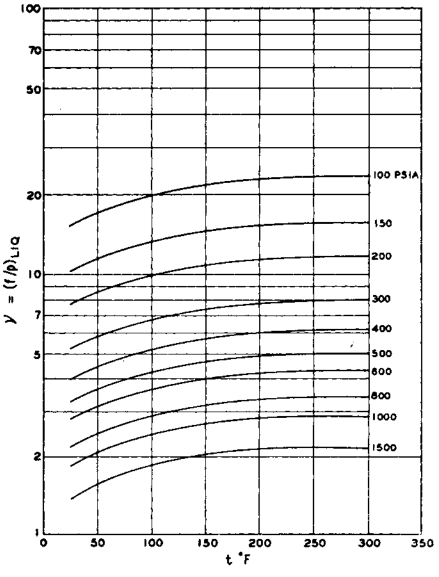

Fig. 5. Liquid fugacity for methane.

TABLE 2. LIQUID-VOLUME CHARACTERISTIC CONSTANTS IN WATSON'S EQUATION

	$V_1\omega_1$, cc./g.-mole
Hydrogen	1.05
Methane	5.00
Ethane	7.77
Propane	9.70
n-Butane	11.62
n-Pentane	14.07
n-Hexane	16.52
n-Heptane	18.96
n-Octane	21.39
n-Nonane	23.83
n-Decane	26.28
Cyclohexane	14.07
Benzene	11.64
Toluene	14.15

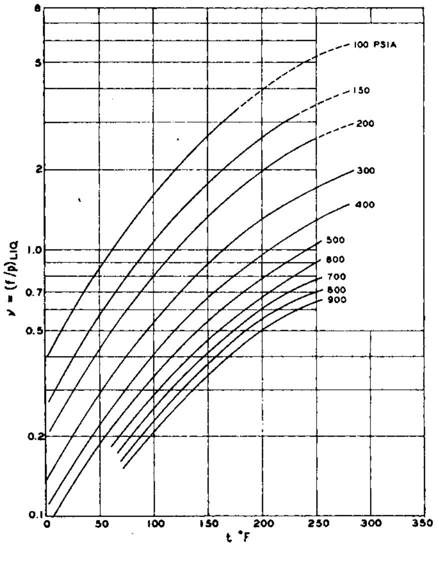

Fig. 7. Liquid fugacity for propane.

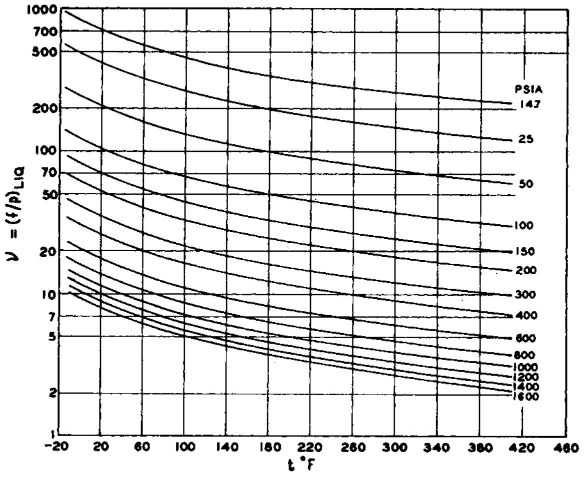

Fig. 8. Liquid fugacity for hydrogen.

Density* at 25°C. = 0.993 × 1.038 = 1.030 g./ml.
V at 25°C. = 209/1.030 = 203 ml./g.-mole.
ΔH at 634°F. = 13,060 cal./g.-mole, from Kistiakowsky equation
ΔH correction factor to 25°C. = 1.369, according to Watson's 0.38 exponential correction (*17*) with T_c = 1,066°F.
ΔH at 25°C. = 1.369 × 13,060 = 17,870 cal./g.-mole
RT at 25°C. = 592 cal./g.-mole
ΔE at 25°C. = 17,870-590 = 17,280 cal./g.-mole
$\Delta E/V$ = 85.1 cal./ml.
δ = 9.23 (cal./ml.)$^{1/2}$

This is a high value for a solubility parameter, typical for aromatic hydrocarbons. (Refer to Figure 1 for comparison with the pure hydrocarbons.)

The pure-component property v of the heavy substances may be estimated from generalized correlations, such as the correlation prepared by Lyderson, Greenkorn, and Hougen (*16*).

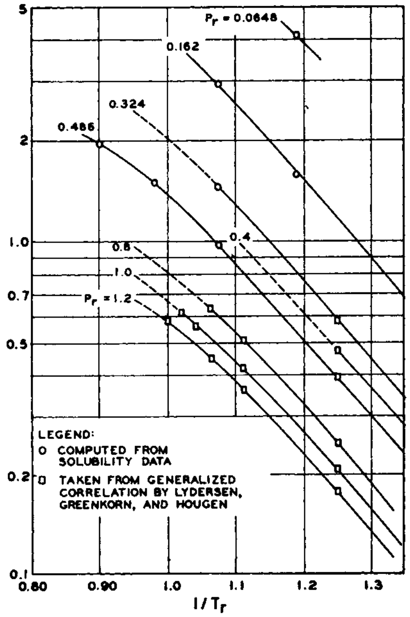

Fig. 9. Liquid fugacity for propane, combination of values from pure component and from solubility data (z_c = 0.277).

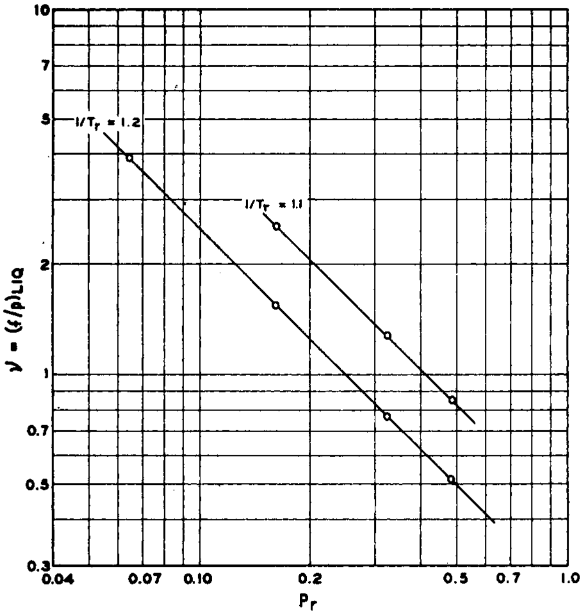

Fig. 10. Isothermal variation of v of propane at low pressure.

Calculation of bubble and dew points of hydrocarbon mixtures according to K values given by Equation (*1*) involves double trial-and-error calculations. Both the temperature and the composition of the equilibrium phase must be assumed and checked through either $\sum_i K_i x_i = 1$, or $\sum_i (y_i/K_i) = 1$.

COMPARISON WITH EXPERIMENTAL DATA

The solubility parameter and liquid fugacity coefficient presented in previous sections were developed from either pure-component properties or solubility data in binary mixtures. These values were used to compute K in multicomponent mixtures under conditions that had been experimentally studied. The results were compared with observed K values. Solomon's (*27*) experimental studies of K values of light hydrocarbons were found the most suitable for the test because of the widely different character of the solvents, including aliphatic, naphthenic, and aromatic oils and compounds under comparable conditions of temperature and pressure.* In addition Kirkbride and Bertetti's (*12*) low-pressure data were tested, but their high-pressures data were beyond the range of the ν charts here developed.

Comparisons were made with the published vapor-liquid-equilibrium data of Kirkbride and Bertetti on the light hydrocarbons, methane through pentane, in naphthenic, paraffin, and aromatic absorption oils at 90 to 92°F. and 123 to 124 lb./sq. in. abs. The average absolute deviation was 15% for the light hydrocarbons. No trend of deviation is observed in the hydrocarbons from methane to pentane, in spite of the difference in source of ν, which is taken from computed values for the

TABLE 3. SOLUBILITY PARAMETER AND LIQUID VOLUME OF SOLVENTS

Solvent	Investigator	t, °F.	δ, (cal./ml.)$^{1/2}$	$\bar{V}$, ml./g.-mole
M.C. gas oil	*27*	100	7.41	324
		220	6.92	346
Hydroformer still bottoms	*27*	220	8.66	214
n-Hexadecane	*27*	100	7.52	297
		220	7.02	316
Dicyclohexyl	*27*	100	8.20	190
		220	7.68	202
Methylnaphthalene	*27*	100	9.53	143
		220	8.94	151
Paraffinic lean oil	*12*	90	7.46	56
Naphthenic lean oil	*12*	90	7.81	61
Aromatic lean oil	*12*	92	9.66	94

lighter compounds and from a generalized correlation for the heavier compounds.

Another comparison was made of Solomon's K of methane with computed values. The experimental studies were on mixtures of methane, ethylene, isobutane, and the heavy solvents at 100° to 220°F. and 500 to 1,000 lb./sq. in. abs. Owing to a lack of suitable equilibrium data, the solubility parameter and liquid molal volume of ethylene were not available from data processing but were estimated from properties of the light paraffins at the same temperature. This admittedly was not accurate, but the estimated quantities were used only in the calculation of average solubility parameter of the liquid mixtures, to which the errors should not contribute to any significant extent. The lack of data also made it impossible to develop a correlation for ethylene. The average absolute deviation was 13%.

K values of isobutane at 100°F. in Solomon's mixtures were calculated by the use of Lydersen's generalized ν values. Results at 100°F. deviated only 5% from the observed.

The solubility parameter and liquid molal volume of the heavy solvents that were used in these calculations are given in Table 3.

DISCUSSION

Calculation of light hydrocarbon vapor-liquid equilibria by the use of solubility parameters appears to give correctly the liquid phase composition effects. Composition-corrected K values are not convenient to apply without electronic digital computers; this method is no exception.

However, simplification has been obtained by taking solubility parameter and liquid volume to be pressure insensitive. As demonstrated in the comparison with experimental data, this lack of sensitivity to pressure appears to be justified up to 1,000 lb./sq. in. abs. at usual temperatures. No trend in deviation was detected with pressure.

Another possibility of simplification may be to take solubility parameter and liquid volume to be temperature independent. There are indications that results of comparable accuracy may be obtained over a range of temperature of practical interest. Since the effect of solubility parameter on the liquid-phase correction is in the form of a difference term, the deviation incurred by taking the individual terms to be constant may be less than suggested by examination of the variation of the individual values with temperatures.

The results presented here are incomplete owing to the scarcity of suitable solubility data, especially at higher temperatures. As more data become available, the correlation developed in this work can no doubt be improved. However the results summarized here indicate that the solubility parameter is a useful tool for the correlation and prediction of hydrocarbon vapor-liquid equilibria.

ACKNOWLEDGMENT

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NOTATION

E = internal energy
f = fugacity
H = enthalpy
K = vaporization equilibrium ratio
P = pressure
R = gas constant
T = absolute temperature
t = temperature
V = molal volume
x = mole fraction in liquid phase
x_v = volume fraction in liquid phase; $x_{vi} = \dfrac{x_i V_i}{\sum_{j=i}^{n} x_j V_j}$
y = mole fraction in vapor phase

Greek Letters

ΔE = energy required to vaporize the liquid to infinite volume
α = coefficient of thermal expansion
γ = activity coefficient in liquid phase, to be given by Hildebrand-Scatchard equation for regular solutions for component $i \equiv f_i/f^L{}_i x_i$
δ = solubility parameter
$\bar{\delta}$ = volume average solubility parameter for the liquid solution $= \sum_{j=i}^{n} x_{vj}\delta_j$
ν = fugacity coefficient of pure liquid, for component $i \equiv f^L{}_i/P$
ϕ = fugacity coefficient in vapor phase, for component $i \equiv f_i/Py_i$
ω = Watson's expansion factor

Superscripts

L = pure liquid

Subscript

c = critical property
i = component i
j = component j
r = reduced property

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