method is limited by the number of available UNIFAC parameters, although experimental determination of new parameters is proceeding rapidly. As more parameters become available, a more extensive evaluation of this method should be accomplished.

NOTATION

A = reactant
B = reactant
k = reaction rate constant
M = activated complex
γ = activity coefficient

Subscripts

$A1$ = cyclohexene reactant
$A2$ = acetone reactant
i = arbitrary solvent
ϕ = benzene solvent
o = ideal solution
1 = cyclohexene hydrogenation reaction
2 = acetone hydrogenation reaction

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Correlation of Hydrogen Solubilities in Nonpolar Solvents Based on Scaled-Particle Theory

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Recent developments in heavy fossil-energy technology have renewed interest in hydrogen-heavy hydrocarbon vapor-liquid equilibria, especially at higher temperatures. In this work we present a correlation for Henry's constants for hydrogen in typical hydrocarbons and nonpolar solvents in the temperature range 248-700°K.

HENRY'S CONSTANT

For hydrogen (2) dissolved in a solvent (1), Henry's constant H is defined by:

$$H \equiv \lim_{x_2 \to 0} f_2/x_2 \tag{1}$$

where x is the liquid-phase mole-fraction and f is the fugacity given by:

$$f_2 = \phi_2 y_2 P \tag{2}$$

where P is the total pressure and y is the vapor-phase mole fraction. The vapor-phase fugacity coefficient ϕ can be calculated from an equation of state (Prausnitz, 1969).

The well-known K factor is related to Henry's constant by:

$$K \equiv y_2/x_2 = \frac{\gamma_2^* H}{\phi_2 P} \tag{3}$$

where γ_2^* is the (unsymmetric) liquid-phase activity coefficient. Since the solubility x_2 is normally small and since hydrogen's gas-phase properties are normally well approximated by those of an ideal gas, the ratio γ_2^*/ϕ_2 is close to unity even at moderately high pressures, provided only that the temperature of the system is well below the solvent's critical.

Figure 1 shows experimental Henry's constants for hydrogen in 14 solvents in the region 248-700°K. Note the scale at the right which refers to carbon disulfide and benzene. For hydrogen in this temperature range, Henry's constants uniformly fall with rising temperature. Over the temperature range indicated, Henry's constants vary by one order of magnitude, depending on temperature and solvent.

SCALED-PARTICLE THEORY

To correlate H, we use the scaled-particle theory of Reiss et al. (1959, 1960) as discussed by Pierrotti (1963, 1976). The partial Gibbs energy of dissolving a solute in a liquid consists of two parts: first, the work needed to create a cavity in the solvent to place a solute molecule and second, the energy of interaction between the dissolved solute and the surrounding solvent. (The entropy of interaction is neglected.)

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TABLE 1. SCALED-PARTICLE-THEORY PARAMETERS

Solvent	$100\sigma_1$, nm	ϵ_1/k, °K	$10^9\sigma_1\left(\frac{P_c}{RT_c}\right)^{1/3}$	ϵ_1/RT_c
n-Heptane	62.3	563	5.28	1.04
Carbon Tetrachloride	53.8	528	5.35	0.95
Benzene	52.3	507	5.31	0.90
n-Octane	65.1	594	5.26	1.04
Toluene	56.3	585	5.30	0.99
Methylcyclohexane	59.8	559	5.38	0.98
Carbon Disulfide	44.6	509	5.35	0.92
n-Hexane	58.4	511	5.22	1.01
Isooctane	66.0	549	5.47	1.01
Bicyclohexyl	71.0	768	5.32	1.05
Tetralin	63.0	728	5.20	1.02
1-Methylnaphthalene	64.0	779	5.10	1.09
Diphenylmethane	68.8	825	5.26	1.07
n-Decane	72.0	679	5.34	1.10

Solute	$100\sigma_1$, nm	ϵ_2/k, °K
Hydrogen	28.7	29.2

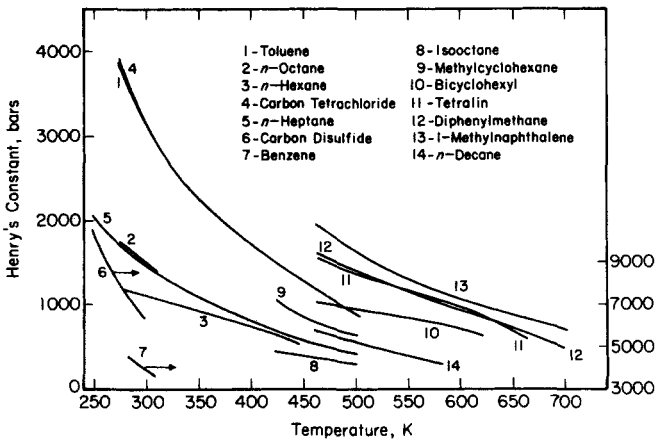

Figure 1. Henry's constants for hydrogen.

$$\frac{\Delta\bar{g}_2}{RT} = \bar{g}_c/RT + \bar{g}_i/RT = \ln Hv_1/RT \quad (4)$$

where subscript c refers to cavity-formation and subscript i refers to interaction; v_1 is the molar liquid volume of solvent. The final term in Equation (4), Hv_1/RT, is a dimensionless quantity.

The scaled-particle theory of fluids (Pierotti, 1963) gives

$$\bar{g}_c = K_0 + K_1\sigma_{12} + K_2\sigma_{12}^2 + K_3\sigma_{12}^3 \quad (5)$$

where

$$K_0 = RT\left[-\ln(1-\xi) + \frac{9}{2}\xi^2/(1-\xi)^2\right] - N\pi P\sigma_1^3/6 \quad (6)$$

$$K_1 = -(RT/\sigma_1)[6\xi/(1-\xi) + 18\xi^2/(1-\xi)^2] + N\pi P\sigma_1^2 \quad (7)$$

$$K_2 = (RT/\sigma_1^2)[12\xi/(1-\xi) + 18\xi^2/(1-\xi)^2] - 2N\pi P\sigma_1 \quad (8)$$

$$K_3 = (4/3)\pi P \quad (9)$$

where $\xi = \pi\sigma_1^3\rho_1/6$, R is the gas constant and N is Avogadro's number.

The density ρ_1 is the number density of the solvent (molecules per unit volume); molecular diameters of solvent and solute are designated by σ_1 and σ_2, respectively. (The number density is related to the molar volume by $\rho_1 = N/v_1$.) We set σ_{12} equal to $(1/2)(\sigma_1 + \sigma_2)$.

The energy of interaction for nonpolar systems is given by:

$$\bar{g}_i \approx \bar{E}_i = N\int_0^\infty \epsilon_i(r)\, 4\pi r^2\rho_1 g(\sigma_2, r)\, dr \quad (10)$$

where $\epsilon_i(r)$ is the energy of interaction between one solute molecule and one solvent molecule separated by distance r and $g(\sigma_2, r)$, the radial distribution function, is a measure of the probability of finding a solvent molecular center at the distance r from the center of a solute molecule. As shown by Wilhelm and Battino (1971) and by Pierotti, when $\epsilon_i(r)$ is given by the Lennard-Jones potential, and when we use the approximation

$$g = 0 \text{ for } r < \sigma_2$$
$$g = 1 \text{ for } r \geq \sigma_2,$$

then,

$$\frac{\bar{g}_i}{RT} = -\left(\frac{32}{9}\right)\left(\frac{\pi\rho_1}{kT}\right)\epsilon_{12}\sigma_{12}^3 \quad (11)$$

where ϵ_{12} is a characteristic solute-solvent interaction parameter and where k is Boltzmann's constant.

DATA REDUCTION

To reduce hydrogen-solubility data we require that such data be given in the form of Henry's constants. In many cases, Henry's constants are given directly by the authors reporting the data. In some cases it was necessary to calculate Henry's constants from the data using Eq. 1.

To fit the data to scaled-particle theory, it is necessary to know the molar liquid volume of the solvent which depends on temperature. Molar liquid volumes at lower temperatures were calculated using the Rackett equation as discussed elsewhere (Prausnitz et al., 1980); for higher temperatures, the correlation of Hankinson and Thomson (1979) was used.

To reduce solubility data, we require three molecular parameters: two unicomponent parameters, σ_1, σ_2 and one binary parameter ϵ_{12}. Calculated Henry's constants are very sensitive to σ_{12} but relatively insensitive to ϵ_{12}.

To correlate data for solubilities in 14 solvents over a wide temperature range, it was necessary to assign a temperature dependence to the parameter σ_{12}. This temperature dependence is most conveniently expressed in the form

$$\sigma_{12} = (\sigma_1 + \sigma_2)/2 \cdot \mathcal{F}(T) \quad (12)$$

For parameter σ_2 we use 0.287 nm as reported by Wilhelm and Battino (1971). For σ_1, we use values determined from the

solubility data. From data reduction for the region 248-700°K, we obtain the generalized correlation:

$$\mathcal{F}(T) = 0.96 + 0.8536815 \times 10^{-3}\tau + 0.1419978 \times 10^{-5}\tau^2 + 0.9024344 \times 10^{-9}\tau^3 \quad (13)$$

where $\tau = (T - 248.15)$, with T in degrees Kelvin. While Eq. 13 is obtained from data below 700°K, it gives reasonable results when extrapolated to 800°K.

For ϵ_{12}, we use the convenient expression:

$$\epsilon_{12} = (\epsilon_1\epsilon_2)^{\frac{1}{2}} \quad (14)$$

with $\epsilon_2/k = 29.2$°K as given by Wilhelm and Battino (1971). Calculated Henry's constants are not sensitive to the choice of ϵ_{12}.

TABLE 2. HENRY'S CONSTANTS FOR HYDROGEN; MOLAR VOLUMES AND VAPOR PRESSURES OF SOLVENTS

Toluene

T, °K	v, 10^6m^3/g · mol	P, bar	H, bar calc	H, bar obs
258.15	102.49	1.01[a]	4339	4383[a]
298.15	106.72	1.01[a]	3352	3199[a]
461.7	133.85	6.45[j]	1235	1189[c]
502.15	(146.28)	12.52[j]	957	848[c]

Methylcyclohexane

T, °K	v, 10^6m^3/g · mol	P, bar[j]	H, bar calc	H, bar obs[b]
424.15	152.70	(5.64)	1066	1037
471.65	167.90	(13.20)	817	723
498.65	180.23	(9.67)	663	635

Carbon Disulfide

T, °K	v, 10^6m^3/g · mol	P, bar[a]	H, bar calc	H, bar obs[a]
248.15	55.61	1.01	9441	10498
273.15	57.08	1.01	8064	8058
298.15	58.68	1.01	6854	6377

n-Hexane

T, °K	v, 10^6m^3/g · mol	P, bar[j]	H, bar calc	H, bar obs[h]
310.93	133.49	0.34	1142	1051
377.59	150.10	2.76	783	810
444.26	178.50	11.05	523	529

n-Heptane

T, °K	v, 10^6m^3/g · mol	P, bar	H, bar calc	H, bar obs
248.15	138.97	1.01[a]	1970	2032[a]
424.15	181.71	3.80[j]	663	679[b]
498.85	230.48	14.76[j]	393	418[b]

Carbon Tetrachloride

T, °K	v, 10^6m^3/g · mol	P, bar[a]	H, bar calc	H, bar obs[a]
273.15	94.43	1.01	3796	3899
298.15	97.11	1.01	3237	3173
308.15	98.26	1.01	3036	2939

Benzene

T, °K	v, 10^6m^3/g · mol	P, bar[a]	H, bar calc	H, bar obs[a]
283.15	87.98	1.01	4408	4497
298.15	89.47	1.01	3989	3929
308.15	90.52	1.01	3733	3611

n-Octane

T, °K	v, 10^6m^3/g · mol	P, bar[a]	H, bar calc	H, bar obs[a]
273.15	157.70	1.01	1758	1726
298.15	162.20	1.01	1502	1483
308.15	164.12	1.01	1412	1399

Isooctane

T, °K	v, 10^6m^3/g · mol	P, bar[j]	H, bar calc	H, bar obs[b]
423.95	202.67	3.62	701	673
471.65	228.68	8.77	499	471
499.35	254.06	13.64	395	404

Bicyclohexyl

T, °K	v, 10^6m^3/g · mol	P, bar[i]	H, bar calc	H, bar obs[e]
462.15	(218.55)	0.29	1066	1054
541.85	(241.25)	2.11	757	836
621.75	(276.96)	9.29	536	595

Tetralin

T, °K	v, 10^6m^3/g · mol	P, bar[d]	H, bar calc	H, bar obs[d]
462.75	(160.15)	0.68	1532	1548
541.85	(177.29)	3.54	1080	1188
621.75	(205.53)	11.83	734	860
662.25	(232.06)	19.23	568	589

1-*Methylnaphthalene*

T, °K	v, 10^6m^3/g · mol	P, bar[g]	H, bar calc	H, bar obs[g]
462.15	(160.17)	0.25	1931	1939
541.85	(174.27)	1.70	1386	1332
621.75	(194.47)	6.42	991	994
701.65	(230.98)	17.56	660	683

Diphenylmethane

T, °K	v, 10^6m^3/g · mol	P, bar[f]	H, bar calc	H, bar obs[f]
462.75	(192.64)	0.14	1578	1580
541.85	(210.25)	1.10	1091	1165
621.75	(235.87)	4.79	761	826
701.65	(283.45)	13.50	495	471

n-Decane

T, °K	v, 10^6m^3/g · mol	P, bar[k]	H, bar calc	H, bar obs[k]
462.45	243.90	1.47	690	679
503.35	264.49	3.53	527	537
542.95	293.79	7.22	400	405
583.45	352.41	13.55	277	274

Equations 12 and 13 indicate that σ_{12} rises with temperature, suggesting that as the solvent expands, the high kinetic energy of the solute "digs" a larger hole for itself in the solvent.

RESULTS

Table 1 presents parameters σ_1 and ϵ_1 for fourteen solvents. Nearly constant values of σ_1 and ϵ_1 are obtained when reduced by critical properties, as shown in the last two columns of Table 1.

Table 2 gives calculated and observed Henry's constants for hydrogen in fourteen solvents. Also shown are the molar liquid volume and the vapor pressure of the solvent. (When $x_2 = 0$, the total pressure of the system is the vapor pressure of the solvent; this pressure is needed in Eq. 5.) When these quantities are uncertain, they are placed in parentheses. Data sources are indicated at the end of Table 2.

In general, calculated and observed Henry's constants agree to within ±15% and often much better. Since large Henry's constants (small solubilities) are difficult to measure accurately, the deviations shown are, in most cases, within the experimental error. Deviations tend to be higher at high temperatures when the system temperature approaches the critical of the solvent.

The correlation presented here is most useful when solubility data are available at only a few temperatures (or possibly, only one temperature) and it is desired to predict the solubility at higher temperatures. In that case, the data (or datum) should be used to find the important parameter σ_1. To do so, we require a value for ϵ_1 but the results are not sensitive to that value. Parameter ϵ_1 can be estimated from the critical temperature of the solvent using results shown in the final column of Table 1.

If no solubility data in a given solvent are available, it is possible to estimate solubilities in a nonpolar solvent using critical data, as indicated in the last two columns of Table 1. To illustrate, we estimate the solubility of hydrogen in meta-xylene for the region 462-582°K. Using the reduced σ_1 and reduced ϵ_1 values for benzene and toluene, we estimate that for meta-xylene:

$$10^9\sigma_1(P_c/RT_c)^{1/3} = 5.29$$

$$\epsilon_1/kT_c = 1.08$$

For meta-xylene, the critical pressure is 35.41 bars and the critical temperature is 617.05°K. We obtain

$$\sigma_1 = 0.599 \text{ nm and } \epsilon_1/k = 663°\text{K}$$

Using these parameters, Henry's constants were calculated as shown in Table 3. Also shown are experimental results; these were *not* used in preparing the correlation. Calculated and experimental Henry's constants are in fair agreement.

Table 3. Predicted and Observed Henry's Constants for Hydrogen in Meta-Xylene

T, °K	v, 10^6m^3/g · mol	P, bar[l]	H, bar predicted	H, bar observed[l]
462.4	152.64	3.20	1096	1205
502.3	164.56	6.96	876	902
542.6	182.03	13.21	682	608
582.1	213.97	22.69	489	365

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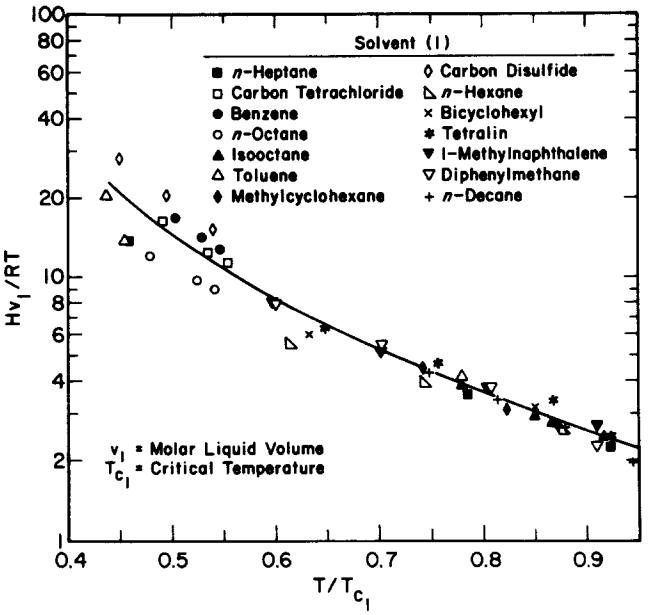

Figure 2. Reduced Henry's constants for hydrogen.

For a fixed gas dissolved in nonpolar solvents, the scaled-particle theory suggests a simplification based on corresponding-states arguments. We assume that at modest pressures

$$v_1/\sigma_1^3 = \text{function of } T/T_{c_1}$$

and further, that

$$\epsilon_{12}/kT_{c_1} = a \text{ constant.}$$

At modest pressures, the final terms in Eqs. 6 to 9 contribute little to $\bar{g}_c$. Therefore, scaled-particle theory suggests that:

$$\ln \frac{Hv_1}{RT} = \text{function of } T/T_{c_1}.$$

To test this suggestion, Figure 2 shows a semilogarithmic plot of reduced Henry's constant Hv_1/RT versus reduced temperature T/T_{c_1} for hydrogen in 14 nonpolar solvents. Considering the simplicity of the correlation method, the data correlate surprisingly well.

ACKNOWLEDGMENT

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NOTATION

$\bar{E}_i$ = partial molar energy

f = fugacity
$\bar{g}$ = partial molar Gibbs energy
g = radial distribution function
H = Henry's constant
k = Boltzmann's constant
K = y_2/x_2
K_0, K_1, K_2, K_3 = functions given by Eqs. 5-9
P = total pressure
P_c = critical pressure
r = intermolecular distance
R = gas constant
T = absolute temperature
T_c = critical temperature
x = liquid-phase mole fraction
y = vapor-phase mole fraction
v = molar volume
ϵ = potential energy parameter
γ^* = liquid-phase activity coefficient
ϕ = vapor-phase fugacity coefficient
σ = molecular diameter
ξ = reduced density
ρ = density (molecules per unit volume)

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Simultaneous Reactions of CO, NO and O_2 in a Tubular Reactor

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INTRODUCTION

Strict federal regulations on automotive exhaust emissions make it necessary to remove carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxides (NO_x) by using so-called three-way catalysts. In automotive exhausts, CO and HC are reducing species, while NO_x and O_2 are oxidizing species. A desired characteristic of a three-way catalyst is that it preferentially favors reactions of the reducing species (i.e., CO and HC) with NO_x rather than with O_2. The actual number of reacting species and reactions possible in automotive three-way catalysis is very large; however, some basic factors involved in catalyst design can be understood by considering only the following two reactions:

$$2CO + O_2 \xrightarrow{k_1} 2CO_2 \tag{1}$$

$$2CO + 2NO \xrightarrow{k_2} 2CO_2 + N_2 \tag{2}$$

For the CO-NO-O_2 system, using an iridium catalyst, Tauster and Murrell (1976) found that under net oxidizing conditions, conversion of NO becomes independent of catalyst loading, and pointed out that this metal concentration-invariant behavior should apply to any catalyst provided that temperature or contact time were high enough for essentially complete CO conversion. Schlatter and Taylor (1977) also observed similar behavior using a rhodium catalyst. The former authors have also attempted to explain this behavior using approximate and numerical approaches (Tauster and Murrell, 1978).

In a recent paper, Hegedus et al. (1979) considered these reactions in an integral plug-flow reactor, under both rich (CO in excess) and lean (NO_x and O_2 in excess) conditions, when the catalyst is equally selective for both reactions ($k = 1$). In this note, we consider the case of *arbitrary* selectivity, and specifically cases where the catalyst is more selective for the second reaction—as with rhodium and iridium catalysts. For example, Tauster and Murrell (1976) found partition factors of 2·8 and 4·5 in favor of the second reaction for iridium catalysts. We also report analytic solutions for values of $k = 2$ and 3.

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BASIC EQUATIONS

Consider an isothermal plug-flow reactor, with simple bimolecular reaction kinetics and no diffusional limitations. To conserve space, the nomenclature of Hegedus et al. (1979) is used. In their notation, then, the relevant conservation equations in dimensionless form are:

$$\frac{dx}{dt} = kR(1 - x)(1 - y) + (S - R)(1 - x)w \tag{3a}$$

$$\frac{dy}{dt} = k(1 - x)(1 - y) \tag{3b}$$

$$\frac{dw}{dt} = -(1 - x)w \tag{3c}$$

with initial conditions at $t = 0$:

$$x = 0, \quad y = 0, \quad w = 1 \tag{4}$$

The various symbols are defined in the Notation. It is important, however, to note here that x and y are CO and NO conversions respectively, and w is the dimensionless O_2 concentration along the reactor length, t. Also by definition,