

# A Generalized Correlation for Henry's Constants in Nonpolar Binary Systems

MASAHIRO YORIZANE

and

YOSHIMORI MIYANO

Department of Chemical Engineering  
Hiroshima University  
Hiroshima, Japan

A generalized correlation for Henry's constant is developed from a three-parameter corresponding states theory for fluid mixtures. Two characteristic parameters are required in each binary system. These parameters are determined for thirty-eight nonpolar binary systems containing quantum gases for solutes. The overall average deviation for calculated Henry's constants is relatively small, about  $\pm 2.5\%$ .

## SCOPE

For the design of industrial equipment for separation processes, Henry's constants are important for phase equilibrium calculations. Thermodynamic properties of a dilute liquid solution can be determined from Henry's law, and the prediction of Henry's constants provides a test of solution theory.

Recently, a number of investigators have given much attention to the calculation of Henry's constants. Preston and Prausnitz (1971) have proposed one of the most widely applicable methods based on a statistical mechanical derivation. Gunn et al. (1974) have developed a Henry's constant correlation from macroscopic corresponding states theory for mixtures. The three-parameter method of Gunn et al. is applied successfully to nonpolar binary systems, with the exception of those containing quantum gases.

A Henry's constant correlation in nonpolar binary systems which include the quantum gases is developed in this work from corresponding states theory for fluid mixtures.

The authors (1968, 1972) reported previously the prediction of high-pressure, vapor-liquid equilibria from a corresponding states theory using the Hirschfelder-Buehler-McGee-Sutton (1958) equation of state.

The proposed method is applied to the correlation for Henry's constants for nonpolar binary systems containing quantum gases. This method requires two characteristic parameters which are correlated for nonpolar binary mixtures involving paraffins, ethylene, benzene, nitrogen, argon, carbon dioxide, carbon monoxide, hydrogen sulfide, hydrogen, and helium.

## CONCLUSIONS AND SIGNIFICANCE

Henry's constants calculated from the proposed method, which requires two characteristic parameters, agree well with the experimental data. In particular for systems containing quantum solutes, this method successfully predicts observed Henry's constants. The overall average deviations for calculated Henry's constants are relatively small, about  $\pm 1.6\%$  (nonquantum solutes) and  $\pm 3.6\%$  (quantum solutes). The procedure of Gunn et al. predicts observed Henry's constants with  $\pm 2.0\%$  deviation (nonquantum solutes), and that of Preston and Prausnitz predicts those with  $\pm 6.9\%$  deviation (nonquantum solutes) and  $\pm 10.6\%$  deviation (quantum solutes).

Frequently, experimental data are lacking for a system of interest. Therefore, the correlations for the characteristic temperature and volume are very useful. For systems for

which experimental data are available at only one temperature, the characteristic temperatures  $T_{C12}$  are determined from experimental data using the correlated values of the characteristic volumes  $V_{C12}$ . In these cases, the average overall deviations are  $\pm 4.8\%$  (nonquantum solutes) and  $\pm 7.2\%$  (quantum solutes). For systems for which experimental data are completely lacking, Henry's constants are calculated using the correlated values of  $T_{C12}$  and  $V_{C12}$ , without using any experimental data. In these cases, the deviations are  $\pm 10\%$  (nonquantum solutes) and  $\pm 20\%$  (quantum solutes).

The characteristic temperature and volume determined from Henry's constant may improve the prediction of vapor-liquid equilibria at low solute concentrations.

Recently, much attention has been given to the calculation of Henry's constant. Neff and McQuarrie (1973) have

---

Correspondence concerning this paper should be addressed to Masahiro YORIZANE, 3 chome Sendamachi, Faculty of Engineering Hiroshima University, Hiroshima, Japan.

0001-1541-78-9956-0181-\$0085 © The American Institute of Chemical Engineers, 1978.

applied a perturbation theory for mixtures to the problem of the solubility of gases in liquids. Tiepel and Gubbins (1972) have applied a simplified form of perturbation theory to the prediction of gas solubility in mixed solvent systems. Uno et al. (1975) have applied the method of Neff and McQuarrie based on perturbation theory to the

calculation of Henry's constants of normal fluids. The statistical mechanical method is theoretical, and the physical significance of parameters in the calculation is clear. However, the calculation procedure is time consuming. Nakahara and Hirata (1969) have applied a solution model to the prediction of Henry's constants in hydrogen-hydrocarbon mixtures. Sagara et al. (1975) have developed a regular solution theory for predicting Henry's constants for hydrogen, nitrogen and paraffins in hydrocarbon solvents. Although the method of Sagara et al. gives good results for hydrocarbon systems, the deviation is large for the calculation of Henry's constants containing hydrogen or nitrogen. Preston and Prausnitz (1971) have proposed one of the most widely applicable methods using statistical mechanical procedure. Gunn et al. (1974) have developed a Henry's constant correlation from a macroscopic

corresponding states theory for mixtures. In their work, the thermodynamic properties are calculated from the following relationship:

$$\Psi = \Psi^{(0)} \left( \frac{T}{T_c}, \frac{P}{P_c} \right) + \omega \Psi^{(1)} \left( \frac{T}{T_c}, \frac{P}{P_c} \right) \quad (1)$$

Equation (1) is a three-parameter corresponding states correlation, where  $\Psi^{(0)}$  and  $\Psi^{(1)}$  are generalized functions which have been tabulated by Pitzer et al. (1955, 1958). Recently, the correlation has been extended to low reduced temperatures down to  $Tr = 0.25$  by Carruth and Kobayashi (1972). Although the procedure of Gunn et al. is more accurate than that of Preston and Prausnitz, it has not been tested for systems including quantum gases.

In this paper, a three-parameter corresponding states theory with two characteristic parameters for each binary

TABLE 1. CRITICAL CONSTANTS FOR SOLUTIONS

Solute	Solvent	Temp. range, °K	$T_{C12},^{***}$ °K	$V_{C12},^{***}$ cm <sup>3</sup> /mole	Average % deviation††		
					Equation (10)	P.P.*	G.Y.W.†
Nitrogen	Methane	126-172	147.3	57.1	1.3	3	1.6
Nitrogen	Ethane	122-278	186.8	107.2	2.2	49	1.9
Nitrogen	n-butane	311-378	207.1	152.1	2.3	4	1.0
Methane	Propane	226-344	263.0	131.0	3.3	6	N.D.**
Methane	n-butane	311-378	275.0	142.4	3.1	2	6.9
Methane	n-pentane	311-411	285.4	153.9	2.4	2	2.0
Methane	n-hexane	311-411	295.0	166.3	3.6	4	3.5
Methane	n-heptane	200-511	302.0	176.1	2.2	23	0.8
Methane	Carbon-dioxide	209-272	237.9	73.3	0.4	1	1.6
Methane	Hydrogen-sulfide	211-344	262.5	51.1	2.1	5	N.D.
Ethane	Propane	311-355	343.7	153.2	0.9	7	2.4
Ethane	n-butane	311-394	359.8	181.4	1.2	4	1.3
Ethane	n-pentane	311-444	380.5	223.9	3.4	7	0.9
Ethane	n-heptane	311-478	402.3	236.2	4.4	6	0.6
Ethane	Benzene	323-473	414.4	200.3	2.2	7	N.D.
Ethane	Hydrogen-sulfide	289-344	323.3	113.8	1.1	5	0.9
Propane	n-butane	344-411	402.5	176.6	0.8	1	1.2
Propane	n-pentane	344-411	414.5	219.2	0.0	1	2.3
Propane	Benzene	378-478	450.2	244.2	1.1	3	N.D.
Butane	n-heptane	422-505	481.2	342.0	0.3	2	2.1
Carbon-dioxide	Propane	294-355	290.1	146.8	1.7	2	2.8
Carbon-dioxide	n-butane	311-378	309.8	185.2	0.8	1	2.8
Carbon-dioxide	Hydrogen-sulfide	293-353	316.1	85.7	0.7	3	N.D.
Hydrogen-sulfide	n-butane	353-394	343.4	254.9	0.9	1	N.D.
Hydrogen	Methane	90-144	107.2	88.1	3.0	19	N.D.
Hydrogen	Ethane	103-255	138.8	97.5	2.9	14	N.D.
Hydrogen	Propane	200-344	159.4	116.2	6.2	10	N.D.
Hydrogen	n-butane	144-297	182.6	134.6	3.5	21	N.D.
Hydrogen	n-hexane	278-444	208.0	161.4	9.0	6	N.D.
Hydrogen	Ethylene	158-255	132.0	75.9	6.9	9	N.D.
Hydrogen	Nitrogen	79-109	70.6	65.9	1.4	6	N.D.
Hydrogen	Argon	87-120	84.5	60.9	1.3	N.D.	N.D.
Hydrogen	Carbon-monoxide	68-88	88.4	97.6	1.8	N.D.	N.D.
Helium	Methane	95-140	58.1	77.0	2.8	1	N.D.
Helium	Ethane	170-260	93.5	100.7	2.6	11	N.D.
Helium	Propane	173-348	101.2	112.4	5.5	12	N.D.
Helium	Argon	86-108	47.5	59.6	0.3	8	N.D.
Helium	Nitrogen	65-112	30.6	55.7	2.1	11	N.D.

\* Preston and Prausnitz (1971).

† Gunn et al. (1974).

\*\* N.D. = No data.

$$\dagger\dagger \text{ Average \% deviation} = \sqrt{\frac{\sum \left( \frac{H_{\text{calcd}} - H_{\text{obsd}}}{H_{\text{obsd}}} \right)^2}{\text{No. of points}}} \times 100.$$

\*\*\*  $T_{C12}$  and  $V_{C12}$  for quantum solutes are rewritten as  $T_{C^{e12}}$  and  $V_{C^{e12}}$ .

system is used for correlating Henry's constants in nonpolar binary systems, some of which include quantum gases.

## THEORY

The solubility of a gas in liquid is often proportional to its partial pressure in the gas phase, provided the partial pressure is not large. This observation is known as Henry's law which is always valid at the limiting condition. For component 2 in a binary mixture, Henry's law may be written as

$$H_{2,1}^{(P_1^s)} = \lim_{x_2 \rightarrow 0} \frac{\bar{f}_2}{X_2} \quad (2)$$

Henry's constant is not a function of composition but depends on temperature and, to a lesser degree, on pressure. The relationship between Henry's constant  $H_{2,1}^{(0)}$  at zero pressure and Henry's constant  $H_{2,1}^{(P_1^s)}$  at the saturation (vapor) pressure  $P_1^s$  of the solvent is written as follows (Fraunhofer and Chueh, 1968):

$$H_{2,1}^{(P_1^s)} = H_{2,1}^{(0)} \exp \int_0^{P_1^s} \frac{\bar{V}_2^\infty}{RT} dP \quad (3)$$

The experimental data used in this work are the values at zero pressure. Therefore, Henry's constant at zero pressure is reduced to that at the saturation pressure with Equation (3).

As indicated by Equation (2), Henry's constant is related to the fugacity coefficient at infinite dilution. According to a three-parameter corresponding states theory, the fugacity coefficient of component  $i$  in the mixture can be written as follows (Gamson and Watson, 1944):

$$\ln \frac{\bar{f}_i}{x_i} = \ln f_m - \frac{n}{Tc'} \left( \frac{\partial Tc'}{\partial n_i} \right) \left( \frac{H^o - H}{RT} \right)_m - \frac{n}{Pc'} \left( \frac{\partial Pc'}{\partial n_i} \right) (Z - 1)_m + n \left( \frac{\partial Zc'}{\partial n_i} \right) \left( \frac{\partial \ln(f_m/P)}{\partial Zc'} \right) \quad (4)$$

An expression for Henry's constant is obtained from Equations (2) and (4). For component 2 in the binary system, it is written as

$$\ln H_{2,1}^{(P_1^s)} = \ln f_1^{(P_1^s)} - \lim_{x_2 \rightarrow 0} \left[ \frac{n}{Tc'} \left( \frac{\partial Tc'}{\partial n_2} \right) \right] \left( \frac{H^o - H}{RT} \right)_1 - \lim_{x_2 \rightarrow 0} \left[ \frac{n}{Pc'} \left( \frac{\partial Pc'}{\partial n_2} \right) \right] (Z - 1)_1^{(P_1^s)} + \lim_{x_2 \rightarrow 0} \left[ n \left( \frac{\partial Zc'}{\partial n_2} \right) \left( \frac{\partial \ln(f_m/P)}{\partial Zc'} \right) \right] \quad (5)$$

Mixture properties in this equation reduce to those of the pure solvent as  $x_2$  approaching zero. Here, expressions for pseudocritical constants are necessary, and van der Waals' one-fluid model is used in this work. These equations are listed below for a binary mixture:

$$Vc' = X_1^2 Vc_1 + 2X_1 X_2 Vc_{12} + X_2^2 Vc_2 \quad (6)$$

$$Tc' = \frac{x_1^2 Tc_1 Vc_1 + 2X_1 X_2 Tc_{12} Vc_{12} + X_2^2 Tc_2 Vc_2}{Vc'} \quad (7)$$

The critical compressibility coefficient is

$$Zc' = X_1 Zc_1 + X_2 Zc_2 \quad (8)$$

The critical pressure is obtained from

$$Pc' = \frac{Zc' RTc'}{Vc'} \quad (9)$$

A similar expression for pseudocritical constants has been derived by Mansoori and Leland (1972). Substituting Equation (6) through (9) into Equation (5), we obtain the expression for Henry's constant:

$$\ln H_{2,1}^{(P_1^s)} = \ln f_1^{(P_1^s)} - 2 \left( \frac{Tc_{12} Vc_{12} - Tc_1 Vc_{12}}{Tc_1 Vc_1} \right) \left( \frac{H^o - H}{RT} \right)_1^{(P_1^s)}$$

TABLE 2. PHYSICAL PROPERTIES OF PURE COMPOUND

Compound	$T_c, ^\circ K$	$P_c, \text{atm}$	$Z_c$	$\omega$	$\alpha$	$c$	$d$
Methane*	190.7	45.8	0.290	0.013	5.86	1.79446††	0.65061††
Ethane*	305.4	48.2	0.285	0.105	6.28	1.82885††	0.73069††
Propane*	369.9	42.0	0.277	0.152	6.54	1.86696††	0.77719††
n-butane*	425.2	37.5	0.274	0.201	6.77	1.946***	0.757***
n-pentane*	469.5	33.3	0.269	0.252	7.03	1.95881††	0.76901††
n-hexane*	507.3	29.9	0.264	0.290	7.27	1.99124††	0.77083††
n-heptane*	540.3	27.0	0.259	0.352	7.27	2.02994††	0.81240††
Ethylene*	283.1	50.5	0.270	(0.089)**	6.18	1.81615††	0.76346††
Benzene*	562.1	48.6	0.274	0.215	6.83	1.89319††	0.82341††
Hydrogen†	43.6	20.2	0.291	0	4.74	—	—
Helium†	10.5	6.67	0.291	0	4.74	—	—
Nitrogen*	126.2	33.5	0.291	0.040	5.98	1.78697††	0.72228††
Argon*	151.0	48.0	0.290	-0.002	5.76	1.72966††	0.80250††
Carbon-monoxide*	133.0	34.5	0.294	0.041	6.04	1.74587††	0.82584††
Carbon-dioxide*	304.2	72.9	0.274	(0.225)**	6.92	1.86488††	0.95331††
Hydrogen-sulfide*	373.6	88.9	0.268	0.100	6.25	1.7462***	1.2117***

\* Reid and Sherwood (1966).

† Gunn et al. (1966).

\*\* Lu et al. (1973).

†† Lu, Ruether, et al. (1973).

\*\*\* Masaki (1974).

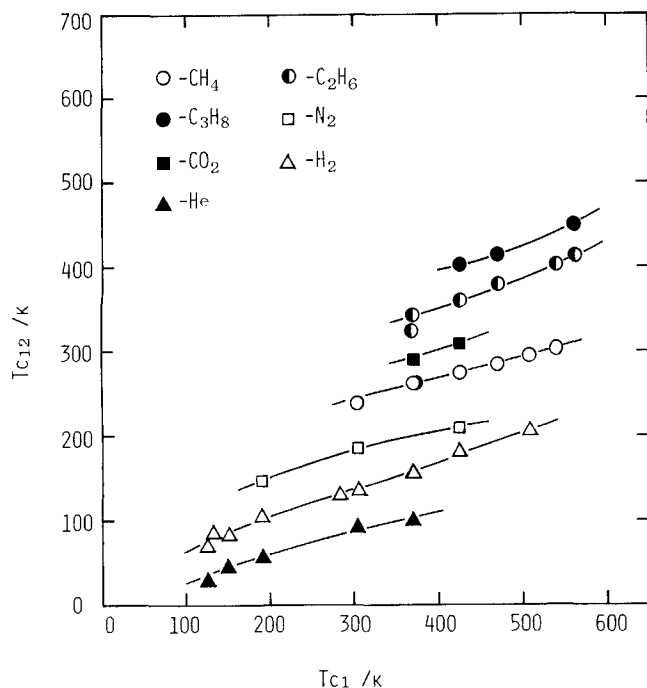


Fig. 1. Characteristic critical temperatures for solutions.

$$-2 \left( \frac{T_{c12}V_{c12} - T_{c1}V_{c12}}{T_{c1}V_{c1}} - \frac{V_{c12} - V_{c1}}{V_{c1}} + \frac{Z_{c2} - Z_{c1}}{2Z_{c1}} \right) (Z - 1)^{(P_1)} + (Z_{c2} - Z_{c1}) \lim_{x_2 \rightarrow 0} \left[ \frac{\partial \ln(f_m/P)}{\partial Z_{c'}} \right] \quad (10)$$

For quantum gases (hydrogen, helium, and neon), slightly temperature-dependent critical constants are used as suggested by Gunn et al. (1966) and Chueh and Prausnitz (1967). When either component 1 or 2 (or both) is a quantum gas, the effective critical constants are given by

$$T_{c12} = \frac{T_{c12}^c}{1 + \frac{C_1}{M_{12}T}} \quad (11)$$

$$V_{c12} = \frac{V_{c12}^c}{1 + \frac{C_3}{M_{12}T}} \quad (12)$$

where

$$\frac{1}{M_{12}} = \frac{1}{2} \left( \frac{1}{M_1} + \frac{1}{M_2} \right) \quad (13)$$

where  $T_{c12}^c$  and  $V_{c12}^c$  are, respectively, the classical critical temperature and the classical critical volume.  $C_1$  and  $C_3$  are constants which were experimentally determined by Gunn et al. (1966).  $C_1 = 21.8^\circ\text{K}$ , and  $C_3 = -9.91^\circ\text{K}$ .

#### DETERMINATION OF $T_{c12}$ AND $V_{c12}$

For each binary system in Table 1, the experimental data of Henry's constants at several temperatures were used to determine best values of the characteristic critical constants  $T_{c12}$  and  $V_{c12}$  by the least-squares method. For experimental data of Henry's constants, the values which were reported by Prausnitz and Chueh (1968), Solen

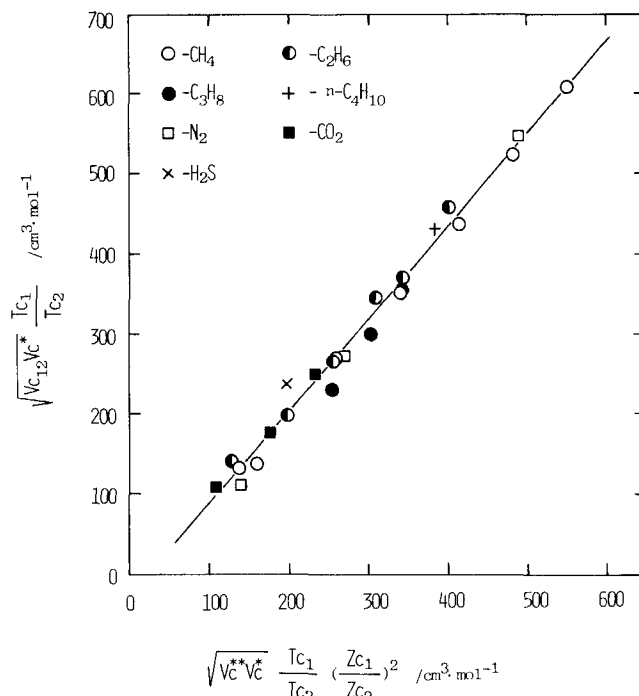


Fig. 2. Characteristic critical volumes for solutions. Solute is a non-quantum gas.

et al. (1970), and Orentlicher and Prausnitz (1964) are used in this study. Each thermodynamic property on the right-hand side of Equation (10) (fugacity, enthalpy departure, compressibility coefficient) was calculated by using the Hirschfelder-Buehler-McGee and Sutton (H.B.M.S.) equation of state. These are written as

Region I  $\rho_r \leq 1$

$$Pr = - (k_0 + k_1 Tr^{-1}) \rho_r^2 + k_2 (-Tr + Tr^{-1}) \rho_r^3 + \frac{\rho_r Tr}{Zc} \cdot \frac{1}{(1 - b\rho_r + b'\rho_r^2)} \quad (14)$$

Region II  $\rho_r \geq 1, Tr \geq 1$

$$Pr = \sum_{j=1}^4 Tr^{j-2} Q_j(\rho_r) \quad (15)$$

Region III  $\rho_r \geq 1, Tr \leq 1$

$$Pr = \sum_{j=1}^4 Tr^{j-2} [Q_j(\rho_r) - Q_j(\rho_{rl})] + Pr^s \quad (16)$$

$$Q_j(\rho_r) = (k_{1j} + k_{2j}\rho_r + k_{3j}\rho_r^2 + k_{4j}\rho_r^3 + k_{5j}\rho_r^4 + k_{6j}\rho_r^5) / \rho_r \quad (17)$$

The expressions of fugacity and enthalpy departure are given in the literature (Hirschfelder et al., 1958).

For the calculation of fugacity and enthalpy, the H.B.M.S. equation of state requires a knowledge of saturated vapor pressure, heat of vaporization, and liquid density. The vapor pressure and heat of vaporization of a pure solvent are calculated from the extension of the correlation of Pitzer et al. (Carruth and Kobayashi, 1972). Guggenheim (1945) and Riedel (1954) proposed the following equation for calculating saturated liquid density:

$$\rho_r = 1 + c(1 - Tr)^{1/3} + d(1 - Tr) \quad (18)$$

This equation was also used in this work for the same purpose. The parameters,  $\alpha$ ,  $c$ , and  $d$  may be treated as

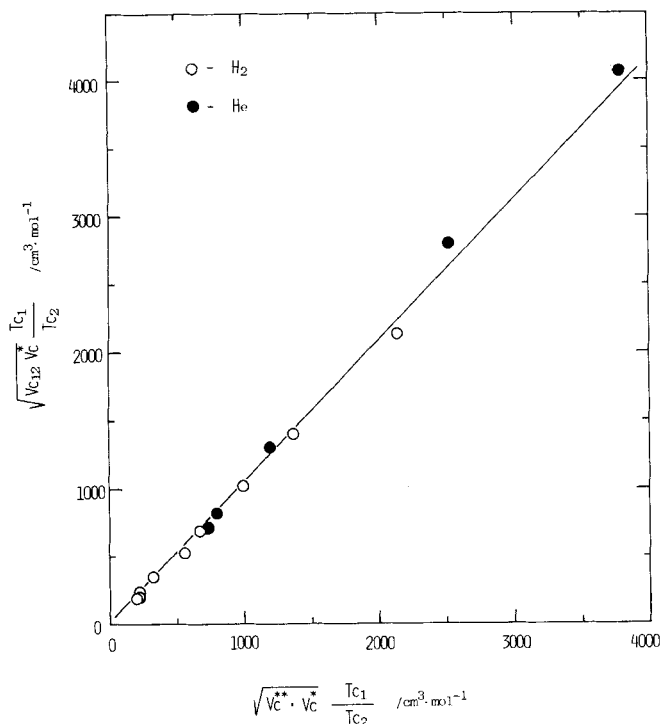


Fig. 3. Characteristic critical volumes for solutions. Solute is a quantum gas.

the functions of a compressibility coefficient, but the functions have not been known. Therefore, the last term on the right-hand side of Equation (10) can not be calculated exactly. Therefore, we used the three-parameter correlation of Gunn et al. (1974) for the calculation of this term. The constants which are required to calculate the thermodynamic properties are shown in Table 2.

## RESULTS

Table 1 summarizes calculated results for a number of the binary mixtures. For comparative purposes, Table 1 also includes calculated results reported by Preston and Prausnitz (1971) and by Gunn et al. (1974). As shown in Table 1, our procedure is more accurate than Preston and Prausnitz's procedure and gives similar accuracy to the procedure of Gunn et al. which uses three interaction parameters, whereas our procedure requires two characteristic parameters. The overall average deviations for calculated Henry's constants from the proposed method, those of Preston and Prausnitz, and that of Gunn et al. are, respectively,  $\pm 1.6\%$  (nonquantum solutes) and  $\pm 3.6\%$  (quantum solutes),  $\pm 6.9\%$  (nonquantum solutes) and  $\pm 10.6\%$  (quantum solutes), and  $\pm 2.0\%$  (nonquantum solutes). These comparisons, of course, are limited to those systems for which data are reported for the other correlations.

For quantum solutes, Equations (11) and (12) are useful. If Henry's constants are calculated using temperature-independent critical constants for quantum solutes, an increase of 50% appears in the average deviation for calculated Henry's constants.

A plot of  $T_{c12}$  vs.  $T_{c1}$  for each solute is shown in Figure 1. The characteristic temperature  $T_{c12}$  for each solute increases with the critical temperature of a solvent. A smooth correlation of  $T_{c12}$  is obtained in this manner.

A plot of  $\sqrt{V_{c12} V_c^*} \frac{T_{c1}}{T_{c2}}$  vs.  $\sqrt{V_c^{**} V_c^*} \frac{T_{c1}}{T_{c2}}$  ( $Z_{c1}/Z_{c2}$ )<sup>2</sup> for all nonpolar solutes which do not contain quantum gases produces a linear relationship as shown in

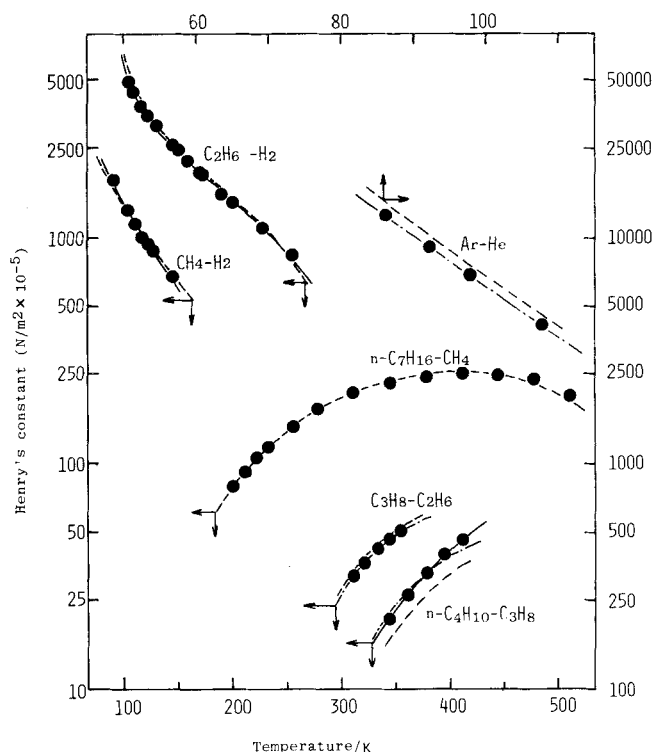


Fig. 4. Comparison of calculated and observed Henry's constants. —, calculated;  $T_{c12}$ ,  $V_{c12}$  from Table 1; ---, calculated;  $T_{c12}$  from Figure 1,  $V_{c12}$  from Equation (19) or (21); - · - ·, calculated;  $V_{c12}$  from Equation (19) or (21);  $T_{c12}$  determined from only one experimental datum with Equation (10) ●; experimental data.

Figure 2. This relationship, determined by the least-squares method, is

$$\sqrt{V_{c12} V_c^*} \frac{T_{c1}}{T_{c2}} = 1.161 \sqrt{V_c^{**} V_c^*} \frac{T_{c1}}{T_{c2}} \left( \frac{Z_{c1}}{Z_{c2}} \right)^2 - 29.2 \quad (19)$$

where

$$V_c^* = \frac{V_{c1} + V_{c2}}{2}, \quad V_c^{**} = \frac{1}{8} (V_{c1}^{1/3} + V_{c2}^{1/3})^3 \quad (20)$$

For quantum gases, a plot of  $\sqrt{V_{c12} V_c^*} \frac{T_{c1}}{T_{c2}}$  vs.  $\sqrt{V_c^{**} V_c^*} \frac{T_{c1}}{T_{c2}}$  is shown in Figure 3. This relationship is

$$\sqrt{V_{c12} V_c^*} \frac{T_{c1}}{T_{c2}} = 1.036 \sqrt{V_c^{**} V_c^*} \frac{T_{c1}}{T_{c2}} + 2.0 \quad (21)$$

As seen in Figures 1, 2, and 3,  $T_{c12}$  and  $V_{c12}$  are correlated successfully.

Typical results for several systems are shown in Figure 4 which compares observed Henry's constants with those calculated using Equation (10). The calculated results for Henry's constants using  $T_{c12}$  and  $V_{c12}$  given in Table 1 are shown by full lines in Figure 4. Frequently, experimental data are completely lacking for a system of interest. Therefore, the correlations shown in Figures 1, 2 and 3 are very useful.

The calculated results using the correlations instead of least-square values for  $T_{c12}$  and  $V_{c12}$  given in Table 1 are shown by dotted lines in Figure 4. The overall average deviations for calculated Henry's constants using the correlations are  $\pm 10\%$  (nonquantum solutes) and  $\pm 20\%$  (quantum solutes).

For a system for which experimental data are available at only one temperature,  $T_{c12}$  is determined from experimental data at only one temperature using  $V_{c12}$  calculated by Equation (19) or (21). These calculated results are shown by one-point dashed lines in Figure 4, and the overall average deviations are  $\pm 4.8\%$  (nonquantum solutes) and  $\pm 7.2\%$  (quantum solutes).

Although the calculated results using the correlations give somewhat larger deviations than those using least-square values for  $T_{c12}$  and  $V_{c12}$  given in Table 1, the temperature dependency of Henry's constant is well expressed.

## CONCLUSIONS

Henry's constants have been correlated from a corresponding states theory and the H.B.M.S. equation of state and can be accurately calculated from Equation (10) using two characteristic parameters,  $T_{c12}$  and  $V_{c12}$ . The characteristic temperature  $T_{c12}$  and the characteristic volume  $V_{c12}$  have been determined for each binary system and have been correlated by simple graphical relationships.

The correlation correctly predicts that Henry's constants increase or decrease with temperature. For the system methane-*n*-heptane, the correlation correctly predicts that a plot of Henry's constants vs. temperature goes through a maximum. For the system ethane-hydrogen, the correlation correctly predicts an S curve.

## NOTATION

- $c, d$  = constants, Equation (18)  
 $C_1, C_3$  = constants, Equations (11) and (12)  
 $f$  = fugacity  
 $H^o - H$  = enthalpy departure  
 $H_{2,1}^{(P,T)}$  = Henry's constant  
 $M$  = molecular weight  
 $n$  = number of moles  
 $P$  = pressure  
 $R$  = gas constant  
 $T$  = temperature  
 $V$  = molar volume  
 $\bar{V}_2^\infty$  = liquid partial molar volume of component 2 at infinite dilution  
 $X$  = mole fraction  
 $Z$  = compressibility coefficient  
 $\alpha$  = Riedel parameter  
 $\rho_r$  = reduced density  
 $\Psi^{(0)}, \Psi^{(1)}$  = function of the reduced temperature and pressure  
 $\omega$  = acentric factor

## Subscripts

- 1 = component 1 (solvent)  
 2 = component 2 (solute)  
 $i, j$  = indicates the individual components in a mixture  
 $c$  = critical property  
 $m$  = mixture property  
 $r$  = reduced property

## Superscripts

- ' = pseudo property  
 $P_1^s$  = property at saturation conditions (vapor pressure of component 1)  
 $c$  = classical value

## LITERATURE CITED

Carruth, G. F., and R. Kobayashi, "Extension to Low Reduced Temperatures of Three-Parameter Corresponding States: Vapor Pressure, Enthalpies and Entropies of Vaporization,

- and Liquid Fugacity Coefficients," *Ind. Eng. Chem. Fundamentals*, **11**, 509 (1972).  
 Chueh, P. L., and J. M. Prausnitz, "Vapor-Liquid Equilibria at High Pressure," *ibid.*, **6**, 492 (1967).  
 Gamson, B. W., and K. M. Watson, "High Pressure Vapor-Liquid Equilibria," *Natl. Petrol. News*, **36**, R623 (1944).  
 Guggenheim, E. A., "The Principle of Corresponding States," *J. Chem. Phys.*, **13**, 253 (1945).  
 Gunn, R. D., P. L. Chueh, and J. M. Prausnitz, "Prediction of Thermodynamic Properties of Dense Gas Mixtures Containing One or More of the Quantum Gases," *AIChE J.*, **12**, 937 (1966).  
 Gunn, R. D., T. Yamada, and D. Whitman, "Corresponding States. III. Henry's Constants for Nonpolar Binary Mixtures," *ibid.*, **20**, 906 (1974).  
 Hirschfelder, J. O., R. J. Buehler, H. A. McGee, and J. R. Sutton, "Generalized Equation of State for Gases and Liquids," *Ind. Eng. Chem.*, **50**, 375 (1958).  
 Lu, B. C. -Y., J. A. Ruether, C. Hsi, and C. -H. Chiu, "Generalized Correlation of Saturated Liquid Densities," *J. Chem. Eng. Data*, **18**, 241 (1973).  
 Lu, B. C.-Y., C. Hsi, S. Chang, and A. Tsang, "Volumetric Properties of Normal Fluids at Low Temperatures: An Extension of Pitzer's Generalized Correlation," *AIChE J.*, **19**, 748 (1973).  
 Mansoori, G. A., and T. W. Leland, Jr., "Statistical Thermodynamics of Mixtures," *Faraday Trans.*, **II**, **68**, 320 (1972).  
 Masaki, S., "Phase Equilibria at High Pressure," M. T. thesis, Hiroshima Univ., Japan (1974).  
 Nakahara, T., and M. Hirata, "The Prediction of Henry's Constants for Hydrogen-Hydrocarbon Systems," *J. Chem. Eng. Japan*, **2**, 137 (1969).  
 Neff, R. O., and D. A. McQuarrie, "A Statistical Mechanical Theory of Solubility," *J. Phys. Chem.*, **77**, 4130 (1973).  
 Orentlicher, M., and J. M. Prausnitz, "Thermodynamics of Hydrogen Solubility in Cryogenic Solvents at High Pressures," *Chem. Eng. Sci.*, **19**, 775 (1964).  
 Pitzer, K. S., D. Z. Lippman, R. F. Curl, Jr., C. M. Huggins, and D. E. Petersen, "The Volumetric and Thermodynamic Properties of Fluids," *J. Am. Chem. Soc.*, **77**, 3427 (1955).  
 Pitzer, K. S., and R. F. Curl, Jr., "Volumetric and Thermodynamic Properties of Fluids-Enthalpy, Free Energy, and Entropy," *Ind. Eng. Chem.*, **50**, 265 (1958).  
 Prausnitz, J. M., and P. L. Chueh, *Computer Calculation for High Pressure Vapor-Liquid Equilibria*, Prentice-Hall, Englewood Cliffs, N.J. (1968).  
 Preston, G. T., and J. M. Prausnitz, "A Generalized Correlation for Henry's Constants in Nonpolar Systems," *Ind. Eng. Chem. Fundamentals*, **10**, 389 (1971).  
 Reid, R. C., and T. K. Sherwood, "The Properties of Gases and Liquids," pp 571-584, McGraw-Hill Book Company, New York (1966).  
 Riedel, L., *Chem. Ind. Tech.*, **26**, 83, 259, 679 (1954).  
 Sagara, H., Y. Arai, and S. Saito, "Calculation of Henry's Constant of Gases in Hydrocarbon Solvent by Regular Solution Theory," *J. Chem. Eng. Japan*, **8**, 93 (1975).  
 Solen, K. A., P. L. Chueh, and J. M. Prausnitz, "Thermodynamics of Helium Solubility in Cryogenic Solvents at High Pressure," *Ind. Eng. Chem., Process Design Develop.*, **9**, 310 (1970).  
 Tiepel, E. W., and K. E. Gubbins, "Theory of Gas Solubility in Mixed Solvent Systems," *Can. J. Chem. Eng.*, **50**, 361 (1972).  
 Uno, K., E. Sarashina, Y. Arai, and S. Saito, "Application of the Perturbation Theory to the Calculation of Henry's Constants for Normal Fluids," *J. Chem. Eng. Japan*, **8**, 201 (1975).  
 Yorzane, M., S. Sadamoto, S. Yoshimura, H. Masuoka, N. Shiki, T. Kimura, and A. Toyama, "Vapor-Liquid Equilibria at Low Temperature," *Kagaku Kogaku*, **32**, 257 (1968).  
 Yorzane, M., S. Yoshimura, H. Masuoka, N. Shiki, T. Kimura, A. Toyama, and I. Funada, "Estimation and Measurement Techniques of Vapor-Liquid Equilibria at Low Temperatures and High Pressures," Paper presented at First Pacific Chemical Engineering Congress, PART III, 140, Kyoto, Japan (Oct., 1972).

Manuscript received March 28, 1977; revision received October 14, and accepted October 27, 1977.