

THE PREDICTION OF HENRY'S CONSTANTS FOR HYDROGEN-HYDROCARBON SYSTEMS*

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The Solution model of hydrogen in hydrocarbons is presented for the calculation of Henry's constant. This model includes the following considerations.

i) To avoid the large volume change of the gas in the dissolving process, the gas before mixing should be brought to the state where its molar volume is the same as that which the hydrogen would have in the dilutely dissolved state. This partial molar volume of hydrogen at infinite dilution is obtained from the fact that in an ideal solution the free volumes of solute and solvent are equal.

ii) The mutual interaction of hydrogen molecules which are dissolved quite dilutely in a liquid phase can be neglected. Then the mixture of hydrogen and hydrocarbons is ideal in both vapor and liquid phase.

For eight hydrogen-hydrocarbon systems, except for the hydrogen-methane system, the calculated Henry's constants agree well with the experimental results.

§ Introduction

In vapor-liquid equilibrium of a binary system, such as the hydrogen-hydrocarbon systems, when the temperature of the system is above the critical temperature of one component, the composition of this light component in the liquid phase can be represented as the solubility of the gas in the liquid. The solution process has been studied from various points of view, but no existing theory explains the process completely, because of the complex nature of liquid mixtures.

Some proposed theoretical treatments for gas-liquid solutions, including hydrogen-hydrocarbon systems, give good approximation in certain limited cases. Prausnitz et al.^{23,24} estimated the solubility of gases on the basis of regular solution theory and of the idea of hypothetical liquified gas at one atmospheric pressure. Pierotti^{21,22} calculated Henry's constants using equations of statistical mechanics derived first by Reiss et al. Katayama et al.^{14,15} presented a useful method for engineering purposes regarding benzene as the standard solvent. Orentlicher et al.²⁰ precisely examined thermodynamical behavior of hydrogen in liquid argon and hydrocarbons and gave an empirical rule for the solubility of hydrogen in solvents. In the present paper, the authors aim to estimate the equilibrium constant at infinite dilution (Henry's constant), analyzing the solution process into a thermodynamical isothermal process of two steps. They also introduce the concept of free volume of solute and solvent to obtain the partial molar volume of a gas in a solvent.

§ Theoretical Treatment of Gas-Liquid Solution

a) Solution model

Compared to the solution process of a liquid in a liquid, the solution process of a gas in a liquid is more complicated because the latter process accompanies a large volume change of the gas. To avoid the volume change of the gas and to make the analysis possible the authors present the following solution model. **Fig. 1** illustrates the solution model of a gas in a solvent. In state *A* the solvent is in thermal equilibrium at $T^\circ\text{K}$ and the gas is at the same temperature. As this state of the gas is a reference state, its pressure can be chosen arbitrarily. So we define it to be sufficiently low, that is nearly zero absolute pressure. The gas in state *A* is compressed to state *B*, where its molar volume becomes equal to the partial molar volume of the gas at infinite dilution in this solvent in order not to cause a volume change of the gas in dissolution process. If the gas before mixing has the same molar volume as the gas would have in the dissolved state, no volume change occurs in the dissolution process. In state *B* the gas exists in two different states corresponding to the vapor and liquid phases of the solvent. Then the mixing of the gas and the solvent is carried out independently in each phase to reach state *C*. State *C* can be considered to be a vapor-liquid equilibrium of the binary system. The gas in the vapor mixture is so dilute that the system pressure can be regarded as the same as the vapor pressure of the solvent P_s . The amount of the gas in the liquid mixture which is in equilibrium with the vapor phase is also very small. In other words the gas is at infinite dilution in each phase.

The authors now discuss the problem of the solution process of a gas in solvents, limiting the gas component to hydrogen and the solvents to hydrocarbons. **Table 1**

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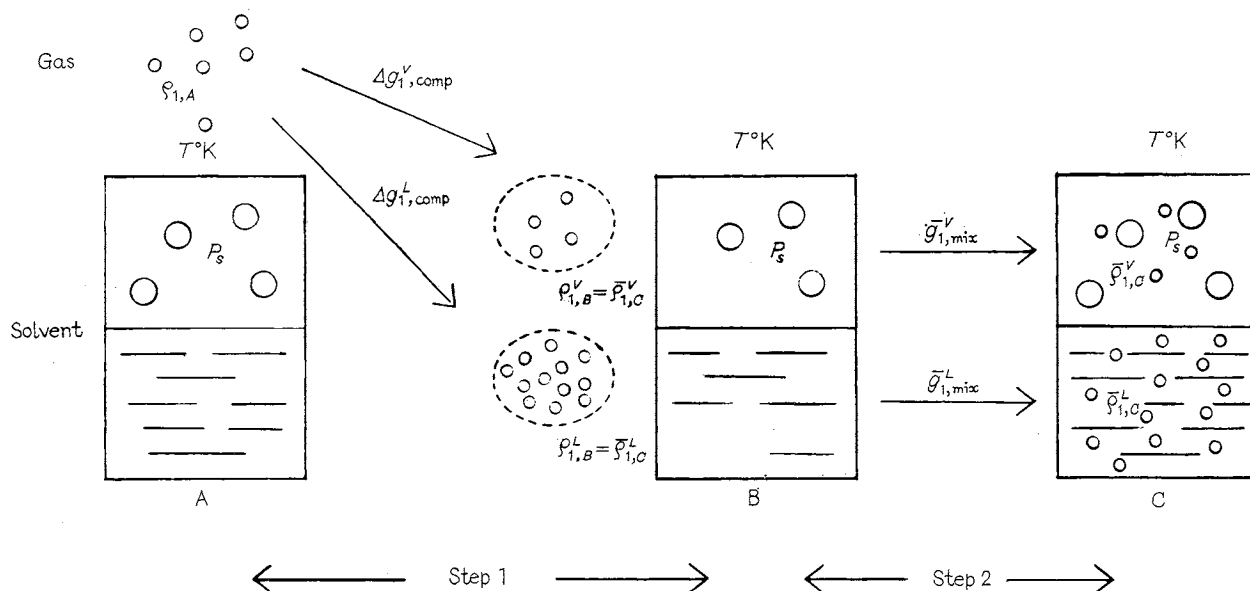


Fig. 1 Solution model of gas into solvent

Table 1 Sources of hydrogen-hydrocarbon equilibrium data

System	Temperature range [°K]	Pressure range [atm]	Reference
Hydrogen-Methane	90.66	17~200	12)
Hydrogen-Methane	90.30~127.16	30~110	10)
Hydrogen-Methane	116.00~173.00	34~103	4)
Hydrogen-Methane	158.16~188.16	20~80	17)
Hydrogen-Ethane	144.30~283.20	17~526	30)
Hydrogen-Ethane	158.20~178.20	S.V.P.*~75	16)
Hydrogen-Propane	172.10~297.10	17~544	28)
Hydrogen-Propane	277.60~361.00	S.V.P.~544	7)
Hydrogen- <i>n</i> -Butane	144.30~297.10	20~500	1)
Hydrogen- <i>i</i> -Butane	311.00~394.30	34~204	9)
Hydrogen-Hexane	277.60~511.40	S.V.P.~680	19)
Hydrogen-Ethylene	158.20~188.20	S.V.P.~75	17)
Hydrogen-Ethylene	158.20~255.40	17~544	30)
Hydrogen-Propylene	200.00~297.00	17~544	30)

* Saturated vapor pressure

shows the hydrogen-hydrocarbon systems considered in this paper.

The mixture of vapor phase in state C is reasonably assumed to be ideal. The mixture of liquid phase also is regarded as an ideal solution, because for sufficiently dilute solutions of non-electrolyte we may neglect all mutual interaction between solute molecules. In this respect the solute molecules behave like the molecules of a perfect gas. Moreover as the temperature is well above the critical point of hydrogen, it is a good assumption to consider hydrogen to behave like a hard-sphere gas. This assumption give good results as is shown afterward in this paper. Therefore in our discussion the behavior of vapor and liquid mixture is treated as ideal.

b) The partial molar volume of a gas at infinite dilution

(i) The entropy of mixing and the concept of free volume.

In the ideal solution of a binary system, Eqs. (1) and (2) should be satisfied.

$$\Delta \bar{H}_1 = 0 \quad \text{Eq. (1)}$$

$$\Delta \bar{S}_1 = -R \ln x_1 \quad \text{Eq. (2)}$$

On the other hand the entropy change of mixing of the two components whose molecules are of different sizes is expressed by Eq. (3) with the concept of the free volume²⁷⁾.

$$\Delta S^M = -R \left(n_1 \ln \frac{n_1 V_1^f}{n_1 \bar{V}_1^f + n_2 \bar{V}_2^f} + n_2 \ln \frac{n_2 V_2^f}{n_1 \bar{V}_1^f + n_2 \bar{V}_2^f} \right) \quad \text{Eq. (3)}$$

The term "free volume" has several meanings⁶⁾. The authors understand free volume as the expansion volume generated by thermal agitation when the substance is heated above 0°K, that is,

$$V^f = V^T - V^0 \quad \text{Eq. (4)}$$

This definition is in line with that of Biltz⁵⁾, who provides relations and data for the estimated volume at 0°K for a wide range of organic compounds.

When the solute is considerably dilute in the solvent the free volume of the solute in the solution is considered to be identical with the free volume of the solvent either when the solvent is in a mixture or in a pure state²⁷⁾. Thus Eq. (5) is obtained.

$$V_2^f = \bar{V}_2^f = \bar{V}_1^f \quad \text{Eq. (5)}$$

Putting Eq. (5) in Eq. (3) and by differentiation with respect to n_1 Eq. (6) is obtained.

$$\Delta \bar{S}_1 = -R \left(\ln x_1 + \ln \frac{V_1^f}{\bar{V}_2^f} \right) \quad \text{Eq. (6)}$$

Comparing Eq. (6) with Eq. (2) gives

$$V_1^f = \bar{V}_2^f, \text{ or } V_1^T - V_1^0 = V_2^T - V_2^0 \quad \text{Eq. (7)}$$

Rewriting Eq. (7), one obtains

$$V_1^T = V_2^T - V_2^0 + V_1^0 \quad \text{Eq. (7')}$$

Eq. (7') is the formula which is applied to both the vapor and liquid phases. For the mixture of the vapor phase, however, V_1^0 and V_2^0 are negligible compared with V_1^T and V_2^T .

(ii) The calculation of molar volume of hydrocarbons

and hydrogen at $T^\circ\text{K}$ and 0°K .

The vapor and liquid volumes of hydrocarbons at saturated state of $T^\circ\text{K}$ are calculated by BWR equation of state. This equation is, however, valid to the density of 1.7 times the critical density. The liquid density at saturated state is generally much larger than this limit. Therefore A. P. I. method²⁸⁾ is also examined for the density of liquid phase. The BWR coefficients for hydrocarbons are taken from the paper of Benedict et al.³⁾ and for hydrogen the coefficients are taken from that of Motard et al.¹⁸⁾

To estimate the molar volume at zero-point the authors present the following two prediction methods since there is no experimental information.

I. If we consider a perfect crystal at absolute zero, the molar volume is determined by the geometrical structure of the lattice. The inert gases, except helium crystallize in face-centered cubic lattices (*c.c.p.*); most mono-atomic solids crystallize in simple lattices; helium in a hexagonal cubic lattice (*h.c.c.*); and alkali metals in body-centered cubic lattices (*b.c.c.*)²⁵⁾. As for the lattice geometry of hydrogen and hydrocarbons no information is available. But their physical properties are more similar to those of the inert gases including helium than to those of the alkali metals or mono-atomic solids. The lattice of hydrogen and hydrocarbons then may be considered as *c.c.p.* or *h.c.p.* Both are types of the tightest possible packing, which means that they have the greatest density of packing. The molar volume of these types of structure is expressed by Eq. (8).

$$V^0 = \frac{\sigma^3 N \times 10^{-3}}{\sqrt{2}} \quad \text{Eq. (8)}$$

where, N ; Avogadro's number, σ ; collision diameter. Eq. (8) is used for the estimation of the molar volume at 0°K . Collision diameter is one of the parameters of potential function which is rigorously related to such properties as the second virial coefficient and viscosity. For this potential function the values of the constants which best fit the experimental data can then be found by trial. Hirschfelder et al.¹³⁾ listed parameters of the Lennard-Jones potential function. Unfortunately these values scatter because of the imperfectness of the experimental data. Hence let us apply the principle of the corresponding state to the volume in Eq. (8). The best average value²⁵⁾ derived from the data for spherical molecules is

$$V_c = 3.14\sigma^3 N, \quad \therefore V^0 = 0.227 V_c \quad \text{Eq. (9)}$$

while the theoretical value is

$$V_c = 1.77\sigma^3 N, \quad \therefore V^0 = 0.400 V_c \quad \text{Eq. (10)}$$

For hydrogen and the hydrocarbons under discussion the best fitting constant is obtained from the line shown in Fig. 2 where $\frac{\sigma^3 N \times 10^{-3}}{\sqrt{2}}$ is plotted against V_c . That is

$$V^0 = 0.243 V_c \quad \text{Eq. (11)}$$

The volume of hydrogen and hydrocarbons at zero-temperature can be read from the smoothed line in Fig. 2.

II. Francis¹¹⁾ presented the equation for the liquid

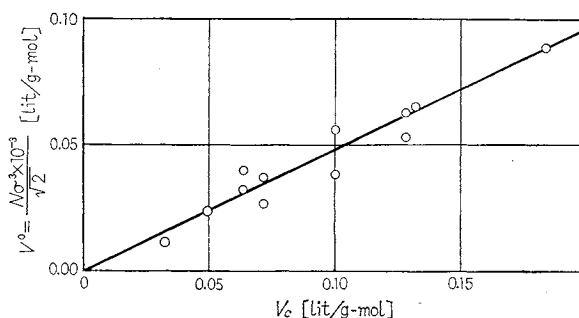


Fig. 2 Molar volumes of hydrogen and hydrocarbons at 0°K from the lattice structure

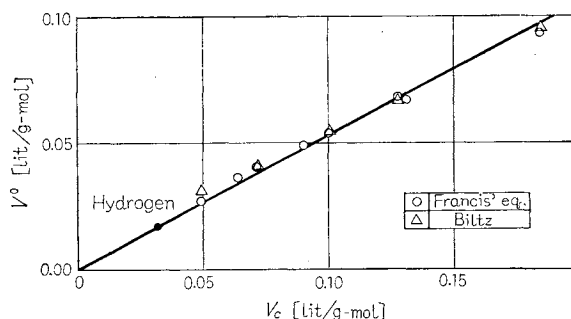


Fig. 3 Molar volumes of hydrogen and hydrocarbons at 0°K from Francis' equation

density of hydrocarbons, which is represented by the following formula.

$$\rho = A - Bt - \frac{C}{E - t} \quad \text{Eq. (12)}$$

where A , B , C , and E are the constants.

Although this equation is applicable to a limited range of temperature, it is possible to calculate the density at absolute zero if t is extrapolated to -273.2°C . The extrapolated values are plotted versus V_c in Fig. 3. The volumes at 0°K calculated by Biltz are plotted in the same figure for reference. The best fitting equation in this case is

$$V^0 = 0.263 V_c \quad \text{Eq. (13)}$$

Though Francis' equation was originally formulated only for the density of hydrocarbons, it is assumed that Eq. (13) is applicable to hydrogen.

Eq. (11) and (13) are in good agreement with each other within 0.005 lit/g-mol.

The partial molar volumes of hydrogen in liquid and vapor mixture are then calculated by Eq. (7') following the process of the combination shown in Table 2. Four kinds of calculation of hydrogen density are applied to liquid phase and two kinds to vapor phase.

Experimental data on the partial molar volume of hydrogen at infinite dilution in liquid benzene⁸⁾ and liquid argon³⁰⁾ are available, and the authors compared them with those calculated in Figs. 4 and 5. The molar volume of liquid argon at $T^\circ\text{K}$ is cited from the literature.²⁶⁾ The only notable difference between observed and calculated values in benzene is that the former increases more rapidly with increasing temperature.

Table 2 Programs for calculation of hydrogen density at system temperature

Phase	Molar volume of hydrogen and hydrocarbons at 0°K	Molar volume of hydrocarbons at T°K	Identifying number of calculation process
Liquid phase	lattice structure	BWR equation of state	(1)
	lattice structure	A. P. I. method	(2)
	Francis's equation	BWR equation of state	(3)
	Francis's equation	A. P. I. method	(4)
Vapor phase	lattice structure	BWR equation of state	(1)
	Francis's equation	BWR equation of state	(2)
	Francis's equation	BWR equation of state	(3)

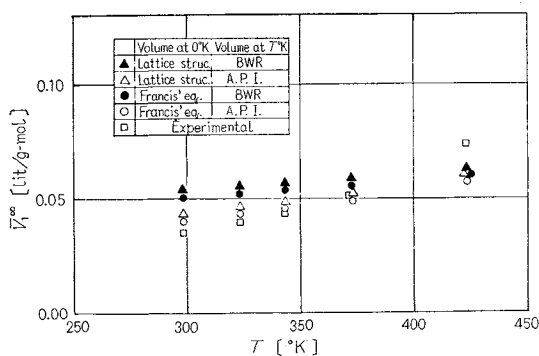


Fig. 4 Partial molar volume of hydrogen in liquid benzene at infinite dilution

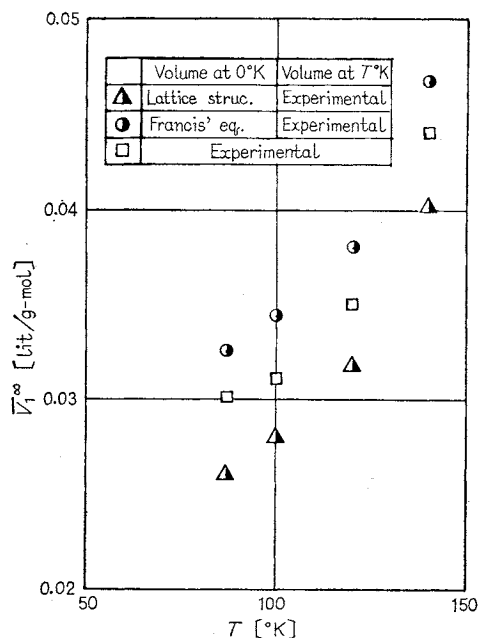


Fig. 5 Partial molar volume of hydrogen in liquid argon at infinite dilution

§ The Calculation of Henry's Constant Based Upon the Solution Model

The solution model can be considered as an isothermal thermodynamical process in a series of two steps. For each step in the process free energy change of the gas

can be given as follows.

Step 1. The free energy of the compression

The free energy change of compression of the gas from state A to B is thermodynamically expressed by Eq. (14).

$$\Delta g_{1, \text{comp}} = \int_A^B v_1 dp \quad \text{Eq. (14)}$$

When the BWR equation of state is taken as the P-V-T relations, the free energy change for the liquid phase is expressed in terms of ρ_1 ,

$$\begin{aligned} \Delta g_{1, \text{comp}}^L = & \left[RT \ln \rho_1 + 2(B_0 RT - A_0 - C_0/T^2)\rho_1 \right. \\ & + \frac{3}{2}(bRT - a)\rho_1^2 + \frac{6}{5}aa\rho_1^5 \\ & + c \exp(-\gamma\rho_1^2) \\ & \left. \times \left(-\frac{1}{\gamma} + \frac{\rho_1^2}{2} + \gamma\rho_1^4 \right) / T^2 \right]_{\rho_{1,A}}^{\rho_{1,B}} \end{aligned} \quad \text{Eq. (15)}$$

and by a similar formula for vapor phase in terms of $\Delta g_{1, \text{comp}}^V$ and $\rho_{1,V}$.

Step 2. The mixing process

The free energy of ideal mixing is expressed by Eq. (16) for liquid phase,

$$\Delta g_{1, \text{mix}}^L = RT \ln x_1 \quad \text{Eq. (16)}$$

and the analogous relations are derived for $\Delta g_{1, \text{mix}}^V$ and y_1 . The two phases of the mixture are in equilibrium and the following equation should be satisfied.

$$\Delta g_{1, \text{mix}}^L + \Delta g_{1, \text{comp}}^L = \Delta g_{1, \text{mix}}^V + \Delta g_{1, \text{comp}}^V \quad \text{Eq. (17)}$$

Substituting Eqs. (15) and (16), into (17) Eq. (18) is obtained.

$$\begin{aligned} K_1^\infty = \lim_{x_1 \rightarrow 0} \frac{y_1}{x_1} \\ = \exp \left\{ \left[RT \ln \rho_1 + 2(B_0 RT - A_0 - C_0/T^2)\rho_1 \right. \right. \\ + \frac{3}{2}(bRT - a)\rho_1^2 + \frac{6}{5}aa\rho_1^5 \\ + c \exp(-\gamma\rho_1^2) \\ \left. \left. \times \left(-\frac{1}{\gamma} + \frac{\rho_1^2}{2} + \gamma\rho_1^4 \right) / T^2 \right]_{\rho_{1,V,B}}^{\rho_{1,L,B}} / RT \right\} \end{aligned} \quad \text{Eq. (18)}$$

The definition of Henry's constant is

$$H = \lim_{x_1 \rightarrow 0} \frac{f_1}{x_1} \quad \text{Eq. (19)}$$

At infinite dilution y_1 is so small that the system pressure is regarded as P_s . In such a case the partial pressure of hydrogen is the same as its fugacity. That is,

$$f_1 = P_s \cdot y_1 \quad \text{Eq. (20)}$$

Henry's constant is then calculated by Eq. (21).

$$H = P_s \cdot K_1^\infty \quad \text{Eq. (21)}$$

§ Calculation Results

The calculation of Henry's constant is carried out by means of a digital computer using the four kinds of calculation process shown in Table 2. The authors also obtained Henry's constant from the equilibrium composition which is calculated from the fugacity by applying the BWR equation of state.

Henry's constant is plotted against the reciprocal of the absolute temperature in **Fig. 6** and **7** for the systems

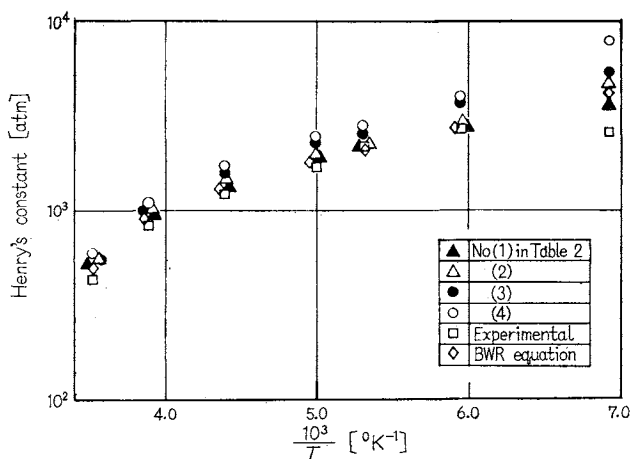


Fig. 6 Henry's constants of hydrogen-ethane system

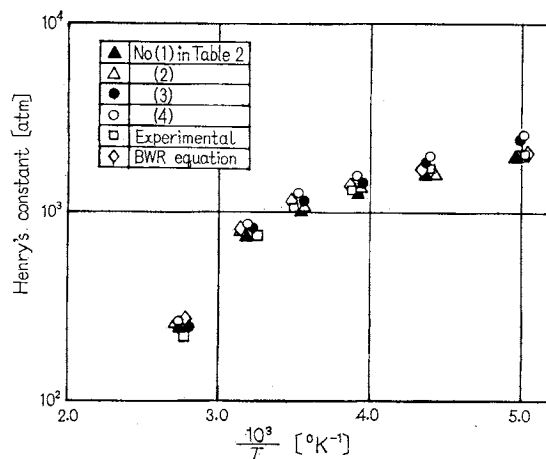


Fig. 7 Henry's constants of hydrogen-propane system

Table 3 Calculated and observed values of Henry's constants

Hydrocarbon of the system	Temperature [°K]	Henry's constant [atm]				Experimental value	BWR*
		Identifying number of calculation process in Table 2					
		(1)	(2)	(3)	(4)		
Methane	110.16	3707	2633	4328	4235	1036	1140
	127.16	2127	2371	2340	2627	787	840
	158.16	947	1054	987	1106	460	485
	168.16	693	759	716	787	415	390
	178.16	456	505	466	518	225	260
<i>n</i> -Butane	144.26	12502	2329	82502	4500	3575	10750
	172.06	3539	1993	7244	3125	2425	4675
	199.86	2177	1765	3238	2456	1750	2850
	227.56	1684	1585	2205	2046	1500	2020
	244.26	1509	1488	1890	1858	1280	1980
	260.96	1374	1395	1666	1696	1180	1780
	297.06	1062	1108	1227	1287	940	1370
Hexane	277.60	1169	1176	1513	1527	1120	2060
	311.00	1020	1055	1248	1300	1000	1710
	344.20	864	891	1019	1056	910	1450
	377.20	741	747	850	858	790	1205
	411.20	610	592	683	661	700	1040
	444.20	477	435	524	474	590	885
	477.20	335	269	361	285	335	—
Ethylene	158.20	3090	3091	3633	3635	2640	2160
	172.10	2401	2547	2724	2906	2010	1800
	178.20	2200	2367	2466	2670	1520	1725
	199.90	1652	1811	1795	1980	1430	1340
	227.60	1117	1204	1182	1280	1065	920
	231.50	1048	1125	1106	1192	720	855
	255.40	644	670	668	696	510	518
Propylene	199.90	2126	2181	2636	2717	2650	2360
	227.60	1656	1776	1934	2094	1910	1850
	255.40	1335	1436	1503	1629	1326	1485
	283.20	1043	1102	1145	1216	1050	1180
	297.10	901	938	978	1022	815	1000
<i>i</i> -Butane	311.00	864	882	979	1001	1030	1165
	338.80	662	668	731	738	815	915
	366.50	462	461	497	496	570	600
	394.30	243	255	253	267	290	345

* Calculated from equilibrium composition which is calculated from fugacity using BWR equation of state.³⁾

of hydrogen-ethane and hydrogen-propane respectively. The results of other systems are tabulated in **Table 3**.

§ Discussion

i. For all the systems except hydrogen-methane the

calculated Henry's constants agree well with those observed. The agreement is particularly good for the systems of hydrogen-ethane, -propane, -*n*-butane, -hexane and -propylene when the molar volume at 0°K is obtained by the lattice structure, and for those of hydrogen -propane, -hexane, -propylene and -*i*-butane when Francis'

equation is used. Generally speaking the results with the application of the lattice structure to the molar volume are better than the application of Francis' equation. In the hydrogen-methane system the calculated values are much larger than those observed.

ii. The difference of the liquid density of hydrocarbons calculated from BWR equation and from Francis' equation is serious for *n*-butane, because the reduced temperature of this system is much lower than that of other systems. The coefficients of BWR equation for *n*-butane are not accurate in a low temperature range. In other systems the liquid densities from these two equations agree with each other quite well.

iii. A very little difference of hydrogen density in liquid phase at $T^\circ\text{K}$ strongly affects Henry's constant, since the free energy which is calculated from the density of hydrogen is related by an exponential function to Henry's constant. For example, in the hydrogen-*n*-butane system at 172.1°K, the densities of hydrogen of 34.386 and 30.080 g-mol/lit. with the same value of 9.766×10^{-5} g-mol/lit. for the density of hydrogen in vapor phase lead to Henry's constants of 7244 and 3125 atm, respectively.

iv. Henry's constant obtained from the equilibrium composition calculated from fugacity applying the BWR equation of state give pretty good results.

§ Conclusion

The proposed solution model of a gas in liquid solvent is successful in predicting Henry's constant for hydrogen-hydrocarbon systems. As a prediction method it has the great advantage that only the properties of pure components are necessary for the evaluation of Henry's constants.

Although this solution model was applied only to hydrogen-hydrocarbon systems, application to other gas-liquid systems may be possible.

Nomenclature

g = free energy	[1-atm/g-mol]
H = Henry's constant	[atm]
H = heat of mixing	
K = equilibrium coefficient	
N = Avogadro's number	
n = moles of a component	
P = pressure	[atm]
R = gas constant	[1-atm/°K, g-mol]
S = entropy	
T = temperature	[°K]
t = temperature	[°C]
f = fugacity	[atm]
V = molar volume	[1/g-mol]
x = mole fraction in liquid phase	
y = mole fraction in vapor phase	
ρ = molar density	[g-mol/l]
σ = collision diameter	[Å]
$A, B, C, a, b, c, \alpha, \gamma$ = coefficients of BWR equation of state	
A, B, C, E = constants of Francis' equation	
Superscripts	
f = free volume	
L = liquid phase	

M = change on mixing process
 T = state at $T^\circ\text{K}$
 V = vapor phase
 0 = state at 0°K
 $-$ = partial molar quantity
 ∞ = at infinite dilution

Subscripts

1 = lighter component
 2 = heavier component
 A = state A in Fig. 1
 B = state B in Fig. 1
 C = critical state
 s = saturated state
 comp = compression process
 mix = mixing process

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