

## 용해도 이론의 여러가지 계에 대한 적용

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한국과학기술연구소 전무식

(1971. 6. 3 접수)

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### Further Applications of the Solubility Theory to Various Systems

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(Received June 3, 1971)

**Abstracts** The theory of solubility proposed by Jhon and Kihara has been tested and applied to various systems.

In the present paper, the systems are the solubilities of gases such as Ar, H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> in liquid benzene and carbon disulfide, those of solids iodine and naphthalene in the nonaqueous solvents, and those of gases H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, Ar, CH<sub>4</sub>, and C<sub>2</sub>H<sub>4</sub> in the electrolyte solutions.

The theoretical values of solubilities are in good agreement with the experimental data in the literature.

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#### Introduction

During the past years, several theories were developed to correlate the solubility data of gases in liquids.

Since Uhlig<sup>1</sup> and Eley<sup>2</sup> had early proposed the theory of solubility, Kobatake and Alder,<sup>3</sup> Pierotti,<sup>4</sup> and Gilson<sup>5</sup> treated solubility problems with their favorite liquid model such as cell theory, scaled particle theory, and significant structure theory, respectively.

And Choi, Jhon, and Eyring<sup>6</sup> studied the curvature dependence of the surface tension and the theory of solubility.

In each case, some improvements are introduced.

Recently, Kihara and Jhon<sup>7</sup> have proposed a new theory of gas solubility in nonpolar liquid on the basis of the core potential of intermolecular forces which considers the size and shapes of molecules.

And Sung, et al.<sup>8</sup> have lately developed the solubility theory of gases in water which is based on the significant liquid structures<sup>9</sup>.

In this paper, the theory of solubility has been tested further and applied to various systems.

### Theory

A common point in these theories is that the activation energy of solution could be divided into two terms.

The first term is the energy to dig holes in the solvent and the second term is the interaction energy between a solute molecule and the surrounding solvent molecules.

Then, Ostwald coefficient,  $C/C^0$ , is defined in the following form

$$C/C^0 = \exp(-\Delta/kT) \quad (1)$$

where  $C^0$  and  $C$  are the number densities of solute molecules in the gas phase and in the solution.  $\Delta$  is the energy of activation,  $T$  is the absolute temperature, and  $k$  is the Boltzmann constant.

The activation energy  $\Delta$  means the work necessary for transferring one solute molecule from the gas phase to the solution at constant pressure and temperature.

The energy of activation can be divided into two terms as follows

$$\Delta = \Delta_1 + \Delta_2 \quad (2)$$

Here, first term  $\Delta_1$  is the energy to create a cavity of the size and shapes of solute molecule against the surface tension of solvent. And the second term  $\Delta_2$  corresponds to the (solute-solvent) interaction energy.

According to Kihara's core potential<sup>10</sup> the intermolecular potential  $U$  is a function of the distance between the molecular centers of cores.

For polyatomic molecules, we assume a core inside each molecule and suppose that the intermolecular potential  $U$  is a function only of the distance  $\rho$  between the cores.

The used cores in the present paper are

listed in Table I. And the core measures and potential parameters are given in Table II, where  $V$  is the volume of core,  $S$  is the surface area of core, and  $M$  is the mean curvature integrated over the surface of core.

Table I. The cores of molecules

Inert gas atoms	Point
Hydrogen	Rod joining H
Nitrogen	Rod joining N
Oxygen	Rod joining O
Ethylene	Rod joining C
Carbon dioxide	Rod joining O
Carbon disulfide	Rod joining S
Iodine	Rod joining I
Naphthalene	Octagon joining midpoints of CH
Methane	Tetrahedron joining midpoints of CH
Ethane	Circular cylinder (radius 0.3 Å, height 1.6 Å)
Benzene	Regular hexagon joining midpoints of CH
Cyclohexane	Truncated double-cone (radius 2.0 Å, height 2.0 Å)

In general, the potential between solute and solvent molecules is assumed to be

$$U_{AB}(\rho) = 4\epsilon_{AB} \left[ \left( \frac{\sigma_{AB}}{\rho} \right)^{12} - \left( \frac{\sigma_{AB}}{\rho} \right)^6 \right] \quad (3)$$

where

$$\epsilon_{AB} = (\epsilon_{AA} \cdot \epsilon_{BB})^{1/2}$$

$$\sigma_{AB} = \frac{1}{2}(\sigma_{AA} + \sigma_{BB})$$

Here, the core is denoted by  $A$  for solute molecules and by  $B$  for solvent molecules. If it is now assumed that the electrolyte is completely dissociated in water, there are solute molecules, water molecules, and ions in the solution.

After averaging the interaction between the permanent dipole over all orientation<sup>11</sup> and ignoring terms due to higher multipole mo-

Table II. Core measures and potential parameters

	$V(\text{\AA}^3)$	$S(\text{\AA}^2)$	$M(\text{\AA})$	$\sigma(\text{\AA})$	$\epsilon/k(^{\circ}\text{K})$	$(\text{\AA}^3)^{(d)}$
$\text{I}_2$	0	0	8.48	3.21	1206	
$\text{C}_{10}\text{H}_8$	0	23.6	20.77	3.03	1449	
$\text{C}-\text{C}_6\text{H}_{12}^{(c)}$	14.7	32.9	21.1	2.40	945	
$\text{C}_6\text{H}_6^{(b)}$	0	10.2	13.2	3.03	850	
$\text{CS}_2^{(a)}$	0	0	9.67	3.21	680	
$\text{H}_2\text{O}^{(c)}$	0	0	0	2.50	167	
$\text{Ar}^{(b)}$	0	0	0	3.42	119	1.626
$\text{H}_2^{(b)}$	0	0	2.32	2.50	39.4	0.802
$\text{N}_2^{(a)}$	0	0	3.44	3.09	124	1.734
$\text{O}_2^{(a)}$	0	0	3.45	2.67	166	1.561
$\text{CO}_2^{(a)}$	0	0	7.23	2.99	316	2.594
$\text{C}_2\text{H}_4^{(b)}$	0	0	4.18	3.74	256	3.702
$\text{CH}_4^{(b)}$	0.084	1.38	5.12	2.81	233	2.699
$\text{C}_2\text{H}_6^{(a)}$	0.45	3.58	7.98	2.76	422	4.326

(a) T. Kihara, K. Yamazaki, M. S. Jhon and U. R. Kim, *J. Chem. Phys. Letter*, to be published.

(b) Data are taken from ref. 10.

(c) J. H. van der Waals and J. C. Platteuw, *Advan. Chem. Phys.*, 2, 1 (1959)

(d) E. A. Moelwyn-Hughes, "Physical Chemistry", Pergamon Press, New York, N. Y. (1964)

ments, the interaction potential<sup>11</sup> between a nonpolar molecule and a polar molecule in the electrolyte solution would be expressed in terms of repulsion, dispersion, induction, and ion-induced dipole interactions.

Thus, the potential between nonpolar solute and polar solvent is assumed to be

$$U_{AB}(\rho) = 4\epsilon_{AB} \left[ \left( \frac{\sigma_{AB}}{\rho} \right)^{12} - \left( \frac{\sigma_{AB}}{\rho} \right)^6 \right] - \frac{\alpha_A \mu_B^2}{\rho^6} - \frac{1}{2} \alpha_A E^2 \quad (4)$$

where  $\alpha_A$  is the polarizability of solute molecule,  $\mu_B$  is the dipole moment of a water molecule, and  $E$  is the electric field at the position of the solute molecule that is produced by all of the surrounding ions.

The electric field  $E$  is the quantity which depends on the distribution of ions about the solute molecule.

If the distribution of ions is assumed to be

uniform, there is on the average a spherically symmetrical charge distribution about the solute molecule.

For such a uniform distribution, the total ion-induced dipole interaction of a solute molecule with all of the surrounding ions become zero<sup>12</sup>.

Now, the first term,  $\Delta_1$ , the energy of cavity formation for nonaqueous systems<sup>7</sup> can be expressed in the following form

$$\Delta_1 = \gamma [S_A + M_A(\sigma_{AA} + b) + \pi(\sigma_{AA} + b)^2] \quad (5)$$

in which  $\gamma$  is the surface tension of solvent and  $b$  is the additional thickness which is a function of temperature.

And the activation energy  $\Delta_1$  for aqueous systems<sup>8</sup> is given by

$$\Delta_1 = \gamma [S_A + M_A(\sigma_{AA} + b) + \pi(\sigma_{AA} + b)^2] \frac{1}{1+K} \quad (6)$$

in which  $K$  is the equilibrium constant between

opened domain (Ice-I-like) and closed domain (Ice-III-like) of water<sup>13</sup>.

The second term,  $\Delta_2$ , the energy of interaction between solute and solvent molecules is given in the form as follows

$$\Delta_2 = fn \int_{\sigma_{AB}}^{\infty} U_{AB}(\rho) \langle S_{A+\rho+B} \rangle_{AV} d\rho \quad (7)$$

in which  $U_{AB}(\rho)$  is the intermolecular potential between solute molecule  $A$  and solvent molecule  $B$ , the quantity  $\langle S_{A+\rho+B} \rangle_{AV}$  means the average value of the effective surface area with respect to the orientation of core  $B$ ,  $n$  is the number density of solvent molecules, and  $f$  is the quantity in order to take account of the fact that the distribution of solvent molecules near the potential minimum is denser than its average value.

According to Steiner's formula<sup>10</sup>,

$$\langle S_{A+\rho+B} \rangle_{AV} = S_A + S_B + (2\pi)^{-1} M_A M_B + 2(M_A + M_B)\rho + 4\pi\rho^2 \quad (8)$$

For nonpolar-nonpolar systems, the equation (7) can be integrated as follows

$$\Delta_2 = -fn\epsilon_{AB} \left[ -\frac{24}{55} \left( S_A + S_B + \frac{1}{2\pi} M_A M_B \right) \sigma_{AB} + \frac{6}{5} (M_A + M_B) \sigma_{AB}^2 + \frac{32}{9} \pi \sigma_{AB}^3 \right] \quad (9)$$

For nonpolar-polar systems, the equation (7) can be integrated as follows

$$\Delta_2 = -fn \left\{ \epsilon_{AB} \left[ -\frac{24}{55} \left( S_A + S_B + \frac{1}{2\pi} M_A M_B \right) \sigma_{AB} + \frac{6}{5} (M_A + M_B) \sigma_{AB}^2 + \frac{32}{9} \pi \sigma_{AB}^3 \right] + \alpha_A \mu_B^2 \left[ \frac{1}{5} (S_A + S_B + \frac{1}{2\pi} M_A M_B) \sigma_{AB}^{-5} + \frac{1}{2} (M_A + M_B) \sigma_{AB}^{-4} + \frac{4}{3} \pi \sigma_{AB}^{-3} \right] \right\} \quad (10)$$

## Results and Discussions

### Solubility of Gases in $C_6H_6$ and $CS_2$

Using the values of core measures and potential

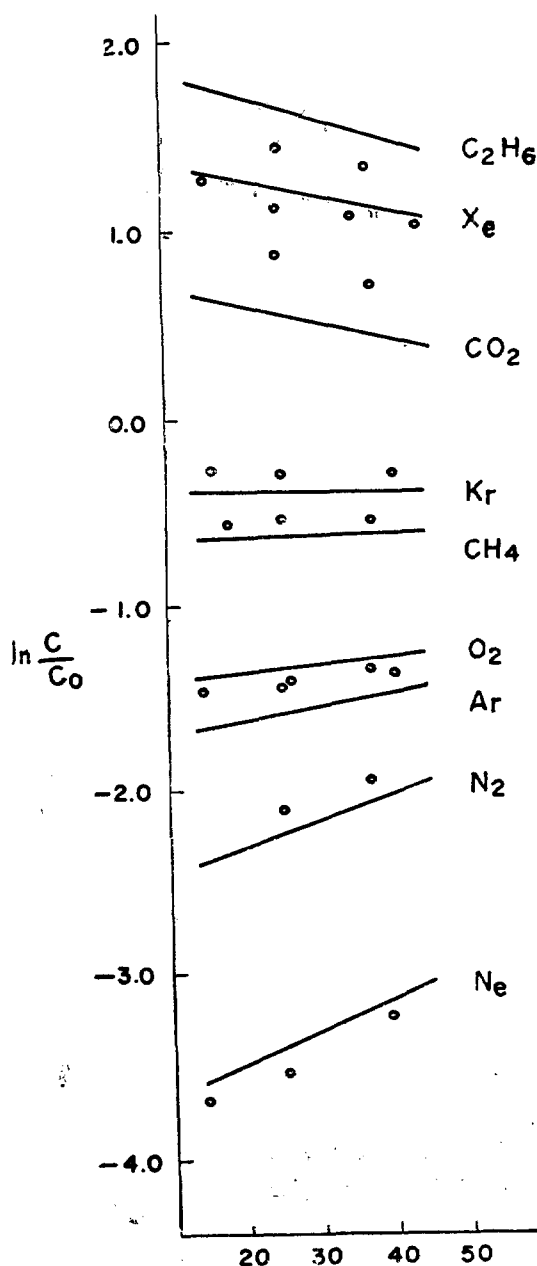


Fig. 1. The solubilities of gases in benzene  
— calculated  
○ observed

parameters in Table II, the applicability of the above theory has been tested and extended to various systems.

The calculated results for the solubility of gases in benzene and carbon disulfide are compared with the experimental values<sup>14,15,16,17</sup> in Figures 1 and 2.

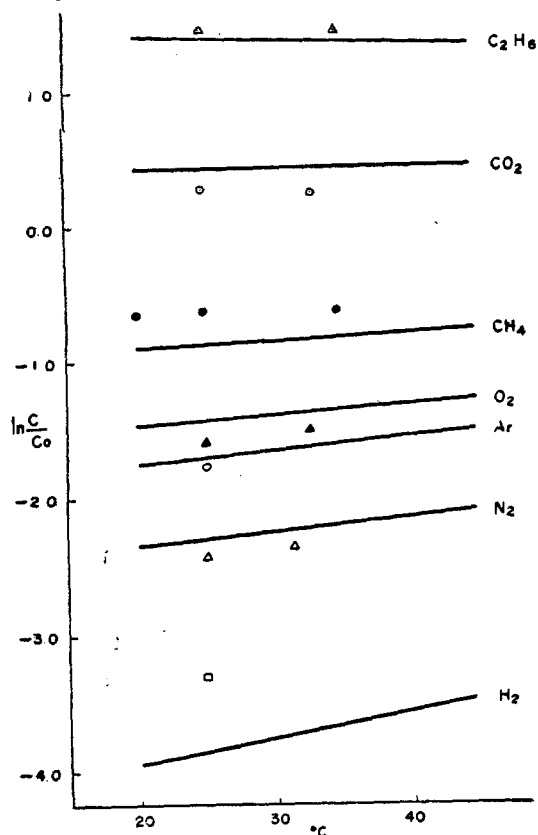


Fig. 2. The solubilities of gases in carbon disulfide

— calculated  
 ○△ observed  
 ●□ observed

In the calculation, besides the known values of  $\gamma^{18}$  and  $\pi^{18}$ , the following empirical parameters are used for benzene,

$$\begin{array}{lll} f=1.46 & b=2.38 & \text{at } 20^\circ\text{C} \\ f=1.43 & b=2.48 & \text{at } 40^\circ\text{C} \end{array}$$

and for carbon disulfide,

$$\begin{array}{lll} f=1.22 & b=2.25 & \text{at } 20^\circ\text{C} \\ f=1.17 & b=2.45 & \text{at } 40^\circ\text{C} \end{array}$$

**Solubility of Solid Iodine and Naphthalene in  $\text{C}_6\text{H}_6$  and  $\text{C}-\text{C}_6\text{H}_{12}$**  To measure the core of solid iodine and naphthalene, their shapes are taken as thin rod and octagon, respectively, and their potential parameters are determined from the Clausius-Clapeyron equation and crystallographic data.

The used core measures and potential parameters are given in Table II.

The experimental Ostwald coefficients are obtained from the mole fraction<sup>19,20</sup> of solid iodine and naphthalene at a certain temperature and vapor pressure of solids<sup>18,21</sup> as follows

$$\frac{C}{C^0} = \frac{760}{P_{(\text{mm})}} \cdot \frac{22414}{M/d} \cdot \frac{(T+t)}{T} \cdot \chi_2 \quad (11)$$

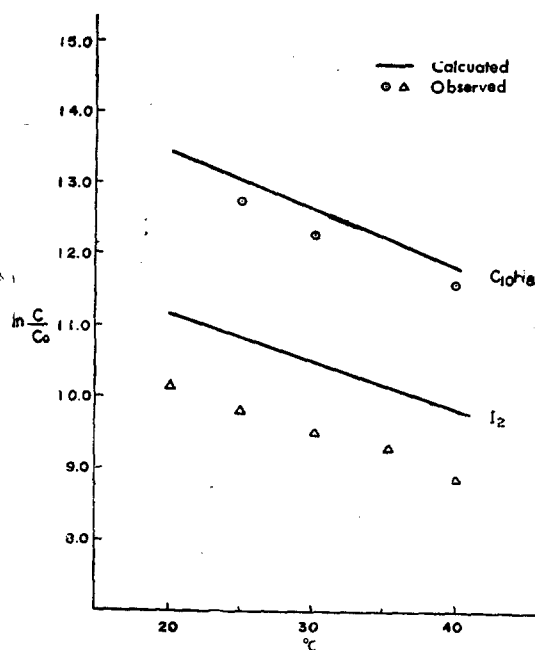


Fig. 3. The solubilities of solids in benzene

where  $P_{(mm)}$  is the vapor pressure of solids,  $M$  is the molecular weight of solvent,  $d$  is the density of solvent,  $T$  is the absolute temperature, and  $X_2$  is the mole fraction of solid in solvent.

For the calculation, the known values of  $\gamma^{18}$  and  $n^{18}$  are used, and  $f$  and  $b$  are taken from the reference 7.

The results are plotted in Figures 3 and 4. The theoretical values agree well with the experimental values in the literature<sup>19,20</sup>.

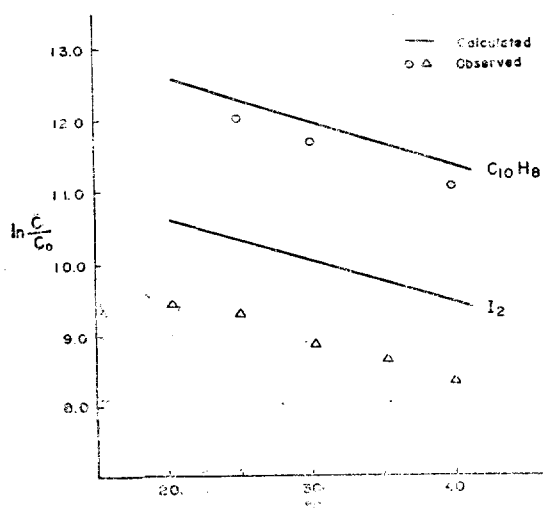


Fig. 4. The solubilities of solids in cyclohexane

**Solubility of Gases in Electrolyte Solutions** The solubilities of gases in aqueous potassium hydroxide solution have been measured by Shoor, Walker, and Gubbins,<sup>22</sup> and those of gases in aqueous sodium chloride solution have been reported by Morrison and Billett.<sup>23</sup>

To calculate the Ostwald coefficient from the equations (6) and (10), the known values of  $\gamma^{18}$  and  $n^{18}$  are used, and  $f$  and  $b$  are taken from the reference 8. And the used core measures and potential parameters are given in Table II.

The calculated values are compared with the experimental data<sup>22,23</sup> in Figure 5 and Table III. The agreement between theory and experiment is quite satisfactory.

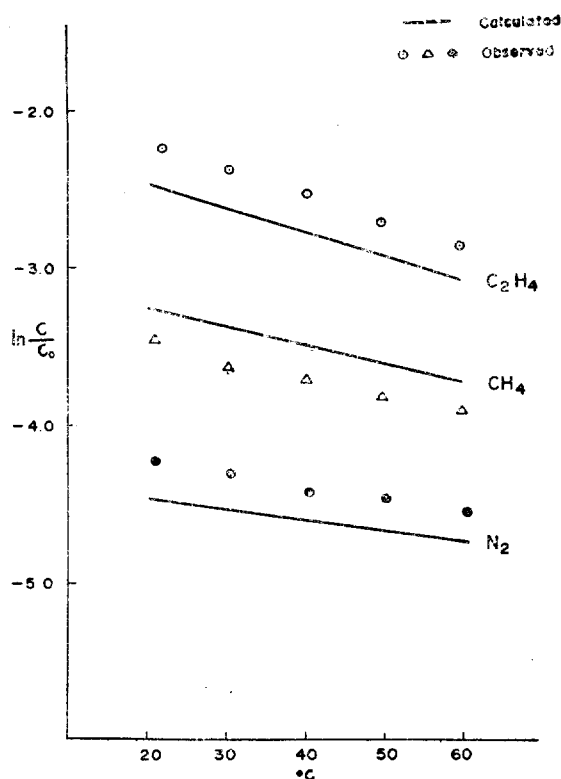


Fig. 5. The solubilities of gases in aqueous NaCl solution

As one sees, the theory includes two empirical parameters,  $b$  and  $f$ . The additional thickness  $b$  is a function of temperature, properly  $db/dT > 0$ , and the factor  $f$  is also a function of temperature, properly  $df/dT > 0$ .

The former is concerned with the effective surface of the cavity and the latter due to the spatial distribution of solvent molecules around a solute molecule.

We assumed that these empirical parameters are independent of the solute species, but they depend on the solvent.

With the reasonable choices of these parameters, the solubilities of a number of gases and solids in solvents can well be represented.

In particular, the good theoretical predictions of solubility of both the gases in electrolyte solutions and the solid in solvents are quite

Table III. The solubilities of gases in aqueous KOH solution

m	O <sub>2</sub>		Ar		CH <sub>4</sub>		H <sub>2</sub>	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
0.00	-3.256	-3.488	-3.734	-3.370	-2.387	-3.390	-5.896	-3.942
0.50	-3.506	-3.735	-4.050	-3.658	-2.714	-3.735	-6.054	-4.908
1.00	-3.728	-3.960	-4.330	-3.950	-3.002	-3.932	-6.202	-4.348
1.50	-3.997	-4.212	-4.669	-4.105	-3.355	-4.265	-6.368	-4.506
2.00	-4.245	-4.445	-4.983	-4.356	-3.680	-4.498	-6.524	-4.652
3.80	-5.071	-5.301	-5.626	-5.198	-4.754	-5.357	-7.063	-5.399

Units: Log. of Ostwald coefficients

encouraging.

These facts support that the theory by Jhon and Kihara is useful and reasonable to understand the solubility phenomena.

### Acknowledgement

The authors express their appreciation to the donors of the Petroleum Research Funds, administered by the American Chemical Society, for support of this research.

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