GROUP CONTRIBUTION MODEL BASED ON THE HOLE THEORY

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A group contribution model is developed, based on the hole theory, for thermodynamic properties of pure liquids of normal alkanes, aromatics and their solutions, including heats of vaporization, pVT relations and activity coefficients. In the present model, the combinatorial factor is approximated by the Flory-Huggins expression, the free volume is expressed by a simplified Henderson's approximation, and a lattice potential energy is made up of pair interaction contributions of segments. By using parameters determined with data reduction of pure liquids and their solutions, pure liquid properties over a wide reduced-temperature range from 0.3 to 0.8 and mixture properties such as activity coefficients are accurately predicted and correlated. Since an equation of state derived from the present new model satisfies the ideal gas limit at infinite volume, it is applied to estimate thermodynamic properties of gaseous phase.

INTRODUCTION

A group contribution method has recently been noted as one of the most useful methods for predicting thermodynamic properties of liquids and their mixtures. This group contribution concept has the advantageous characteristic that all compounds can be regarded as mixtures of group species. Therefore, we can estimate thermodynamic properties of thousands of compounds from the physical properties of a much smaller number of groups.

There have been two kinds of method related to this concept. One is a method for estimating activity coefficients and some excess quantities by using the group activity coefficients, proposed by Wilson and Deal(2), Derr and Deal(5), Rone and Ratcliff(24) and Fredenslund et al.(9). The other is a method based on statistical thermodynamics, developed by Chao and coworkers(13,14,18). The latter method seems better because it is capable of estimating not only activity coefficients but also other thermodynamic properties.

However, the group contribution method of Chao et al. cannot be used to estimate thermodynamic properties of vapor phase, because their method is based on the cell theory of Prigogine and Flory(2,21).

Thus, we have proposed here a new group contribution model based on the hole theory in order to use the new model to estimate all thermodynamic properties of both liquid and vapor phases.

1. GROUP CONTRIBUTION MODEL BASED ON THE HOLE THEORY

According to the hole theory, the configurational partition function for a mixture is given by

$$Q = g A^\nu \exp \left( -E_0/kT \right)$$

where $g$ is the combinatorial factor when groups and holes are placed on well-defined lattice sites, $v_f$ the free volume of a molecule $A$, $E_0$ the sum of lattice energy, and $A_d = m/(2\pi m k T)^{1/2}$. They are derived in the following manner.

The combinatorial factor is derived here for the system containing groups and holes according to the Flory-Huggins procedure, namely,

$$\ln g = \sum_{A} \{ N_a \ln (\eta_A/N_A) - N_a (r_A - 1) \} - N' \ln N'$$

$$+ (N + N') \ln (\sum_{A} N_a r_A + N')$$

where $N$ is the total number of molecules ($= \sum N_A$), $N_A$ the number of molecule $A$, $N'$ the number of holes, and $\eta_A$ is the constant in the Flory-Huggins' approximation. And $r_A$ is the number of segments per molecule $A$ and is given by the sum of the number of segments as follows:

$$r_A = \sum_{i} n_{Ai} r_i$$

where $r_i$ is the number of segments per group $i$ and $n_{Ai}$ is the number of group of type $i$ in molecule $A$. In this work, all segments are defined as being the same size and the group of type $i$ consists of $r_i$ segments.

Following Nitta et al.(18), the free volume of a mole-
The free volume of a group is expressed in terms of the free volume of a group, $v_{fi}$, that is,

$$\frac{v_{fi}}{A_i} = \prod_{\ell} \left[ \frac{v_{f\ell}}{A_\ell} \right]^{-c_i}$$  \hspace{1cm} (4)

where $A_i = h/(2\pi m_i kT)^{1/2}$ and $c_i$ is the external degree of freedom proposed by Prigogine.

Although several different forms have been published for the expression of free volume, Henderson's approximation seems to be reasonable. We have adopted here this approximation for the free volume of segment:

$$v_f = (1 - \alpha)v_0^f + \alpha \tau$$  \hspace{1cm} (5)

where $v_0^f$ is the free volume of segment in the solid state. According to Arai and Saito, the first term in Eq. (5) can be negligible in comparison with the second term. Then, the free volume of group $i$ becomes

$$v_{fi}/A_i = (\alpha \tau / A_i)^i$$  \hspace{1cm} (6)

where $A_i = h/(2\pi m_i kT)^{1/2}$, $\alpha$ is the hole fraction, defined as

$$\alpha = N'/(\sum r_A N_A + N')$$  \hspace{1cm} (7)

and $\tau$ is defined as a unit cell volume per segment and is given by $V_N/(\sum r_A N_A + N')$.

The sum of lattice energy $E_o$ in Eq. (1) is approximated by the sum of the pair potential energy of the nearest-neighbor pairs as follows:

$$-E_o = \sum_i \sum_j N_{ij} u_{ij}$$  \hspace{1cm} (8)

where $N_{ij}$ is the number of $i-j$ segment pairs and $u_{ij}$ is the pair potential energy between $i$ and $j$ segments. When random distribution of segments and holes at lattice sites is assumed as a crude approximation by neglecting difference in the pair potential energies, $N_{it}$ and $N_{jt}$ are readily obtained as

$$N_{it} = (z/2)(N_i r_i)((\sum r_A N_A + N'))$$  \hspace{1cm} (9)

$$N_{jt} = z((r_j N_j)/(\sum r_A N_A + N'))$$  \hspace{1cm} (10)

where

$$\zeta_i = \sum_j N_{ij}$$  \hspace{1cm} (11)

and $z$ is the coordination number. In derivation of Eqs. (9) and (10), chemical bonds in molecules are neglected.

Thus, from the above equations, the complete expression of the partition function is derived as

$$\ln Q = \sum_A N_A \left[ \ln(V_A/N_A) - r_A + 1 \right] - N' \ln N'$$

$$+ (N + N') \ln(\sum r_A N_A + N')$$

$$+ \left( \sum N_A c_A \right) \ln \left( (N'/\zeta_i) / \left( \sum r_A N_A + N' \right) \right)$$

$$+ \left( N' / T \sum (r_n n_n) (r_n n_n) u_{ij} \right)$$  \hspace{1cm} (12)

where

$$c_A = \sum_n n_A c_n r_n$$  \hspace{1cm} (13)

$$n_i = \sum_A n_A x_A$$  \hspace{1cm} (14)

$$u_{ij} = z e_{ij} / 2 \kappa$$  \hspace{1cm} (15)

In Eq. (12) the number of segments $r_A$, the number of holes $N'$, the unit cell volume per segment $\tau$, the external degree of freedom of group $c_i$ and the pair potential energy $u_{ij}$ defined by Eq. (15) are the parameters which must be evaluated from experimental data. These several parameters are determined here in the following manner.

The number of segments $r_A$ is assumed to be given by the ratio of the solid-state molar volume of group species $i$ $V_{oi}$ to that of a reference segment $V^s_o$, as follows:

$$r_A = V_{oi} / V^s_o$$  \hspace{1cm} (16)

The choice of a reference segment is somewhat arbitrary. In the present study, a methane molecule is adopted as a reference segment. Therefore, the solid-state molar volume of methane corresponds to $V^s_o$. Further, the unit cell volume per segment $\tau$ is taken as equal to the solid-state volume of methane molecule $v_0^s$.

The number of holes $N'$ can be calculated by Eq. (7) when the value of hole fraction $\alpha$ is known. The value of $\alpha$ is given by the following expression:

$$\alpha = (V_N - (V^s_o N / V^s_o) V_0) / V_N$$  \hspace{1cm} (17)

In Eq. (18) $V_{oi}$ denotes the solid-state molar volume of component $A$, and $x_A$ denotes mole fraction of component $A$.

The pair potential energy $u_{ij}$ is expressed by the empirical temperature-dependent equation

$$u_{ij} = u_{ij}^{(0)} + u_{ij}^{(1)} T + u_{ij}^{(2)} T^2$$  \hspace{1cm} (19)

where $u_{ij}^{(0)}$, $u_{ij}^{(1)}$, and $u_{ij}^{(2)}$ are coefficients which must be determined by fitting the present theory to experimental data. Combining Eqs. (7), (12), (17), and (18), the final expression of the partition function is given as

$$\ln Q = \sum_A N_A \ln \frac{v_A}{N_A} - N_A \left( \frac{V_{oi}}{V^s_o} - 1 \right) + N' \ln \frac{V_N}{V^s_o}$$

$$- V_N - \left( (V^s_o N / V^s_o) V_0 \right) \ln \frac{V_N - (V^s_o N / V^s_o) V_0}{V_N}$$

$$+ \left( \sum A N_c A \right) \ln \frac{V^s_o}{A^2 V_N} - \left( V_N - (V^s_o N / V^s_o) V_0 \right)$$

$$+ \frac{N^2 V^s_o}{V_N} \sum_{\ell} \sum (V_0 n_\ell n_\ell) u_{ij}$$  \hspace{1cm} (20)

2. Derivation of Thermodynamic Functions

All thermodynamic functions can be derived from the partition function Eq. (20) by following standard procedures.
2.1 Equation of state

Differentiating Eq. (20) with respect to $V_N$ at constant $T$ and $N_A$, an equation of state can be obtained as

$$\frac{p V_N}{kT} = 1 - \frac{V_N}{V_o^*} - \frac{V_N}{V_o^*} \ln \frac{V - V_o^*}{V} + \frac{c V_o}{V_V - V_o^*} \frac{T*}{T}$$

(21)

where

$$c = \sum_{A} c_A x_A = \sum_{A} \sum_{i} c_{A,i} x_{A,i} \frac{V_o^{i}}{V_o^*}$$

(22)

and

$$T^* = \frac{1}{V_o^2} \sum_{i} \sum_{j} (n_i V_o)(n_j V_o) \mu_{i,j}$$

(23)

It is easily shown that Eq. (21) becomes $p V_N = kT$ when we let $V_N = \infty$. That is, the present equation of state satisfies consistency at the ideal gas limit.

2.2 Heat of vaporization

The heat of vaporization is thermodynamically related to the internal energy which can be obtained by differentiating Eq. (20) with respect to $T$ at constant $V_N$ and $N_A$, that is:

$$\Delta H_{vap} = U_v - U_l + p(V_v - V_l) - RT$$

(24)

At low pressure where vapor can be regarded as an ideal gas and the volume of liquid is negligible compared with that of vapor, Eq. (24) is adequately approximated by

$$\Delta H_{vap} = \frac{R}{V_v^*} \sum_{i} \sum_{j} (n_i V_o)(n_j V_o) \mu_{i,j}$$

(25)

2.3 Activity coefficient

The activity coefficient of component $A$ in a solution is derived by the thermodynamic relation

$$\ln \gamma_A = (\mu_A - \mu_A^*)/kT - \ln x_A$$

(26)

where $\mu_A$ is chemical potential of molecule $A$ and can be obtained by differentiating Eq. (20) with respect to $N_A$ at constant $T$, $V_N$, and $N*_{A,B}$. Finally, the activity coefficient of component $A$ in a solution is given by

$$\ln \gamma_A = \frac{V_A}{V} + \frac{V_o^*}{V_o} - \ln \frac{V(V_A - V_o^*)}{V_o}$$

$$-c_A \ln \frac{V_A(V - V_o)}{V_A - V_o} + c_A \frac{V_o^* - V_o}{V}$$

$$-c_A \frac{V_o^*}{V_o^*} + \frac{2V_o^* T^*}{TV}$$

$$-\frac{2}{TV} \sum_{i} \sum_{j} (n_i V_o)(n_j V_o) \mu_{i,j}$$

(27)

where

$$T^* = \frac{1}{V_o^*} \sum_{i} \sum_{j} (n_i V_o)(n_j V_o) \mu_{i,j}$$

(28)

3. Determination of the Parameters

In this work, normal alkanes, aromatics and their solutions are employed to examine the applicability of the present model. These compounds are made up of four groups: methyl, methylene, aromatic carbon and aromatic methyl. The characteristic parameters in this model are the solid-state molar volume of group $V_o$, the external degree of freedom of respective group $c_A$, the coefficients of Eq. (19) $u_A^{i,j}$, and $u_A^{i,j}$, and the solid-state molar volume of methane $V_m^*$. These parameters have been determined by the following procedure. First, $V_m^*$ has been determined by referring to data on liquid molar volume and the heat of vaporization of pure methane. In this case, the value of $c_A$ for methane can be regarded as unity. Remaining parameters: $V_o$, $c_A$, $u_A^{i,j}$, and $u_A^{i,j}$ have been determined by referring to data on liquid molar volume and heat of vaporization of nine pure normal alkanes and three aromatics, $C_2$, $C_3$, $C_4$, $C_5$, $C_6$, $C_7$, $C_8$, $C_{10}$, benzene, toluene, and p-xylene, and activity coefficient data of a few binary systems consisting of these components. The liquid molar volume is taken from Francis' correlation or Flory's correlation at reduced temperatures from 0.3 to 0.8. The heat of vaporization in the same temperature range is taken from the correlation of Carruth and Kobayashi or Pitzer et al. The values of the above-mentioned parameters can be determined by using $\Delta H_{vap}$ and $V_v^*$ data in principle. Further, activity coefficient data on $C_9-C_{18}$ at 20°C and 60°C, $C_9$-benzene at 30°C and 50°C, and $C_9$-toluene at 20°C and 40°C have been used for fine adjustment of the parameters. A method of least squares is adopted to find the suitable values, and they are shown in Tables 1 and 2. The liquid molar volume, heat of vaporization, and activity coefficient correlated by using these parameters are shown in Figs. 1 to 7.

4. Comparison of Calculation with Experimental Data

By using the present model with the parameters shown in Tables 1 and 2, the thermodynamic properties of pure substances and phase equilibria have been predicted and are compared with the experimental values.

4.1 Liquid molar volume

By using Eq. (21) with the necessary group parameters shown in Tables 1 and 2, the liquid molar volume of $C_{14}$, $C_{18}$, and $C_{18}$ have been predicted. Comparisons of the predicted results with experimental data are shown in Fig. 1. As demonstrated by this figure, the predictions from the present model are in good agreement with experimental data.

4.2 Vapor-liquid equilibria

Vapor-liquid equilibria near atmospheric pressure...
Table 1 Group parameters

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<th>Group</th>
<th>$V_{c}$ [cc/mol]</th>
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<td>CH₃</td>
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<td>0.8110</td>
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Table 2 Group interaction parameters (available down to $T_r=0.3$)

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<td></td>
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<td>-1.448</td>
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</table>

Fig. 1 Liquid-phase molar volumes of normal alkanes

Fig. 2 Heats of vaporization of normal alkanes

Fig. 3 Liquid-phase molar volumes of aromatic hydrocarbons

Fig. 4 Heats of vaporization of aromatic hydrocarbons

Fig. 5 Activity coefficients for the $n$-hexane(1)-$n$-hexadecane(2) system

Fig. 6 Activity coefficients for the $n$-hexane(1)-benzene(2) system
can be predicted when the activity coefficient of liquid phase is known. Activity coefficients of liquid phase were predicted by Eq. (27) and are compared with experimental results in Figs. 8 to 11. As demonstrated by these figures, good agreement is obtained. Therefore, the group contribution model derived here can be successfully used to predict vapor-liquid equilibria.

4.3 Solid-liquid equilibria

The present model was adopted to predict solid-liquid equilibria in order to examine whether or not it is applicable in lower-temperature regions. Assuming that the solid phase is pure solute, the mole fraction of solute A in the solution can be expressed by

\[ x_A = \left( \frac{f_A^S}{f_A^L} \right) \left( \frac{1}{f_A^L} \right) \]

(29)

where \( f_A^S \) is the fugacity of solid phase for pure A, \( f_A^L \) the fugacity of subcooled liquid phase for pure component A. The fugacity ratio \( f_A^S/f_A^L \) can be estimated by

\[ \ln \frac{f_A^S}{f_A^L} = \frac{\Delta S_{f,A}}{R} \left( 1 - \frac{T_{m,A}}{T} \right) \]

(30)

where \( T_{m,A} \) and \( \Delta S_{f,A} \) are respectively the melting temperature and molar entropy of fusion at \( T_{m,A} \) for the solute A. The values of \( T_{m,A} \) and \( \Delta S_{f,A} \) can be taken from the literature. Therefore, solubilities expressed by mole fraction \( x_B \) can easily be predicted from Eq. (29) by calculating activity coefficients from Eq. (27). Figures 12 to 15 show comparisons between predicted and experimental solubilities. There is fairly good agreement. It is noted that no physical properties of...
these systems have been adopted to determine the group parameters.

4.4 Vapor pressure, saturated vapor volume and second virial coefficient

The vapor pressures of normal alkanes (C₂, C₄, C₆ and C₈) have been predicted, based on a thermodynamic condition, that is, the equality of chemical potentials for component \( i \) in both vapor and liquid phases. The saturated molar volume of vapor can be predicted by Eq. (21) by adopting the experimental values of \( p^\circ \) and \( T \). The comparisons between predicted and experimental vapor pressures and saturated molar volume of vapor are illustrated in Figs. 16 and 17, respectively. From Eq. (21), the second virial coefficient can be readily derived as

\[
B = \frac{V^\circ}{2V^\circ} + cV^\circ - \frac{V^\circ T^*}{T}
\]

The second virial coefficients of several substances predicted by the present model are given in Fig. 18 and
are compared with the experimental values. It is shown that the prediction for saturated molar volume of vapor gives good results. As shown in Fig. 16, the predicted vapor pressures show fairly good agreement with the experimental values, except for n-octane. However, a somewhat large discrepancy is shown for the second virial coefficient.

Conclusion

A new group contribution model is proposed based on the hole theory. The group parameters required for the calculation have been determined by using the molar volume of liquid and the heat of vaporization for pure normal alkanes and aromatics, and the activity coefficient data of binary mixtures consisting of these compounds. The present model can successfully be used to predict the liquid molar volume and the heat of vaporization. It can also be used to predict the activity coefficient of liquid phase, so that vapor-liquid equilibria and solid-liquid equilibria can be calculated with good agreement.

The equation of state derived from the present model satisfies the ideal gas limit \( pV_N = NkT \) at \( V_N = \infty \). Therefore, it can be used to calculate thermodynamic properties of gaseous phase. Although agreement with the experimental results is not necessarily good, it is noted that the group contribution model based on the hole theory is capable of calculating the thermodynamic properties of vapor phase as well as liquid phase.

Nomenclature

- \( B \) = second virial coefficient \([\text{cc/mol}]\)
- \( c \) = molar volume of component \( A \) \([\text{cc/mol}]\)
- \( c_{i_A} \) = external degree of freedom for molecule \( A \) \([\text{cc/mol}]\)
- \( c_i \) = external degree of freedom for group \( i \) \([\text{cc/mol}]\)
- \( E_0 \) = sum of lattice energy \([\text{cal}]\)
- \( f_{L}^{A} \) = fugacity of pure component \( A \) in liquid phase \([\text{atm}]\)
- \( f_{S}^{A} \) = fugacity of pure component \( A \) in solid phase \([\text{atm}]\)
- \( g \) = combinatorial factor
- \( \Delta H^{vap} \) = heat of vaporization \([\text{cc-atm/mol}]\)
- \( k \) = Boltzmann constant \([\text{erg/K}]\)
- \( m_A \) = mass per molecule \( A \) \([\text{g}]\)
- \( m_i \) = mass per group \( i \) \([\text{g}]\)
- \( m_0 \) = mass per segment \([\text{g}]\)
- \( \bar{N} \) = sum of the number of molecules
- \( N_{A} \) = number of molecule \( A \)
- \( N' \) = number of holes
- \( N_{i} \) = number of group \( i \)
- \( N_{i,j} \) = number of \( i-j \) segment pairs
- \( n_{i,A} \) = number of group \( i \) in molecule \( A \)
- \( n_i \) = number of molecule \( i \)
- \( p \) = pressure \([\text{atm}]\)
- \( p^{s} \) = saturated vapor pressure \([\text{atm}]\)
- \( Q \) = configurational vapor pressure \([\text{cal}]\)
- \( r_A \) = number of segments per molecule \( A \)
- \( r_i \) = number of segments per group \( i \)
- \( R \) = gas constant \([\text{cc-atm/mol-K}]\)
- \( \Delta S^{A}_{f} \) = entropy of fusion of pure component \( A \) at \( T_{m.A} \) \([\text{cal/mol-K}]\)
- \( T \) = system temperature \([\text{K}]\)
- \( T_{m.A} \) = melting-point temperature of pure component \( A \) \([\text{K}]\)
- \( T_c \) = critical temperature \([\text{K}]\)
- \( T_r \) = reduced temperature \( = T/T_c \) \([\text{--}]\)
- \( T^* \) = reduced temperature defined by Eq. (23) \([\text{K}]\)
- \( u_{ij} \) = \( i-j \) segment interaction parameter defined by Eq. (15) \([\text{K}]\)
- \( V \) = molar volume of mixture \([\text{cc/mol}]\)
- \( V_{A} \) = molar volume of component \( A \) \([\text{cc/mol}]\)
- \( V_{0} \) = solid-state molar volume of component \( A \) \([\text{cc/mol}]\)
- \( V_{0,A} \) = solid-state molar volume of mixture \([\text{cc/mol}]\)
- \( V_{0,i} \) = solid-state molar volume of group \( i \) \([\text{cc/mol}]\)
- \( V_{0}^{*} \) = solid-state molar volume of methane \([\text{cc/mol}]\)
- \( V_{N} \) = system volume containing \( ar{N} \) molecules \([\text{cc}]\)
- \( v_{f} \) = free volume of segment \([\text{cc}]\)
- \( v_{S}^{A} \) = free volume of component \( A \) in solid state \([\text{cc}]\)
- \( v_{S,i} \) = free volume of group \( i \) \([\text{cc}]\)
- \( v_{S}^{*} \) = free volume of methane \([\text{cc}]\)
- \( x_A \) = mole fraction of component \( A \) \([\text{--}]\)
- \( z \) = coordination number
- \( \alpha \) = hole fraction \([\text{--}]\)
- \( \gamma_A \) = activity coefficient of component \( A \) \([\text{--}]\)
- \( \varepsilon_{i,j} \) = pair potential energy between \( i \) and \( j \) segments \([\text{cal}]\)
- \( \eta_A \) = constant in Flory-Huggins’ approximation \([\text{cal}]\)
- \( \mu_A \) = chemical potential of molecule \( A \) in mixture \([\text{cal}]\)
- \( \mu_A^{S} \) = chemical potential of molecule \( A \) (pure state) \([\text{cal}]\)
- \( \tau \) = unit cell volume \([\text{cc}]\)

Literature Cited

SOLUBILITIES OF NITROGEN IN BINARY SOLUTIONS OF ACETONE WITH CYCLOHEXANE, BENZENE, CHLOROFORM AND 2-PROpanol

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Experimental data of nitrogen solubilities in four binary solvents with acetone and those of excess molar volumes of the solvents are presented at 25°C. Cyclohexane, benzene, chloroform, and 2-propanol are selected as the other component. The experimental excess quantities of gas solubility are represented almost quantitatively by a generalized equation of Flory-Huggins type with physical and chemical terms. It is also shown that the similarity between the excess quantity of gas solubility and the relative excess molar volume holds for the systems investigated except for the benzene-acetone system.

Gas solubility in liquid is a fundamental property for designing gas absorption and stripping columns in chemical industries. Gas solubility data in mixed solvents are especially required in both practical and theoretical fields; however, there are few reliable data available to evaluate some predictive methods for gas solubilities in mixed solvents. From the viewpoint of molecular thermodynamics, a dissolved gas molecule in a solvent is considered to be a probe for detecting intermolecular forces between the gas and the solvent.

In this work, experimental data for nitrogen solubilities in four binary mixtures with acetone at 25°C are presented. Density measurements were also performed for obtaining the excess volumes of the binary mixtures. Cyclohexane, benzene, chloroform, and 2-propanol were selected as a component of each binary mixture because they are different from each other in their physical and chemical interactions with acetone.

1. Experimental

1.1 Apparatus and procedure

The solubility apparatus and procedures were the same ones as previously described\(^{9,14}\), which were similar to those of Horii\(^{11}\). The dissolution vessel was 80 cm\(^3\) in volume and immersed in a water bath controlled to \(\pm 0.03^\circ\)C. The gas buret was housed in an air thermostat regulated within \(\pm 0.06^\circ\)C. Mixed solvent of a known composition was first boiled under reflux at atmospheric pressure. It was then transfer-