intensity for flowing gas mixtures with a pilot-stabilized flame.

2. Butane-air mixtures for the system investigated will remain unignited for velocities greater than 666 ft./sec.

3. Turbulent boundary formation and, to a lesser extent quenching, adversely affected ignition to a great degree in the 1-in. combustion chamber. Any future studies should thoroughly consider these factors.

## NOTATION

$A, B, C$ = constants
$d_w$ = thickness of screen wire
$f$ = % turbulent intensity/100
$l$ = scale of turbulence, in.
$U$ = cold stream velocity ft./sec, based on empty combustion chambers
$Y$ = composition, mole %

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# A Thermodynamic Correlation of Nonpolar Gas Solubilities in Polar, Nonassociated Liquids

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The regular-solution theory of Hildebrand (*15*) and Scatchard (*31*) has received much attention in recent years. But the Hildebrand equation, Equation (23), is applicable only to nonpolar systems. Furthermore, because of its approximate nature, the Hildebrand equation has not been used as successfully in theoretical predictions of gas solubilities in liquids as in forming the basis of some semiempirical correlations (*5, 11, 29*). While the regular-solution equation consists of two terms, the internal energy of mixing and the ideal entropy of mixing, it should be noted that both terms are approximate even for nonpolar solutions. The errors resulting from these approximations however have been fortunately cancelled (*32*). The Hildebrand equation has thus been well accepted by chemical engineers and chemists because of its overall fitness to the nonpolar solutions and its convenience in application.

This paper deals mainly with nonpolar gas solubilities in polar, nonassociated liquids. Those polar liquids which exist in the form of monomers are here considered nonassociated. For internal energy of mixing the general equation of Hildebrand and Wood (*16*) is used to extend the regular-solution theory to binary solutions consisting of a nonpolar and a polar, nonassociated liquid. The entropy of mixing can also be considered ideal for such solutions especially if the solution is dilute. Empirically the partial molal entropy of mixing can be evaluated for gas-liquid solutions from the slope of the straight line when log $x_2$ is plotted vs. log $T$ (*28*). Examining plots of this kind one will find that for each nonpolar gas studied in this work the slopes for polar, nonassociated liquids generally follow the slope pattern of nonpolar liquids very well. This suggests that the degree of randomness for both kinds of solution may be considered as approximately the same, and the ideal solution model for entropy of mixing can be retained for binary solutions consisting of a nonpolar and a polar, nonassociated component. Together with considerations of intermolecular forces caused by dipole-dipole interactions, an equation is derived to express the activity coefficient of the nonpolar component in such systems. This equation is then applied to gas-liquid solutions to provide the thermodynamic framework for the correlation of experimental solubility data of nonpolar gases in polar, nonassociated liquids. With this correlation it is possible to estimate low pressure gas solubilities in other polar, nonassociated liquids when no experimental data are available.

## PREVIOUS APPROACHES

Most of the previous correlations, empirical or semiempirical, concerning nonpolar gas solubilities in liquids have been confined to nonpolar liquids (*5, 11, 20, 24*) or to a specific liquid (*14*). Gjaldbaek and Anderson (*10*) studied the solubilities of carbon dioxide, oxygen, carbon monoxide, and nitrogen at 25°C. in polar, nonassociated liquids and found empirically that the difference between the values of experimental solubility data and those predicted by the Hildebrand equation is qualitatively proportional to the dipole moments of the liquids for each gas. Empirically, Gjaldbaek (*8, 9*) also correlated the solubilities of methane, nitrogen, argon, and ethane in alcohols and water with the dielectric constants of the liquids and the polarizabilities of the gases. His results were satisfactory for alcohols but not for water. Recently Prausnitz and Shair (*29*), in their semiempirical correlation of nonpolar gas solubilities in nonpolar liquids, suggested an empirical plot to estimate certain gas solubilities in polar liquids, provided solubility data for other gases in this solvent are available. This empirical plot was based on the

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functional equation of the following form for gaseous component 2:

$$\ln \gamma_2 = V_2 F(T, \delta_2, \text{properties of solvent}) \qquad (1)$$

## THEORETICAL DEVELOPMENT

From statistical considerations Hildebrand and Wood (*15, 16*) derived an equation for binary mixtures forming regular solutions. The internal energy of mixing can be expressed as

$$\Delta E^M = 2\pi N^2 (N_1V_1 + N_2V_2)\phi_1\phi_2 \left[ \frac{2}{V_1V_2} \int_0^\infty \Phi_{12}\rho^*{}_{12} r^2 dr - \frac{1}{V_1^2}\int_0^\infty \Phi_{11}\,\rho_1\, r^2 dr - \frac{1}{V_2^2}\int_0^\infty \Phi_{22}\,\rho_2\, r^2 dr \right] \qquad (2)$$

The following assumptions were made in the derivation of Equation (2):

1. The additivity of the energies of molecular pairs.
2. No change in volume on mixing at constant pressure and temperature.
3. $\rho^*{}_{11} = \rho_1$, $\rho^*{}_{22} = \rho_2$, $\rho^*{}_{12} = \rho^*{}_{21}$ where $\rho^*{}_{11} = (\rho_{11})/(\phi_1)$, $\rho^*{}_{12} = (\rho_{22})/(\phi_2)$, $\rho^*{}_{12} = (\rho_{12})/(\phi_2)$, $\rho^*{}_{21} = (\rho_{21})/(\phi_1)$.

For liquids, especially for liquid mixtures, very little is known about the radial distribution function, and the validity of the third assumption cannot be rigorously justified. For $\rho^*{}_{21} = (\rho_{21})/(\phi_1)$ this assumption means that the probability of finding molecules of type 1 surrounding a molecule of type 2 is directly proportional to the volume fraction of component 1 in the solution. It can be true only if the solution is truly random. In Hildebrand's opinion (*15*) however this introduces a small and usually negligible correction for nonpolar binary solutions, although even nonpolar solutions are not truly random as indicated by their nonideal entropy of mixing (*20*). For binary solutions consisting of a nonpolar and a polar, nonassociated component the degree of randomness has been compared with that for nonpolar solutions previously. The third assumption is therefore retained in this work.

Table 1. Solubility Parameters for Nonpolar Liquids

| Nonpolar liquids | $\delta_1$, (cal./cc.)$^{1/2}$ (*15, 20*) |
|---|---|
| $n$-$C_7F_{16}$ | 5.70 |
| $(C_4F_9)_3N$ | 5.90 |
| $C_7F_{14}$* | 6.00 |
| $C_8F_{16}$† | 6.10 |
| $i$-$C_8H_{18}$** | 6.85 |
| $n$-$C_6H_{14}$ | 7.30 |
| $n$-$C_7H_{16}$ | 7.45 |
| $n$-$C_8H_{18}$ | 7.55 |
| $C_7H_{14}$†† | 7.85 |
| $c$-$C_6H_{12}$ | 8.20 |
| $CCl_4$ | 8.60 |
| $C_6H_6$ | 9.15 |
| $CS_2$ | 10.0 |

* Perfluoromethylcyclohexane.
† Perfluorodimethylcyclohexane.
** 2, 2, 4-trimethylpentane.
†† Methylcyclohexane.

There is generally a volume change on mixing. However this change is small compared with the volumes of the pure components for most of the binary liquid mixtures. For gas-liquid mixtures the volume of the gas decreases enormously during its dissolution in liquids, and the second assumption is no longer valid. However this difficulty can be overcome by the use of the Prausnitz-Shair hypothesis (29) that the gaseous component is first converted to a hypothetical liquid and is then mixed with the liquid solvent at constant volume.

The first assumption is not exactly true but has been used successfully as the basis for most of the theories of liquids and solutions. As pointed out by Hirschfelder, Curtiss, and Bird (*17*) this assumption is generally valid for nonpolar and polar, nonassociated molecules but not for molecules which tend to associate or for molecules which are capable of hydrogen bonding.

Equation (2) has hitherto been used to derive the familiar equation of regular-solution theory for nonpolar systems, Equation (26), by employing the Lennard-Jones potential function to evaluate the integrals in Equation (2). Since the assumptions discussed above can be expected to hold for polar, nonassociated molecules, if an appropriate form of potential function is employed, Equation (2) can be used to derive a relation for binary mixtures consisting of a nonpolar and a polar, nonassociated liquid. This derivation, parallel to Hildebrand's (*15*), is carried out in the following manner.

While the Lennard-Jones potential function is still used for the nonpolar liquid, designated as *component 2*, the Stockmayer potential function is used for the polar, nonassociated liquid, designated as *component 1*, in the evaluation of the integrals in Equation (2).

Lennard-Jones potential function (*17*)

$$\Phi_{22} = 4\epsilon_2 \left[ \left(\frac{\sigma_2}{r}\right)^{12} - \left(\frac{\sigma_2}{r}\right)^{6} \right]$$

where (3)

$$\sigma = \left(\frac{1}{2}\right)^{1/6} d_0 \qquad (4)$$

Stockmayer potential function (*17*)

$$\Phi_{11} = 4\epsilon_1 \left[ \left(\frac{\sigma_1}{r}\right)^{12} - \left(\frac{\sigma_1}{r}\right)^{6} \right] - \frac{\mu_1^2}{r^3} g(\theta, \phi) \qquad (5)$$

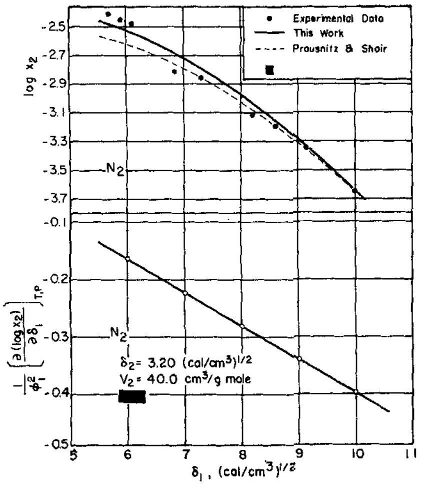

**Fig. 1. Determination of $V_2$ and $\sigma_2$. Gas, nonpolar; liquid, nonpolar; temperature, 25°C.; partial pressure of gas, 1 atm.**

The potential function between molecule 1 and molecule 2 can be expressed as (*17*)

$$\Phi_{12} = 4\epsilon'_{12} \left[ \left(\frac{\sigma'_{12}}{r}\right)^{12} - \left(\frac{\sigma'_{12}}{r}\right)^{6} \right] \qquad (6)$$

where

$$\epsilon'_{12} = \sqrt{\epsilon_1\epsilon_2\xi^2} \qquad (7)$$

$$\sigma'_{12} = \frac{1}{2}(\sigma_1 + \sigma_2)\,\xi^{-1/6} \qquad (8)$$

$$\xi = 1 + \frac{1}{4} \cdot \frac{\alpha_2}{\sigma_2^{\,3}\sqrt{\epsilon_2}} \cdot \frac{\mu_1^{\,2}}{\sigma_1^{\,8}\sqrt{\epsilon_1}} \qquad (9)$$

In accordance with Hildebrand and Scott (*15*) the potential energy per mole of liquid $E'$, or the internal energy of vaporization with opposite sign $-\Delta E^V$, can be expressed as

$$E' = -\Delta E^V = \frac{2\pi N^2}{V}\int_0^\infty \Phi\,\rho(r) r^2 dr \qquad (10)$$

and $\rho\ (y)$ is a universal function if $y = r/d_m$, where $d_m$ is the position of the first maximum in the plot of $\rho\ (r)$ vs. $r$. Hence

$$-\Delta E^V = \frac{2\pi N^2}{V}\int_0^\infty \Phi\,\rho(y) d_m^{\,3} y^2 dy \qquad (11)$$

Assuming $d_0 \cong d_m \cong d$, and applying Equation (3) to Equations (10) and (11), one gets

$$\frac{\Delta E_2^{\,V}}{V_2} = -\frac{2\pi N^2}{V_2^2}\int_0^\infty \Phi_{22}\rho_2 r^2 dr = \frac{8\pi N^2}{V_2^2 d_2^3} \cdot \epsilon_2\sigma_2^{\,6}[f] \qquad (12)$$

where

$$[f] = \int_0^\infty \left[\frac{1}{y^4} - \frac{1}{2y^{10}}\right] \rho(y) dy \qquad (13)$$

Similarly, applying Equation (5) to

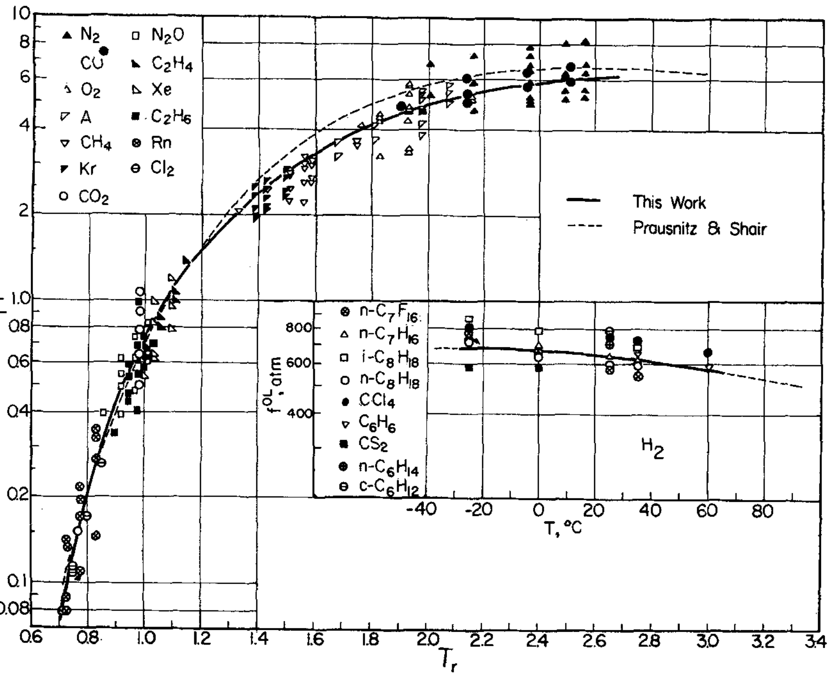

**Fig. 2. Fugacity of hypothetical liquid at pressure of 1 atm.**

Equations (10) and (11), one obtains

$$\frac{\Delta E_1^V}{V_1} = -\frac{2\pi N^2}{V_1^2}\int_0^\infty \Phi_{11}\rho_1 r^2 dr$$

$$= \frac{8\pi N^2}{V_1^2 d_1^3}\cdot \epsilon_1\sigma_1^6[\int]$$

$$+\frac{2\pi N^2\mu_1^2}{V_1^2}\int_{g_1}^{g_2}\int_0^\infty \frac{g\rho(y)}{y}\,dydg \tag{14}$$

where $dg = d\theta_1 d\theta_2 d(\phi_2 - \phi_1)$

$$\int_{g_1}^{g_2} = \int_0^{2\pi}\int_0^{\pi}\int_0^{\pi}$$

Rearranging one gets

$$\frac{8\pi N^2}{V_1^2 d_1^3}\cdot \epsilon_1\sigma_1^6[\int] = \frac{\Delta E_1^V}{V_1} + \Delta \tag{15}$$

where

$$\Delta = -\frac{2\pi N^2\mu_1^2}{V_1^2}\int_{g_1}^{g_2}\int_0^\infty \frac{g\rho(y)}{y}\,dydg \tag{16}$$

It should be noted here that $\Delta$ is a function of the properties of liquid 1 alone under a given condition of pressure and temperature, and each should be a constant for any polar, nonassociated liquid. Now applying Equations (6), (7), and (8), taking $d_{12} = (d_1 + d_2)/2$, and assuming the equality of the geometric mean and the arithmetic mean of $\sigma$ for component 1 and component 2, one gets

$$\frac{2\pi N^2}{V_1 V_2}\int_0^\infty \Phi_{12}\rho^*_{12} r^2 dr$$

$$= \frac{2\pi N^2}{V_1 V_2}\int_0^\infty \Phi_{12}\rho(y)\, d^3_{12} y^2 dy$$

$$= -\xi\ \delta_2(\delta_1^2 + \Delta)^{1/2} \tag{17}$$

where $\delta = \left(\frac{\Delta E^V}{V}\right)^{1/2}$ solubility parameter.

Substituting Equations (12), (14), and (17) into Equation (2) one obtains for the internal energy of mixing

$$\Delta E^M = (N_1V_1 + N_2V_2)\phi_1\phi_2[\delta_1^2 + \delta_2^2 - 2\xi\delta_2(\delta_1^2 + \Delta)^{1/2}] \tag{18}$$

and the partial molal internal energy of mixing for component 2 is

$$\Delta E_2^{-M} = \left(\frac{\partial\,\Delta E^M}{\partial N^2}\right)_{N_1,\,T,\,P}$$

$$= V_2\phi_1^2[\delta_1^2 + \delta_2^2 - 2\xi\delta_2(\delta_1^2 + \Delta)^{1/2}] \tag{19}$$

The partial molal entropy of mixing for component 2 is ideal as discussed previously. Hence

$$\Delta S_2^{-M} = -R\ln x_2 \tag{20}$$

If the volume change on mixing can be neglected, the partial molal free energy of mixing can be expressed as

$$\Delta G_2^{-M} = \Delta E_2^{-M} - T\Delta S_2^{-M} \tag{21}$$

When one substitutes Equations (19) and (20) into Equation (21), the final equation for systems consisting of a nonpolar and a polar, nonassociated liquid is

$$RT\ln\gamma_2 = V_2\phi_1^2[\delta_1^2 + \delta_2^2 - 2\xi\delta_2(\delta_1^2 + \Delta)^{1/2}] \tag{22}$$

For nonpolar binary systems, $\mu = 0$, $\Delta = 0$, $\xi = 1$, Equation (22) reduces to the familiar form of the Hildebrand equation

$$RT\ln\gamma_2 = V_2\phi_1^2(\delta_1 - \delta_2)^2 \tag{23}$$

In the above derivations all the assumptions are those used by Hildebrand in his derivation of Equation (23) except those introduced by the Stockmayer potential function, Equations (5) and (6).

## APPLICATION OF EQUATIONS (22) AND (23) TO GAS-LIQUID SOLUTIONS

Equations (22) and (23) were derived on the assumption that there is no volume change on mixing. They cannot be applied to gas-liquid solutions because of the great change of gas volume on mixing and the difficulty in evaluating the solubility parameter and the activity coefficient of the gaseous component as discussed by Prausnitz (*28*). To overcome these difficulties Prausnitz and Shair (*29*) hypothesized a two-step dissolution process. They arrived at the following equation:

TABLE 2. MOLAL VOLUMES OF HYPOTHETICAL LIQUID AND SOLUBILITY PARAMETERS FOR GASEOUS SOLUTES

| Gas | $\delta_2'$ (cal./cc.)$^{1/2}$ This work | $\delta_2'$ (cal./cc.)$^{1/2}$ Prausnitz and Shair | $V_2$, cc./g. mole This work | $V_2$, cc./g. mole Prausnitz and Shair | $\overline{V}_2$, cc./g. mole, experimental partial molal volume of gaseous component (*15, 18*) at 25°C. |
|---|---|---|---|---|---|
| $N_2$ | 3.20 | 2.58 | 40.0 | 32.4 | 53 in benzene and in $CCl_4$ |
| CO | 3.61 | 3.13 | 40.2 | 32.1 | 52 in benzene<br>53 in $CCl_4$ |
| $H_2$ | 3.83 | 3.25 | 37.3 | 31.0 | 36 in benzene<br>38 in $CCl_4$ |
| $O_2$ | 4.70 | 4.0 | 49.6 | 33.0 | 46 in benzene<br>45 in $CCl_4$ |
| A | 5.00 | 5.33 | 55.0 | 57.1 | |
| $CH_4$ | 5.28 | 5.68 | 50.7 | 52.0 | 52 in benzene and in $CCl_4$ |
| Kr | 5.90 | 6.4 | 52.0 | 65.0 | |
| $CO_2$ | 6.00 | 6.0 | 62.0 | 55.0 | |
| $N_2O$ | 6.20 | | 51.0 | | |
| $C_2H_4$ | 6.30 | 6.6 | 50.0 | 65.0 | 61 in benzene and in $CCl_4$ |
| Xe | 6.30 | | 45.8 | | |
| $C_2H_6$ | 6.35 | 6.6 | 70.0 | 70.0 | 67 in benzene and in $CCl_4$ |
| Rn | 6.80 | 6.83 | 60.0 | 70.0 | |
| $Cl_2$ | 8.60 | 8.70 | 55.0 | 74.0 | 53 in *n*-heptane (*12*) |

$$-\log x_2 = \frac{V_2\phi_1^2}{2.303RT}(\delta_1-\delta_2)^2 + \log f^{0L} \quad (24)$$

Equation (24), together with the theorem of corresponding states, forms the thermodynamic framework of the Prausnitz-Shair correlation of nonpolar gas solubilities in nonpolar liquids (*29*) [Correlation (A)].

Similarly, when Equation (22) is applied to the two-step dissolution process, the solubility of a nonpolar gas in a polar, nonassociated liquid, in the absence of any chemical effects, can be expressed theoretically as

$$-\log x_2 = \frac{V_2\phi_1^2}{2.303RT}[\delta^2_1 + \delta_2^2 - 2\xi\delta_2(\delta_1^2+\Delta)^{1/2}] + \log f^{0L} \quad (25)$$

$\xi$ is defined by Equation (9). Values of $\alpha$, $\sigma$, and $\epsilon$ were taken from reference *17*, and $(\alpha_2)/(\sigma_2^3\sqrt{\epsilon_2})$ was calculated for the gases correlated here. Except for hydrogen with a value of about $0.04 \times 10^7$ erg.$^{-1/2}$, all of the other gases have a value for $(\alpha_2)/(\sigma_2^3\sqrt{\epsilon_2})$ of about $0.03 \times 10^7$ erg.$^{-1/2}$. Hence $\xi$ has a value of approximately 1.01 to 1.05 as $(\mu_1^2)/(\sigma_1^3\sqrt{\epsilon_1})$ for the liquid solvents ranges from $1 \times 10^{-7}$ to $5 \times 10^{-7}$ erg.$^{1/2}$. For binary solutions of different gases with a specific liquid solvent, $\xi$ is about the same for all gases except hydrogen. For practical purposes $\xi$ can be taken as having a value of 1 without serious error. This is exactly the same as neglecting the induction force between a nonpolar and a polar molecule, which usually is small compared with other intermolecular forces, such as dispersion and orientation (*17*).

As a result of the above discussion Equation (25) becomes

$$-\log x_2 = \frac{V_2\phi_1^2}{2.303RT}[\delta_1^2 + \delta_2^2 - 2\delta_2(\delta_1^2+\Delta)^{1/2}] + \log f^{0L} \quad (26)$$

which reduces to Equation (24) for nonpolar systems. Equation (26) will be used in this paper as the thermodynamic basis for the proposed correlation of nonpolar gas solubilities in polar, nonassociated liquids [Correlation (B)]. This proposed correlation will utilize the result of Correlation (A). It is important therefore to review the latter correlation.

## CORRELATION (A): NONPOLAR GAS SOLUBILITIES IN NONPOLAR LIQUIDS

TABLE 3. SOURCE AND TEMPERATURE RANGE OF GAS SOLUBILITY DATA IN NONPOLAR LIQUIDS
Partial pressure of gas: 1 atm.

| Gas | Literature cited | Temperature range, °K. |
|---|---|---|
| $N_2$ | (*11, 18, 20, 21*) | 253 → 323 |
| CO | (*6, 18*) | 253 → 333 |
| $H_2$ | (*5, 18*) | 248 → 333 |
| $O_2$ | (*6, 18, 20*) | 273 → 333 |
| A | (*4, 13, 20, 25, 30*) | 253 → 313 |
| $CH_4$ | (*9, 18, 20*) | 253 → 333 |
| Kr | (*3*) | 289 → 313 |
| $CO_2$ | (*7, 20*) | 298 |
| $N_2O$ | (*18, 38*) | 263 → 313 |
| $C_2H_4$ | (*18*) | 283 → 323 |
| Xe | (*2, 4*) | 289 → 316 |
| $C_2H_6$ | (*13, 18, 20*) | 273 → 313 |
| Rn | (*25*) | 273 → 313 |
| $Cl_2$ | (*12, 20, 22, 35, 36*) | 298 → 353 |

In correlating nonpolar gas solubilities in nonpolar liquids Prausnitz and Shair (*29*) determined the three parameters according to Equation (24) for the gaseous component as a hypothetical liquid: the fugacity, the molal volume, and the solubility parameter from experimental solubility data taken from the literature. The procedure has been described in detail in their original paper. Since more experimental solubility data for nonpolar gases in nonpolar liquids were available than those they have used, the numerical values for the parameters, $f^{0L}$, $V_2$, and $\delta_2$ were redetermined in this work. In the work of Prausnitz and Shair $f^{0L}$ was considered to be independent of the properties of the liquid solvent in accordance with the two-step dissolution process, and thus it was possible to correlate $f^{0L}$ by means of the theorem of corresponding states. Both $V_2$ and $\delta_2$ were treated as constants. $\delta_1$ was also taken as a constant, and the value calculated from its thermodynamic definition $\delta_1 = \left(\frac{\Delta E_1^V}{V_1}\right)^{1/2}$ at 25°C. was used (Table 1). To check these simplifications the necessary conditions in using Correlation (A) with the above assumptions will be examined.

Since $f^{0L}$ is independent of the properties of the liquid solvent and $\phi_1$ changes only slightly with liquid solvents, differentiating Equation (26) with respect to $\delta_1$ one gets

$$\frac{T}{\phi_1^2}\left[\frac{\partial(\log x_2)}{\partial\delta_1}\right]_{T,P} = -\frac{2V_2}{2.303R}\delta_1 + \frac{2V_2}{2.303R}\delta_2 \quad (27)$$

and

$$\frac{T}{\phi_1^2}\left[\frac{\partial^2(\log x_2)}{\partial\delta_1^2}\right]_{T,P} = -\frac{2V^2}{2.303R} \quad (28)$$

Equations (27) and (28) require the following necessary conditions of the experimental solubility data:

1. A plot of $\log x_2$ vs $\delta_1$ at any temperature should give a curve of negative curvature.
2. $\frac{T}{\phi_1^2}\left[\frac{\partial(\log x_2)}{\partial\delta_1}\right]_{T,P}$ evaluated from the above plot should be linear with $\delta_1$.
3. Since $V_2$ is always positive, to be of any physical significance the curve of $\log x_2$ vs. $\delta_1$ may have a maximum, at which $\delta_2 = \delta_{1\,\max}$, and $-\log x_2 = \log f^{0L}$ in accordance with Equation (28).
4. From the plot of

$$\frac{T}{\phi_1^2}\left[\frac{\partial(\log x_2)}{\partial\delta_1}\right]_{T,P}$$

vs. $\delta_1$, $V_2$ can be determined from the slope which must be negative in order to obtain positive values for $V_2$, and $\delta_2$ can be determined from the intercept which must be positive in order to obtain positive values for $\delta_2$.

All low-pressure solubility data of nonpolar gases in nonpolar liquids available in the literature were collected. The reliability of these data was examined by carefully comparing data from different sources and observing the linearity of $\log x_2$ with $\log T$ in accordance with Kobatake and Hildebrand (*20*). The experimental results of early investigators, such as Just (*19*) and McDaniel (*26*), disagreed with those of several later investigators and were excluded in this work. Horiuti (*18*) reported very reliable solubility data of many gases in both nonpolar and polar liquids. His data were used extensively for the correlations in this work.

TABLE 4. VALUES OF $\Delta$ AND $\delta_1$ FOR POLAR, NONASSOCIATED LIQUIDS

| Liquid | $\Delta$, cal./cc. | $\delta_1$, (cal./cc.)$^{1/2}$ | Source of $\delta_1$ |
|---|---|---|---|
| Ethyl ether, $(C_2H_5)_2O$ | –2.80 | 7.45 | (*15*) |
| Toluene, $C_6H_5CH_3$ | 1.79 | 8.90 | (*15*) |
| Octanol, $C_8H_{17}OH$ | 7.52 | 9.20 | (*1*) |
| Chloroform, $CHCl_3$ | 8.53 | 9.25 | (*10*) |
| Methyl acetate, $CH_3COOCH_3$ | 5.80 | 9.50 | (*10*) |
| Chlorobenzene, $C_6H_5Cl$ | 7.76 | 9.50 | (*15*) |
| Acetone, $CH_3COCH_3$ | 6.87 | 9.65 | (*10*) |
| 1, 2-dibromoethane, 1, 2-$C_2H_4Br_2$ | 17.4 | 10.5 | (*10*) |
| Pyridine, $C_5H_5N$ | 27.5 | 10.7 | (*10*) |
| Aniline, $C_6H_5NH_2$ | 39.6 | 11.55 | (*10*) |

To determine $V_2$ and $\delta_2$ the experimental data were treated by a trial-and-error graphical method in accordance with the necessary conditions discussed above for a total of fourteen gases in thirteen nonpolar liquid solvents (Tables 1 and 2). A representative plot of this graphical method is shown in Figure 1 for nitrogen. For comparison values of log $x_2$ were also calculated by the use of the values of $V_2$, $\delta_2$, and $f^{oL}$ reported by Prausnitz and Shair with the aid of Equation (24) and were plotted in Figure 1 as shown by the dotted line. The results for fourteen gases are tabulated in Table 2, where the values of $V_2$ determined in this work and those by Prausnitz and Shair are compared with the experimental partial molal volumes of the gaseous component taken from the literature. The comparison shows qualitative agreement.

Values of $f^{oL}$ were then calculated with Equation (24) and the values of $V_2$ and $\delta_2$ just determined. A single, smooth curve of $f^{oL}/P_c$ (at 1 atm.) was obtained for all of the gases according to the theorem of corresponding states (Figure 2). The results of Prausnitz and Shair are also compared.

The sources and temperature range of the solubility data used in this correlation are summarized in Table 3. For 213 selected data points the average deviation for fourteen gases in thirteen nonpolar liquids is 13.1%. The detailed calculation of percentage deviation for each experimental point is tabulated in reference *38*.

### CORRELATION (B): NONPOLAR GAS SOLUBILITIES IN POLAR, NONASSOCIATED LIQUIDS

Before Equation (26) is used to correlate nonpolar gas solubilities in polar, nonassociated liquids, the five parameters in Equation (26) are now considered separately.

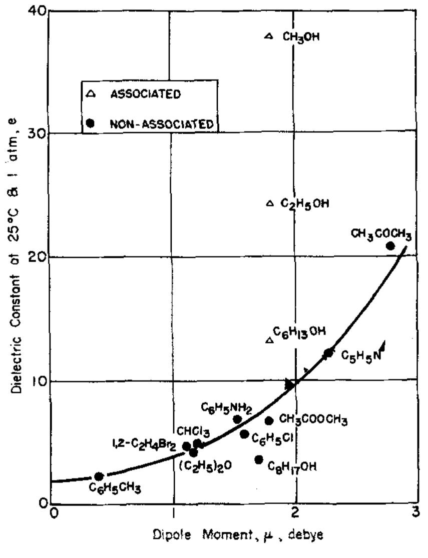

**Fig. 3. Dielectric constant vs. dipole moment for polar liquids.**

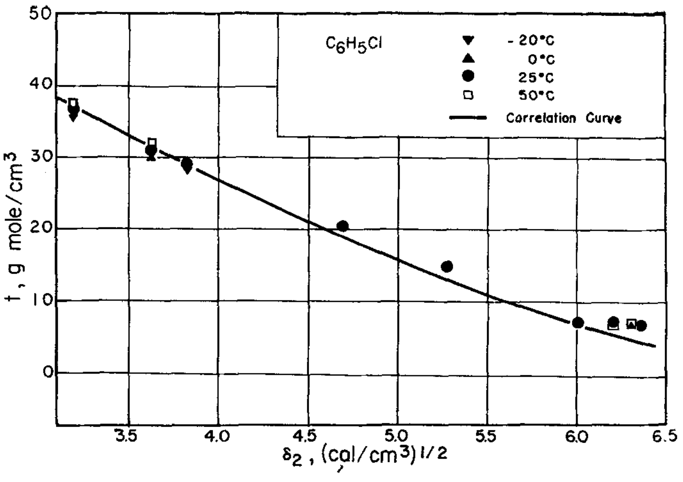

**Fig. 4. Correlation of nonpolar gas solubilities in polar, nonassociated liquids, determination of**

$V_2$. Some literature data show that the volume of nonpolar gas solute in both nonpolar and polar, nonassociated liquid solvents are about the same (*15*, *18*). Values of $V_2$ for nonpolar gases determined in Correlation (A) will therefore be used here to correlate their solubilities in polar, nonassociated liquids.

$\delta_2$. Since $\delta_2$ is considered only as a function of the physical properties of the pure gaseous component and is assumed to be a constant for any gas, the values of $\delta_2$ determined in Correlation (A) will be used here.

$\delta_1$. As in Correlation (A) $\delta_1$ will be taken as a constant, and its value calculated from its thermodynamic definition at 25°C. will be used (Table 4).

$f^{oL}$. $f^{oL}$ is considered as independent of the properties of the liquid solvent, so the reduced fugacity plot prepared in Correlation (A) should be applicable here.

$\Delta$. As Equation (16) indicates $\Delta$ consists of a multiple integral of $y$ and the angular dependence of the dipole-dipole interaction. To evaluate this integral theoretically with present knowledge of liquids and solutions is difficult, if not impossible. However this evaluation depends only upon the properties of the liquid solvent. In this work $\Delta$ is treated as a characteristic constant for each polar, nonassociated liquid at any temperatures, since for a regular solution ln $\gamma$ is directly proportional to the reciprocal of $T$ (*29*). This simplification will also be justified by the results of this correlation.

As a result of the above discussions it can be seen that Correlation (B) of nonpolar gas solubilities in polar, nonassociated liquids can be based on Correlation (A) of same gas solubilities in nonpolar liquids. Only one additional parameter $\Delta$ is introduced and it can be determined for each polar, nonassociated liquid from experimental solubility data taken from the literature.

Rearranging Equation (26) one gets

$$t = \frac{-2.303RT}{\phi_1^2}\left(\frac{\log x_2 + \log f^{oL}}{V_2}\right) = \delta_1^2 + \delta_2^2 - 2\delta_2(\delta_1^2 + \Delta)^{1/2} \qquad (29)$$

Differentiating with respect to $\delta_2$ and neglecting the small change of $\phi_1$ with $\delta_2$ one obtains

$$t' = \frac{-2.303RT}{2\phi_1^2}\left\{\frac{\partial[(\log x_2 + \log f^{oL})/V_2]}{\partial \delta_2}\right\}_{T,P} = \delta_2 - (\delta_1^2 + \Delta)^{1/2} \qquad (30)$$

and

$$t'' = \frac{-2.303RT}{2\phi_1^2}\left\{\frac{\partial^2[(\log x_2 + \log f^{oL})/V_2]}{\partial \delta_2^2}\right\}_{T,P} = +1 \qquad (31)$$

Equations (29), (30), and (31) require the following necessary conditions of the experimental solubility data:

1. A plot of $t$ vs. $\delta_2$ should give a curve of positive curvature.
2. $t'$ evaluated from the above plot should be linear with $\delta_2$. The slope of this straight line should be 1.
3. The curve of $t$ vs. $\delta_2$ could have a minimum, at which $\Delta = \delta_{2\,\max}^2 - \delta_1^2$.

To determine whether or not a polar liquid is associated, Pauling's criterion (*27*) used by Gjaldbaek and Anderson (*10*) was adopted for its simplicity and convenience. The dielectric constant at 25°C. and 1 atm. is plotted vs. the dipole moment for the polar liquids (*34*). In accordance with Pauling's criterion those molecules which are

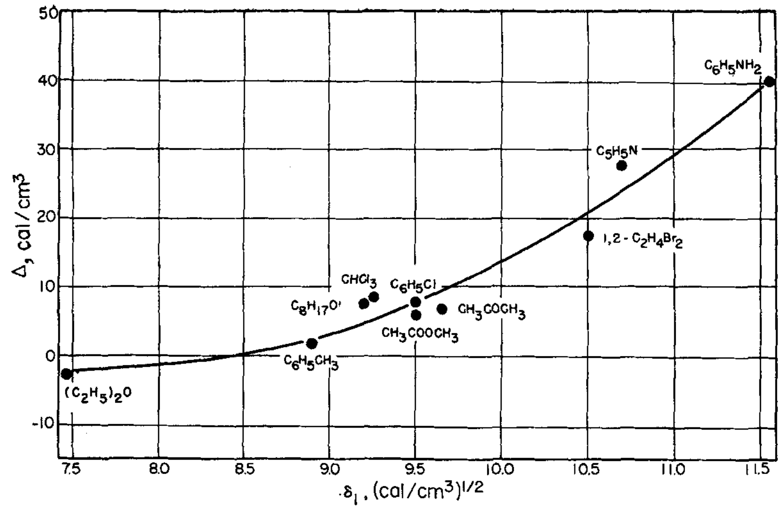

Fig. 5. Δ vs. $\sigma_1$ for polar, nonassociated liquids.

nonassociated can be connected empirically by a single, smooth curve, as shown in Figure 3. Based on this plot ten polar, nonassociated liquids were chosen (Table 4) for this correlation, since solubility data of gas in these liquids are available in the literature.

All of the low-pressure solubility data of nonpolar gases in the ten polar, nonassociated liquids were collected from the literature. The reliability of these data were examined. Theoretically to determine Δ for any polar, nonassociated liquid only one solubility measurement of any nonpolar gas in this liquid is necessary in accordance with Equation (26). However because of the approximate nature of Equation (26) all of the data were used in a trial-and-error procedure for the determination of Δ. This is graphically illustrated in Figure 4 for chlorobenzene. The final value of Δ, 7.76, gives a correlation curve which represents the experimental points satisfactorily, and all of the three necessary conditions were fulfilled.

Values of Δ for ten different polar, nonassociated liquids have been determined and tabulated in Table 4. For 119 selected data points representing the solubilities of ten gases (nitrogen, carbon monoxide, hydrogen, oxygen, argon, methane, carbon dioxide, nitrous oxide, ethylene, and ethane) in ten polar, nonassociated liquids the average deviation of the above correlation is 16.7%. Although the detailed calculation of percentage deviation for each experimental point is tabulated in reference *38*, the sources and temperature range of the solubility data used in this correlation are summarized in Table 5.

The values of Δ increase with increasing solubility parameter of the liquids, as may be observed from Table 4. Figure 5 shows that they can be correlated empirically by a single curve which should be useful in estimating gas solubilities in other polar, nonassociated liquids when experimental data are not available.

## DISCUSSION OF RESULTS

### Correlation (A)

The values of the three parameters, $V_2$, $\delta_2$, and $f^{\circ L}$, determined in this work do not agree very well with those reported by Prausnitz and Shair (Table 2 and Figure 2). This disagreement is believed to be caused by the following facts: 1. The approximate nature of the Hildebrand equation and of the theorem of corresponding states, as well as the scattering of the experimental data points. In certain cases, such as those for carbon dioxide and ethane, the correlation curve could have been drawn in different ways, and different values of the parameters would have been obtained. 2. The solubility data of gas in those solvents of relatively small solubility parameters, such as fluorocarbons ($\delta_1 \cong 6$) and iso-octane ($\delta_1 = 6.85$), were for the most part neglected by Prausnitz and Shair, while in this work the Hildebrand equation was applied to all of the nonpolar solvents, for which reliable solubility data are available. For example normal perfluoroheptane and iso-octane were not included in the table which listed the solubility data source for hydrogen in the original paper of Prausnitz and Shair (*29*). This can also be seen in Figure 1 as represented by nitrogen.

Although certain binary solutions involving fluorocarbons do not obey the regular-solution theory very well, there have been cases where systems involving fluorocarbons are in good agreement with the theory (*32, 39*). A critical review on this subject has been given by Scott (*32*). Moreover the Hildebrand equation in the form of Equation (24) is used in this work semi-empirically, and the only necessary conditions to be fulfilled in using Correlation (A) are those listed previously. The solubility data of gases in fluorocarbons and in iso-octane satisfy the necessary conditions just about as well as those in the solvents of large solubility parameters ($\delta_1 = 7$ to 10) within the capacity of the Hildebrand equation and the theorem of corresponding states. All of the data were therefore included in this work to retain the generality of Correlation (A).

Carbon monoxide and nitrous oxide are weak polar gases as indicated by their dipole moments of 0.11 and 0.17, respectively (*34*). Theoretical considerations including dipole-dipole interactions between these molecules require insignificant corrections. They are therefore treated as nonpolar gases.

### Correlation (B)

As modifications of the Hildebrand equation, Equations (22) and (26) derived in this paper extend the regular-solution theory to binary mixtures involving nonpolar and polar, nonassociated molecules. Equation (22) is also a quantitative expression of the functional equation of Prausnitz and Shair, Equation (1). In the derivation of Equations (22) and (26) most of the assumptions were those used in the derivation of Equations (23) and (24) for nonpolar systems. It is realized that at least some of the polar, nonassociated molecules would not behave as regularly as nonpolar molecules in gas-liquid solutions. Therefore Equation (26) should be of an even more approximate nature when used in Correlation (B) than Equation (24) in Correlation (A). This fact was indicated by the average percentage deviation of these two correlations.

The treatment of Δ as a characteristic constant independent of temperature was mentioned earlier. Within the accuracy of this correlation the effect of temperature on Δ is generally small and irregular as may be seen in Figure 4; thus this simplification is justified.

TABLE 5. SOURCES AND TEMPERATURE RANGE OF GAS SOLUBILITY DATA IN POLAR, NONASSOCIATED LIQUIDS

Partial pressure of gas: 1 atm.

| Liquid | Literature cited | Temperature range, °K. |
|---|---|---|
| $(C_2H_5)_2O$ | (*18, 23*) | 233 → 298 |
| $C_6H_5CH_3$ | (*5, 10, 30, 37*) | 233 → 298 |
| $C_8H_{17}OH$ | (*1, 21*) | 298 |
| $CHCl_3$ | (*6, 10, 11, 23, 33*) | 298 |
| $CH_3COOCH_3$ | (*18*) | 233 → 298 |
| $C_6H_5Cl$ | (*10, 18*) | 253 → 323 |
| $CH_3COCH_3$ | (*18, 25*) | 233 → 313 |
| 1,2-$C_2H_4Br_2$ | (*10, 23*) | 298 |
| $C_5H_5N$ | (*6, 10, 23*) | 298 |
| $C_6H_5NH_2$ | (*10, 23, 33*) | 298 |

By examining the values of $\Delta$ tabulated in Table 4 one will see that such liquid of small dipole moment as toluene has a *small* value of $\Delta$. This is in qualitative agreement with Equation (16) and with the boundary condition that $\Delta = 0$ when $\mu = 0$ for nonpolar liquids. However dipole moment is not the only factor in determining $\Delta$ as indicated by Equation (16). This is probably the reason why Gjaldbaek and Anderson could not correlate nonpolar gas solubilities in polar, nonassociated liquids by considering dipole moment alone (*10*).

Because of the complexity of $\Delta$, as indicated by Equation (16), further attempts to correlate $\Delta$ with the properties of the liquid component based on theoretical considerations were fruitless. Only the empirical correlation of $\Delta$ with $\delta_1$ as shown in Figure 5 could be concluded. Whenever possible $\Delta$ should be determined from experimental solubility data. This curve shown in Figure 5 is to be used to estimate gas solubilities in other polar, nonassociated liquids when experimental data are not available.

## CONCLUSIONS

The regular-solution theory of Hildebrand and Scatchard may be used to correlate semiempirically the low-pressure solubilities of nonpolar gases in nonpolar liquids in accordance with Equation (24). $V_2$, $\delta_1$, and $\delta_2$ may be treated as constants, and $f^{oL}$ can be correlated with the theorem of corresponding states as initiated by Prausnitz and Shair.

The regular-solution theory may be extended to binary systems consisting of a nonpolar and a polar, nonassociated liquid. When applied to gas-liquid solutions the mole fraction of the nonpolar gaseous component may be expressed by Equation (26). $\Delta$ is a characteristic constant for the polar, nonassociated liquid component, and it increases with increasing solubility parameter of the liquid component.

## ACKNOWLEDGMENT

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## NOTATION

$a$ = activity
$d_m$ = position of first maximum of $\rho$ vs. $r$ plot
$d_o$ = equilibrium intermolecular distance
$e$ = dielectric constant at 25°C. and 1 atm.
$E'$ = average intermolecular potential
$\Delta E$ = internal energy change between two states
$f$ = fugacity, atm.
$f^{oL}$ = fugacity of hypothetical liquid at pressure of 1 atm., atm.
$F$ = function
$g(\theta, \phi)$ = angular dependence of dipole-dipole interaction
$G$ = free energy
$H$ = enthalpy
$N$ = Avogadro's number
$N_1$ or $N_2$ = number of g. moles of 1 or 2
$P$ = pressure, atm.
$r$ = intermolecular distance
$R$ = gas constant
$T$ = temperature, °C. or °K.
$V_1$ = molal volume of pure component 1, ml./g. mole
$V_2$ = molal volume of hypothetical liquid, ml./g. mole
$x$ = mole fraction
$y$ = $r/d_m$

### Greek Letters

$\alpha$ = polarizability
$\gamma$ = activity coefficient
$\delta$ = solubility parameter, (cal./cc.)$^{1/2}$
$\Delta$ = characteristic constant for polar, nonassociated liquid, defined by Equation (16)
$\epsilon$ = minimum potential energy
$\mu$ = dipole moment, debye
$\xi$ = defined by Equation (9)
$\rho$ or $\rho(r)$ = radial distribution function, or radial distribution function as a function of $r$
$\rho^*$ = concentration independent radial distribution function, defined in text
$\sigma$ = intermolecular distance where $\Phi = 0$
$\Phi$ = intermolecular potential function
$\phi$ = volume fraction

### Superscripts

$I$, $II$ = step $I$ or $II$ of the two-step dissolution process
$M$ = mixing
$V$ = vaporization

### Subscripts

1 = liquid, as solvent
2 = gas, as solute
$ij$ = molecule $j$ surrounding molecule $i$
$c$ = critical
$r$ = reduced

### Marks above nomenclature

– = partial molal quantities

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