Regular Solution Theory for Gas-liquid Solutions

J. M. PRAUSNITZ, **University of California, Berkeley, California**

Regular-solution equations developed by Hildebrand and others are useful for obtaining semiquantitative estimates of phase equilibria in nonpolar systems. These equations, however, do not take into account the volume change on mixing and therefore require modification for solutions of gases in liquids. The required modifications are presented in this paper, and the resulting equations give reasonable estimates of the solubilities of gases and of the temperature coefficient of solubility. In the modified form the regular-solution theory may be used to estimate gas-liquid phase equilibria at high pressures.

The aim of solution theory is to predict the thermodynamic properties of a solution using only data for the pure components. No existing theory completely fulfills this aim, but various proposed theoretical treatments give good approximations in certain restricted cases. The most successful is the theory of regular solutions, and its most useful formulation for chemical engineering purposes is that of Hildebrand (*6*). This theory provides a simple method for estimating solubility and partial-pressure relationships for solutions of nonpolar liquids. The extension of Hildebrand's equations to solutions of nonpolar gases in nonpolar liquids is the subject of this paper. This extension provides a simple means for estimating the solubility of gases in liquids and for determining approximate values of the temperature coefficient of gas solubility.

IDEAL SOLUBILITY OF GASES

A rough estimate of the solubility of a gas, known as the ideal solubility, is given by Raoult's Law

$$x_1 = P_1/P_1^0 \qquad (1)$$

where x_1 = mole fraction of gaseous solute in liquid solution.

The utility of Equation (1) has two serious limitations. First, Equation (1) implies that the ideal solubility of a given gas is the same in all solvents. Second, the method for extrapolating the vapor pressure beyond the critical temperature is nesessarily quite arbitrary. The usual procedure is to assume a linear relationship between the logarithm of the vapor pressure and the reciprocal temperature; consequently, Equation (1) also implies that the solubility of all gases must always decrease with rising temperature. These implications are, in general, contrary to the experimental facts.

REGULAR SOLUTION EQUATIONS

The regular-solution equations assume 1) that there are no orienting or chemical effects acting between the molecules of the solution, 2) that therefore the entropy of solution at constant volume is equal to that of an ideal solution, and 3) that the energy of interaction between two molecules of unlike species is given by the geometric mean of the energies of interaction for the two species of like molecules. Since data on the volume change in mixing are scarce and since volume changes are usually very small for liquids, a further assumption made is that mixing at constant temperature and pressure effects no change in the total volume. On the basis of these assumptions it was shown (*6*) that for a binary solution

$$RT \ln \gamma_1 = V_1\phi_2^2(\delta_1 - \delta_2)^2 \qquad (2)$$

where the solubility parameter δ is given by $(\Delta E/V)^{1/2}$.

ΔE is the isothermal molar change in energy for a pure component in going from liquid to the ideal gas state. ΔE is essentially the molar energy of vaporization. Subscripts 1 and 2 refer respectively to components 1 and 2. The activity coefficient γ_1 is defined by

$$\gamma_1 = \frac{\bar{f}_1}{x_1 f_1^{\,L}}$$

Equation (2) cannot be applied to a gaseous solute in liquid solution for two reasons—1) the isothermal, isopiestic dissolution of a gas in a liquid is not a constant volume process since the volume of the gas decreases enormously; 2) the definitions of solubility parameter and activity coefficient as given cannot be applied readily to a component at a temperature above its critical. The regular solution equations as originally formulated are therefore not applicable to gas-liquid solutions.

ISOMETRIC MIXING OF GAS AND LIQUID

The difficulties encountered when applying regular-solution equations to solutions of gases in liquids can be overcome by considering the mixing process as an isothermal thermodynamic process in a series of three steps, the most important being the first:

1. Isothermal compression of the pure gas from its partial pressure and the pure liquid from its vapor pressure to the isometric mixing pressure. (At the isometric mixing pressure the pure gas has a volume equal to its partial molar volume in solution.)
2. Isothermal, isometric, and isopiestic mixing of the pure components at the isometric mixing pressure.
3. Isothermal expansion of the solution from the isometric mixing pressure to the equilibrium pressure.

For each step in this process it is possible to write an expression giving the molar free energy change of the gaseous component, designated by subscript 1:

Step 1

Isothermal compression of pure gas from P_1 to the isometer mixing pressure π.

$$\Delta F_1^{\,I} = \int_{P_1}^{\pi} V_1\,dp = RT \ln \frac{f_1(\pi)}{f_1(P_1)} \qquad (3)$$

Step 2

Mixing at constant pressure, temperature, and volume.

The regular solution equation applies.

$$\Delta \bar{F}_1^{\,II} = \bar{V}_1\phi_2^2(\delta_1 - \delta_2)^2 + RT \ln x_1 \qquad (4)$$

$\bar{V}_1$ = partial molar volume of gaseous solute at pressure π and mole fraction x_1

δ_1 = solubility parameter of gaseous solute = $(\Delta E_1/\bar{V}_1)^{1/2}$

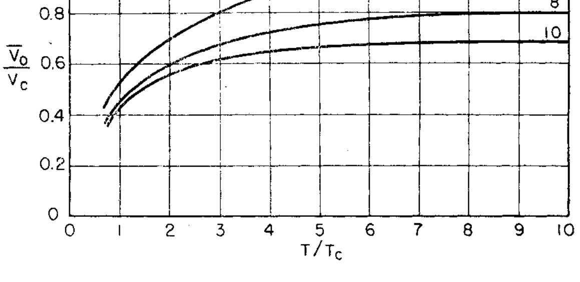

Fig. 1. Partial molar volumes of gases in nonpolar liquid solutions.

ΔE_1 = isothermal change in internal energy for the pure gas in going from molar volume $\bar{V}_1$ to the ideal gas state
ϕ_2 = volume fraction of liquid solvent = $(x_2\bar{V}_2)/(x_1\bar{V}_1 + x_2\bar{V}_2)$
$\bar{V}_2$ = partial molar volume of liquid solvent at pressure π
δ_2 = solubility parameter of liquid solvent at pressure π

At conditions remote from the critical, very little error is introduced by conconsidering the solvent incompressible and by equating the partial molar volume of solvent to the molar volume of the pure component.

Step 3

Isothermal expansion of the solution at constant composition from π to P.

$$\Delta \bar{F}_1^{III} = \int_\pi^P \bar{V}_1 \, dp \qquad (5)$$

If x_1 is the equilibrium composition corresponding to the partial pressure P_1 and if the excellent assumption is made that the Lewis fugacity rule holds for the gas at the low pressure, then the total free energy change for the gaseous component 1 is zero:

$$\Delta F_1^{I} + \Delta \bar{F}_1^{II} + \Delta \bar{F}^{III} = 0 \qquad (6)$$

Substitution of Equations (3), (4) and (5) into (6) yields

$$RT \ln \frac{f_1(P_1)}{x_1 f_1(\pi)} = \bar{V}_1 \phi_2^2 (\delta_1 - \delta_2)^2 - \int_P^\pi \bar{V}_1 \, dp \qquad (7)$$

Equation (7) relates x_1 to $\bar{V}_1$. The pressure at which the pure gas has a molar volume equal to $\bar{V}_1$ is π. Computation of the solubility of a gas in a liquid solvent, therefore, requires information on the partial molar volume of the gas; once this is known, the thermodynamic properties of the pure gas and those of the pure solvent are sufficient for determining the other quantities in Equation (7).

PARTIAL MOLAR VOLUMES

Accurate measurements of partial molar volumes of gases in liquid solutions are scarce. Recent experimental work, however, has helped to establish the two conclusions that the partial molar volume of a gaseous component in liquid solution 1) is considerably larger than the liquid volume of that component at its normal boiling point and 2) tends to decrease as the internal pressure (solubility parameter) of the solvent increases. For estimation purposes all reliable data have been collected and correlated in the generalized plot shown in Figure 1. The reduced, partial molar volume at infinite dilution is plotted against the reduced temperature of the solute*; the effect of the solvent is indicated by lines of constant solubility parameter of the solvent at 25°C. This correlation reproduces the available reliable data with a standard deviation of about ±5%.

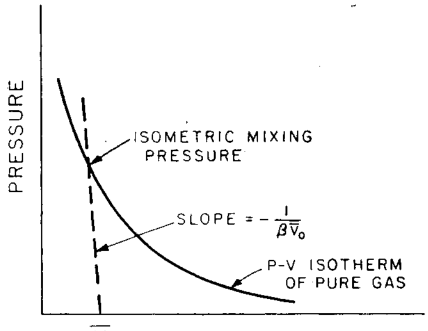

Fig. 2. Computation of isometric mixing pressure.

THE ISOMETRIC MIXING PRESSURE

The isometric mixing pressure is the pressure at which gaseous solute and liquid solvent mix isothermally and isopiestically without change of volume. To compute it the thermodynamic properties of the pure gas and an estimate of the partial molar volume are necessary. In general, the partial molar volume is itself a function of pressure, and since the isometric mixing pressure is large—usually in the vicinity of 1,000 atm.—this effect is not negligible. The correlation in Figure 1 gives the partial molar volume at very low pressure; this volume is smaller at high pressures. There are only a few experimental studies of the compressibility β of dissolved gases (*9*, *10*), but these indicate that it is about the same as that observed for normal liquids; a good estimate for the compressibility, therefore, is $\beta \approx 10^{-4}$ atm.$^{-1}$. An approximate relation for $\bar{V}$, the partial molar volume of the gas at any pressure, is therefore given by

$$\bar{V} = \bar{V}_0[1 - \beta P] \qquad (8)$$

The isometric mixing pressure can be computed by finding the intersection of Equation (8) with the isothermal pressure-versus-volume curve for the pure gas as illustrated in Figure 2. Volumetric properties have been reported for numerous pure gases (*1*, *4*) or may be estimated with fairly good accuracy from generalized correlations (*2*, *11*). The uncertainty in β introduces considerable uncertainty in π. However, as shown later, for estimation purposes this uncertainty is not serious. Calculations presented below indicate that reasonable estimates of gas solubility can be made by using Equations (7) and (8) with Figure 1 and with thermodynamic properties of the pure gas under consideration.

SOLUBILITY PARAMETERS

The solubility parameter of the gaseous solute is computed from the thermodynamic properties of the pure gas at the temperature of the solution and at the isometric mixing pressure. When volumetric and enthalpy data for the gas are available, ΔE is found by

$$\Delta E = E(\text{at } P = 0) - E(\text{at } P = \pi)$$

or

$$\Delta E = \Delta H - \Delta(pv) = \Delta H - RT + \pi \bar{V}_1$$

where $\Delta H = H$ (at $P = 0$) $- H$ (at $P = \pi$), all at the temperature of the solution. Generalized charts for $\Delta E/T_c$ have been published by Lydersen *et al.* (*11*).

The solubility parameters of most common nonpolar solvents are tabulated, and their temperature dependence is discussed by Hildebrand and Scott (*6*). The effect of pressure is to increase somewhat the solubility parameter of the solvent. This increase can be calculated if the volumetric properties of the liquid solvent are known; it can be estimated

Table 1. Solubility of Gases at 1-atm. Partial Pressure

Gas	Solvent	Temp., °C.	Solubility parameter of solvent, (cal./cc.)$^{1/2}$	Partial molar volume $\bar{V}_0$	Isometric mixing pressure, atm.	Solubility parameter of Gas, (cal./cc.)$^{1/2}$	Solubility: x_1 10^4 Equation (9)	Observed	Ref.
Nitrogen	*n*-Perfluoro heptane	25	5.7	67.5	545	2.9	29.1	39.1	*5*
Nitrogen	Carbon disulfide	25	10.0	52.2	1310	4.0	2.98	2.23	*5*
Krypton	Iso-octane	25	6.85	52.6	620	4.6	68.1	78.8	*1*
Krypton	Benzene	25	9.15	47.0	1130	5.8	29.9	27.3	*1*
Hydrogen	*n*-Heptane	0	7.80	38.1	1280	3.1	6.22	5.90	*3*
Hydrogen	Carbon tetrachloride	0	9.0	34.8	1760	2.9	3.15	2.60	*3*

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*Pseudocritical values were used for hydrogen as recommended by Newton (12); T_c = 41.3°K. and V_c = 47 cc./g.-mole.

TABLE 2. ENTROPIES OF SOLUTION FOR GASES IN BENZENE AT 25°C. AND 1-ATM. PARTIAL PRESSURE

Gas	Solubility $x_1 10^4$ observed (*8*)	$\bar{V}_0\alpha$, cc./(g.-mole)(°K.)	π, atm.	Entropy of solution, cal./(g.-mole)(°K.) Equation (15)	Observed (*8*)
Nitrogen	4.42	0.058	1,050	2.9	3.3
Carbon monoxide	6.7	0.064	1,000	+1.0	+1.8
Ethane	148	0.131	1,450	−7.6	−7.5

roughly but not very accurately from Lydersen's charts. The simplest procedure is to consider the solvent as an incompressible liquid. For estimation purposes, the error introduced by this simplification is not very serious.

ESTIMATING THE SOLUBILITY OF GASES

Measured solubilities are available for a number of gases, the vast majority of such data having been taken at 25°C. and 1 atm. partial-gas pressure. Equations (7) and (8) have been used to estimate the solubilities of a few gases in several solvents. Table 1 gives a comparison of the calculated and observed results. At a partial gas pressure of 1 atm. the fugacity of the gas is very close to 1 atm., and the mole fraction of gaseous solute is so small that $\phi_2 = 1$. The equation used in these calculations, therefore, becomes

$$-RT \ln x_1 f_1(\pi) = \bar{V}_0(1 - \beta\pi)(\delta_1 - \delta_2)^2 - \bar{V}_0\pi\left[1 - \frac{\beta\pi}{2}\right] \qquad (9)$$

Table 1 also gives the partial molar volume at low pressure as computed from Figure 1, the isometric mixing pressure, and the solubility parameter of the gaseous solute. In these calculations the value of β was 10^{-4} atm.$^{-1}$, and the solvents were considered incompressible.

MULTICOMPONENT SYSTEMS

The theory of regular solutions for binary systems is readily extended to multicomponent systems as discussed in detail by Hildebrand and Scott (*6*). For the estimation of the solubility of a gas in a mixture of n liquids Equation (7) is modified to

$$RT \ln \frac{f_1(P_1)}{x_1 f_1(\pi)} = \bar{V}_1(\delta_1 - \bar{\delta})^2 - \int_P^\pi \bar{V}_1\, dp \qquad (10)$$

where

$$\bar{\delta} = \sum_{i=1}^{n+1} \phi_i \delta_i.$$

The symbol δ denotes an average solubility parameter. The average, taken on a volume fraction basis, comprises all components, including the gaseous solute.

TEMPERATURE COEFFICIENT OF SOLUBILITY

The solubility of gases in liquids is, in general, a strong function of temperature. In the vicinity of room temperature most gases become less soluble as the temperature is raised; there are, however, several exceptions, of which hydrogen is probably the best known. At higher temperatures many gases become less soluble with rising temperature. The temperature coefficient of solubility is directly related to the entropy of mixing, the exact relationship being

$$\frac{d \ln x_1}{d \ln T} = \frac{\Delta\bar{S}_1}{R\left(\dfrac{\partial \ln a_1}{\partial \ln x_1}\right)_T} \qquad (11)$$

where $\Delta\bar{S}_1$ = entropy of solution = $\bar{S}_1 - S_1$.

In all cases $(\partial \ln a_1)/(\partial \ln x_1)$ is positive. The solubility therefore increases with temperature if the partial entropy change is positive and decreases with temperature if it is negative. In many cases the gaseous solute is sufficiently dilute to permit the assumption of Henry's Law. In that case $(\partial \ln a_1)/(\partial \ln x_1) = 1$, and Equation (11) becomes

$$R\frac{\partial \ln x_1}{\partial \ln T} = \Delta\bar{S}_1 \qquad (12)$$

A three-step analysis analogous to that used to derive equations for the partial free energy also computes the partial entropy change of the gas $\Delta\bar{S}_1$. The equations for the entropy (per mole of gas) are

Step 1

Isothermal compression from P_1 to π

$$\Delta S_1^{I} = -\int_{P_1}^{\pi}\left(\frac{\partial V}{\partial T}\right)_P dP \qquad (13)$$

Step 2

Isothermal, isopiestic, and isometric mixing

$$\Delta\bar{S}_1^{II} = -R \ln x_1 \qquad (14)$$

Step 3

Isothermal expansion (in liquid solution) from π to P

$$\Delta\bar{S}_1^{III} = -\int_\pi^P\left(\frac{\partial \bar{V}_1}{\partial T}\right)_P dP \qquad (15)$$

The partial molar entropy of solution $\Delta\bar{S}_1$ is then given by

$$\Delta\bar{S}_1 = \Delta\bar{S}_1^{I} + \Delta\bar{S}_1^{II} + \Delta\bar{S}_1^{III} \qquad (16)$$

To compute $\Delta\bar{S}_1$ the isometric mixing pressure must first be estimated. The entropy change ΔS_1^{I} can then be found from the thermodynamic properties of the pure gas or from generalized charts. $\Delta\bar{S}_1^{II}$ is computed from the solubility, and $\Delta\bar{S}_1^{III}$, a relatively small term, can be found approximately by rewriting Equation (15)

$$\Delta\bar{S}_1^{III} \approx \bar{V}_0\alpha(\pi - P) \qquad (17)$$

Experimental values of α are rare, but they can be estimated from the slopes of the generalized plots in Figure 1 by the relationship

$$\bar{V}_0\alpha \equiv \left(\frac{\partial \bar{V}_0}{\partial T}\right)_P = \frac{V_c}{T_c}\left[\frac{\partial \dfrac{\bar{V}_0}{V_c}}{\partial \dfrac{T}{T_c}}\right] \qquad (18)$$

Table 2 compares observed entropies of mixing for nitrogen, carbon monoxide, and ethane with those calculated by Equation (16). The agreement is quite good. The calculated entropies show that at 25°C. the solubility of nitrogen in benzene rises considerably, that of carbon monoxide rises moderately, and that of ethane falls strongly as the temperature is increased.

To illustrate the use of entropies of solution consider the following problem: Cook *et al.* (*3*) have measured the solubility of hydrogen in benzene at 25°C. and 1-atm. partial pressure: $x_1 = 2.58 \times$

TABLE 3. SOLUBILITY AND ENTROPY OF SOLUTION FOR ETHYLENE IN CARBON TETRACHLORIDE FOR VARIOUS ISOMETRIC MIXING PRESSURES

Isometric mixing pressure, atm.	Solubility Parameter for ethylene, (cal./cc.)$^{1/2}$	Solubility $x_1\, 10^4$ at 25°C. and 1-atm. partial pressure Calculated	Observed (*8*)	Entropy, cal./(g.-mole)(°K.) Calculated*	Observed (*8*)
400	6.2	128	145	−7.9	−7.9
600	6.6	158	145	−8.0	−7.9
900	7.1	196	145	−8.1	−7.9

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*Based on the observed solubility.

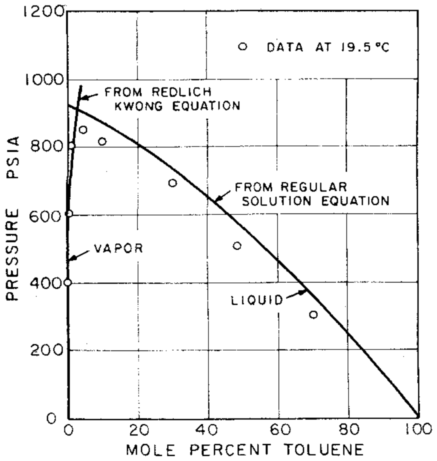

Fig. 3. Phase equilibria for toluene-ethylene system.

10^{-4}. Using this information estimate the solubility of hydrogen in benzene at 100°C. and at a partial pressure of 97 atm. To solve this problem the entropy of solution at 25°C. and 1 atm. is first computed by Equation (16) and found to be 4.9 cal./gmol. °K. At 1 atm., therefore, using Equation (12) and assuming the entropy of solution to be independent of temperature,

$$\ln \frac{x_1(100°\text{C.})}{2.58 \times 10^{-4}} = \frac{4.9 \ln \frac{373}{298}}{1.987}$$

This gives $x_1(100°\text{C.}) = 4.56 \times 10^{-4}$. At a partial pressure of 97 atm. a good estimate for the solubility is

$$x_1 = (97)(4.56 \times 10^{-4}) = 4.41 \times 10^{-2}.$$

The observed value (7) is 4.01×10^{-2}. The assumption of constant entropy of solution is good only for small temperature intervals. Also, Henry's Law is valid only at low solute concentrations.

UTILITY

Since the theory of regular solutions makes a variety of simplifying assumptions, it can only approximately describe the thermodynamic behavior of nonpolar solutions. The solubilities of gases and their temperature coefficients can therefore only be estimated by the given equations. The regular-solution equations as discussed here are not applicable for exact quantitative work. Rather, they should be regarded as first-order corrections to Raoult's Law.

One of the major computational difficulties in the application of regular-solution theory to gas-liquid solutions is the uncertainty of β for which almost no experimental results are available. The value of β has a large effect on π, but the effect of π on the computation of the solubility x_1 and the entropy $\Delta\bar{S}_1$ is not excessively serious. Thus a change in the isometric mixing pressure by as many as several hundred atmospheres usually produces in x_1 and $\Delta\bar{S}_1$ changes amounting to perhaps a factor of 2 or less. To illustrate this point solubilities and entropies for ethylene in carbon tetrachloride at 25°C. and 1 atm. have been calculated for several isometric mixing pressures. The results, given in Table 3, indicate that a very accurate value of the isometric mixing pressure is not required for estimation purposes. In fact, the simplest procedure is to assume $\beta = 0$ and to evaluate the isometric pressure using just the partial molar volume of the gas at low pressure. Solubilities based on this assumption, however, tend to be on the low side.

The main uses of these equations for chemical engineering purposes are to extend available data to new conditions and to make preliminary phase-equilibria estimates for nonpolar systems having no existing data. To illustrate, consider as a final example phase equilibrium in a system containing a gas near its critical temperature. (These systems have become interesting in connection with possible applications for fluid-liquid extraction.) The example chosen is the ethylene-toluene system, and, using only data for the pure components, a pressure-versus-composition diagram at 19.5°C. has been constructed. The liquid-phase equilibrium line is calculated from Equation (7) assuming that the partial molar volume of solvent is independent of composition. At high pressures P_1 must be replaced by a fugacity; at high pressures ϕ_2 is not unity, and therefore finding x_1 involves some trial-and-error algebra. The vapor-phase equilibrium line is computed from the Redlich and Kwong equation of state (*13*). The results, shown in Figure 3, are in better than qualitative agreement with the experimental values reported by Todd and Elgin (*14*).

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NOTATION

a_1 = activity of gaseous solute
ΔE = change in internal energy
ΔF = change in free energy
f_1 = fugacity of pure gas
f_1^L = fugacity of pure component 1 as a liquid at the temperature and pressure of the solution
$\bar{f}_1$ = fugacity of component 1 in solution
ΔH = change in enthalpy
P = total pressure
P_1 = partial pressure of gas
P_1^0 = extrapolated vapor pressure of the gas
R = gas constant
S_1 = entropy of pure gas
$\bar{S}_1$ = partial molar entropy of gaseous solute
T = absolute temperature
T_c = critical temperature of gas
V = molar liquid volume of pure component
$\bar{V}_2$ = partial molar volume of liquid solvent
$\bar{V}_1$ = partial molar volume of gaseous solute
$\bar{V}_0$ = partial molar volume of gaseous solute at infinite dilution
V_c = critical volume of gas
x_1 = mole fraction of component 1 in liquid phase

Greek Letters

α = coefficient of thermal expansion
β = compressibility
δ = solubility parameter = $(\Delta E/V)^{1/2}$
γ = activity coefficient
ϕ = volume fraction
π = isometric mixing pressure

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