An Introduction to the Understanding of Solubility

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The phenomenon of the solubility of one substance in another has been at the forefront of chemistry and held the fascination of both scientists and the lay public for eons. How is it that one substance can "disappear" or dissolve into another—a gas or a solid or a liquid into a liquid solvent? There appear to be strange limits to this solubility: depending on the solution, raising *or* lowering the temperature can result in phase separation! At a particular temperature you can add one liquid dropwise to another and observe miscibility, followed by phase separation, followed by miscibility again at higher quantities of the added solvent. There is an appearance of magic here.

Solubility (defined as the concentration of dissolved solute in a solvent in equilibrium with undissolved solute at a specified temperature and pressure) has a practical side in terms of industrial processes, sewage treatment, oxygen transport in the blood, oceanography, and extraction, to mention just a few areas. The Solubility Data Commission (V.8) of IUPAC has already produced more than 60 volumes of critically selected and evaluated solubility data and has more than 50 additional volumes in preparation in its *Solubility Data Series*. This enormous international effort is driven by a universal need for reliable solubility data.

Table 1. Solubility of Gases in Water

Gas	Mole Fraction $\times 10^5$ [a]
He	0.708
Ne	0.8223
Ar	2.532
Kr	4.546
Xe	7.949
H_2	1.411
N_2	1.177
O_2	2.301
CH_4	2.552
C_2H_6	3.404
C_3H_8	2.732
C_4H_{10}	2.244
SF_6	0.4385
CF_4	0.383
C_2F_6	0.0972
CH_3F	106.2
CH_3Cl	187.8
CO_2	61.5
NH_3	18,760
H_2S	183
SO_2	2, 460
HCl	25,900

[a]Values are for 25 °C and 0.101 MPa partial pressure of gas.

In this paper we explore the process of solubility from several perspectives. In principle, we can consider the water in a glass or Teflon or stainless-steel beaker to actually dissolve some of the container material to attain an equilibrium state, even though the amount may be undetectable. Table 1 gives the solubilities of some selected gases in water at 25 °C and a partial pressure of gas of 0.101 MPa. The solubilities range from a low of one molecule of C_2F_6 per one million water molecules to 35 HCl molecules per 100 water molecules. You will note that the gases below the line are either polar or they react "chemically" with water, as is the case for CO_2, NH_3, SO_2, and HCl.

How can we account for this wide range of solubilities? The very large value for HCl is due to the ionization of the gas in water, followed by hydration of the ions. The case of NH_3, SO_2, or CO_2 is very different. Although we speak of NH_4OH, H_2SO_3, and H_2CO_3, these "compounds" are really strongly hydrogen-bonded species and should be written as $NH_3{\cdot}H_2O$, etc. Hydrogen bonding or dipole–dipole interaction between the solute and water is responsible for the high values for CH_3F, CH_3Cl, and H_2S.

Table 2. Solubility Products for Some Salts in Water

Salt	K_{sp}	T/°C
NaCl	39	20
$CaCrO_4$	2.3×10^{-2}	18
Li_2CO_3	1.7×10^{-3}	25
$CaSO_4$	2.01×10^{-4}	10
$BaCO_3$	7×10^{-9}	16
$PbCrO_4$	1.8×10^{-14}	18
ZnS	1.2×10^{-23}	18
CdS	3.6×10^{-29}	18
$Fe(OH)_3$	1.1×10^{-36}	18
Ag_2S	1.6×10^{-49}	18
HgS	10^{-49}–10^{-53}	18

Before going on let us examine some more solubility data. Table 2 gives the solubility products for a number of salts in water. Again there is a very wide range of solubilities, from 11 Na^+ ions and 1 Cl^- ion per 100 water molecules to, for HgS, one ion each of Hg^{2+} and S^{2-} per 10 L (or 3×10^{26} molecules) of water, if we assume the lower value of K_{sp}. The solubility of HgS is almost inconceivably small. We normally think of mercury as being insoluble, yet its mole fraction solubility at 25 °C is, in water, 5.4×10^{-9}; in benzene, 1.1×10^{-6}; in *n*-hexane, 8.4×10^{-7}; and in methanol, 1.2×10^{-7}. The solubility of water at 25 °C in some hydrocarbons is, in *n*-heptane 5.1×10^{-4}; in *n*-decane, 5.7×10^{-4}; and in *n*-hexadecane, 6.8×10^{-4}. There is also an extensive literature on the solubility of solids in compressed gases, as well as a recent explosion of information on solubilities in supercritical fluids.

As a general rule we can use the old adage "like dissolves like." By "like" we mean the structure and polar nature of the molecules. For example, nonpolar solutes dissolve in nonpolar solvents, and polar solutes in polar solvents. The solubilities of the 1-alkanols in water are a good example. Methanol, ethanol, and 1-propanol are miscible in all proportions in water at room temperature. They are polar solutes with nonpolar hydrocarbon tails. But as the chain length increases the nonpolar tails become dominant. We therefore find the follow-

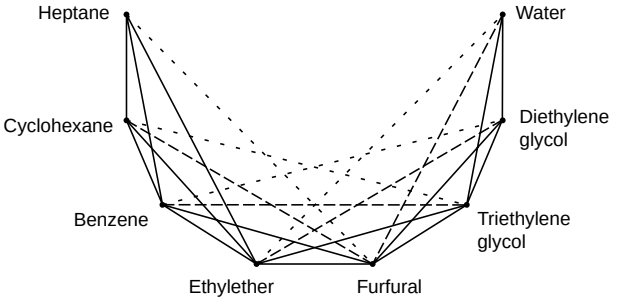

Figure 1. Mutual solubility of liquids (adapted from ref *1*). (——) complete miscibility; (– – –) high solubility; (- - -) low solubility; (no line) very low solubility.

ing solubilities in g solute/100 g H_2O at 20 °C: 1-butanol, 7.9; 1-pentanol, 2.3; 1-hexanol, 0.6; 1-heptanol, 0.17.

Finally, we have modified Figure 1 from Francis (*1*) as an interesting example of the mutual solubility of eight solvents.

The Ideal Solution

The ideal solution provides a useful limit for considering the solution process. If you mix two substances that form an ideal mixture, there are no volume or heat (enthalpy) effects due to the mixing. Thus,

$$\Delta V_{m,mix} = 0 \quad \text{and} \quad \Delta H_{m,mix} = 0 \tag{1}$$

for an ideal solution. Many real solutions approximate this behavior.

For the ideal solution of a pure solid in *any* liquid,

$$-R \ln x_2 = \Delta H_{fusion,2}(1/T - 1/T_{fusion,2}) \tag{2}$$

where R is the gas constant, x_2 is the mole fraction solubility at T, $\Delta H_{fusion,2}$ is the enthalpy change on fusion for pure component 2, and $T_{fusion,2}$ is the melting point of component 2. (The derivation of eq 2 is given in all standard thermodynamics and physical chemistry texts.) A similar equation can be derived for the ideal solubility of a gas in a liquid:

$$-R \ln x_2 = \Delta H_{vap,2}(1/T_{b,2} - 1/T) \tag{3}$$

where $\Delta H_{vap,2}$ is the enthalpy change on evaporation of the pure solute at its normal boiling point $T_{b,2}$.

Equations 2 and 3 only contain information about the solid or gaseous *solute* (species 2) and are independent of the nature of the solvent (species 1). As an illustration, the solubility of several aromatic solids in benzene at 25 °C is presented in Table 3. Equation 2 may be used to calculate the ideal phase diagram of binary mixtures, including an estimate for the eutectic composition and temperature.

The Second Law of Thermodynamics and Ideal Mixtures

The theoretical basis for solubility or mixing lies in the second law of thermodynamics: for a process to take place in an isolated system the overall entropy change must be positive (*2*). The mixing of nonreacting gases, such as nitrogen and oxygen at ordinary temperatures and pressures, is such a process. The underlying *raison d'être* for the phenomenon can be expressed in terms of the second law as

$$\Delta S = k \ln[W(\text{mixed})/W(\text{unmixed})] \tag{4}$$

where ΔS is the entropy change and W is the number of different ways in which the energy of the system can be achieved by rearranging the molecules among the states available to them (*2*).

Assuming that the gas molecules have kinetic energy, calculations show that for a binary mixture (*3*)

$$\Delta_{mix}S_m = -y_1 R \ln y_1 - y_2 R \ln y_2 \tag{5}$$

where $\Delta_{mix}S_m$ is the molar entropy of mixing and y_i refers to the mole fraction of gas i in the mixture. The same relationship can be obtained from simple thermodynamic considerations (*4*). You will notice that for these ideal gas mixtures, $\Delta_{mix}S_m$ will always be positive as $0 < y_i < 1$.

For *ideal liquids*, where the interactive forces between all the molecules of the mixture are identical and the molecules have enough kinetic energy to mix completely, an equation similar to eq 5 can be derived (*4*):

$$\Delta_{mix}S_m = -x_1 R \ln x_1 - x_2 R \ln x_2 \tag{6}$$

where x_i is the mole fraction of liquid i in the mixture. Again $\Delta_{mix}S_m$ is always positive.

Taking stock of what we have done so far, we see that the mixing of ideal gases and the mixture of ideal liquids are natural phenomena that are driven by probability on the assumption that the molecules have sufficient kinetic energy to interchange. Our understanding of the mixing process is based on the statistical nature of the second law of thermodynamics.

Table 3. Solubility of Aromatic Solids in Benzene at 25 °C

Solute	ΔH_{fus} / (kJ mol^{-1})	$T_{fus,1}$ / K	x_1	
			Ideal	Exptl
Biphenyl	16.8	299.2	0.39	0.39
Naphthalene	19.1	353.4	0.30	0.24
Phenanthrene	16.5	373	0.25	0.19
Anthracene	28.8	490	0.011	0.0063

Real Liquid Mixtures

For *real liquid* mixtures, eq 4 still applies, but because of the complexity of the system, it is now impossible to calculate the values of W. A different approach is necessary. One way around this dilemma is to consider another expression for the second law and the criterion of spontaneous change, namely (*2*):

$$dG_{T,P} \leq 0 \tag{7}$$

For a real mixture (5),

$$\mu_i = \mu_i^* + RT \ln x_i \gamma_i \tag{8}$$

and as

$$\Delta_{mix}G_m = \Sigma x_i(\mu_i - \mu_i^*) \tag{9}$$

$$\Delta_{mix}G_m = \Sigma x_i RT \ln x_i + \Sigma x_i RT \ln \gamma_i \tag{10}$$

where the first term on the right relates to ideal mixing and the second term to non-ideal mixing. The latter term is often called the excess Gibbs energy of mixing ($\Delta_{mix}G_m^E$). The term μ_i is the chemical potential of i in the liquid mixture, μ_i^* is the chemical potential of pure liquid i at the temperature and pressure of the mixture, and γ_i is the activity coefficient defined so that $\gamma_i \to 1$ as $x_i \to 1$.

Looking at eq 10, we see that the ideal term is always negative. However, for mixing to take place $\Delta_{mix}G_m$ must be negative. A proper understanding of the applications of eq 10 requires a knowledge of activity coefficients.

Activity Coefficients

The activity coefficient, γ_i, in a liquid mixture has been defined above. It can also be considered as a measure of the deviation from Raoult?s law:

$$p_i = \gamma_i x_i p_i^\circ \tag{11}$$

where p_i and p_i° are the partial pressure of i and the vapor pressure of pure i at the temperature of the mixture, respec-

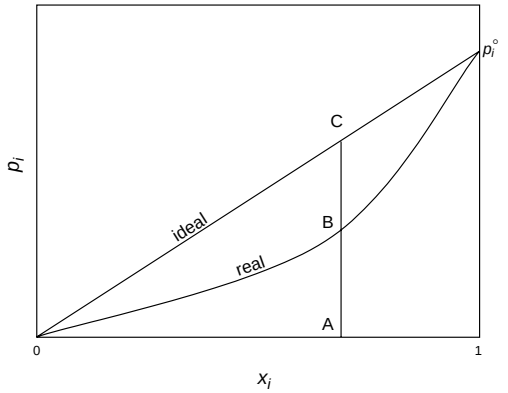

Figure 2. The activity coefficient, γ_i of a component *i*, based on the convention $\gamma_i \rightarrow 1$ as $x_i \rightarrow 1$; p_i is the partial pressure of species *i*; p_i° is the vapor pressure of pure *i* at the temperature *T*; and x_i is the mole fraction of species *i*. At x_A, γ_i = AB/AC.

tively, and can be written as a ratio of two partial pressures:

$$\gamma_i \text{ (at } x_i = x_A) = \text{AB/AC} \qquad (12)$$

where AB and AC are distances representing the real and ideal partial pressures as shown in Figure 2.

Negative deviations occur when the mixing liquids are strongly associated (e.g., chloroform plus acetone) and the vapor pressure of the mixture, and indeed the partial pressures, are less than the values predicted by Raoult's law. In such mixtures $\gamma < 1$ (see Fig. 2).

Positive deviations occur when strongly associated species (e.g., polar liquids) are mixed with nonpolar liquids (e.g., an alkanol plus an alkane). In these cases, the total vapor pressure and the partial pressures in the real mixture are greater than the calculated values for a "Raoult's law" liquid and $\gamma > 1$.

The sign of the Raoult's law deviation often correlates with the sign of the $\Delta_{mix}H_m$ and $\Delta_{mix}V_m$. The only reason for this is that the $\Delta_{mix}H_m$ is usually the dominant effect in the mixing process. The $\Delta_{mix}V_m$ effect is often dictated by a packing effect, which masks the chemical effect.

The many methods available for determining γ_i include the measurement of vapor pressures (*5*). The activity coefficient is one of the most important properties in chemistry, so it is not surprising that so many workers have added to our understanding of it through theoretical concepts.

The activity coefficient, like the excess Gibbs energy of mixing, $\Delta_{mix}G_m^E$, is a function of *T*, *P*, and *x* and can be written as

$$RT \ln \gamma_i = (\partial \Delta_{mix} G_m^E / \partial x_i)_{T,P} \qquad (13)$$

As expected, there are many expressions for $\Delta_{mix}G_m^E$ and the "γ_i as functions of composition". Some of these expressions are empirical; for example, the two- and three-suffix Margules and the Van Laar equations (see Table 4) (*6*). The two-suffix Margules equation is actually a "one-parameter" equation and has limited application. The three-suffix Margules and the Van Laar equations are two-parameter equations and are much more reliable. For binary liquid mixtures at a fixed *T* and *P*, the activity coefficients over the whole composition range can be predicted from only two experimental values of γ_i. The two most reliable activity coefficients to use in these circumstances are the activity coefficients at infinite dilution (γ_i^∞). Again, there are many methods for determining γ_i^∞, including gas-liquid chromatography (*7*) and ebulliometry (*8*).

The Wilson equation (Table 4) is also a "two-parameter" equation but does have a theoretical foundation. Other popular equations used in summarizing activity coefficient data are the four-suffix Margules equation (an empirical equation), the non-random two-liquid (NRTL) equation (*6*), and the universal quasi chemical (UNIQUAC) equation (*6*).

Another approach has been the development of methods for correlating activity coefficients at infinite dilution for liquid mixtures through the summing of "group contributions". The earliest work in this area was by Pierotti et al. (*9*). They proposed a series of empirical equations involving parameters depending on the nature of the solute and solvent functional groups and other parameters depending on the class of liquids used. For example, for ethanol (1) + *n*-hexane (2) at 60 °C,

$$\ln \gamma_1^\infty = A_{1,2} + C_1(1/N_1 - 1) + D(N_1 - N_2)^2 \qquad (14a)$$

with $A_{1,2} = 3.22$ (an interpolated value), $C_1 = 0.898$, and $D = -0.00131$; N_1 and N_2 refer to the carbon number of species 1 and 2 respectively. Also,

$$\ln \gamma_2^\infty = A_{2,1} + B_2(N_2/N_1) + D(N_2 - N_1)^2 + F_2/N_1 \qquad (14b)$$

with $A_{2,1} = 1.842$, $B_2 = 0.318$, and $F_2 = -1.022$. Substitution gives

$$\ln \gamma_1^\infty = 2.75 \quad \text{and} \quad \gamma_1^\infty = 15.7$$

$$\ln \gamma_2^\infty = 2.26 \quad \text{and} \quad \gamma_2^\infty = 9.65$$

and hence

$$A = 7163.18 \quad \text{and} \quad B = -692.70$$

and

$$RT \ln \gamma_1 = 5085.0x_2^2 + 2770.8x_2^3$$

$$RT \ln \gamma_2 = 9241.3\, x_1^2 - 2770.8\, x_1^3$$

and

$$\Delta_{mix}G_m^E = x_1x_2[7163.18 - 692.70(x_1 - x_2)]$$

Other methods used for making reasonable estimates of γ_1 for non-ideal liquid mixtures include the analytical solution of groups (ASOG) (*10*) and the universal quasi chemical equation functional group activity coefficients (UNIFAC) (*11, 12*) methods.

Real Liquids Revisited

Referring back to where we left off, the fundamental equations for looking at mixtures are eqs 7 and 10:

$$\Delta_{mix}G_m = \Sigma x_i RT \ln x_i\gamma_i \qquad (10a)$$

For mixtures which mix over the whole composition range, $\Delta_{mix}G_m$ will be negative for any value of x_i. The shape of $\Delta_{mix}G_m$ given in Figure 3 is typical for this type of mixture.

For liquids in mixtures that do not mix over the whole composition range, $\Delta_{mix}G_m$ as a function of x_i takes on an interesting shape (see Fig. 4). The shape is dependent on the values of γ_i, which is a function of composition. This function is usually logarithmic, as is seen from the equations for γ in Table 4. This shape leads to an interesting phenomenon, which is unique to liquids. Phase separation takes place between the concentrations defined by the troughs of the $\Delta_{mix}G_m$ curve (x_i' and x_i'') in such a way that in the region between x_i' and x_i'', the composition of each phase remains constant and only the relative volumes of each phase change. This is because the lowest $\Delta_{mix}G_m$ defines the most stable situation, and in this case, this can be achieved by drawing a tangent between the

Table 4. Some Models for Excess Gibbs Energy and Activity Coefficients for Binary Systems

Model [a]	$\Delta_{mix}G_m^E$	Binary Parameters	$\ln\gamma_1$ $\ln\gamma_2$	$\ln\gamma_1^\infty$ $\ln\gamma_2^\infty$
1	Ax_1x_2	A	$RT\ln\gamma_1 = Ax_2^2$ $RT\ln\gamma_2 = Ax_1^2$	A/RT A/RT
2	$x_1x_2[A + B(x_1 - x_2)]$	A, B	$RT\ln\gamma_1 = (A + 3B)x_2^2 - 4Bx_2^3$ $RT\ln\gamma_2 = (A - 3B)x_1^2 + 4Bx_1^3$	$(A - B)/RT$ $(A + B)/RT$
3	$\dfrac{Ax_1x_2}{x_1(A/B) + x_2}$	A, B	$RT\ln\gamma_1 = A\left(1 + \dfrac{A}{B}\dfrac{x_1}{x_2}\right)^{-2}$ $RT\ln\gamma_2 = B\left(1 + \dfrac{B}{A}\dfrac{x_2}{x_1}\right)^{-2}$	A/RT B/RT
4	$RT[-x_1\ln(x_1 + \Lambda_{12}x_2) - x_2\ln(x_2 + \Lambda_{21}x_1)$	$\Lambda_{12}, \Lambda_{21}$	$\ln\gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2$ $\ln\gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left(\dfrac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \dfrac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right)$	$1 - \Lambda_{21} - \ln\Lambda_1$ $1 - \Lambda_{12} - \ln\Lambda$
5	$x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2]$	A, B, C	$RT\ln\gamma_1 = (A + 3B + 5C)x_2^2 - 4(B + 4C)x_2^3 + 12Cx_2^4$ $RT\ln\gamma_2 = (A - 3B + 5C)x_2^2 - 4(B + 4C)x_2^3 + 12Cx_2^4$	$A - B + C$ RT
6	$RT\left[x_1x_2\left(\dfrac{\tau_{21}G_{21}}{x_1 + x_2G_{21}} + \dfrac{\tau_{12}G_{12}}{x_2 + x_1G_{12}}\right)\right]$ where $\tau_{12} = \Delta g_{12}/RT$; $\tau_{21} = \Delta g_{21}/RT$ $\ln G_{12} = -\alpha_{12}\tau_{12}$; $\ln G_{21} = -\alpha_{12}\tau_{21}$	$\Delta g_{12}, \Delta g_{21}, \alpha_{12}$ where: $\Delta g_{12} = g_{12} - g_{22}$ $\Delta g_{21} = g_{21} - g_{11}$	$\ln\gamma_1 = x_2^2\left[\tau_{21}\left(\dfrac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \dfrac{\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2}\right]$ $\ln\gamma_2 = x_1^2\left[\tau_{12}\left(\dfrac{G_{12}}{x_2 + x_1G_{12}}\right)^2 + \dfrac{\tau_{21}G_{21}}{(x_1 + x_2G_{21})^2}\right]$	—
7 [b]	$\Delta_{mix}G_m = g^E(\text{combinatorial}) + g^E(\text{residual})$ $\dfrac{g^E(\text{combinatorial})}{RT} = x_1\ln\dfrac{\Phi_1}{x_1} + x_2\ln\dfrac{\Phi_2}{x_2} + \dfrac{z}{2}\left(q_1x_1\ln\dfrac{\theta_1}{\Phi_1} + q_1x_2\ln\dfrac{\theta_2}{\Phi_2}\right)$ $\dfrac{g^E(\text{residual})}{RT} = -q_1x_1\ln(\theta_1 + \theta_2\tau_{21}) - q_2x_2\ln(\theta_2 + \theta_1\tau_{12})$ $\ln\tau_{21} = -(\Delta u_{21}/RT)$ $\ln\tau_{12} = -(\Delta u_{12}/RT)$	$\Delta u_{12}, \Delta u_{21}$ where: $\Delta u_{12} = u_{12} - u_{22}$ $\Delta u_{21} = u_{21} - u_{11}$	$\ln\gamma_i = \ln\dfrac{\Phi_i}{x_1} + \dfrac{z}{2}q_i\ln\dfrac{\theta_i}{\Phi_i} + \Phi_j\left(\lambda_i - \dfrac{r_i}{r_j}\lambda_j\right) - q_i\ln(\theta_i + \theta_j\tau_{ij}) + \theta_jq_i\left(\dfrac{\tau_{ji}}{\theta_i + \theta_j\tau_{ji}} - \dfrac{\tau_{ij}}{\theta_j + \theta_i\tau_{ij}}\right)$ where $i = 1, j = 2$ or $i = 2, j = 1$ $\lambda_i = \dfrac{z}{2}(r_i - q_i) - (r_i - 1)$ $\lambda_j = \dfrac{z}{2}(r_j - q_j) - (r_j - 1)$	—

[a] The numbers represent the following models: 1, two-suffix Margules; 2, three-suffix Margules; 3, van Laar; 4, Wilson; 5, four-suffix Margules; 6, NRTL; 7, UNIQUAC.

[b] r and q are pure-component parameters and z, the coordination number, is equal to 10.

troughs as shown in Figure 4. At an overall composition of x_i^*, the value of $\Delta_{mix}G_m$ on the tangent will be more negative than the value of $\Delta_{mix}G_m$ on the hump. In practice, this "tangent situation" can be achieved by taking some liquid defined by x_i' and adding to it some liquid defined by x_i'' so that the overall composition is satisfied.

A practical demonstration will help to explain this. Consider adding triethylamine (1) to water (2) at 298.2 K (*13*). At first, the two liquids mix, but at a particular composition (x_1', x_2'), phase separation takes place and a minute amount of liquid at composition x_1'', x_2'' forms. Further addition of 1 to 2 will result in the relative volumes of the two phases (defined by x_1', x_2' and x_1'', x_2'', respectively) changing until a point is reached when most of the mixture is composed of x_1'', x_2'' and only a minute amount of x_1', x_2' remains. Further addition of 1 results in the complete mixing of 1 in 2.

Two important points remain. First, the tangent drawn between the troughs in Figure 4 does not necessarily coincide exactly with the minimum of the $\Delta_{mix}G_m$ curve. Second, we must not forget that in the phase-splitting region, mixing, albeit partial mixing, does take place, and in this region $\Delta_{mix}G_m$ must be negative.

The shape of the $\Delta_{mix}G_m$ curve can be calculated from a knowledge of γ_i and hence it should be possible to predict phase separation. We can illustrate this with a problem.

Problem 1. Estimate the mutual solubilities for the water (1) 1-butanol (2) system at 293.2 K given that $\gamma_1^\infty = 3.7$ and $\gamma_2^\infty = 70$ (*12*). Assume that the excess Gibbs energy function can be summarized using the van Laar equation

$$\Delta_{mix}G_m^E = \frac{Ax_1x_2}{x_1(A/B) + x_2}$$

and

$$\ln\gamma_1^\infty = A/RT; \quad \text{hence } A = 3188.7$$

$$\ln\gamma_2^\infty = B/RT; \quad \text{hence } B = 10354.4$$

Now

$$\Delta_{mix}G_m = \Sigma x_i RT\ln x_1 + \Delta_{mix}G_m^E =$$

$$x_1RT\ln x_1 + (1 - x_1)RT\ln(1 - x_1) + 3188.7x_1(1 - x_1)/[0.3080x_1 + (1 - x_1)]$$

(the first line of this equation is identical to eq 10). A plot of $\Delta_{mix}G_m$ vs x_1 is given in Figure 5. The tangent occurs at $x_1' = 0.40$ and $x_1'' = 0.98$. The literature value (*12*) is $x_1' \approx 0.60$ and $x_1'' = 0.90$.

If the value of γ_1^∞ is very very large, that is, $\gamma_1^\infty >> 1000$, then $x_1 \approx 1/\gamma_1^\infty$. Such values for γ_1^∞ are very common and this simplification is used extensively in pollution studies of organic liquids in water. A problem illustrates this point.

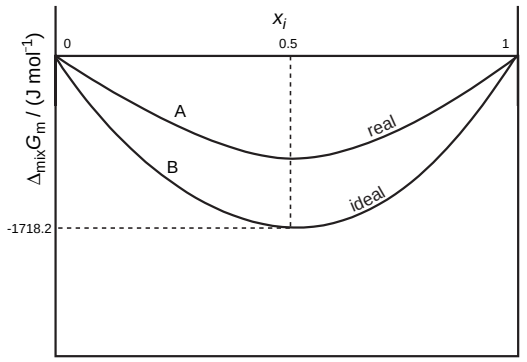

Figure 3. The shape of $\Delta_{mix}G_m$ as a function of x_i for (curve A) a real mixture and (curve B) an ideal mixture. For curve A, $\Delta_{mix}G_m = \Delta_{mix}G_m^{ideal} + \Delta_{mix}G_m^{E}$ where $\Delta_{mix}G_m^{ideal} = \Sigma x_i RT \ln x_i$.

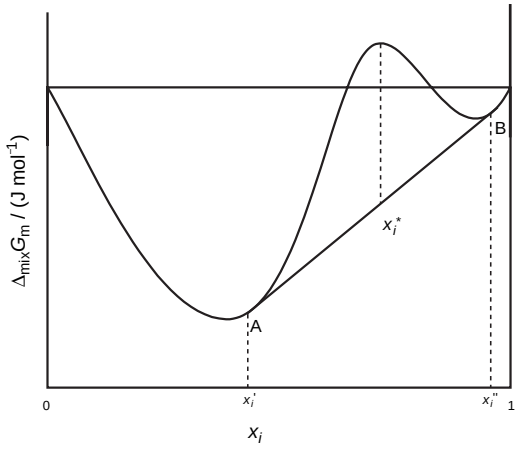

Figure 4. The graph of $\Delta_{mix}G_m$ vs x_i for a mixture whose phases separate.

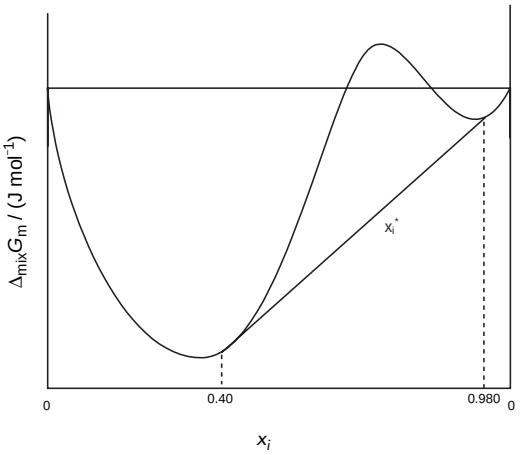

Figure 5. The graph of $\Delta_{mix}G_m$ as a function of x_1. The tangent joins phase-separated mixtures that are in equilibrium, x_1' and x_1''.

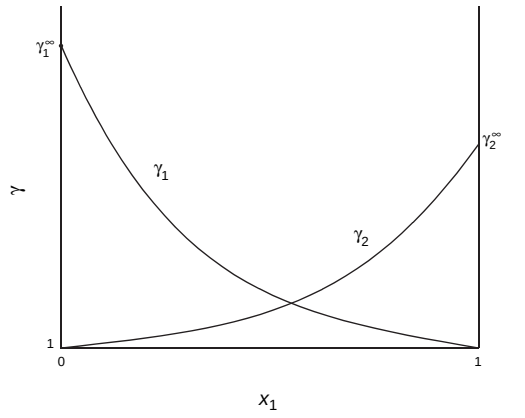

Figure 6. A typical graph of γ_1 and γ_2 as a function of x_1 for a binary liquid mixture system.

Problem 2. For the liquid mixture 1-methlynaphthalene (1)–water (2) at 298.2 K, $\gamma_1^\infty = 282{,}000$. Calculate the solubility of 1-methylnaphthalene in water at this temperature.

It is important to know that at this temperature both substances are liquids.

$$x_1 = 1/\gamma_1^\infty = 1/282{,}000 = 3.5 \times 10^{-6} \text{ mole fraction}$$

The literature value for this is 3.55×10^{-6} mole fraction (*14*).

The reason for the simplification used in the previous problem can be understood by again referring to eq 10 written for a binary system:

$$\Delta_{mix}G_m = x_1 RT \ln x_1\gamma_1 + x_2 RT \ln x_2\gamma_2 \qquad (15)$$

If γ_1^∞ is very large (e.g., 10,000), then at low concentrations ($x < 0.001$ mole fraction) $\gamma_1 \approx \gamma_1^\infty$ (see Fig. 6). At these low concentrations $x_2 \approx 1$ and hence $\gamma_2 \approx 1$, and the second term on the right disappears. Therefore, at these concentrations $\Delta_{mix}G_m$ will be dominated by γ_1 (i.e., γ_1^∞) and will be positive for most values of x_1. But at some values of x_1, $\Delta_{mix}G_m$ will be negative and mixing will take place. For example, if $\gamma_1^\infty = 10{,}000$ then at $x_1 = 10^{-6}$ mole fraction $\gamma_1 \approx \gamma_1^\infty \leq 10^4$ and $\Delta_{mix}G_m = 10^{-6}RT \ln 10^{-2}$. This is a negative quantity. Now at $x_1 = 10^{-3}$ mole fraction we can again safely say that $\gamma_1 \approx \gamma_1^\infty = 10^4$ and $\Delta_{mix}G_{mm} = 10^{-3}RT \ln 10$, which is a positive quantity! Somewhere in between (at the limit of solubility)

$$0 = x_1 RT \ln x_1\gamma_1^\infty \quad \text{and} \quad x_1 = 1/\gamma_1^\infty$$

Continuing with this idea we can show that the magnitude of $\ln \gamma_1^\infty$ gives a good idea of the possibility of phase separation. If $\ln \gamma_1^\infty$ is large and negative, we would assume that $\ln \gamma_2^\infty$ was also negative (a consequence of the Gibbs–Duhem equation 7) and that it is most likely that $\ln \gamma_1$ and $\ln \gamma_2$ would be negative at finite compositions. As a result $\Delta_{mix}G_m$ would be negative at all compositions and complete mixing would take place at all compositions. If, however, $\ln \gamma_1^\infty$ (and consequently $\ln \gamma_2^\infty$) was positive, phase instability could arise because it was possible to obtain positive values for $\Delta_{mix}G_m$ from eq 10 or 15. Experience has shown that if $\ln \gamma_1^\infty > 2$, it is most likely that phase separation will take place.

Solubility of Liquids in Terms of Intermolecular Forces

When mixing takes place between two liquids the liquids are dispersed, one in the other. The process can be divided into three stages: (i) the dispersion of the molecules of liquid A (always an endothermic effect); (ii) the dispersion of the molecules of liquid B (also endothermic); and (iii) the association of molecules A and B (always exothermic). If the last stage is the dominant process and the energy of interactions

A–B > A–A or B–B, then the overall process is exothermic, the values of γ_A and γ_B will very likely be <1 (a negative deviation from Raoult's law), and mixing will take place. This is true for the system acetone-plus-chloroform. However, if the energy of interaction A–A or B–B is very much greater than A–B, then we can expect a large positive deviation from Raoult's law and, as γ_A and γ_B >>1, phase separation (i.e., limited miscibility).

Summing up our understanding of real liquid mixtures, we see that liquids *always* mix to form a single phase, albeit at very low concentrations for some liquid mixtures. Phase separation takes place when the intermolecular forces between the molecules of one liquid are very much stronger than the intermolecular forces between that liquid and the other liquids in the system (γ >>> 1).

Solids in Liquids

When dealing with solids dissolved in liquids, the process is a little more complex. To understand the process, it is best to consider dissolution taking place in four stages.

1. The solid is heated (at a fixed pressure p) from T to T_m, its normal melting point.
2. The solid is melted at T_m.
3. The liquid is super-cooled from T_m to T.
4. The supercooled liquid is mixed with the solvent as discussed above, with eq 10 describing this stage.

The overall Gibbs energy change for these four stages can be summarized as

$$\Delta_{mix}G_m = \Delta G_L + \Sigma RTx_i \ln \gamma_i x_i \qquad (16)$$

where ΔG_L refers to the Gibbs energy changes involved in stages 1, 2, and 3. This is a positive quantity and increases with increasing amount of dissolved solid. It will also depend on the magnitude of T_m with respect to T and on the magnitude of ΔH°_{fusion}, the enthalpy of fusion of the solid. The sign of the second term on the right will depend on the magnitude and sign of $\ln \gamma_i$ but will be negative at some value of x_i. Therefore, the larger is the value of ΔH°_{fusion} and T_m the smaller will be x_1, the limit of solubility. This is supported by solubility data in the literature and an example is given in Table 5. Anthracene has a larger ΔH°_{fusion} and T_m and a lower solubility in organic solvents than phenanthrene.

A more quantitative result can be obtained by analyzing the chemical potential for a solution, as defined in eq 8. When dealing with a solid species, i, μ_i^* and γ_i have no meaning as there is no liquid state at $x_i \rightarrow 1$. To overcome this a new definition is used for the solid solute (*5*):

$$\gamma_i \rightarrow 1 \text{ as } x_i \rightarrow 0$$

and μ_i becomes a *hypothetical* property but one which can be calculated (*5*). The chemical potential μ_i of the solvent remains as defined earlier, and $\gamma_i \rightarrow 1$ and $x_i \rightarrow 1$.

At the limit of solubility, a minute trace of pure solid s (1) is in equilibrium with the solute in solution:

$$\mu_1^s(T,P) = \mu_1(\text{solution}) = \mu_1^*(T,P) + RT \ln x_1\gamma_1(T,P,x_1) \qquad (17)$$

and

$$\ln x_1\gamma_i(T,P,x_1) = \frac{\mu_1^s(T,P) - \mu_1^*(T,P)}{RT} = \frac{\Delta G^\circ_{fusion}}{RT} \qquad (18)$$

Table 5. Solubility of Phenanthrene and Anthracene at 293.2 K (*16*)

Solvent	x_1	
	Phenanthrene	Anthracene
n-Hexane	0.048	0.0018
Acetone	0.145	0.0031
Chloroform	0.238	0.0094
Diethylether	0.133	0.0029
Carbon tetrachloride	0.145	0.0041
Ideal solubility	*0.206*	*0.00871*

NOTE: Solubility decreases with increasing ΔH°_{fusion} and T_m. For phenanthrene ΔH°_{fusion} = 18.6 kJ mol^{-1} and T_m = 369.5 K. For anthracene ΔH°_{fusion} = 28.8 kJ mol^{-1} and T_m = 489.7 K.

At constant P we have

$$\Delta G^\circ_{fusion}(T) = \Delta H^\circ_{fusion}(T) - T\Delta S^\circ_{fusion}(T) \qquad (19)$$

To calculate $\Delta H^\circ_{fusion}(T)$ we must consider heating the solid to T_m, melting it, and then super-cooling it back to T:

$$\Delta H^\circ_{fusion}(T) = \int_T^{T_m} C_p^s dT + \Delta H^\circ_{fusion}(T_m) + \int_{T_m}^T C_p^\ell dT \qquad (20)$$

and

$$\Delta S^\circ_{fusion}(T) = \int_T^{T_m} \frac{C_p^s}{T} dT + \Delta S^\circ_{fusion}(T_m) + \int_{T_m}^T \frac{C_p^\ell}{T} dT \qquad (21)$$

Combining the last expression of eq 18 with eqs 19–21 we get (*15*)

$$\ln x_1\gamma_1 = -\left\{ \frac{\Delta H^\circ_{fusion}(T_m)}{RT}\left[1 - \frac{T}{T_m}\right] + \frac{\Delta C_p}{R}\left[1 - \frac{T_m}{T} + \ln\left(\frac{T_m}{T}\right)\right]\right\} \qquad (22)$$

where ΔC_p refers to $C_p^\ell - C_p^s$ and ℓ and s refer to liquid and solid, respectively. If we assume ideal solubility (similar intermolecular forces in solute and solvent, e.g., naphthalene [1] and toluene [2]), that is, $\gamma_1 = 1$, then eq 22 becomes

$$\ln x_1^{ideal} = -\left\{ \frac{\Delta H^\circ_{fusion}(T_m)}{RT}\left[1 - \frac{T}{T_m}\right]\right\} \qquad (23)$$

with $\Delta C_p = 0$.

The ideal solubility for phenanthrene and anthracene are 0.206 and 0.00871, respectively, and these values are reasonably close to some experimental values (see Table 5). Similar success is found for the related compound naphthalene, as is seen in Table 6. It is reasonable to expect the solubility of these related compounds in aromatic solvents to be close to the ideal solubility because for these solutions $\gamma_1 \approx 1$. However, the solubility for naphthalene, anthracene, and phenanthrene in water are 4.3×10^{-6}, 7.5×10^{-9}, and 1.19×10^{-7} mole fraction, respectively (*14*). We expect large deviation from ideality for these systems.

Table 6. Solubility of Naphthalene (*17*)

Solvent	x_1
Chlorobenzene	0.256
Benzene	0.241
Toluene	0.224
Carbon tetrachloride	0.205
n-Hexane	0.090
Ideal solubility	*0.273*

NOTE: ΔH°_{fusion} = 18.58 kJ mol^{-1} and T_m = 353.20 K for naphthalene.

To better predict the solubility of solids in liquids through the application of eq 22, it is necessary to have some way of predicting γ_1. Many methods are available, including the UNIFAC method (*15*) and the solubility parameter method (*17, 18*). The latter is based on the equation

$$RT \ln \gamma_1 = V_1^{\ell}(\delta_1 - \delta_2)^2 \phi_2^2 \qquad (24)$$

where V_1^{ℓ} is an estimate of the molar volume of the solute as a liquid, δ is the solubility parameter defined by

$$\delta = \left(\frac{\Delta U_{vap}}{V^{\ell}}\right)^{1/2} \qquad (25)$$

where ΔU_{vap} is the molar internal energy change of vaporization of the supercooled liquid (1) and

$$\Delta U_{vap} = \Delta H_{vap} - P\Delta V = \Delta H_{vap} - RT \qquad (26)$$

and ϕ_2 is the volume fraction defined by

$$\phi_2 = x_2 V_2^{\ell}/(x_2 V_2^{\ell} + x_1 V_1^{\ell}) \qquad (27)$$

where V_2^{ℓ} is the molar volume of the solvent at temperature T.

To illustrate the application of the solubility parameter theory, let us predict the solubility for one of the mixtures that did not show ideal behavior in Table 6.

Problem 3. Estimate the solubility of solid naphthalene (1) in liquid *n*-hexane (2) at 293.2 K given that for naphthalene $\Delta H^{\circ}_{fusion}$ = 18.58 kJ mol^{-1}, T_m = 353.20 K, molar mass = 128.19 g mol^{-1}, ρ_{solid} = 1.0253 g cm^{-3}, and the vapor pressure is given by ln P (in bars) = 20.083 – 8708/T.

For *n*-hexane, δ_2 = 14.92 (J cm^{-3})$^{1/2}$ and V_2^{ℓ} = 132 cm^3 mol^{-1}.

Our main problem is to find δ_1 from ΔU_{vap}.

$$\Delta U_{vap} = \Delta H^{\circ}_{vap} - RT = \Delta H^{\circ}_{sub} - \Delta H^{\circ}_{fusion} - RT$$

Now

$$\frac{\Delta H^{\circ}_{sub}}{RT^2} = \frac{d \ln P}{dT} = \frac{\ln P}{dT} = \frac{8708}{T^2}$$

$$\Delta H^{\circ}_{sub} = (8708 \times 8.314)\ \text{J mol}^{-1} = 72.43\ \text{kJ mol}^{-1}$$

$$\Delta U_{vap} = \left[72.43 - 18.58 - \left(\frac{8.314 \times 293.15}{1000}\right)\right] \text{kJ mol}^{-1} = 51.41\ \text{kJ mol}^{-1}$$

$$\delta_1 = \left(\frac{51.41}{125}\right)^{1/2} (\text{J cm}^{-3})^{1/2} = 20.28\ (\text{J cm}^{-3})^{1/2}$$

Assuming that the molar volume of the solid is the same as that of the liquid and assuming that ΔC_p = 0, we have from eqs 22 and 24

$$\ln x_1 = \frac{-V_1^{\ell}(\delta_1 - \delta_2)^2 \phi_2^2}{RT} - \frac{\Delta H_f^{\circ}(T_m)}{RT}\left(1 - \frac{T}{T_m}\right) \qquad (28)$$

Because x_1 and ϕ_2 are unknown, it is necessary to iterate. Assuming ϕ_2 = 1 for the first iteration, x_1 = 0.063. Substituting back into eq 28 and calculating ϕ_2 each time, x_1 = 0.078 after three iterations. The literature value for x_1 is 0.090 (see Table 6).

The activity coefficient at this concentration is γ_1 = 0.273/0.090 = 3.0; and as before, it reflects the solution's deviation from ideality. In general, if the solute–solvent interactions are weaker than the solute–solute interactions, the solubility will be less than expected for the ideal solution and $\gamma > 1$. This is a typical situation for solid in liquids. The converse is also true.

An interesting example to consider before leaving the dissolution of nonelectrolyte solids in nonelectrolyte liquids is that of buckminsterfullerene (C_{60}) in benzene. In spite of the aromatic nature of C_{60}, its solubility in benzene is very low and $x_1 = 2 \times 10^{-4}$ mole fraction at 298 K (*19*). The dominant features here are the large T_m and $\Delta H^{\circ}_{fusion}$ values.

Solubility of a Solid in a Liquid in Terms of Intermolecular Forces

As in all dissolution processes, the solute is dispersed throughout the solvent. For solids in liquids this involves two stages (we have assumed only limited solubility):

1. The separation of solute molecules (or ions in the case of ionic material) from one another; and
2. The association of separated solute molecules (or ions) and the solvent molecules.

Stage 1 is always endothermic and for ionic compounds in water this enthalpy of ionization is usually very large. It is in fact the lattice energy, $\Delta H^{\circ}_{lattice}$. Stage 2 is always exothermic and for ions in water it is called the *hydration* enthalpy, $\Delta H^{\circ}_{hydration}$. For solutes in other solvents, it is the *solvation* enthalpy. The overall enthalpy is the enthalpy of solution ($\Delta H^{\circ}_{solution}$) and may be large or small and positive or negative. The value of $\Delta H^{\circ}_{solution}$ is responsible for the effect of temperature on solubility as reflected by Le Châtelier's principle. For example, if $\Delta H^{\circ}_{solution}$ is positive (endothermic), then an increase in temperature will result in an increase in solubility. This is true for KNO_3. Its solubility increases from 15 to 60 g KNO_3 per 100 g water as the temperature increases from 0 to 40 °C. For NaCl the effect is small: over the same temperature change the solubility increases from 35 to 37 g NaCl per 100 g water. The effect is opposite for Li_2SO_4: over the same temperature change the solubility decreases from 36 to 33 g per 100 g water.

The range of solubility of ionic solids in water is enormous (see Table 2). The dominant effect is not the magnitude or sign of $\Delta H^{\circ}_{solution}$, but the magnitude of the $\Delta H^{\circ}_{fusion}$ and T_m.

Summing up our understanding of the solubility of solids in liquids, we see that like liquids dissolving in liquids, solubility depends on the relative nature of the molecular interactions in the solute and solvent. But, unlike liquids, the solubility of a solid depends largely on the magnitude of the enthalpy of fusion and the melting point of the solute.

Gases in Liquids

For gases dissolved in liquids a similar approach to that taken with solids can be used. The resultant equation (analogous to eq 22) is

$$\ln x_1\gamma_1 = -\frac{\Delta H^{\circ}_{vap} T_b}{RT}\left(1 - \frac{T}{T_b}\right) - \frac{\Delta C_p}{R}\left[1 - \frac{T_b}{T} + \ln\left(\frac{T_b}{T}\right)\right] \qquad (29)$$

with γ_1 defined in a similar way (*4*) from

$$\mu_i = \mu_i^0 + RT \ln x_i \gamma_i \qquad (30)$$

with $\gamma_i \rightarrow 1$ or $x_i \rightarrow 0$ and μ_i^0 is the hypothetical chemical potential at $x_1 = 1$, extrapolated from infinite dilution behavior (see Fig. 7). The ideal gas solution follows Henry's law (5):

$$P_i = x_i H_i \tag{31}$$

where H is the Henry's law constant. The activity coefficient is again a measure of deviation from ideality and can be related to vapor pressure as shown in Figure 7, where, at x_A,

$$\gamma_1 = \mathrm{AC/AB} \tag{32}$$

The ideal gas solubility can be calculated from eq 29, assuming $\gamma_1 = 1$. A simple equation, ignoring ΔC_p, is

$$\ln x_1^{\mathrm{ideal}} = -\frac{\Delta H^\circ_{\mathrm{vap}} T_b}{RT}\left(1 - \frac{T}{T_b}\right) \tag{33}$$

To illustrate this equation, let us calculate the solubility of hydrocarbon gases in a hydrocarbon liquid—a near-ideal situation.

Problem 4. Estimate the solubility of methane and ethane in *n*-heptane and in water at 298.2 K and 1.013 bar, given the following data:

Solute	T_b/K	$\Delta H^\circ_{\mathrm{vap}}$/kg mol^{-1}
CH_4	111.54	8.18
C_2H_6	184.55	14.70

The results, calculated from eq 33, are given below, together with literature values.

Solvent	Solute	x_1^{ideal}	x_1 (Lit.)	Ref
n-Heptane	CH_4	0.004	0.0051	*20*
n-Heptane	C_2H_6	0.025	0.0315	*20*
Water	CH_4	0.004	2.51×10^{-5}	*21*
Water	C_2H_6	0.025	3.34×10^{-5}	*21*

As expected, the predicted solubility results for the gases in *n*-heptane are reasonably close to the experimental values. The predicted results for the gases in water are two orders of magnitude different from the measured values.

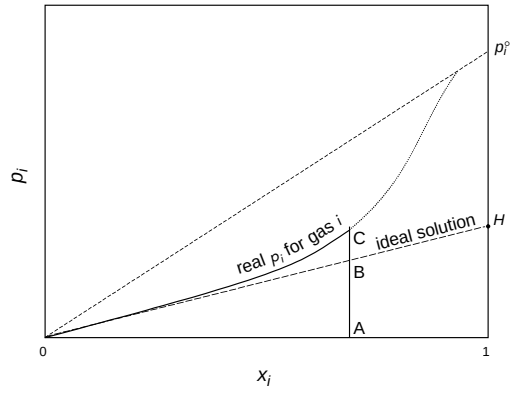

Figure 7. The partial pressure p_i of gas (1) in a gas–liquid system. The "ideal" solution is defined at infinite dilution, $x_1 = 0$; the ideal solubility is defined in terms of the extrapolation to H, the Henry's law constant, at infinitely dilute partial pressure (at $x_1 = 1$); $p_i = x_i H$; and $\gamma_1 = \mathrm{AC/AB}$.

Another way to predict gas solubilities is to assume that the gases behave according to Raoult's law:

$$p_1 = x_1 p_1^\circ \tag{34}$$

where p_1 is the partial pressure of the solute (taken as 1.013 bar in problem 6) and p_1° is the extrapolated pressure of the gas to $x = 1$. For permanent gases the solubility is so low at partial pressures of 1 bar that the Henry's law line approximates the Raoult's law line. The following example illustrates this method of predicting solubilities.

Problem 5. Calculate the ideal solubility of nitrogen, oxygen, and hydrogen at 298.15 K in liquids using (a) Raoult's law and (b) eq 33 and the following data:

Gas	$\Delta H^\circ_{\mathrm{vap}}$/kg mol^{-1}	T_b/K	T_c/K	P_c/MPa
N_2	5.590	77.300	126.2	3.394
O_2	6.828	87.290	154.6	5.046
H_2	0.904	20.370	33.2	1.297

The p_1° values were calculated from the Clausius–Clapeyron equation using P_c and T_c:

$$p_1 = p_2 \exp\left[-\frac{\Delta H^\circ_{\mathrm{vap}}}{R}\left(\frac{1}{T_1} - \frac{T}{T_2}\right)\right]$$

The solubilities for these gases using eqs 33 and 34 are given below.

Gas	x_1^{ideal}		x_1 in *n*-Heptane		x_1 in Water	
	eq 33	eq 34	Value	Ref	Value	Ref
N_2	1.59×10^{-3}	1.38×10^{-3}	1.35×10^{-3}	*20*	1.17×10^{-5}	*21*
O_2	1.29×10^{-3}	1.55×10^{-3}	2.1×10^{-3}	*20*	2.30×10^{-5}	*21*
H_2	6.92×10^{-3}	4.25×10^{-3}	6.88×10^{-4}	*20*	1.41×10^{-5}	*21*

The predicted results for nitrogen and oxygen in *n*-heptane are remarkably good, but the other predictions are too high. For the solutions, $\gamma > 1$, reflecting a great disparity in intermolecular forces between solute and solvent. As in the case of solids in liquids, theories such as the solubility parameter theory can be successfully used to predict solubility (*15*).

Our understanding of the solubilities of gases in liquids follows very much the approach used for solids in liquids. The predictions made for gas solubilities using very basic and simple theories are remarkably good. Pollack (*22*) has done a detailed analysis of why gases dissolve in liquids using xenon solubilities in simple organic liquids for illustrative purposes.

Conclusions

We have found that the solution process in an isolated system at constant T and P is spontaneous; the entropy of solution is positive, which in probabilistic terms indicates more complexions or a more random distribution of the particles involved. The enthalpy change for mixing for an ideal solution is zero. For real systems it may be positive or negative, the magnitude being usable as an indicator of "non-ideality". Each of the changes in thermodynamic functions may be used as a reason for the common-sense observation that substances dissolve in fluids.

We have shown the importance of intermolecular forces in predicting solubility, thus supporting the old adage like dissolves

like. We have shown that liquids always mix, although the mixing may only be partial. We have shown the importance of properties such as $\Delta H^{\circ}_{fusion}$ and T_m for solids and ΔH°_{vap} and T_b (for gases) in determining solubilities and illustrated how modern theories of solutions can be used to make very good estimates of complex solubilities.

Literature Cited

1. Francis, A. W. *Critical Solution Temperatures*; Advances in Chemistry Series 31; American Chemical Society: Washington, DC, 1961.
2. Atkins, P. W. *Physical Chemistry*, 5th ed.; Oxford University Press: New York, 1994; Chapter 4.
3. Moore, W. J. *Physical Chemistry*, 5th ed.; Prentice Hall: Englewood Cliffs, NM, 1972; Chapter 7.
4. Atkins, P. W. Op. cit.; Chapter 7.
5. Denbigh, K. G. *Principles of Chemical Equilibria*, 4th ed.; Cambridge University Press: New York, 1981; Chapter 9.
6. Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed., McGraw-Hill: New York, 1987; Chapter 8, Table 8-3.
7. Letcher, T. M. *Faraday Symp.* **1980**, *15*, 103–111.
8. Eckert, C. A.; Newman, B. A.; Nicolaides, G. L.; Long, T. C. *Am. Inst. Chem. Eng. J*. **1981**, *27*, 33–40.
9. Pierotti, R.; Deal, C. H.; Derr, E. *Ind. Eng. Chem*. **1959**, *51*, 95–102.
10. Palmer, D. A. *Chem. Eng*. **1975**, *82*, 80–85.
11. Friedenslund, A.; Jones, R. L.; Praunsnitz, J. M. *Am. Inst. Chem. Eng. J*. **1975**, *21*, 1086–1093.
12. Friedenslund, A.; Gmehling, T.; Rasmussen, P. *Vapor Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, 1977.
13. Atkins, P. W. Op. cit.; Chapter 8.
14. Mackay, D.; Shiu, W. Y. *J. Chem. Eng. Data* **1977**, *22*, 359–402.
15. Sandler, S. I. *Chemical & Engineering Thermodynamics*, 2nd ed.; Wiley: New York, 1989; Chapter 8.
16. Gmehling, J. G.; Anderson, T. F.; Prausnitz, J. M. Ind. Eng. Chem. Fundamentals **1978**, *17*, 269–273.
17. Hildebrand, J. H.; Scott, R. L. *The Solubility of Non-electrolytes*, 3rd ed.; Reinhold: New York, 1950; Chapter XVII.
18. Scatchard, G. *Chem. Rev*. **1931**, *8*, 321–333.
19. Letcher, T. M.; Domanska, U.; Crosby, P. B.; Fowler, P.; Legan, T. *South Afr. J. Chem*. **1993**, *46*, 41–44.
20. Wilhelm, E.; Battino, R. *Chem. Rev*. 1973, *73*, 1–10.
21. Wilhelm, E.; Battino, R.; Wilcock, R. J. *Chem. Rev*. **1977**, *77*, 219–262.
22. Pollack, G. L. *Science* **1991**, *251*, 1323.