Chapter 10. Solubilities of Gases in Liquids

The solubility of a gas in a liquid is determined by the equations of phase equilibrium.
If a gaseous phase and a liquid phase are in equilibrium, then for any component *í* the fugacities in both phases must be the same.

$$f_i^{\text{gas}} = f_i^{\text{liquid}} \tag{10-1}$$

10.1 The Ideal Solubility of a Gas

The simple way to reduce Eq. (10-1) to a more useful form is to rewrite it in a manner suggested by Raoult's law.

① neglecting all gas-phase nonidealities as well as the effect of pressure on the condensed phase

② neglecting any nonidealities due to solute-solvent interactions

$$p_i = x_i P_i^s \tag{10-2}$$

$p_í$: the partial pressure of component *í* in the gas phase
$x_í$: the solubility of *í* in the liquid
$p_í^s$: the saturation vapor pressure of pure liquid *í*

An obvious difficulty presents itself in finding a value for $p_í^s$, whenever the solution temperature is above the critical temperature of pure *í*.
In that case it has been customary to extrapolate the saturation pressure of pure liquid *í* beyond its critical temperature to the solution temperature.

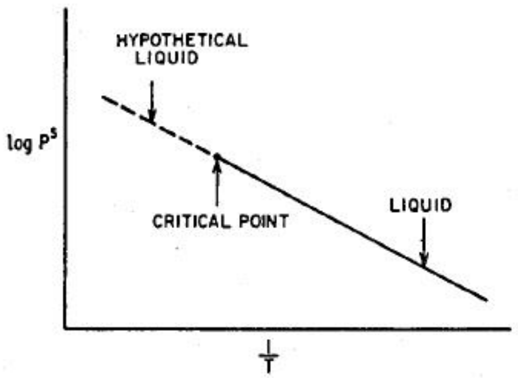


Figure 10-1 Convenient but arbitrary extrapolation of liquid saturation pressure into the hypothetical liquid region.

The ideal solubility, as calculated by Eq. (10-2) and the extrapolation scheme indicated in Fig. 10-1, usually gives correct order-of-magnitude. In some case, where the physical properties of solute and solvent are similar, the ideal solubility is remarkably close to the experimental value.

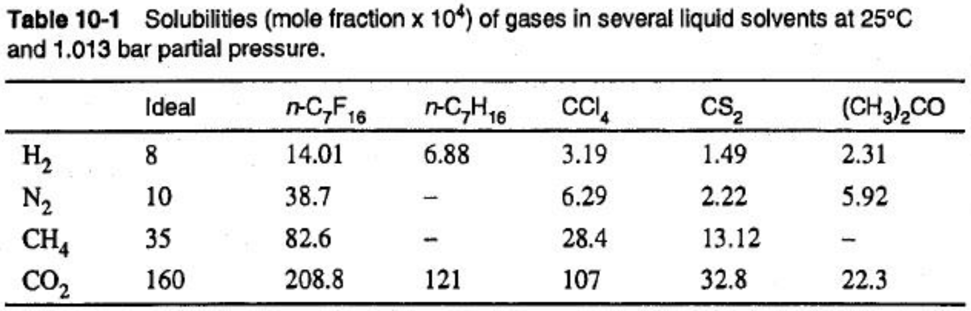


Table 10-1 Solubilities (mole fraction x 10^4) of gases in several liquid solvents at 25°C and 1.013 bar partial pressure.

	Ideal	n-C_7F_{16}	n-C_7H_{16}	CCl_4	CS_2	$(CH_3)_2CO$
H_2	8	14.01	6.88	3.19	1.49	2.31
N_2	10	38.7	–	6.29	2.22	5.92
CH_4	35	82.6	–	28.4	13.12	–
CO_2	160	208.8	121	107	32.8	22.3

The ideal solubility is significantly different from observed solubilities, but it is of the right order of magnitude.

The ideal solubility given by Eq. (10-2) suffers from two serious defects.

① at a fixed temperature and partial pressure, has the same solubility in all solvents

② at constant partial pressure, the solubility of a gas always decreases with rising temperature

10.2 Henry’s Law and Its Thermodynamic Significance

$$p_i = y_i P = kx_i \qquad (10\text{-}3)$$

κ : constant of proportionality depending only on temperature (for any given solute and solvent)

For Eq. (10-3), there are two constraints

① the solubility and the partial pressure of the solute are small
② the temperature is well below the critical of the solvent

When compared with Eq. (10-1) and Eq. (10-3),

$$f_2^L = kx_2 = H_{2,1}x_2 = \gamma_2 x_2 f_2^0 \qquad (10\text{-}4)$$

Thus,

$$k = H_{2,1} = \gamma_2 f_2^0 \qquad (10\text{-}5)$$

1 : stands for solvent
2 : stands for solute

At a given temperature and pressure, the standard-state fugacity is a constant and does not depend on the solute mole fraction in the liquid phase.
Since κ does not depend on x_2, the activity coefficient γ_2 must also be independent of x_2.
So,

$$RT \ln \gamma_2 = A(1-x_2)^2 + B(1-x_2)^3 + \ldots \qquad (10\text{-}6)$$

A, B, … : constants depending on temperature and on intermolecular forces between solute and solvent

When $x_2 \ll 1$, γ_2 is only weakly dependent on χ_2 and Henry's law provides a good approximation.

Coefficient A is a measure of nonideality.

① A is positive : 'dislike' between solute and solvent
② A is negative : 'tendency' between solute and solvent

In any case, it is the absolute value of A/RT that determines the range of validity of Henry's law.

① $A/RT = 0$: ideal solution. Henry's law holds for the entire range of composition ($0 \le x_2 \le 1$)
② A/RT is small : activity coefficient γ_2 does not change much even for appreciable x_2
③ A/RT is large : even a small x_2 can produce a significant change in the activity coefficient with composition
④ $x_2 \to 0$: the logarithm of the activity coefficient approaches the constant value A/RT (So, Henry's law is valid)

In Eq. (10-3), Henry's law assumes that the gas-phase fugacity is equal to the partial pressure.
If this assumption is not used, Henry's law for solute i is,

$$\boxed{f_i = \varphi_i y_i P = H_{i,\,\text{solvent}}\, x_i} \qquad (10\text{-}7)$$

Table 10-2 Henry's constants (bar) for four gases in ethylene oxide.*

Temperature (°C)	N_2	Ar	CH_4	C_2H_6
0	2837	1692	621	85.4
25	2209	1439	622	110
50	1844	1287	603	131

* J. D. Olson, 1977, *J. Chem. Eng. Data*, 22: 326. The estimated experimental uncertainty is about 2%.

Table 10-3 Some volumetric properties of four ethylene oxide (1)/gas (2) systems.*

		cm^3 mol^{-1}			
	Temperature (°C)	N_2	Ar	CH_4	C_2H_6
$-B_{22}$	0	10.3	21.5	53.6	223
	25	4.7	15.8	42.8	187
	50	0.3	11.2	34.2	157
$-B_{12}$	0	85.9	119	160	331
	25	69.4	98.6	133	273
	50	56.2	82.3	112	229
$\bar{v}_2^\infty$	0	41.1	35.9	44.4	61.3
	25	43.3	39.5	47.5	64.5
	50	48.5	43.6	52.0	68.6

* J. D. Olson, 1977, *J. Chem. Eng. Data*, 22: 326. Second virial coefficient ($-B_{22}$) from sources quoted in J. H. Dymond and E. B. Smith, 1980, *The Virial Coefficients of Pure Gases and Mixtures* (Oxford: Clarendon Press). Second-virial cross coefficient ($-B_{12}$) are estimated from a correlation by C. Tsonopoulos, 1974, *AIChE J.*, 20: 263. Liquid-phase partial molar volumes at infinite dilution ($\bar{v}_2^\infty$) are estimated from the correlation of E. Lyckman, C. A. Eckert, and J. M. Prausnitz, 1965, *Chem. Eng. Sci.*, 20: 685.

10.3 Effect of Pressure on Gas Solubility

Actually, the pressure dependence can be neglected as long as the pressure is not large.
At high pressures, however, the effect is not negligible and therefore it is necessary to consider how Henry’s constant depends on pressure.

$$\left(\frac{\partial \ln f_i^L}{\partial P}\right)_{T,x} = \frac{\overline{v}_i}{RT} \qquad (10\text{-}8)$$

$\overline{V}_i$: partial molar volume of *i* in the liquid phase

The thermodynamic definition of Henry’s constant is,

$$H_{i,\text{solvent}} \equiv \lim_{x_i \to 0} \frac{f_i^L}{x_i} \quad \text{(at constant temperature and pressure)} \qquad (10\text{-}9)$$

Substitution of Eq. (10-9) into Eq. (10-8) gives

$$\boxed{\left(\frac{\partial \ln H_{i,\text{solvent}}}{\partial P}\right)_T = \frac{\overline{v}_i^{\infty}}{RT}} \qquad (10\text{-}10)$$

$\overline{V}_i^{\infty}$: partial molar volume of solute *i* in the liquid phase at infinite dilution

Integrating Eq. (10-10) and assuming that the fugacity of *i* at constant temperature and pressure is proportional to x_i,

$$\ln \frac{f_i}{x_i} = \ln H_{i,\text{solvent}}^{(P^r)} + \frac{\int_{P^r}^{P} \overline{v}_i^{\infty} dP}{RT} \qquad (10\text{-}11)$$

$H_{i,solvent}^{(P^r)}$: Henry’s constant evaluated at an arbitrary reference pressure P^r.

There are two constraints

① the activity coefficient of the solute does not change noticeably over the range of x_2 considered
→ x_2 must be small

② the infinitely dilute liquid solution must be essentially incompressible
→ temperatures far removed from the critical temperature of the solution

Using two constraints and letting subscript 1 refer to the solvent and subscript 2 to the solute, Eq. (10-11) becomes

$$\boxed{\ln\frac{f_2}{x_2} = \ln H_{2,1}^{(P_1^s)} + \frac{\bar{v}_2^{\infty}(P - P_1^s)}{RT}} \tag{10-12}$$

(*Krichevsky – Kasarnovsky*)

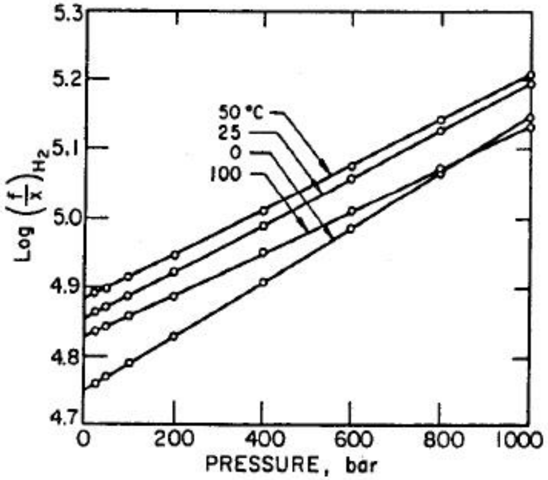


Figure 10-2 Solubility of hydrogen in water at high pressures.

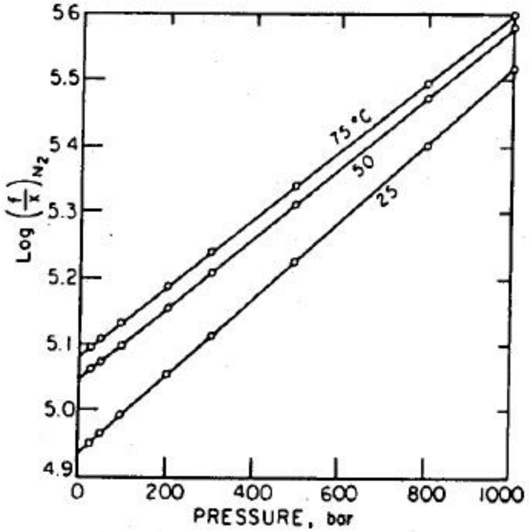


Figure 10-3 Solubility of nitrogen in water at high pressures.

Fig. 10-4 shows limitation of the Krichevsky – Kasarnovsky equation.

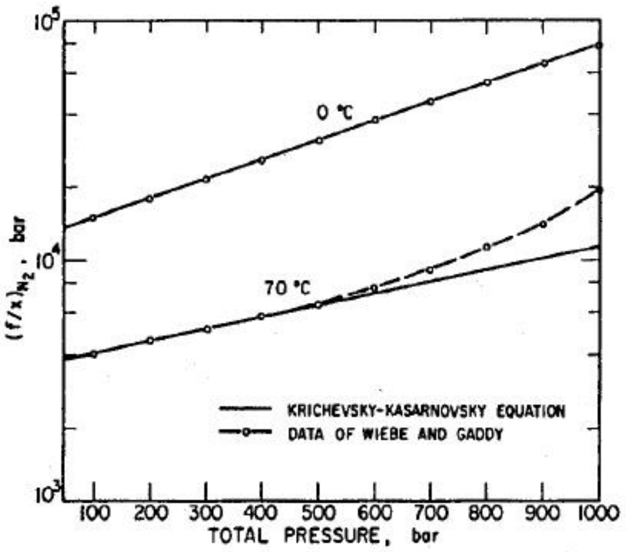


Figure 10-4 Success and failure of the Krichevsky-Kasarnovsky equation. Solubility of nitrogen in liquid ammonia.

At 70℃, Krichevsky – Kasarnovsky equation breaks down after about 600 bar.

In case of 0℃, the assumptions of Eq. (10-12) are reasonably satisfied.

① 0℃ liquid ammonia is an unexpanded liquid solvent
(the critical temperature of ammonia is 132.3℃)

② the solubility of nitrogen is small throughout, only 2.2 mol % at 1000 bar

However

① 70℃ liquid ammonia is already quite expanded (and compressible)

② the solubility of nitrogen is no longer small (12.9 mol % at 1000 bar)

As a result, it is not surprising that Krichevsky – Kasarnovsky equation fails at higher pressures for the data at 70℃.

Variation of the activity coefficient of the solute with mole fraction can be taken into account by one of the methods discussed in Chap. 6. Among them, the simplest way is to use two-suffix Margules equation.

$$\ln\gamma_1 = \frac{A}{RT}x_2^2 \qquad (10\text{-}13)$$

A : an empirical constant determined by intermolecular forces in the solution.
(Typically, A is a weak function of temperature)

The activity coefficient γ^*_2 of the solute, normalized according to the unsymmetric convention (Sec. 6.4), is then found from the Gibbs-Duhem equation.

$$\ln\gamma_2^* = \frac{A}{RT}(x_1^2 - 1) \qquad (10\text{-}14)$$

The fugacity of component 2 at pressure P_1^s is

$$f_2 = \gamma_2^* H_{2,1}^{(P_1^s)} x_2 \qquad (10\text{-}15)$$

instead of Eq. (10-12) we obtain

$$\boxed{\ln\frac{f_2}{x_2} = \ln H_{2,1}^{(P_1^s)} + \frac{A}{RT}(x_1^2 - 1) + \frac{\overline{v}_2^{\infty}(P - P_1^s)}{RT}} \tag{10-16}$$

(*Krichevsky – Ilinskaya*)

Because of the additional parameter, it has a wider applicability than does Eq. (10-12).

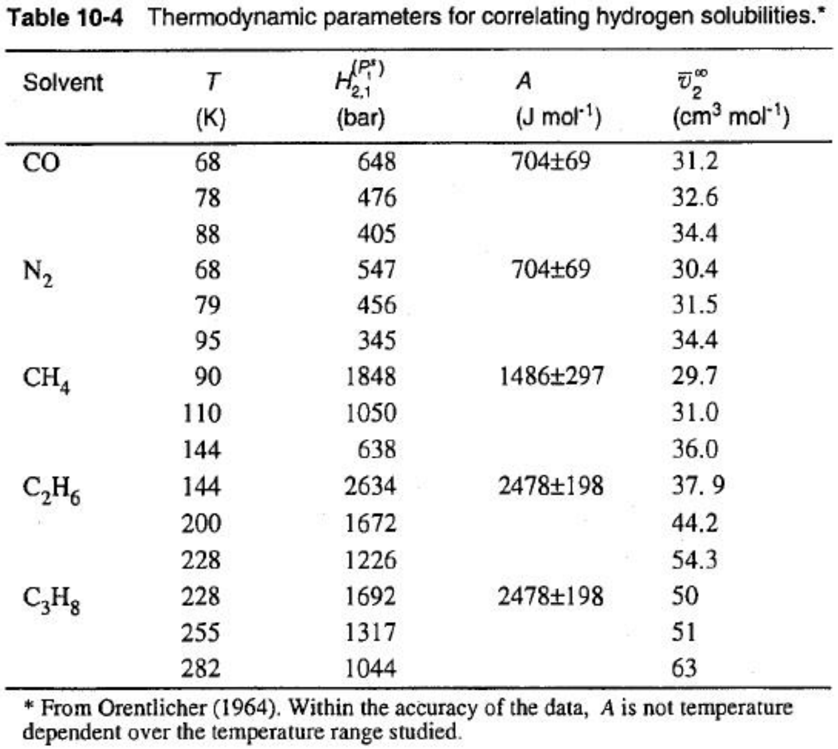


Table 10-4 Thermodynamic parameters for correlating hydrogen solubilities.*

Solvent	T (K)	$H_{2,1}^{(P_1^s)}$ (bar)	A (J mol^{-1})	$\overline{v}_2^{\infty}$ (cm^3 mol^{-1})
CO	68	648	704±69	31.2
	78	476		32.6
	88	405		34.4
N_2	68	547	704±69	30.4
	79	456		31.5
	95	345		34.4
CH_4	90	1848	1486±297	29.7
	110	1050		31.0
	144	638		36.0
C_2H_6	144	2634	2478±198	37. 9
	200	1672		44.2
	228	1226		54.3
C_3H_8	228	1692	2478±198	50
	255	1317		51
	282	1044		63

* From Orentlicher (1964). Within the accuracy of the data, A is not temperature dependent over the temperature range studied.

When, for a given temperature, gas-solubility data alone are available as a function of pressure, it is difficult to obtain three isothermal parameters ($H_{2,1}^{(P_1^S)}$, $\overline{v}_2^{\infty}$, A) from data reduction.

Let $W = \ln(f_2/x_2)$ & isothermal changes in the region $P = P_1^s$ and $x_2 = 0$.

At a constant temperature T, we write a Taylor series

$$W(P,x_2) = W(P_1^s,0) + \left(\frac{\partial W}{\partial x_2}\right)_{P=P_1^s,\, x_2=0} x_2 + \left(\frac{\partial W}{\partial P}\right)_{P=P_1^s} (P - P_1^s) \tag{10-17}$$

Comparison with Eq. (10-16) shows that

$$W(P_1^s,0) = \ln H_{2,1}^{(P_1^s)} \tag{10-18}$$

$$\left(\frac{\partial W}{\partial P}\right)_{P_1^s} = \frac{\overline{v}_2^{\infty}}{RT} \tag{10-19}$$

$$\left(\frac{\partial W}{\partial x_2}\right)_{x_2=0} = -\frac{2A}{RT} \tag{10-20}$$

We can calculate parameters ($H_{2,1}^{(P_1^S)}$, $\overline{v}_2^{\infty}$, A) from an equation of state.

First,

$$H_{2,1}^{(P_1^s)} = P_1^s \varphi_2^{L,\infty} \tag{10-21}$$

$\varphi_2^{L,\infty}$: fugacity coefficient of solute 2 in the liquid phase at temperature T at infinite dilution ($x_2 = 0$)

Second,

$$\bar{v}_2^{\infty} = -\left[\frac{(\partial P / \partial n_2)_{T,V,n_1}}{(\partial P / \partial V)_{T,n_1,n_2}}\right]_{n_2=0} \tag{10-22}$$

n : the number of moles
V : the total volume

Finally,

$$A = -\frac{RT}{2}\left(\frac{\partial \ln \varphi_2^L}{\partial x_2}\right)_{P=P_1^s, T, x_2=0} \tag{10-23}$$

(EOS be valid for the entire density range, because fugacity coefficients depend on an integral of the EOS)

Calculated thermodynamic properties of mixtures often depend strongly on the mixing rules.
(especially on the cross term for the characteristic energy parameter)

① in equations of the van der Waals form, the constant a (for a binary mixture) is

$$a = x_1^2 a_1 + x_2^2 a_2 + 2x_1 x_2 (a_1 a_2)^{1/2}(1 - k_{12}) \tag{10-24}$$

k_{12} : binary parameter that has a large effect on φ_2^L

② Redlich – Kwong – Soave

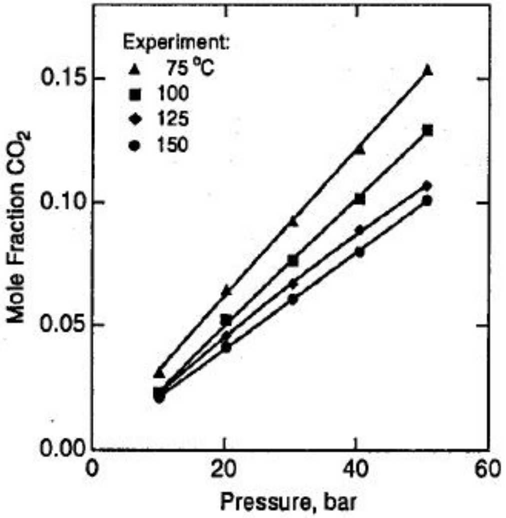


Figure 10-5 Solubility of carbon dioxide in phenol. Solid lines are calculated from the Krichevsky-Ilinskaya equation [Eq. 10-16)] with the parameters listed in Table 10-5 for the Redlich-Kwong-Soave equation of state. Experimental data from Yau *et al.* (1992).

Table 10-5 Thermodynamic parameters for correlating carbon dioxide solubility in phenol. Parameter k_{12} was obtained from regression of vapor-liquid equilibrium data for the carbon dioxide/phenol system at each isotherm.

Temp. (°C)	$k_{12}\times10^2$	$H_{2,1}^{(P_1^s)}$ (bar)	A (J mol^{-1})	$\bar{v}_2^\infty$ (cm^3 mol^{-1})
75	7.53	330	1347	45.3
100	7.72	384	1465	48.6
125	7.19	436	1531	52.1
150	6.31	473	1597	56.3

10.4 Effect of Temperature on Gas Solubility

No simple generalizations can be made concerning the effect of temperature on solubility as indicated by Fig. 10-6 that shows Henry's constants as a function of temperature.

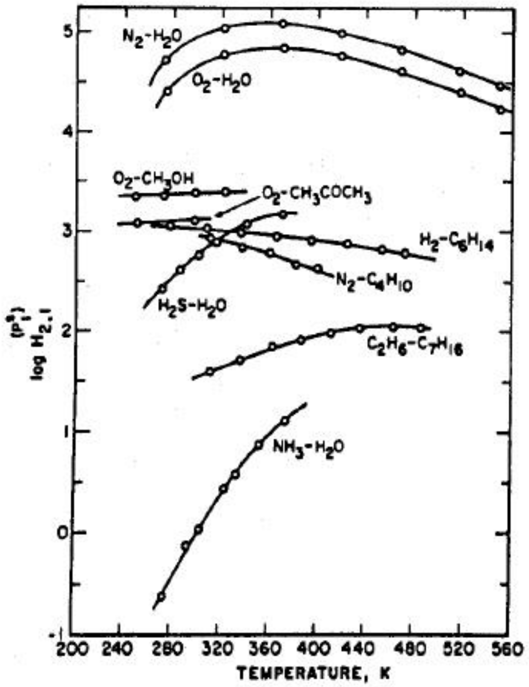


Figure 10-6 Henry's constants (bar) for typical gases range over five orders of magnitude. The effect of temperature differs qualitatively from one system to another.

The effect of temperature depends strongly on the properties of the particular system and also on the temperature.

The temperature derivative of the solubility, as calculated from the Gibbs-Helmholtz equation, is directly related to either the partial molar enthalpy or the partial molar entropy of the gaseous solute in the liquid phase.
Therefore, if something can be said about the enthalpy or entropy change of solution, insight can be gained on the effect of temperature on solubility.

$$\left(\frac{\partial \ln x_2}{\partial 1/T}\right)_P = -\frac{\Delta \bar{h}_2}{R} \qquad (10\text{-}25)$$

$$\left(\frac{\partial \ln x_2}{\partial \ln T}\right)_P = \frac{\Delta \bar{s}_2}{R} \qquad (10\text{-}26)$$

x_2 : the mole fraction of gaseous solute at saturation

$$\Delta \bar{h}_2 \equiv \bar{h}_2^L - h_2^G, \qquad \Delta \bar{s}_2 \equiv \bar{s}_2^L - s_2^G$$

h_2^G and s_2^G : the enthalpy and the entropy of pure 2 gas at system temperature and pressure, respectively

In Eq. (10-26),

① $\Delta \bar{s}_2 > 0$: the solubility increases with rising temperature
② $\Delta \bar{s}_2 < 0$: the solubility decreases with rising temperature

$$\Delta \bar{s}_2 = (s_2^L - s_2^G) + (\bar{s}_2^L - s_2^L) \qquad (10\text{-}27)$$

s_2^L : the entropy of the (hypothetical) pure liquid at the temperature of the solution

In Eq. (10-27),

① the first term on the right-hand side : the entropy of condensation of the pure gas
(in general) negative (the entropy of a liquid is lower than that of a saturated gas at the same temperature)

② the second term : the partial molar entropy of solution of the condensed solute

$$\bar{s}_2^L - s_2^L = -R \ln x_2 \tag{10-28}$$

(assuming ideal entropy of mixing for the two liquids)

positive ($x_2 < 1$)
the smaller the solubility, the larger this term

So (in Eq. 10-27),

① gases have very small solubilities : $\Delta \bar{s}_2 > 0$
② the others : $\Delta \bar{s}_2 < 0$

Therefore (combining Eq. 10-26 and Eq. 10-27),

① sparingly soluble gases (very small x_2) : positive temperature coefficients of solubility
② readily soluble gases (relatively large x_2) : negative temperature coefficients of solubility

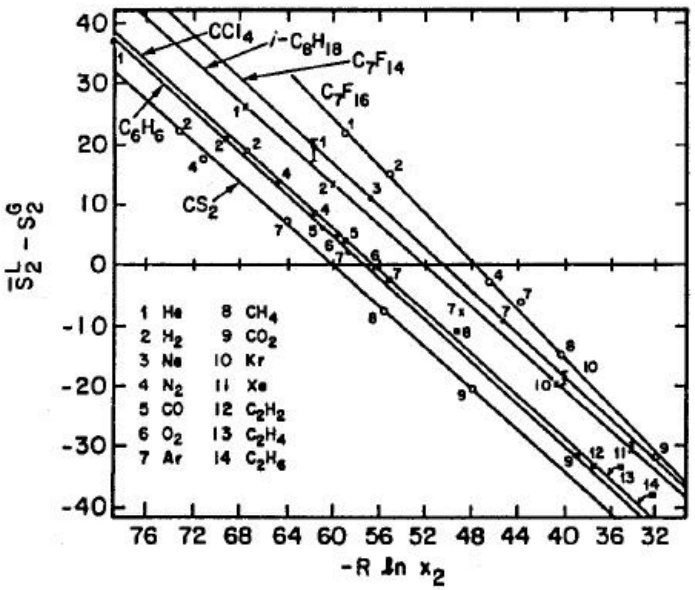


Figure 10-7 Entropy of solution of gases in liquids as a function of gas solubility (mole fraction) x_2 at 25°C and 1.013 bar (Hildebrand and Scott, 1962). Units of entropy and gas constant R are J mol $^{-1}$ K^{-1}.

In Eq. (10-25),

① $\Delta\bar{h}_2 > 0$: the solubility increases with rising temperature

② $\Delta\bar{h}_2 < 0$: the solubility decreases with rising temperature

$$\Delta\bar{h}_2 = (h_2^L - h_2^G) + (\bar{h}_2^L - h_2^L) \qquad (10\text{-}29)$$

h_2^L : the enthalpy of the (hypothetical) pure liquid at the temperature of the solution

In Eq. (10-29),

① the first term on the right-hand side : the enthalpy of condensation of pure solute
(in general) negative (the enthalpy of a liquid is lower than that of a gas at the same temperature)

② the second term : the partial enthalpy of mixing for the liquid solute
(in general) positive / endothermic (the absence of salvation between solute and solvent)
the larger the difference between the cohesive energy density of the solute and that of the solvent, the larger the enthalpy of mixing

So (in Eq. 10-29),

① the difference between the cohesive energy density is large (the second term dominates) : $\Delta \bar{s}_2 > 0$

② the difference between the cohesive energy density is small (the first term dominates) : $\Delta \bar{s}_2 < 0$

If there are specific chemical interactions between solute and solvent, then both terms in Eq. (10-29) are negative (exothermic) and the solubility decreases rapidly as the temperature rises.
Actually, when the partial pressure of the solute is small, the solubility typically decreases with temperature, goes through a minimum, and then rises.

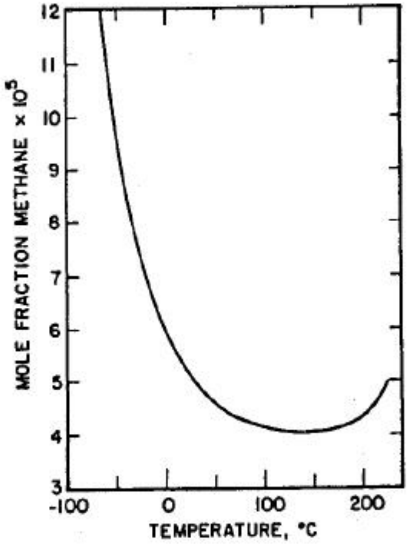


Figure 10-8 Solubility of methane in *n*-heptane when the vapor-phase fugacity of methane is 0.01 bar.

The effect of temperature on Henry's constant over narrow temperature ranges (0℃ ~ 50℃) is

$$\ln H_{2,1} = \alpha_2\left(1-\frac{T_2}{T}\right) - \beta\left(1-\frac{T_2}{T}\right)^2 + \ln 1.01325 \qquad (10\text{-}30)$$

$H_{2,1}$: Henry's constant for solute 2 in solvent 1
α_2 and T_2 : constants specific to the solute
β : universal constant

Table 10-6 Parameters for Eq. (10-30) (with $\beta = 36.855$) giving Henry's constants (in bar) for seven gaseous solutes in water in the region 0 to 50°C (Benson and Krause, 1976).

Solute	T_2 (K)	α_2
Helium	131.42	41.824
Neon	142.50	41.667
Nitrogen	162.02	41.712
Oxygen	168.85	40.622
Argon	168.87	40.404
Krypton	179.21	39.781
Xenon	188.78	39.273

Over a wider range of temperatures, simple equations such as Eq. (10-30) are unable to describe Henry's constant. Harvey developed a semiempirical correlation of Henry's constants over large temperature ranges.

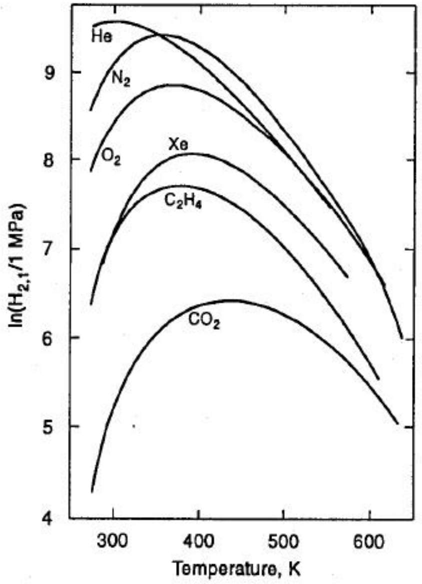


Figure 10-9 Henry's constants $H_{2,1}$ for several gases in water. Curves represent data fitted by the correlation of Harvey (1996).

At the critical point of solvent 1, Henry's constant for solute 2 is given by

$$H_{2,1} = P_{c_1} \varphi_2^\infty$$

P_{C_1} : the solvent's critical pressure

φ_2^∞ : the solute fugacity coefficient at infinite dilution at the critical temperature and pressure of the solvent

The derivative d$H_{2,1}$/dT diverges to negative infinity (or positive infinity for some solute/solvent pairs) due to the diverging compressibility of the solvent.
The corrected functional form for this divergence is Eq. (10-31).
Near the solvent's critical point, a function of Henry's constant is linear in density.

$$T \ln(H_{2,1} / f_1) = A + B(\rho_1 - \rho_{c_1}) \qquad (10\text{-}31)$$

f_1 and ρ_1 : the fugacity and the density of the pure solvent, respectively
ρ_{c1} : the solvent's critical density

Constant A is related to $H_{2,1}$ at the solvent's critical-point as determined by φ_2^∞.
Constant B is related to a thermodynamic derivative called the *Krichevsky parameter*, the key quantity describing dilute mixtures near the solvent's critical point.

$$T \ln K^\infty = 2B(\rho_{L_1}^s - \rho_{c_1}) \qquad (10\text{-}32)$$

$\rho_{L_1}^S$: the saturated liquid density of the solvent

K^{∞} : infinite dilution partition coefficient, defined along the solvent's coexistence curve

$$K^{\infty} \equiv \lim_{x_2 \to 0} (y_2 / x_2) \qquad (10\text{-}33)$$

While Eqs. (10-31) and (10-32) are only asymptotic results, they describe experimental data over a wide range of conditions.

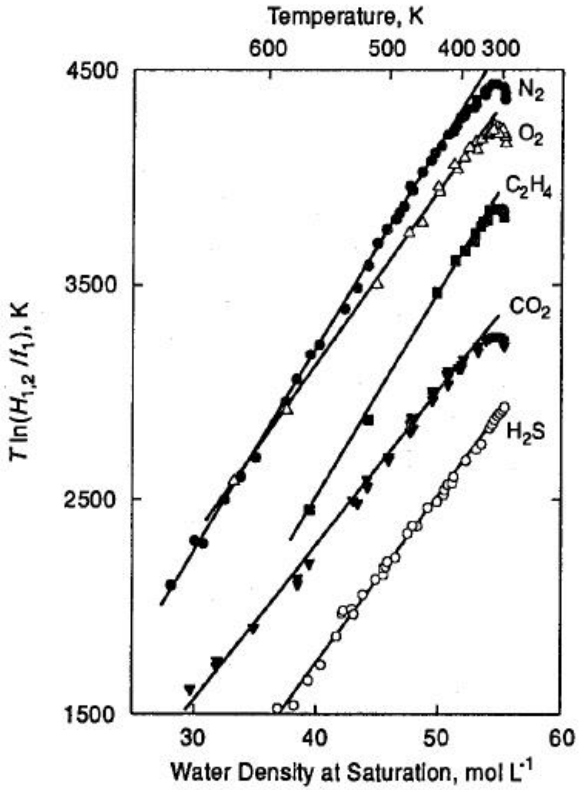


Figure 10-10 Henry's constants for several gases in water plotted according to Eq. (10-31).

10.5 Estimation of Gas Solubility

Reliable data on the solubility of gases in liquids are not plentiful. So we consider first the semiempirical correlations.

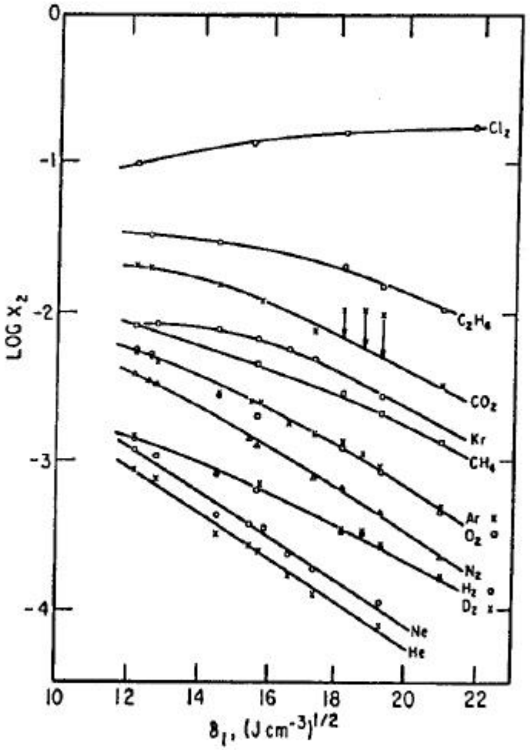


Figure 10-11 Solubilities of gases in liquids at 25°C and at a partial pressure of 1.013 bar as a function of solvent solubility parameter δ_1 (Hildebrand and Scott, 1962).

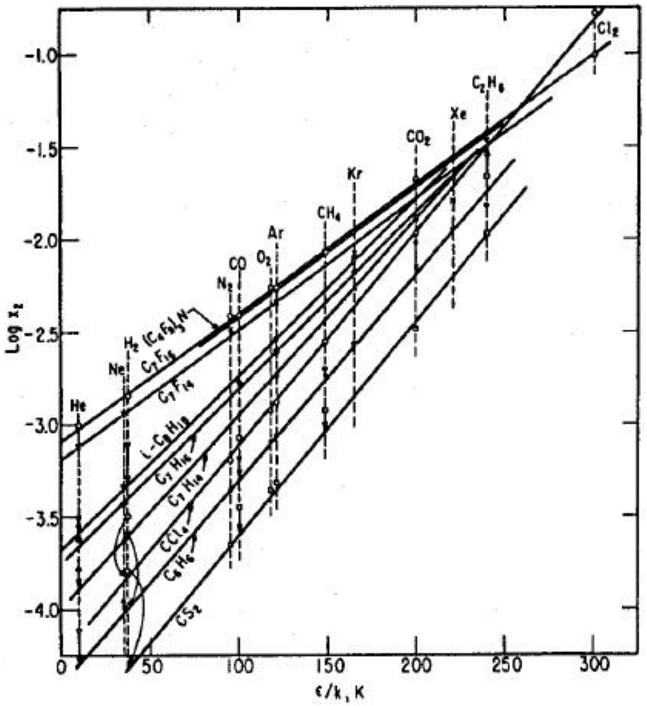


Figure 10-12 Solubilities of gases in liquids at 25°C and at a partial pressure of 1.013 bar as a function of solute characteristic ε/k (Lennard-Jones 6-12-potential) (Hirschfelder *et al.*, 1954).

Figures 10-11 and 10-12 may be used to predict solubilities in nonpolar systems where no experimental data are available.

These predictions are necessarily limited to systems at 25℃.

But, with the help of Eq. (10-26) and the entropy data shown in Fig. 10-7, it is possible to predict solubilities at other temperatures not far removed from 25℃.

In Fig. 10-11, Lewis acid-base interaction → higher solubility
(CO_2 in basic aromatic system)

In Fig. 10-12, the solubilities of the quantum gases are a little higher than expected, the discrepancies becoming larger as the solubility parameter of the solvent increases.

Unfortunately, solubility data at temperatures much larger or smaller than room temperature are scarce.
For theoretical methods, the theory of regular solutions and the theorem of corresponding states can serve as the basis for a correlating scheme.

The solution process for the gas is accompanied by a large decrease in volume because the partial molar volume of the solute in the condensed phase is much smaller than that in the gas phase.
Therefore, to apply regular solution theory, the isothermal solution process of the gaseous solute is then considered in two steps,

$$\Delta g = \Delta g_{\mathrm{I}} + \Delta \bar{g}_{\mathrm{II}} \tag{10-34}$$

$$\Delta g_{\mathrm{I}} = RT \ln \frac{f_{\mathrm{pure}\,2}^{L}}{f_2^G} \tag{10-35}$$

$$\Delta \bar{g}_{\mathrm{II}} = RT \ln \gamma_2 x_2 \tag{10-36}$$

f_{pure2}^{L} : the fugacity of (hypothetical) pure liquid solute
γ_2 : the symmetrically normalized activity coefficient of the solute referred to the (hypothetical) pure liquid
($\gamma_2 \rightarrow 1$ as $x_2 \rightarrow 1$)

Ⅰ Step)

the gas isothermally “condensed” to a hypothetical state having a liquid-like volume

Ⅱ Step)

liquid-like fluid dissolves in the solvent

The solute in the liquid solution is in equilibrium with the gas that is at fugacity f_2^G.
So, the equation of equilibrium is

$$\Delta g = 0 \tag{10-37}$$

We assume that the regular-solution equation gives the activity coefficient for the gaseous solute

$$RT \ln \gamma_2 = v_2^L (\delta_1 - \delta_2)^2 \Phi_1^2 \tag{10-38}$$

δ_1 : the solubility paremeter of solvent
δ_2 : the solubility paremeter of solute
v_2^L : the molar liquid volume of solute
Φ_1 : the volume fraction of solvent

Substitution of Eqs. (10-34), (10-35), (10-36), and (10-38) into Eq. (10-37) gives the solubility.

$$\frac{1}{x_2} = \frac{f_{\text{pure }2}^L}{f_2^G} \exp\left[\frac{v_2^L (\delta_1 - \delta_2)^2 \Phi_1^2}{RT}\right] \tag{10-39}$$

Eq. (10-39) requires three parameters (these parameters are all temperature dependent).

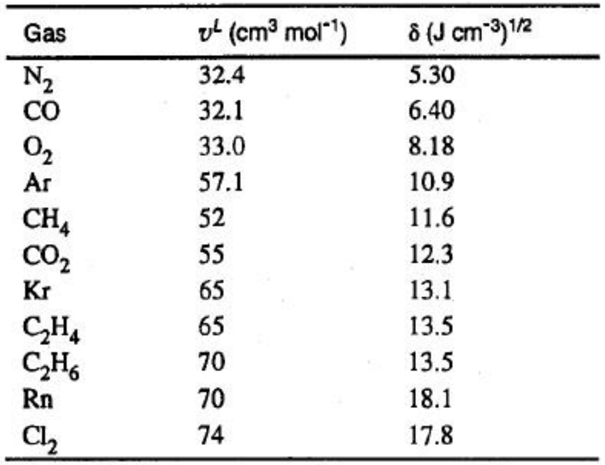
① the pure liquid fugacity
② the liquid volume
③ the solubility parameter

However, the theory of regular solutions assumes that at constant composition Eq. (10-40), the quantity $v_2^L (\delta_1 - \delta_2)^2 \Phi_1^2$ is not temperature-dependent.

$$\ln \gamma_2 \propto \frac{1}{T} \qquad (10\text{-}40)$$

Therefore, any convenient temperature can be used for v_2^L and δ_2 provided that the same temperature is also used for δ_1 and v_1^L.

Table 10-7 "Liquid" volumes and solubility parameters for gaseous solutes at 25°C.



Gas	v^L (cm^3 mol^{-1})	δ (J cm^{-3})$^{1/2}$
N_2	32.4	5.30
CO	32.1	6.40
O_2	33.0	8.18
Ar	57.1	10.9
CH_4	52	11.6
CO_2	55	12.3
Kr	65	13.1
C_2H_4	65	13.5
C_2H_6	70	13.5
Rn	70	18.1
Cl_2	74	17.8

For nonpolar systems, where the molecular size ratio is far removed from unity, it is necessary to add a Flory-Huggins entropy term to the regular-solution equation for representing gas solubility.

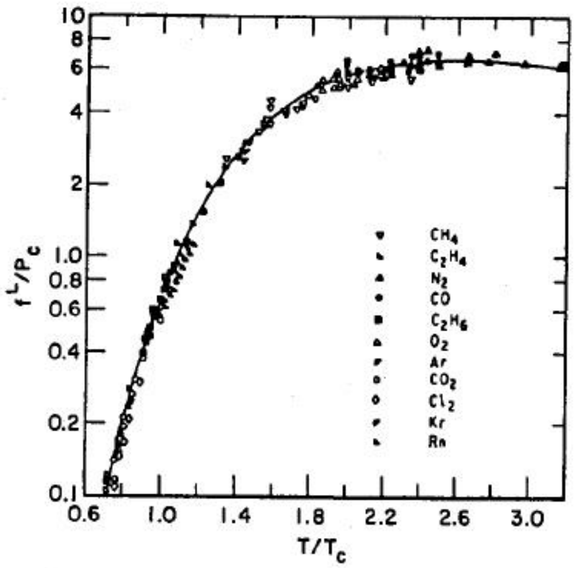


Figure 10-13 Fugacity of hypothetical liquid at 1.013 bar.

If the solution under consideration is at a considerably higher pressure, the Poynting correction should be applied to the fugacity as read from Fig. 10-13,

$$\underset{\text{(at total pressure } P)}{f^L_{\text{pure 2}}} = \underset{\text{(from Fig.10–13)}}{f^L_{\text{pure 2}}} \exp\left[\frac{v_2^L(P-1.013)}{RT}\right] \tag{10-41}$$

Shair’s technique for correlating gas solubilities with regular-solution theory can readily be extended to mixed solvents.
Eq. (10-39) is replaced by,

$$\frac{1}{x_2} = \frac{f^L_{\text{pure 2}}}{f_2^G}\exp\left[\frac{v_2^L(\delta_2-\bar{\delta})^2}{RT}\right] \tag{10-42}$$

$$\bar{\delta} = \sum_i \Phi_i \delta_i$$

$\bar{\delta}$: an average solubility parameter for the entire solution

The correlation given by Eq. (10-39), Table 10-7, and Fig. 10-13 gives fair estimates of gas solubilities over a moderate temperature range for nonpolar gases and liquids.

Gas solubilities can also be calculated from an equation of state using the methods discussed in Chaps.3 and 12.
(the equation of state must be valid for the solute-solvent mixture from zero density to the density of the liquid)

$$H_{2,1} = \varphi_2^{L,\infty} P \qquad (10\text{-}43)$$

$\varphi_2^{L,\infty}$: the fugacity coefficient of the solute in the liquid solvent at infinite dilution

[Gas Solubilities from Scaled-Particle Theory]

Consider a very dilute solution of nonpolar solute 2 in nonpolar solvent 1 at low pressure and at a temperature well below the critical of the solvent.
Henry's constant is,

$$\ln \frac{H_{2,1}^{(P_1^s)} v_1}{RT} = \frac{\bar{g}_c}{RT} + \frac{\bar{g}_i}{RT} \qquad (10\text{-}44)$$

v_1 : the molar volume of the solvent

Equation (10-44) assumes that the dissolution process can be broken into two steps.

Ⅰ Step)

a cavity is made in the solvent to allow introduction of a solute molecule

Ⅱ Step)

the solute molecule interacts with surrounding solvent

If the total pressure is low,

$$\frac{\bar{g}_c}{RT} = \frac{6Y}{1-Y}(2r^2 - r) + \frac{18Y^2}{(1-Y)^2}\left(r - \frac{1}{2}\right)^2 - \ln(1-Y) \qquad (10\text{-}45)$$

$$r = \frac{a_1 + a_2}{2a_1}$$

$$Y = \frac{\pi a_1^3 N_A}{6v_1}$$

a_1 : the hard-sphere diameter for solvent
a_2 : the hard-sphere diameter for solute
N_A : Avogadro’s constant

To obtain an expression for $\overline{g_i}$, we assume two things.

① all changes in entropy that result from dissolution of a gas in a solvent are given by the cavity-formation calculation

② some potential function are used for describing solute-solvent intermolecular forces.

$$\bar{g}_i = -\left(\frac{32\pi R}{9v_1}\right)\left(\frac{N_A \sigma_{12}^3 \varepsilon_{12}}{k}\right) \qquad (10\text{-}46)$$

Lennard-Jones-12,6 potential is used

σ_{12} and ε_{12} : parameters in the Lennard-Jones potential
k : Boltzmann's constant
R : the universal gas constant

Within the approximations used here, it is reasonable to set $\sigma_{12} = 1/2(a_1 + a_2)$.
The adjustable parameters are a_1, a_2, and ε_{12}/k.

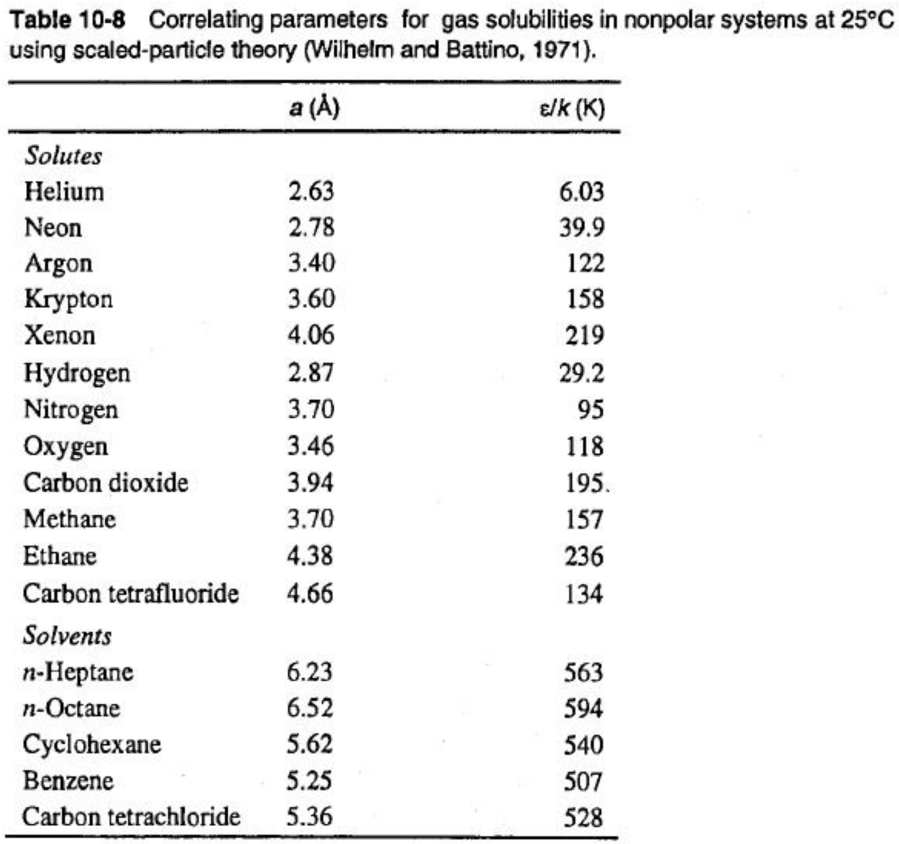


Table 10-8 Correlating parameters for gas solubilities in nonpolar systems at 25°C using scaled-particle theory (Wilhelm and Battino, 1971).

	a (Å)	ε/k (K)
Solutes		
Helium	2.63	6.03
Neon	2.78	39.9
Argon	3.40	122
Krypton	3.60	158
Xenon	4.06	219
Hydrogen	2.87	29.2
Nitrogen	3.70	95
Oxygen	3.46	118
Carbon dioxide	3.94	195
Methane	3.70	157
Ethane	4.38	236
Carbon tetrafluoride	4.66	134
Solvents		
n-Heptane	6.23	563
n-Octane	6.52	594
Cyclohexane	5.62	540
Benzene	5.25	507
Carbon tetrachloride	5.36	528

10.6 Gas Solubility in Mixed Solvents

Solubility data in mixed solvents are scarce.
However, with the aid of a simple molecular-thermodynamic model, it is often possible to make a fair estimate of the solubility of a gas in a simple solvent mixture.

Let subscript 2 stand for the gas as before, and let subscripts 1 and 3 stand for the two (miscible) solvents.
To simplify matters, we confine attention to low or moderate pressures where the effect of pressure on liquid-phase properties can be neglected.
For the ternary liquid phase, we write the simplest (two-suffix Margules) expansion for the excess Gibbs energy at constant temperature

$$\frac{g^{E\,(\text{ternary})}}{RT} = a_{12}x_1x_2 + a_{13}x_1x_3 + a_{23}x_2x_3 \qquad (10\text{-}47)$$

a_{ij} : a constant characteristic of the *ij* binary pair

From Eq. (10-47) we can compute the symmetrically normalized activity coefficient γ_2 of the gaseous solute using Eq. (6-25).
The unsymmetrically normalized activity coefficient γ_2^* can be found by

$$\gamma_2^* = \gamma_2 \exp(-a_{12}) \qquad (10\text{-}48)$$

$$\gamma_2^* \equiv \frac{f_2}{x_2H_{2,1}} \qquad (10\text{-}49)$$

Parameters a_{23} and a_{12} are related to the two Henry's constants

$$a_{23} = a_{12} + \ln\left(\frac{H_{2,3}}{H_{2,1}}\right) \qquad (10\text{-}50)$$

$H_{2,3}$: Henry's constant for the solute in solvent 3 at system temperature

From Eqs. (10-47) and (10-48), utilizing Eq. (6-25), we obtain

$$\ln\gamma_2^* = a_{12}[x_1(1-x_2)-1] + a_{23}x_3(1-x_2) - a_{13}x_1x_3 \qquad (10\text{-}51)$$

$$H_{2,\text{mixture}} \equiv \lim_{x_2 \to 0} \frac{f_2}{x_2} = \lim_{x_2 \to 0} \gamma_2^* H_{2,1} \qquad (10\text{-}52)$$

$H_{2,\text{mixture}}$: Henry's constant for the solute in the mixed solvent

From Eq. (10-51),

$$\lim_{x_2 \to 0} \gamma_2^* = (a_{23} - a_{12})x_3 - a_{13}x_1x_3 \qquad (10\text{-}53)$$

Substitution of Eqs. (10-50) and (10-53) into Eq. (10-52) gives the desired result

$$\boxed{\ln H_{2,\text{mixture}} = x_1 \ln H_{2,1} + x_3 \ln H_{2,3} - a_{13}x_1x_3} \qquad (10\text{-}54)$$

① when the two solvents (without solute) form an ideal mixture, $a_{13} = 0$

② when the solute-free mixture exhibits positive deviations from Raoult's law, a_{13} 〉 0
(Henry's constant in the mixture is smaller or solubility is larger than that corresponding to an ideal mixture of the same composition)

③ when the solute-free mixture exhibits negative deviations from Raoult's law, a_{13} 〈 0
(Henry's constant in the mixture is larger or solubility is smaller)

④ Constant a_{13} must be estimated from vapor-liquid equilibrium data for the solvent mixture

$$a_{13} \approx \frac{(\delta_1 - \delta_3)^2 (v_1^L + v_3^L)}{2RT}$$

According to Eq. (10-54), the effect of nonideal mixing of the solvents is not large.

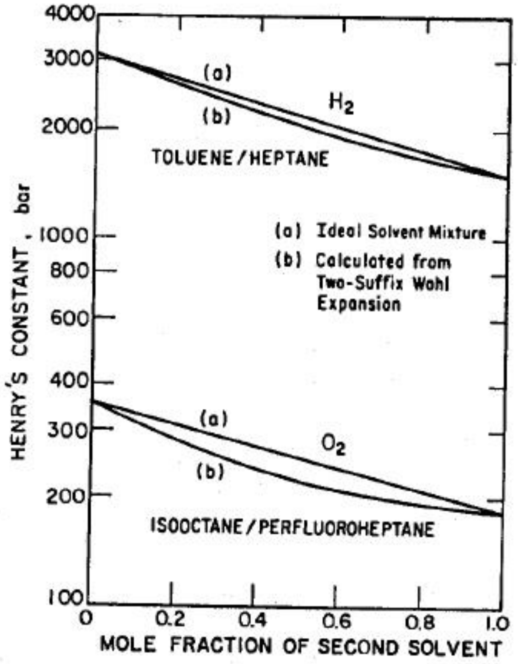


Figure 10-16 Calculated Henry's constants in solvent mixtures at 25°C.

Eq. (10-54) is readily generalized to solvent mixtures containing any desired number of solvents.
For an *m*-component system where the gas is designated by subscript 2, Henry's constant for the gaseous solute is given by

$$\ln H_{2,\mathrm{mixture}} = \sum_{\substack{j=1 \\ j\neq 2}}^{m} x_j \ln H_{2,j} - \sum_{\substack{j=1 \\ j\neq 2}}^{m-1} \sum_{\substack{k>j \\ k\neq 2}}^{m} a_{jk} x_j x_k \qquad (10\text{-}55)$$

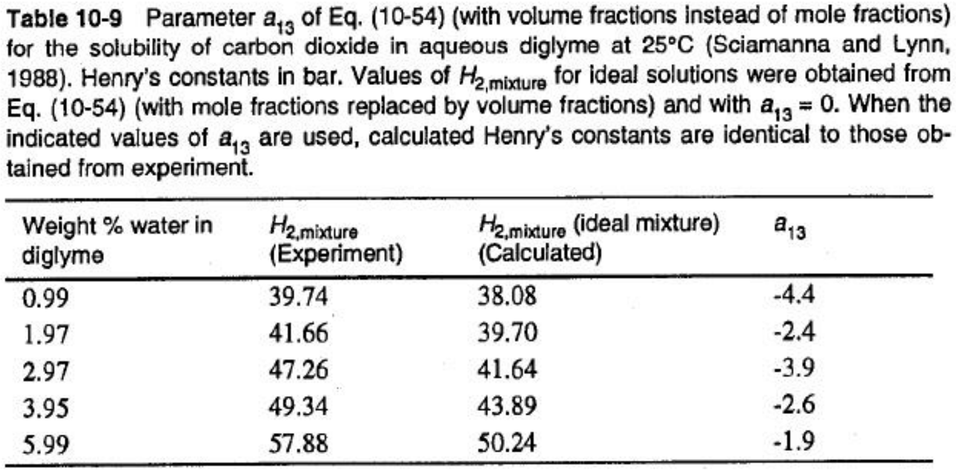


Table 10-9 Parameter a_{13} of Eq. (10-54) (with volume fractions instead of mole fractions) for the solubility of carbon dioxide in aqueous diglyme at 25°C (Sciamanna and Lynn, 1988). Henry's constants in bar. Values of $H_{2,\text{mixture}}$ for ideal solutions were obtained from Eq. (10-54) (with mole fractions replaced by volume fractions) and with $a_{13} = 0$. When the indicated values of a_{13} are used, calculated Henry's constants are identical to those obtained from experiment.

Weight % water in diglyme	$H_{2,\text{mixture}}$ (Experiment)	$H_{2,\text{mixture}}$ (ideal mixture) (Calculated)	a_{13}
0.99	39.74	38.08	-4.4
1.97	41.66	39.70	-2.4
2.97	47.26	41.64	-3.9
3.95	49.34	43.89	-2.6
5.99	57.88	50.24	-1.9

The negative values for a_{13} indicate that the water-solvent mixture exhibits negative deviations from Raoult's law, probably due to hydrogen bonding between water and solvent molecules.

The important assumption is that Eq. (10-47) gives a valid description of the excess Gibbs energy of the ternary mixture.
This assumption provides a reasonable approximation for some solutions of simple fluids, but for mixtures containing polar or hydrogen-bonded liquids a better model is required.
For such cases, binary data may not be sufficient.
A ternary constant may be necessary.

define a residual quantity $\mathfrak{R}$ by

$$\mathfrak{R} = \ln H_{i,\text{mixture}} - \sum_{j=1}^{m} \Phi_j \ln H_{i,j} \qquad \text{(10-56)}$$

$H_{\text{i,mixture}}$: Henry's constant for solute *i* in the solvent mixture containing *m* solvents
$H_{\text{i,j}}$: Henry's constant for solute *i* in the solvent *j*

Φ_j : the volume fraction of solvent *j* in the solvent mixture on a solute-free basis

$$\mathfrak{R} = (\mathfrak{R})_{\text{size}} + (\mathfrak{R})_{\text{physical interaction}} \tag{10-57}$$

$$(\mathfrak{R})_{\text{size}} = \sum_{j=1}^{m} \Phi_j \ln \frac{v_j}{v} \tag{10-58}$$

$$(\mathfrak{R})_{\text{physical interaction}} = -\frac{v_i}{RT} \sum_{j>k}^{m} \Phi_j \Phi_k \chi_{jk} \tag{10-59}$$

$$v = \sum_{j=1}^{m} x_j v_j \tag{10-60}$$

v : the molar volume of the solute-free solvent mixture
x : mole fraction
v_i : the molar “liquid” volume of solute *i*
x_{jk} : Flory interaction parameter for solvents *j* and *k*

If one of the solvents (solvent *k*) is an alcohol or amine that associates continuously,

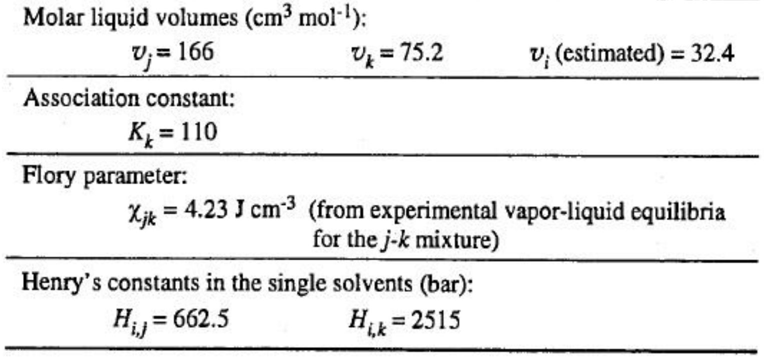
$$\mathfrak{R} = (\mathfrak{R})_{\text{size}} + (\mathfrak{R})_{\text{physical interaction}} + (\mathfrak{R})_{\text{association}} \tag{10-61}$$

$$(\mathfrak{R})_{\text{association}} = -\left(\frac{v_j}{v_k}\right)\Phi_k\left(\frac{2}{1+\sqrt{1+4K_k\Phi_k}} - \frac{2}{1+\sqrt{1+4K_k}}\right) \tag{10-62}$$

$$K_k = \left(\frac{c_n}{v_k}\right)\frac{1}{(c_{n-1}c_1)} \tag{10-63}$$

c_1 : the concentration of monomer
c_n : the concentration of polymer of degree n

Table 10-10 Parameters for calculating Henry's constant for nitrogen (i) in the mixed solvent system isooctane (j)/n-propanol (k) at 25°C (Nitta *et al.*, 1973).



Molar liquid volumes (cm^3 mol^{-1}):
$v_j = 166$ $v_k = 75.2$ v_i (estimated) $= 32.4$

Association constant:
$K_k = 110$

Flory parameter:
$\chi_{jk} = 4.23$ J cm^{-3} (from experimental vapor-liquid equilibria for the j-k mixture)

Henry's constants in the single solvents (bar):
$H_{i,j} = 662.5$ $H_{i,k} = 2515$

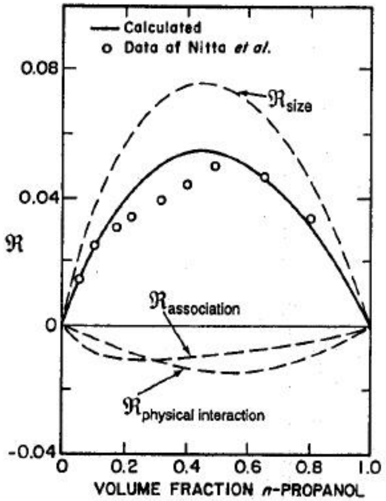


Figure 10-17 Solubility of nitrogen in a mixed solvent containing isooctane and n-propanol at 25°C. See Eq. (10-56).

10.7 Chemical Effects on Gas Solubility

The gas-solubility correlations discussed in Sec. 10.5 are based on a consideration of physical forces between solute and solvent.
But they are not useful for those cases where chemical forces are significant.
Specific chemical forces are not subject to simple generalizations.

The importance of chemical effects is shown in Figure 10-18.

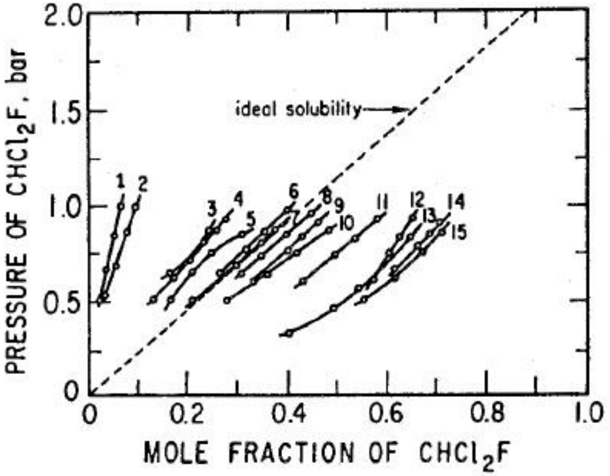


Figure 10-18 Solubility of Freon-21 in liquid solvents at 32.2°C. Solvents are: 1. Ethylene glycol; 2. Trimethylene glycol; 3. Decalin; 4. Aniline; 5. Benzotrifluoride; 6. Nitrobenzene; 7. Tetralin; 8. Bis-β methylthioethyl sulfide; 9. Dimethylaniline; 10. Dioxan; 11. Diethyl oxalate; 12. Diethyl acetate; 13. Tetrahydrofurfuryl laurate; 14. Tetraethyl oxamide; 15. Dimethyl ether of tetraethylene glycol.

Figure 10-18 indicates that the solvents fall roughly into three groups.

① the solubility is less than ideal (positive deviations from Raoult’s law)
→ the solvent molecules are strongly self-associated, they will not be available to form hydrogen bonds with the solute
→ as a result, strongly associated substances are poor solvents for solute that can form only weak hydrogen bonds
→ cannot compete successfully for proton acceptors

② the solubility is similar to ideal (deviations from Raoult’s law are very small)
→ aromatic solvents aniline, benzotrifluoride, and nitrobenzene are weak proton acceptors
→ for these solvents, chemical forces (causing negative deviations from Raoult’s law) are just strong enough to overcome physical forces (usually cause positive deviations from Raoult’s law)

③ the solubility is larger than ideal (negative deviations from Raoult’s law)
→ solvents that are powerful proton acceptors and whose molecules are free to accept protons

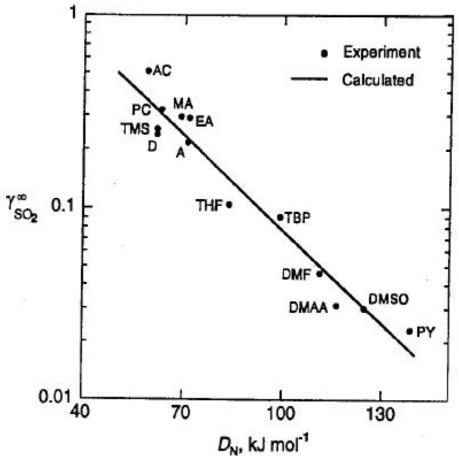


Figure 10-19 Correlation of infinite-dilution activity coefficients of SO_2 with solvent Gutmann donor number at 25°C. The solvents shown are: A - Acetone; AC - Acetonitrile; D - 1,4-Dioxane; DMAA - *N,N*-Dimethylacetamide; DMF - *N,N*-Dimethylformamide; DMSO - Dimethyl sulfoxide; EA - Ethyl acetate; MA - Methyl acetate; PC - Propylene carbonate; PY- Pyridine; TBP - Tributyl phosphate; THF - Tetrahydrofuran; TMS - Tetramethylene sulfone. —— Calculated from Eq. (10-64); ● Experiment.

As discussed earlier, Henry's constant is directly related to the activity coefficient at infinite dilution (see Eq. 6-43).
In this case, Henry's constant is the product of $\gamma_{SO_2}^{\infty}$ and the vapor pressure of pure SO_2 liquid at 25℃.

To characterize the electron-donor ability of a molecule, the *donor number* D_N (or donicity) as the molar enthalpy value ($-\Delta h$) for the reaction of the donor (D) with $SbCl_5$ was defined.

$$D + SbCl_5 \rightleftharpoons D{\bullet}SbCl_5 \qquad (-\Delta h_{D\bullet SbCl_5} \equiv D_N)$$

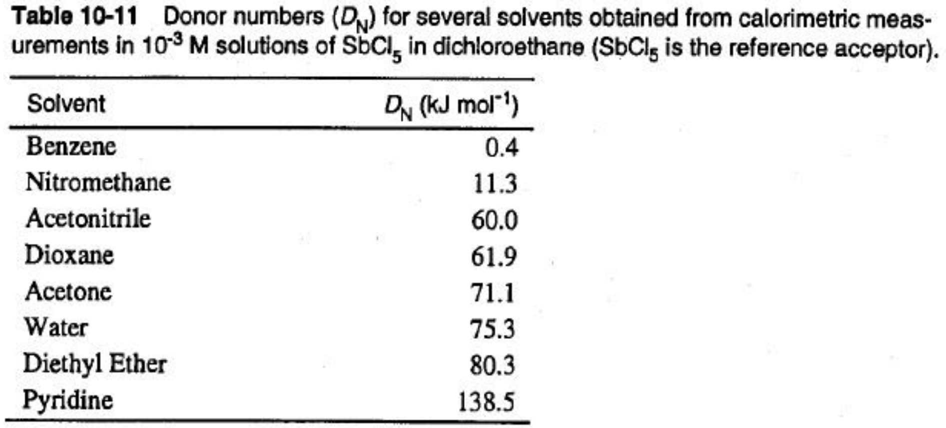


Table 10-11 Donor numbers (D_N) for several solvents obtained from calorimetric measurements in 10^{-3} M solutions of $SbCl_5$ in dichloroethane ($SbCl_5$ is the reference acceptor).

Solvent	D_N (kJ mol^{-1})
Benzene	0.4
Nitromethane	11.3
Acetonitrile	60.0
Dioxane	61.9
Acetone	71.1
Water	75.3
Diethyl Ether	80.3
Pyridine	138.5

$$\ln \gamma_{SO_2}^{\infty} = 1.18 - 0.0375 D_N \qquad (10\text{-}64)$$

Using this linear relation, it is possible to estimate Henry's constants for sulfur dioxide in a variety of "chemical" organic solvents.

While the chemical characteristics of solvents can be used to correlate gas solubilities, it is also possible to use gas-solubility data to characterize solvents.

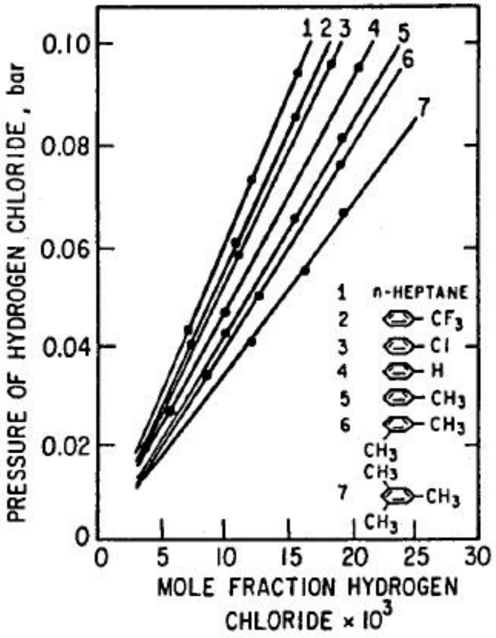


Figure 10-20 Solubility of hydrogen chloride at -78.51°C in *n*-heptane and in 5 mol % solutions of aromatics in *n*-heptane.

Table 10-12 Henry's constants for solubility of HCl in 5 mol % solutions of aromatics in *n*-heptane, and dissociation constants *K* for complex formation (all at -78.51°C).

Aromatic solute	*H* (bar)	*K* (bar)
None (pure heptane)	6.026	–
Benzotrifluoride	5.626	4.266
Chlorobenzene	5.333	2.000
Benzene	4.666	0.960
Toluene	4.226	0.613
m-Xylene	3.973	0.480
Mesitylene	3.400	0.320

The solubility data show that addition of small amounts of aromatics to heptanes increases the solubility of hydrogen chloride. This increase is a result of the electron-donating properties of aromatic molecules that, because of their π–electrons, can act as Lewis bases.

The evidence that hydrogen chloride and aromatics form stable complexes at low temperatures is given by the freezing point data of for mixtures of hydrogen chloride and mesitylene shown in Fig. 10-21.

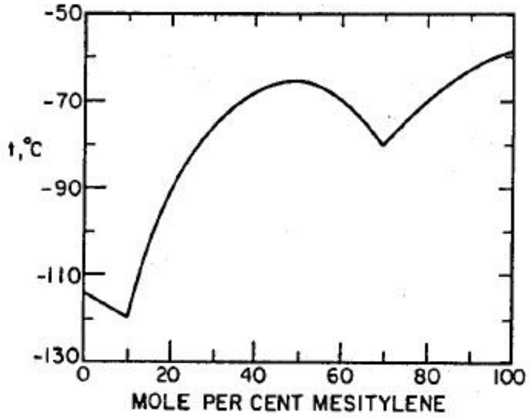


Figure 10-21 Evidence for complex formation: freezing points for hydrochloric acid/mesitylene mixtures.

The maximum at a mole fraction of one-half shows that the stoichiometric ratio of hydrogen chloride to aromatic in the complex is 1:1.

Brown and Brady reduced their solubility data by calculating dissociation equilibrium constants for the complexes.
The dissociation constant is defined by

$$K = \frac{x_{\text{free aromatic}}\, p_{\text{HCl}}}{x_{\text{complex}}} \qquad (10\text{-}65)$$

x : mole fraction
p : partial pressure

According to this definition, the stability of a complex falls as the dissociation constant rises.
By simple stoichiometry and by assuming that the complex is nonvolatile, Brown and Brady were able to calculate K from the change in Henry's constant in heptanes that results when aromatic molecules are added to the solvent.
Their results are shown in Table 10-12.
The aromatic components are listed in order of rising basicity.
As basicity increases, the solubility also increases and Henry's constant falls.

Deviations from Henry's law may result from chemical effects even at very low solute concentrations.
However, whenever the gaseous solute experiences a chemical change such as association or dissociation in the solvent, Henry's law fails because the equilibrium between the vapor phase and the liquid phase is then coupled with an additional (chemical) equilibrium in the liquid phase.

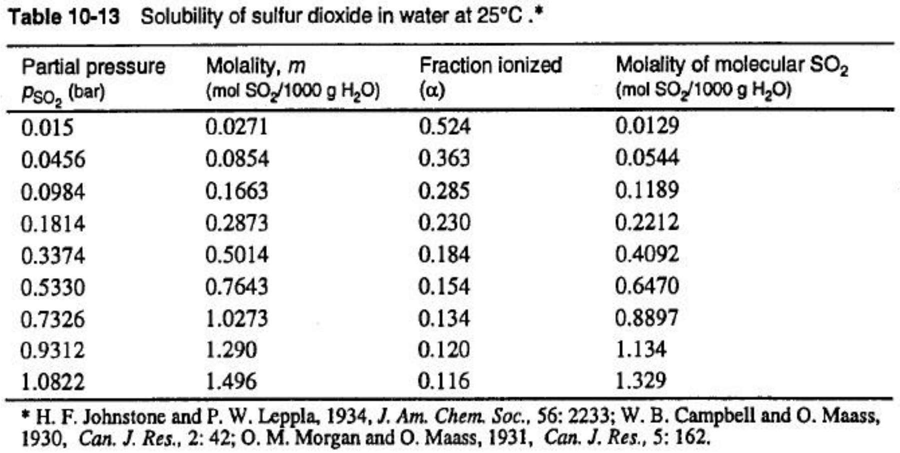


Table 10-13 Solubility of sulfur dioxide in water at 25°C .*

Partial pressure p_{SO_2} (bar)	Molality, m (mol SO_2/1000 g H_2O)	Fraction ionized (α)	Molality of molecular SO_2 (mol SO_2/1000 g H_2O)
0.015	0.0271	0.524	0.0129
0.0456	0.0854	0.363	0.0544
0.0984	0.1663	0.285	0.1189
0.1814	0.2873	0.230	0.2212
0.3374	0.5014	0.184	0.4092
0.5330	0.7643	0.154	0.6470
0.7326	1.0273	0.134	0.8897
0.9312	1.290	0.120	1.134
1.0822	1.496	0.116	1.329

* H. F. Johnstone and P. W. Leppla, 1934, *J. Am. Chem. Soc.*, 56: 2233; W. B. Campbell and O. Maass, 1930, *Can. J. Res.*, 2: 42; O. M. Morgan and O. Maass, 1931, *Can. J. Res.*, 5: 162.

In Table 10-13, when plotted, these data do not yield a straight line.
The reason for the failure of Henry’s law becomes apparent when we consider that sulfur dioxide plus water produces hydrogen ions and bisulfate ions.
When sulfur dioxide gas is in contact with liquid water, we must consider two equilibria

$$\begin{array}{lll} \text{Gas Phase} & SO_2 & \\ & \updownarrow & \\ \text{Liquid Phase} & SO_2\,(\text{aqueous}) & \rightleftharpoons H^+ + HSO_3^- \end{array}$$

Henry’s law governs only the vertical equilibrium between the two phases.
In this case,

$$p = H\,m_M \qquad (10\text{-}66)$$

p : the partial pressure of sulfur dioxide
H : a “true” Henry’s constant
m_M : the molality of molecular (nonionized) sulfur dioxide in aqueous solution

When the partial pressure of sulfur dioxide is plotted against m_M, a straight line is obtained.

This case is particularly fortunate because independent conductivity measurements are available.
In a more typical case, independent data on the liquid solution would not be available.

For equilibrium between sulfur dioxide in the gas phase and molecular sulfur dioxide in the liquid phase,

$$p = H m_M = H m(1-\alpha) \qquad (10\text{-}67)$$

For ionization equilibrium in the liquid phase,

$$K = \frac{m_{\mathrm{H}^+} m_{\mathrm{HSO}_3^-}}{m_{\mathrm{M}}} = \frac{\alpha^2 m^2}{m_{\mathrm{M}}} \qquad (10\text{-}68)$$

K : the ionization equilibrium constant

Substituting Eq. (10-67),

$$K = \frac{\alpha^2 m^2}{p/H} \qquad (10\text{-}69)$$

$$\alpha = \frac{\sqrt{p}}{m}\sqrt{\frac{K}{H}} \qquad (10\text{-}70)$$

Finally,

$$\frac{m}{\sqrt{p}} = \frac{\sqrt{p}}{H} + \sqrt{\frac{K}{H}} \qquad (10\text{-}71)$$

Equation (10-71) shows the effect of ionization on Henry’s law.

If there were no ionization, *K* = 0 and Henry’s law is recovered.
The ability of a solute to ionize in solution increases its solubility.
However, as the concentration of solute in the solvent rises, the fraction ionized falls.
Therefore, the “effective” Henry’s constant *p/m* rises with increasing pressure.

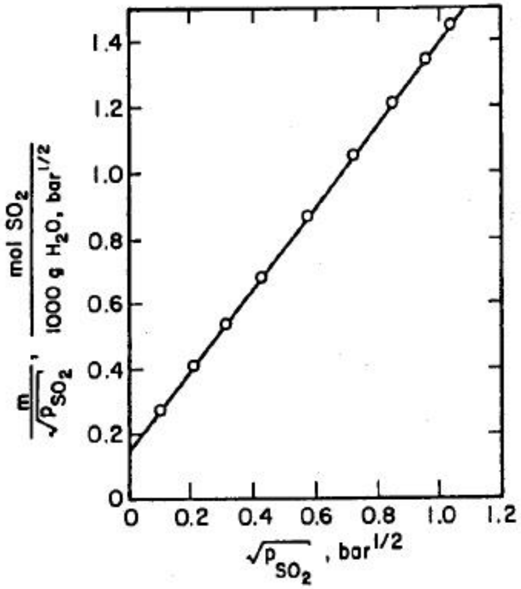


Figure 10-22 Effect of ionization on solubility. Linearization of solubility data for sulfur dioxide in water at 25°C.

Figure 10-22 presents solubility data for the sulfur dioxide/water system plotted according to Eq. (10-71).

The effect of ionization on solubility is particularly strong when two volatile, ionizing solutes, one basic and one acidic, are dissolved in an ionizing (high-dielectric constant) solvent.

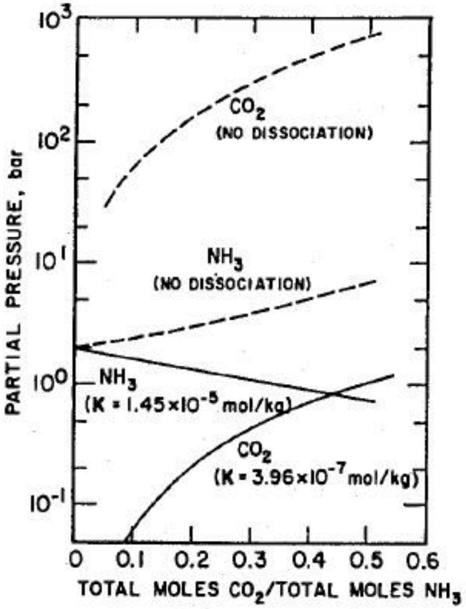


Figure 10-23 Enhancement of solubilities due to chemical interactions. The system carbon dioxide/ammonia/water contains 6.75 molal ammonia at 100°C.

The indicated values of *K* are ionization equilibrium constants for the reactions

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$

The preceding examples illustrate how chemical effects may have a large influence on solubility behavior. It must be remembered that a solvent is never an inert material that merely acts as a cage for the solute.