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SOLUBILITIES OF NONPOLAR SOLUTES IN WATER AND IN METHANOL

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Solubilities of Nonpolar Solutes in Water and in Methanol

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ABSTRACT

Since many chemical processes are concerned with dilute solutions in water or in methanol, an analytical correlation of solubilities may be useful for computer-aided design. Such a correlation is presented here. Based on a perturbed-hard-sphere equation of state, this correlation gives Henry's constants for nonpolar solutes over a wide range of temperature. Unlike most other correlations of solubilities, the one presented here correctly reproduces the often-observed maximum when Henry's constant is plotted against temperature.

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Introduction

Estimates of phase equilibria are often essential for chemical process design. While much effort has been spent on such equilibria for distillation, much less attention has been given to those equilibria which are required for absorption of gases or for extraction (or stripping) of solutes from dilute aqueous solution, especially at temperatures remote from ambient. Since aqueous solutions are common in chemical processes, and since methanol is a popular solvent (for example in sweetening of sour gases), we present here a correlation for solubilities of nonpolar solutes in water and in methanol.

The literature contains numerous correlations for estimating gas solubilities, including those by Prausnitz and Shair (1961), Hildebrand and Scott (1962), Yen and McKetta (1962), Pierotti (1963, 1965), Preston (1971), Tiepel and Gubbins (1972, 1973), Gunn et al.(1974), Cysewski (1976), and Wilcock et al.(1978). A variety of techniques was used to develop these correlations, including regular-solution theory, corresponding-states theory, and concepts taken from perturbation theory. More recently, models based on group-contribution methods have been reported by Antunes and Tassios (1983), Sander et al.(1983), and Gmehling (1983). One advantage of group-contribution methods is its direct applicability to multicomponent mixtures (Sander et al., 1983, Skjold-Jørgensen, 1983); as demonstrated by

Takeuchi et al.(1983), the solubility of a component in a mixed solvent may be appreciably different from those in the single solvent. Unfortunately, many of these methods are limited to nonpolar solutes and solvents and nearly all are applicable only to a limited temperature range.

Among promising correlations are those derived from perturbation theory. Pierotti (1965) was able to predict Henry's constants to within a factor of 2 for many nonpolar solutes in water at 25°C, while Schulze and Prausnitz (1981) have extended Pierotti's work to the range 0-300°C for simple solutes in water. While a factor of 2 may seem large, experimental uncertainties are also large, especially for solutes at temperatures well removed from 25°C.

For engineering design, our objective is to obtain a correlation which is easy to use and which extends over a wide temperature range. Towards this end, we have developed a semiempirical correlation for predicting Henry's constants of nonpolar solutes in two common industrial solvents: water and methanol. Aqueous streams abound in chemical technology. Refrigerated methanol, as used, for example, in the Rectisol process (Lurgi) is important for synthesis-gas purification because of its low energy consumption and its selective removal of undesired constituents (Kohl and Riesenfeld, 1979). Because molecular theory is not adequate and because reliable experimental data are scarce (especially remote from 25°C), our correlation does not provide

high accuracy. Nevertheless, because it is predictive, we expect that it may be useful for chemical process design.

Our correlation is for Henry's constants; this constant is defined as the ratio of the solute's fugacity to its mole fraction at very high dilution. For a given solute/solvent pair, Henry's constant is a function only of temperature. When Henry's constant is divided by the liquid-phase standard-state fugacity (essentially the solute's vapor pressure), we obtain the activity coefficient at infinite dilution.

Thermodynamic Framework

To obtain an expression for Henry's constant, we start with an equation of state of the van der Waals form; the total pressure is given by the sum of repulsive (rep) and attractive (att) contributions:

$$p = p^{rep} + p^{att} \tag{1}$$

where

$$p^{rep} = \frac{6kT}{\pi}\left[\frac{\xi_0}{1-\xi_3} + 3\xi_1\frac{\xi_2}{\left(1-\xi_3\right)^2} + 3\frac{\xi_2^3}{\left(1-\xi_3\right)^3} - \xi_3\frac{\xi_2^3}{\left(1-\xi_3\right)^3}\right] \tag{1a}$$

and

$$p^{att} = -\frac{a_m}{v^2} \tag{1b}$$

Here

$$\xi_\beta = \frac{\pi}{6}\sum_{i=1}^{i=nc} \rho_i \sigma_i^\beta, \qquad \beta = 0,1,2,3 \quad ,$$

nc is total number of components, k is Boltzmann's constant, ρ_i is number density of molecule i, and σ_i is the hard-sphere diameter of molecule i.

Van der Waals parameter a_m characterizes the attractive forces in the mixture and v is the molar volume of the mixture. For a binary mixture,

$$a_m = a_{11}x_1^2 + 2a_{12}x_1x_2 + a_{22}x_2^2 \qquad (1c)$$

Equation (1a) is for a hard-sphere mixture, as given by Mansoori, Carnahan, Starling, and Leland (1971). Equation (1b) is the simple form orginally proposed by van der Waals.

From classical thermodynamics we obtain Henry's constant (H) through fugacity (f); we obtain the fugacity from chemical potential (μ) which, in turn, follows from Helmholtz energy (A):

$$P = -\left[\frac{\partial A}{\partial V}\right]_{T,n_j} \qquad (2) \qquad\qquad \mu_i = \left[\frac{\partial A}{\partial n_i}\right]_{T,V,n_{j\neq i}} \qquad (3)$$

$$\mu_i - \mu_i^o = RT\ln\frac{f_i}{f_i^o} \qquad (4) \qquad\qquad H_{ij} = \lim_{x_i \to 0}\left[\frac{f}{x}\right]_i \qquad (5)$$

Here V is total volume, n is mole number, x is liquid-phase mole fraction, and H_{ij} is Henry's constant for solute i in solvent j. Henry's constant is evaluated at the saturation pressure of solvent j at temperature T.

Using equations 1-5 for solute 1 in solvent 2, we

obtain for the reduced Henry's constant $\tilde{H}$:

$$\ln\tilde{H} = \ln\tilde{H}^{rep} + \ln\tilde{H}^{att} \tag{6}$$

where $\tilde{H} = H_{12}v_2/RT$

$$\ln\tilde{H}^{rep} = -\ln(1-\alpha_2) + \alpha_1\left[\frac{1+\alpha_2+\alpha_2^2-\alpha_2^3}{(1-\alpha_2)^3}\right] + 3\frac{\alpha_2}{1-\alpha_2}\left[\frac{\sigma_1}{\sigma_2}\right] \tag{6a}$$

$$+ 3\left[\frac{\sigma_1}{\sigma_2}\right]^2\left[\ln(1-\alpha_2) + \alpha_2\left(\frac{2-\alpha_2)}{(1-\alpha_2)^2}\right]\right]$$

$$- \left[\frac{\sigma_1}{\sigma_2}\right]^3\left[2\ln(1-\alpha_2) + \alpha_2\left(\frac{2-\alpha_2)}{1-\alpha_2}\right]\right]$$

where $\alpha_1 = \frac{\pi}{6}\rho_2\sigma_1^3$ and $\alpha_2 = \frac{\pi}{6}\rho_2\sigma_2^3$. Equation (6a) follows from an expression for the chemical potential given by Reed and Gubbins (1973).

$$\ln\tilde{H}^{att} = -2\rho_2\frac{a_{12}}{RT} \tag{6b}$$

where $\rho_2=\frac{1}{v_2}$ is the solvent molar density, R is the gas constant, and a_{12} characterizes the attractive forces between molecules 1 and 2. Equation (6) shows that for a binary system, Henry's constant is a function of temperature, hard-sphere diameters, solvent density, and one binary parameter, a_{12}. To determine that parameter we reduce solubility data.

Data Reduction

For water and methanol, ρ_2 is known as a function of

temperature. Tables 1 and 2 give saturated densities for water and methanol.

For numerous nonpolar solutes, H_{12} is known at a few values of T. Figure 1 shows a semilog plot of Henry's constant versus temperature for selected solutes in water. As shown, Henry's constant is a strong, nonlinear function of temperature, with values ranging over 5 orders of magnitude. To reduce solubility data like those shown in Figure 1, we require first a consistent set of collision diameters.

Corresponding-states theory suggests that the hard-sphere diameter is proportional to the cube root of the critical volume. Using the hard-sphere diameter and critical volume of one reference substance, we can estimate the hard-sphere diameter for some other fluid. For reference we use the collision diameter of argon reported by Dymond and Alder (1969) as 3.28×10^{-8} cm. The critical volume of argon is 74.9 cm^3/mole. Therefore, the hard-sphere diameter of any nonpolar solute i is obtained from

$$\sigma_i \text{ (cm)} = 3.28 \times 10^{-8} \left[\frac{v_{c_i}}{74.9} \right]^{\frac{1}{3}} \tag{7}$$

where v_{c_i} is in cm^3/mole. While the choice of diameter σ_i is very important, it is also somewhat arbitrary. The main advantages of Equation (7) are simplicity and consistency. For water we use $\sigma = 2.977 \times 10^{-8}$ and for methanol we use

$\sigma=3.817\times10^{-8}$ cm.

Given H_{12}, T, ρ_2, σ_1, σ_2, the only unknown is a_{12}. Using experimental Henry's constants, we obtain a_{12} from Equation (6).

Dimensional analysis suggests that a_{12} is related to $RT_{c_{12}}v_{c_{12}}$. For convenience we set $T_{c_{12}} = (T_{c_1}T_{c_2})^{1/2}$ and $v_{c_{12}} = \left[\frac{1}{2}(v_{c_1}^{1/3}+v_{c_2}^{1/3})\right]^3$; here T_{c_1} and T_{c_2} are the critical temperatures and v_{c_1} and v_{c_2} are the critical volumes, respectively. We recognize that these well-known combining rules provide only very rough approximations. Empirical corrections to these rules are, in effect, accounted for by a solute-specific constant, as shown below.

When we plot $\tilde{a}_{12} = \frac{a_{12}}{RT_{c_{12}}v_{c_{12}}}$ versus $\tilde{T} = \frac{T}{T_{c_{12}}}$, we find the curves to be approximately parallel to one another. Therefore, we factor a_{12} into three parts: a generalized (reduced) $\tilde{A}_{12}$ which depends strongly on temperature; a system-specific, characteristic part A^*_{12} which is independent of temperature; and a system-specific, weakly temperature-dependent part F(T):

$$a_{12} = \tilde{A}_{12}A^*_{12}F(T) \tag{8}$$

where $F(T) = 1+C_{12}(T-300)$ with T in kelvin. Here $\tilde{A}_{12}$ is a generalized reduced van der Waals parameter that is a function of temperature only and A^*_{12} is a temperature-

independent parameter that reflects characteristics of the solute/solvent pair. Parameter C_{12} is an empirical constant that accounts for the small secondary temperature dependence not included in $\tilde{A}_{12}$. We choose 300 K as a convenient reference point because most experimental data are available near that temperature. Therefore F(T) is usually close to unity.

The generalized $\tilde{A}_{12}$ is a reduced function that is the same for all solutes in a particular solvent. To obtain $\tilde{A}_{12}$, we choose experimental results for a reference solute where extensive reliable data are available for a large temperature range: For water we use xenon and for methanol we use krypton.

Figure 2 shows $\tilde{A}_{12}$ as a function of temperature, once for water and once for methanol. Empirical equations have been fitted to the data. These equations should be used only within the indicated temperature range. (A relation for $\tilde{A}_{12}$ as a function of $\tilde{T} = T/T_{c_{12}}$ has theoretical advantage but was less successful for correlating solubility data.)

Substituting equation (8) into equation (6) provides a fair method for correlating Henry's constants. For a fixed solute/solvent pair, only A^*_{12} and C_{12} remain unknown. Using these two adjustable parameters, we vary A^*_{12} and C_{12} until we obtain the "best" fit. In general "best" fit means the smallest root-mean-square percent deviation over the entire temperature range. However, for a few solutes more emphasis

was given to data at temperatures near 300 K where the data tend to be more reliable. For solutes in water, C_{12} was set equal to zero whenever possible; in that event, A^*_{12} is the only adjustable binary parameter.

Results

Tables 3 and 4 show data sources and the best values for A^*_{12} and C_{12} for 22 nonpolar solutes in water and for 19 nonpolar solutes in methanol. Not all experimental points were used. Judgement as to which points were omitted was based on whether agreement was found between two independent sources. It is remarkable how much disagreement there is between published experimental results for identical systems at the same temperature.

With the tabulated values of A^*_{12} and C_{12}, we can reproduce many of the experimental Henry's constants over a large temperature range. It is particularly gratifying that calculated results show the temperature maxima exhibited by the data.

Figures 3-5 show A^*_{12} plotted versus $RT_{c_{12}}v_{c_{12}}$. As suggested by theory, there appears to be a linear dependence. Figure 6 shows a plot of C_{12} versus $(T_{c_1}T_{c_2})^{1/2}$ for solutes in water and in methanol. While we were unsuccessful in finding a general relation for C_{12}, except for the quantum gases, C_{12} tends to be small for most solutes. To illustrate, for H_2S in water, F(T)=0.994 at 0°C and F(T)=1.065 at

315°C.

Figure 3 shows two regions for solutes in water. For low values of $RT_{c_{12}}v_{c_{12}}$, a straight line was drawn through the points for argon and xenon, while for high values of $RT_{c_{12}}v_{c_{12}}$, the line was obtained by a least-squares fit. Figure 4 shows both regions joined by a least-squares line drawn through all the points. The points lie close to the line because the scales are condensed. Since small changes in A^*_{12} may have a large effect on calculated Henry's constants, the two regions should be considered separately.

Figure 5 shows A^*_{12} versus $RT_{c_{12}}v_{c_{12}}$ for solutes in methanol. Because reliable data at infinite dilution were not available for hydrocarbons higher than butane, we show only one region with the line drawn through all points by a least-squares fit.

Equation (6) provides a correlation for Henry's constants for nonpolar solutes over a wide range of temperatures. Using critical data for the solute and solvent, we use the equations on Figures 3-5 to calculate A^*_{12}. From Figure 2 we obtain $\tilde{A}_{12}$.

We have calculated Henry's constants for all the solutes used in the correlation and compared them to experiment. Results are shown in Tables 5 and 6. In addition, a comparison was made between calculated and experimental values for 10 solutes in methanol which were not used in the

correlation; these results are shown in Table 7. For all predicted Henry's constants, C_{12} was set to zero, except for hydrocarbons larger than pentane in water. Effective critical constants (Prausnitz, 1969) were used for the quantum gases (H_2, He, Ne).

Tables 5 and 6 indicate that for most solutes, calculated Henry's constants agree with experiment to within a factor of 2 over the temperature range shown. For water, the temperature range is about 300 K, while for methanol the temperature range is about 100 K for many of the solutes.

While the correlation does well for most of the solutes, there are a few where predicted values vary significantly from experiment. For CO we underpredict solubilities; a partial explanation may follow from Jung's observation (1971) that there is appreciable chemical reaction between water and carbon monoxide at temperatures above 250°C.

While we expect the correlation to be poor as we depart from non-spherical molecules, we do not understand why the predictions for 1-octene are so much worse than those for n-octane, especially since the correlation is satisfactory for some other unsaturated hydrocarbons. While we cannot be sure, it may be that at least part of the disagreement is due to experimental uncertainties.

None of the calculated results for solutes in methanol

differ grossly from experiment; this may follow from the smaller temperature range and from the fewer solutes considered. The predicted Henry's constant of carbon disulfide is too low, but there is reason to question the validity of the data. As in water, we do worse for the quantum gases, and as hydrocarbon length increases, we seem to make increasingly poorer predictions. Finally, while it is not apparent from Tables 5 and 6, we overpredict Henry's constants for CO_2 and H_2S in both water and methanol. This is not surprising because both solutes are weak electrolytes; ionic dissociation in water increases solubility.

Table 7 shows the limitations of the correlation. Since ammonia and sulfur dioxide are both strongly polar and are weak electrolytes, it is not surprising that their predicted solubilities are low. Similarly, acetylene and methylacetylene have low predicted solubilities because they are weak acids while methanol is slightly basic. Finally, the calulated Henry's constant for hydrogen chloride is an order of magnitude larger than experiment; this solute was included only to demonstrate that the correlation is not suitable for strong electrolytes.

Sensitivity to Collision Diameter of Solute

Deviations between calculated and experimental Henry's constants for nitrogen and cyclohexane in water are surprisingly large compared to those for other molecules of similar shape and size. If, however, we retain A_{12}^* but decrease the

hard-sphere diameter by about 3.5% for N_2, the average deviation for Henry's constant over the entire temperature range is now only 5.5%. For example, at 0°C, decreasing σ_i by 3.5% results in a decrease in H_{12} by 74.5%. Similarly, for cyclohexane, keeping A^*_{12} the same and setting $C_{12}=0$, and increasing the hard-sphere diameter by about 1.3%, improves the fit to 15.5% average deviation over the entire temperature range. At 10°C this change produces an increase in predicted H_{12} by 350%, while at 230°C it produces an increase of 130% in H_{12} for the same A^*_{12} and C_{12}. From these results we see once again, as noted by others, that Henry's constants are extremely sensitive to small changes in hard-sphere diameter. While individual adjustment of σ_i would very much improve the calculations, such adjustment necessarily requires solubility data; for our engineering purposes here, we use a generalized procedure to calculate σ_i so that the correlation can be used for prediction, i.e., for making solubility estimates as needed in process design when no binary data are available.

Conclusions

While various previously published correlations are helpful for estimating solubilities, most of them are limited to nonpolar solvents and nonpolar solutes, or to temperatures near ambient. Because aqueous streams are common in technology and because methanol is a popular solvent for absorption processes, the correlation presented here is for

nonpolar solutes in water and in methanol over a large temperature range.

The accuracy of calulated Henry's constants is not high partly because many of the experimental solubility data are not accurate and partly because, to retain its engineering-oriented form, the correlation uses only pure-component parameters.

Predicted Henry's constants must be used with caution. However, for many solutes over a wide temperature range, the correlation produces Henry's constants within a factor of 2 or 3 compared to what are often doubtful experimental results. To our best knowledge, no presently available predictive correlation can do better, especially at temperatures remote from ambient. Significant improvement will require on the one hand, better and more extensive experimental data and on the other, a much improved theory of liquid solutions reduced to practice. Until such improvements are attained, the correlation presented here may be useful for facilitating chemical process-design calculations.

For convenient engineering application in computer-aided design, our correlation is in analytical form; the authors will be glad to make a computer program available to interested readers.

Nomenclature

A	= Helmholtz Energy
$\tilde{A}_{12}$	= Reduced Interaction Parameter
A^*_{12}	= Generalized Interaction Parameter
a_m	= Parameter Which Characterizes Attractive Forces in the Mixture
a_{12}	= van der Waals Binary Interaction Constant
$\tilde{a}_{12}$	= Reduced Binary Interaction Constant
C_{12}	= Constant for Secondary Temperature Dependence of a_{12}
f	= Fugacity
f^o	= Standard State Fugacity
H_{ij}	= Henry's Constant of Solute i in Solvent j
$\tilde{H}$	= Reduced Henry's Constant
i	= Component
k	= Boltzmann's Constant
n	= Mole Number
nc	= Total Number of Components
P	= Pressure
P^{rep}	= Repulsive Contribution to Pressure
P^{att}	= Attractive Contribution to Pressure
R	= Gas Constant
T	= Temperature
T_c	= Critical Temperature
$T_{c_{12}}$	= Binary Constant: $(T_{c_1} T_{c_2})^{1/2}$
$\tilde{T}$	= Reduced Temperature

V = Total Volume

v = Molar Volume of Mixture

v_c = Critical Molar Volume

$v_{c_{12}}$ = Binary Constant: $[0.5(v_{c_1}{}^{1/3}+v_{c_2}{}^{1/3})]^3$

v_2 = Saturated Molar Volume of Solvent, $1/\rho_2$

x = Liquid-Phase Mole Fraction

<u>Greek Letters</u>

α = Reduced Density (Equation 6a)

β = Index

μ = Chemical Potential

ξ = A Density Function (Equation 1a)

ρ = Density (Number Density in Eq. 1a, Molar Density Elsewhere)

σ = Hard-Sphere Diameter

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Table 1 - Saturated Densities for Water

(Density ρ is in moles/cm^3)

T, °C	100ρ	T, °C	100ρ	T, °C	100ρ
0	5.550	75	5.411	200	4.799
10	5.549	100	5.319	225	4.629
20	5.541	125	5.212	250	4.436
25	5.534	150	5.090	275	4.215
50	5.484	175	4.952	300	3.955

from "Steam Tables", 1964. Department of Scientific and Industrial Research, National Engineering Laboratory, Edinburgh, Her Majesty's Stationery Office.

Table 2 - Saturated Densities for Methanol

(Density ρ is in moles/cm^3)

t^oC	100ρ	t^oC	100ρ
-97.6	2.813	-20	2.587
-80	2.762	0	2.528
-60	2.703	25	2.455
-40	2.645	50	2.385

Density calulated by Francis Equation

$$d = A - Bt - \frac{C}{E-t} \quad , \quad d \text{ in g/cm}^3, \quad t \text{ in } ^oC$$

A=0.84638 B=0.9321×10^{-3} C=423.28 E=11641 for -97.6† to 50 ^oC

A=0.86867 B=0.6111×10^{-3} C=17.267 E=283.08 for 40 to 180 ^oC

Constants from Wilhoit, R.C.; Zwolinski, B.J. "Physical and Thermodynamical Properties of Aliphatic Alcohols", J. Phys. Chem. Ref. Data 1973, Vol. 2, Suppl. No. 1.

† The temperature range for this set of constants is listed as -20 to 50 ^oC. However, because the calculations compare favorably with experimental density data of Katayama and Nitta (J. Chem. Eng. Data 1976, 21, 194.) to -60 ^oC, the temperature range was extended to -97.6 ^oC.

Table 3 - Best A^*_{12} and C_{12} for Solutes in Water

Solute	Temp. Range, K	A^*_{12}, l^2-bar/mole^2	C_{12}, 1/K	Average % Dev.	Ref.
Helium	273-589	0.268	1.06e-03	8.0	a,i,j,l
Neon	273-543	0.299	2.70e-04	5.3	a,b,l
Hydrogen	273-616	0.420	6.21e-04	20.8	j,l
Argon	273-568	0.632	0	3.1	b,l
Oxygen	273-617	0.617	0	11.3	e,j,l
Nitrogen	273-573	0.701	0	7.8	a,e,j,l
Carbon Monoxide	273-573	0.749	2.06e-04	23.8	f,l
Methane	273-518	0.810	0	8.8	b,l
Krypton	273-523	0.780	0	6.1	b,i,l
Carbon Dioxide	273-533	0.930	0	14.3	c,l
Xenon	273-557	1.000	0	3.5	b,i,l
Hydrogen Sulfide	273-588	1.020	2.25e-04	25.2	c,l
Benzene	283-503	2.103	1.24e-04	13.8	k
n-Pentane	311-469	2.130	0	16.0	c
Cyclohexane	283-503	2.245	0	15.4	k
1-Hexene	298-494	2.453	7.10e-05	10.7	d,g
n-Hexane	273-493	2.500	1.21e-04	20.3	k
Ethylbenzene	273-553	2.780	9.50e-05	33.2	d,g,h
1-Octene	298-550	3.083	1.22e-04	8.2	d,g
Ethylcyclohexane	311-553	3.066	3.85e-05	78.4	d
n-Octane	298-553	3.182	8.77e-05	17.4	d,g
1-Methylnapthalene	311-550	3.362	3.99e-05	88.4	d

$$\text{Ave.\%Dev.} = \left\{ \frac{\sum \left[\frac{H_{calcd} - H_{exptl}}{H_{exptl}} \right]^2}{\text{No. of points}} \right\}^{1/2} \times 100$$

Note: A number followed by e+n should be multiplied by 10^n

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Table 4 - Best A^*_{12} and C_{12} for Solutes in Methanol

Solute	Temp. Range, K	A^*_{12}, l^2-bar/mole^2	C_{12}, 1/K	Average % Dev.	Ref.
Helium	288-310	0.2362	2.63e-03	1.78	q
Neon	288-310	0.2950	1.70e-03	0.199	k
Hydrogen	213-298	0.4804	1.27e-03	1.59	a,k
Nitrogen	213-323	0.8517	6.17e-04	1.27	b,d,h,n
Argon	278-313	0.7949	5.55e-04	0.429	p
Oxygen	253-323	0.7741	5.58e-04	0.257	r
Methane	213-298	1.058	3.24e-04	5.62	b,n
Krypton	173-293	1.000	0	0.555	o
Carbon Dioxide	213-298	1.259	-3.05e-04	10.8	b,c,j,n,v,w
Nitrous Oxide	291-305	1.258	3.74e-04	1.60	s
Ethylene	203-298	1.443	-1.30e-04	10.7	b,u,v
Hydrogen Sulfide	194-298	1.418	-5.57e-04	10.2	v,w,x
Ethane	283-303	1.588	2.52e-04	2.08	l,t
Carbonyl Sulfide	194-298	1.692	-1.72e-04	25.7	e,g,v,y
Propylene	220-298	1.965	1.86e-04	12.3	g,v
Propane	273-323	2.087	8.17e-05	4.78	i
Carbon Disulfide	194-298	2.154	-3.47e-04	5.22	v,y
Isobutane	298-323	2.541	2.92e-04	1.91	i
n-Butane	298-323	2.538	1.12e-04	1.44	i

$$\text{Ave.\%Dev.} = \left[\frac{\sum \left(\frac{H_{calcd} - H_{exptl}}{H_{exptl}} \right)^2}{\text{No. of points}} \right]^{1/2} \times 100$$

Note: A number followed by e+n should be multiplied by 10^n

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Table 5 - Comparison of Predicted and Experimental Solubilities in Water

Solute	Temp. Range, K	A^*_{12}, l^2-bar/mole^2	Average %Deviation	Range of H^c/H^e
Helium	273-589	0.243	83.2	1.44-2.50
Neon	273-543	0.351	60.9	0.322-0.633
Hydrogen	273-616	0.372	155.	1.56-3.63
Argon	273-568	0.649	26.9	0.696-0.853
Oxygen	273-617	0.650	39.9	0.509-1.00
Nitrogen	273-573	0.652	161.	1.38-2.85
Carbon Monoxide	273-573	0.676	324.	3.89-4.63
Methane	273-518	0.801	22.9	1.03-1.30
Krypton	273-523	0.803	33.0	0.630-0.757
Carbon Dioxide	273-523	0.950	30.8	0.610-1.23
Xenon	273-557	1.035	44.7	0.475-0.719
Hydrogen Sulfide	273-588	1.058	56.1	0.396-2.29
Benzene	283-503	2.115	16.4	0.770-1.30
n-Pentane	311-469	2.138	41.6	0.430-0.893
Cyclohexane	283-503	2.326	78.5	0.137-0.317
1-Hexene	298-494	2.404	121.	1.43-2.90
n-Hexane	273-493	2.495	31.3	0.980-1.83
Ethylbenzene	273-553	2.754	89.2	0.700-2.74
1-Octene	298-550	3.028	158.	1.97-3.24
Ethylcyclohexane	311-553	3.073	39.4	0.541-1.62
n-Octane	298-553	3.149	76.3	1.36-2.16
1-Methylnapthalene	311-550	3.417	54.8	0.298-1.05

$$\text{Ave.\%Dev.} = \left[\frac{\left[\frac{H_{calcd} - H_{exptl}}{H_{exptl}} \right]^2}{\text{No. of points}} \right]^{1/2} \times 100$$

$$H^c/H^e = H_{calcd}/H_{exptl}$$

$$A^*_{12} = 0.1499 + 0.2954(RT_{c_{12}} v_{c_{12}})$$

For the first 12 solutes $C_{12} = 0$. For the remainder, $C_{12} = 10^{-4}$.

Table 6 - Comparison of Predicted and Experimental Solubilities in Methanol

Solute	Temp. Range, K	A^*_{12}, l^2-bar/mole^2	Average %Deviation	Range of H^c/H^e
Helium	288-310	0.1897	48.6	1.42-1.57
Neon	288-310	0.3640	45.5	0.512-0.594
Hydrogen	213-298	0.3921	90.4	1.48-2.11
Nitrogen	213-313	0.8129	25.8	0.921-1.49
Argon	278-313	0.8171	19.7	0.740-0.875
Oxygen	253-323	0.8196	36.9	0.506-0.761
Methane	213-298	1.038	14.7	0.779-1.18
Krypton	173-293	1.046	40.8	0.504-0.671
Carbon Dioxide	213-298	1.270	23.2	0.744-1.59
Nitrous Oxide	291-305	1.302	32.8	0.642-0.691
Ethylene	203-298	1.426	47.2	1.12-1.89
Hydrogen Sulfide	194-298	1.434	57.9	0.833-2.40
Ethane	283-303	1.587	2.89	0.949-1.02
Carbonyl Sulfide	194-298	1.706	25.9	0.433-1.40
Propylene	220-298	1.921	38.5	1.13-1.53
Propane	273-323	2.055	27.5	1.20-1.32
Carbon Disulfide	194-298	2.278	55.8	0.350-0.601
Isobutane	298-323	2.485	69.3	1.60-1.75
n-Butane	298-323	2.492	50.2	1.47-1.52

$$\text{Ave.\%Dev.} = \left[\frac{\sum\left[\frac{H_{calcd}-H_{exptl}}{H_{exptl}}\right]^2}{\text{No. of points}}\right]^{1/2} \times 100$$

$$H^c/H^e = H_{calcd}/H_{exptl}$$

$$A^*_{12} = 0.0375 + 0.3557(RT_{c_{12}}v_{c_{12}})$$

$$C_{12} = 0 \text{ for all solutes}$$

Table 7 - Comparison of Predicted vs. Experimental Henry's Constants for Solutes in Methanol not Used in Correlation

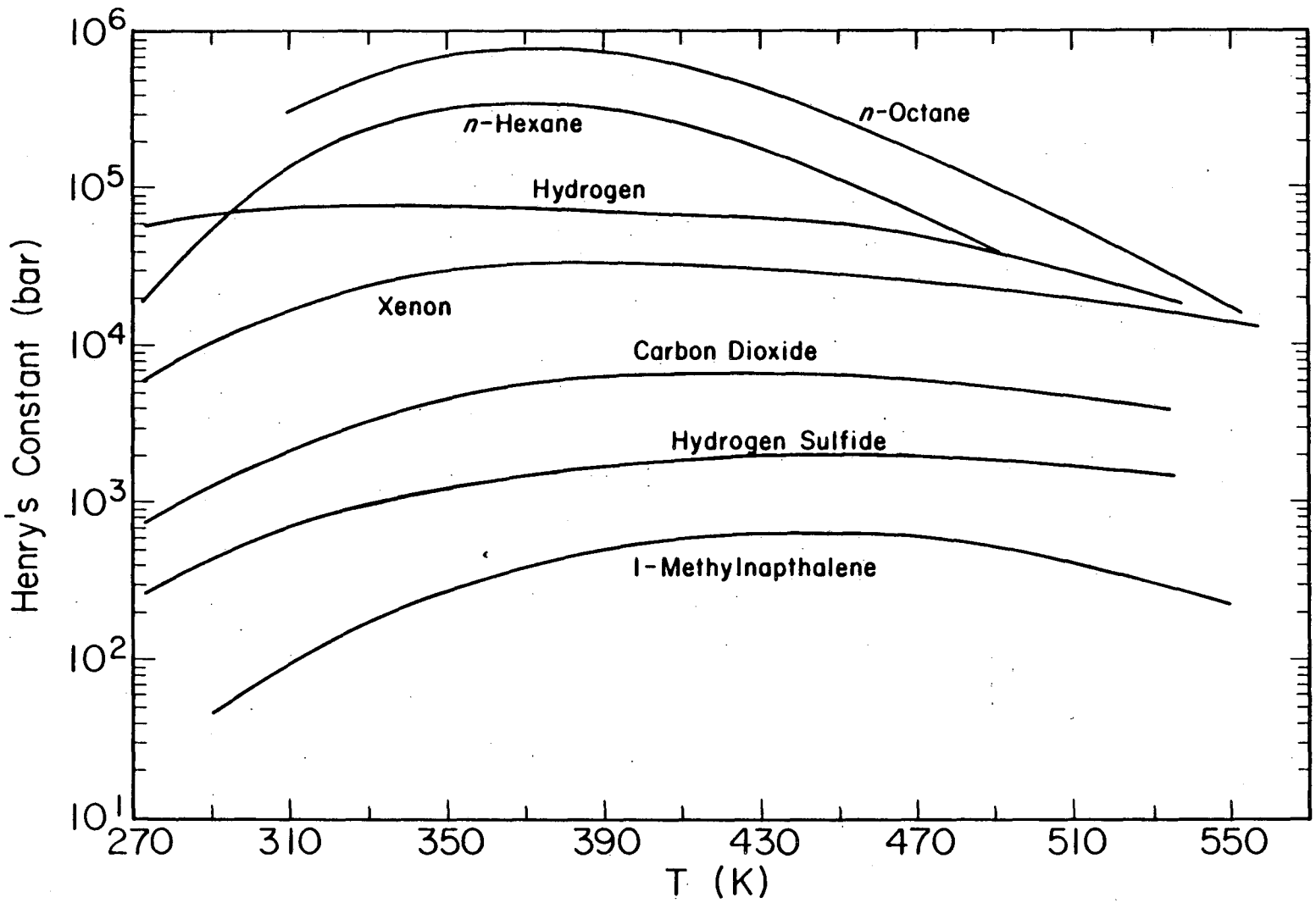
Solute	$RT_{c_{12}} v_{c_{12}}$, l^2-bar/mole^2	A^*_{12}, l^2-bar/mole^2	T, K	H^{expt}_{12}, bar	H^{calcd}_{12}, bar
Nitrous Oxide	2.134	0.796	298	1808.	674.9
				1604.	674.9
Carbon Monoxide	2.280	0.848	298	3294.	4790.
				2465.	4790.
Hydrogen Chloride	3.335	1.224	298	2.43	86.0
Ammonia	3.541	1.297	298	2.60	25.8
Xenon†	3.781	1.382	293	278.	222.
Acetylene	3.817	1.395	298	66.7	158.
				39.6	158.
Sulfur Dioxide	4.688	1.705	298	2.80	19.4
Propadiene	5.181	1.880	293	31.5	41.8
Methylacetylene	5.277	1.914	298	9.68	39.6
1-Butene	6.626	2.394	298	19.7	45.5

$$A^*_{12} = 0.0375 + 0.3557(RT_{c_{12}} v_{c_{12}})$$

$$C_{12} = 0 \text{ for all solutes}$$

Unless otherwise indicated, all reported Henry's constants were taken from Weber, W., "Experimentelle Bestimmung und Korrelation der Löslichkeit von Gasen in Alkoholen," Dissertation, Technischen Universität Berlin, 1981.

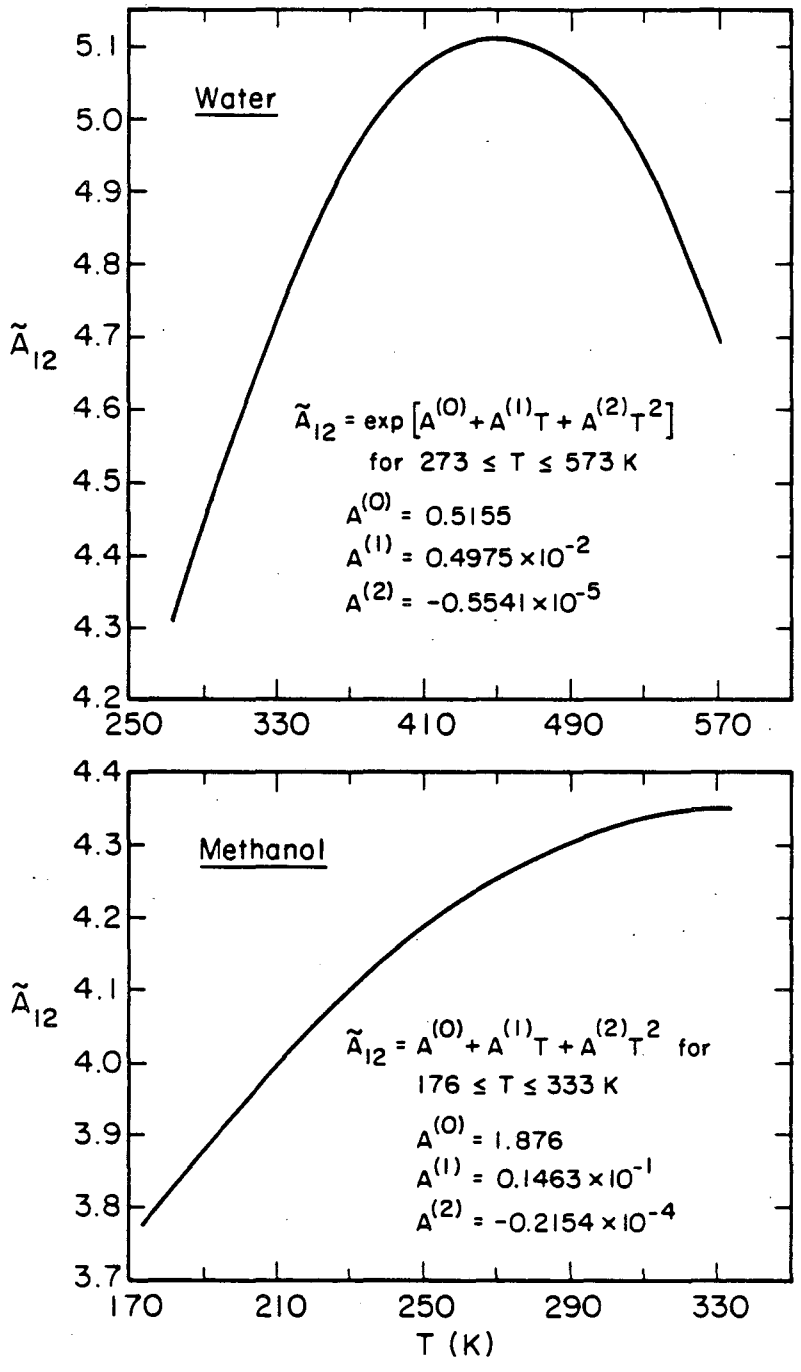
† Taken from Cejnar, F.; Wilhelmova, L.; Vrzala, P. Int. J. Appl. Radiat. Isot. 1977, 28, 281.



Selected Experimental Henry's Constants for Nonpolar Solutes in Water

XBL 841-540

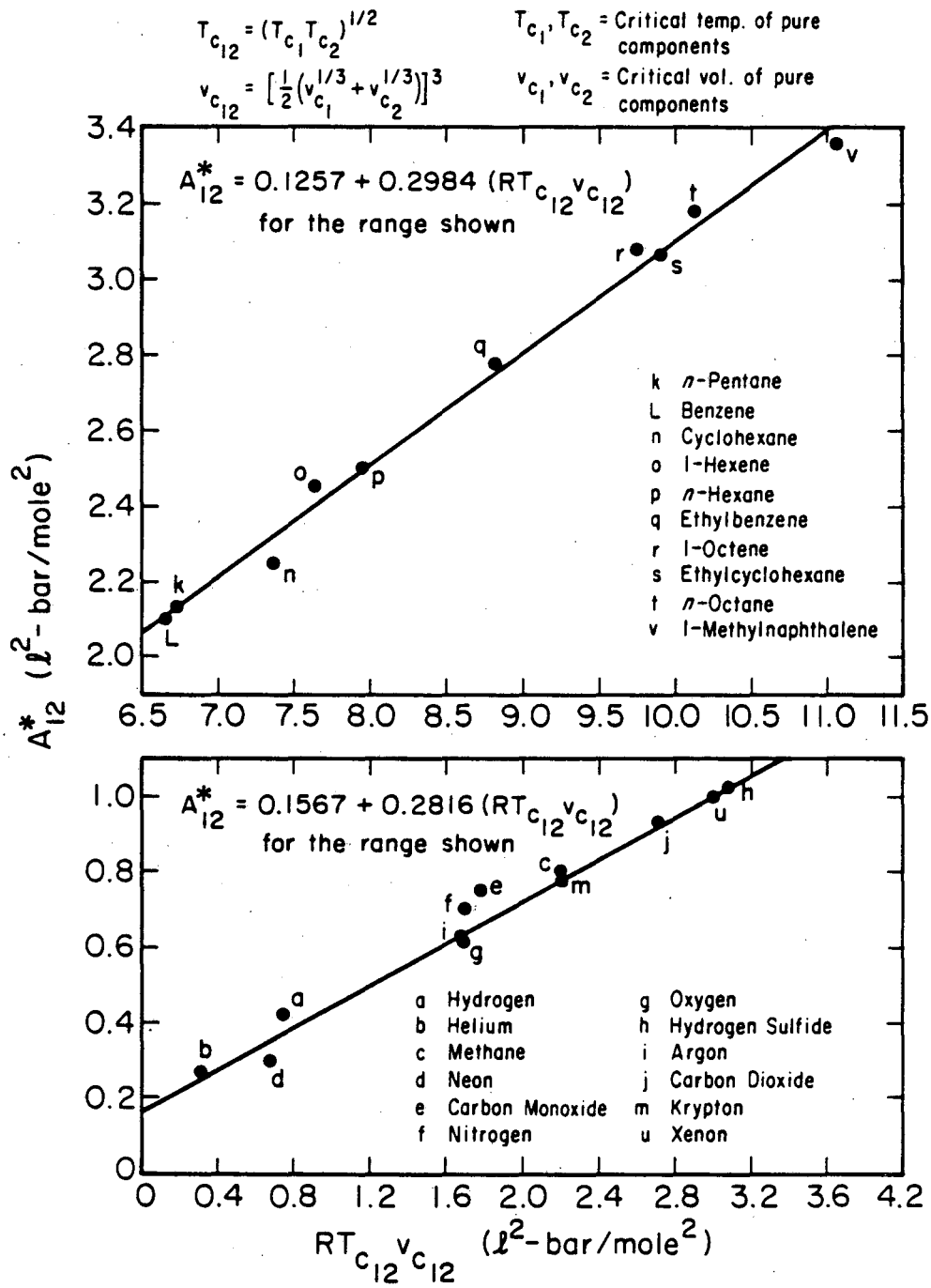
Figure 1



Reduced van der Waals Interaction Parameter for Nonpolar Solutes in Water and in Methanol

XBL 841-536

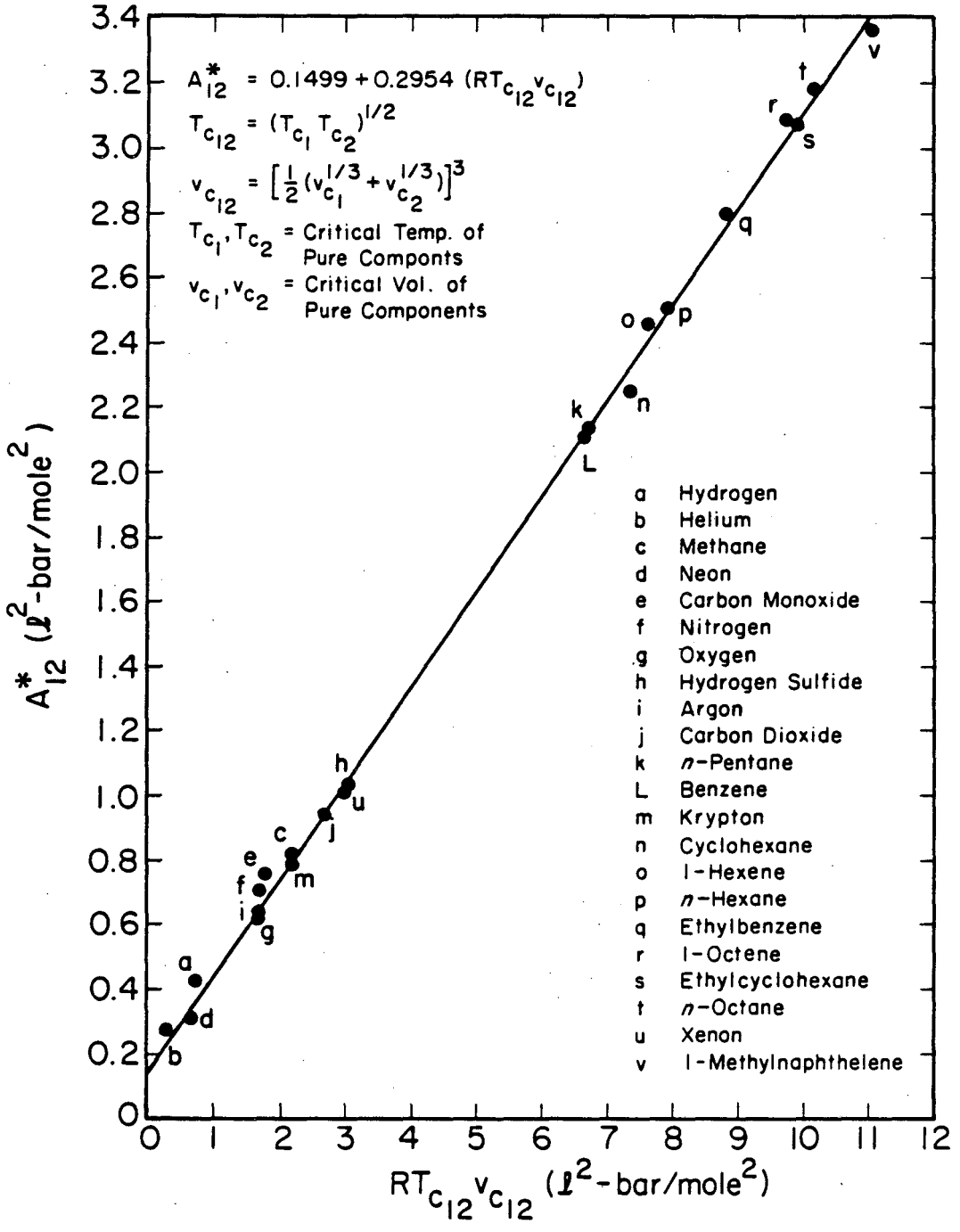
Figure 2



Generalized van der Waals Interaction Parameter for Nonpolar Solutes in Water at 300 K

XBL 841-538

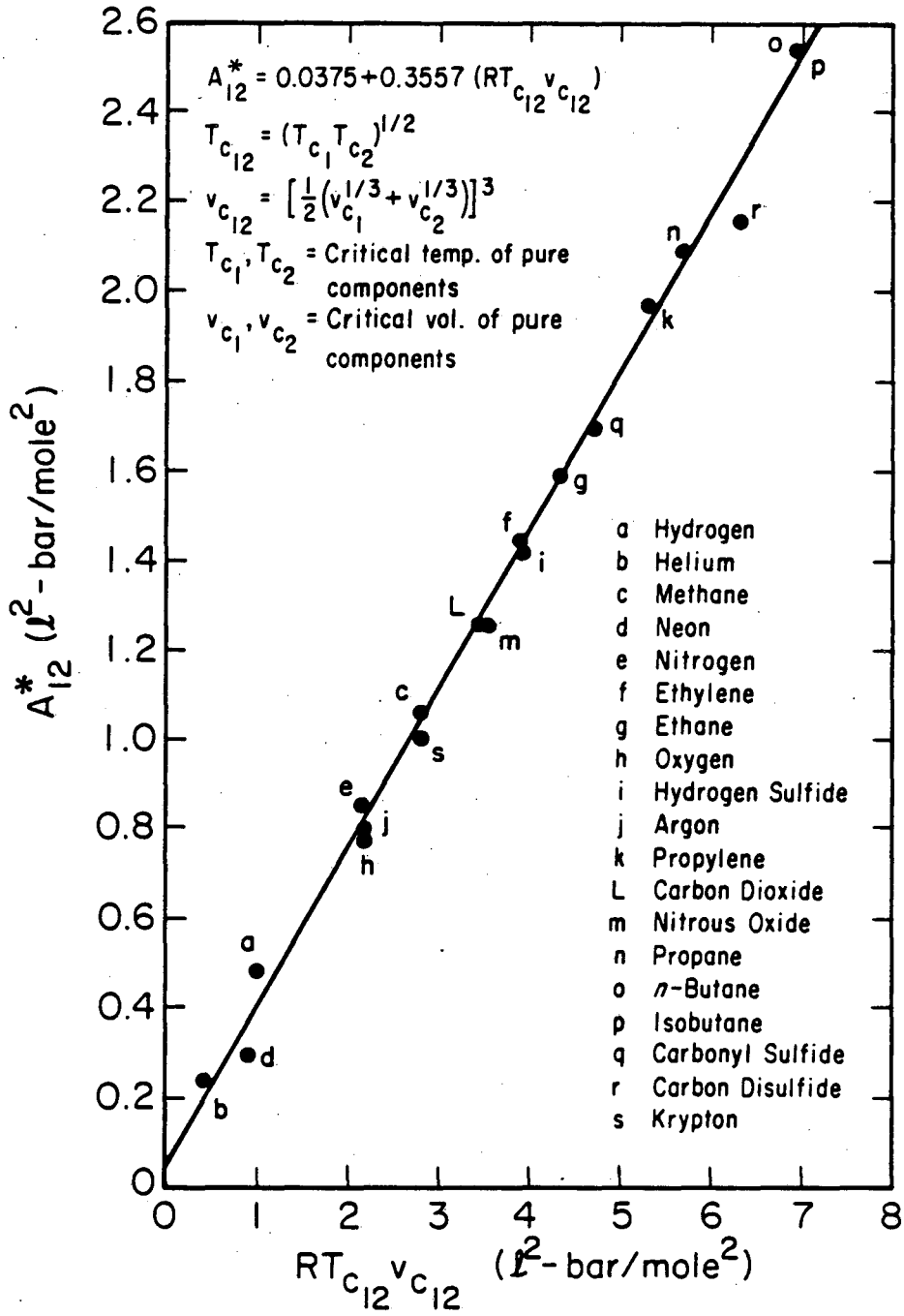
Figure 3



Generalized van der Waals Interaction Parameter for Nonpolar Solutes in Water at 300 K

XBL 841-539

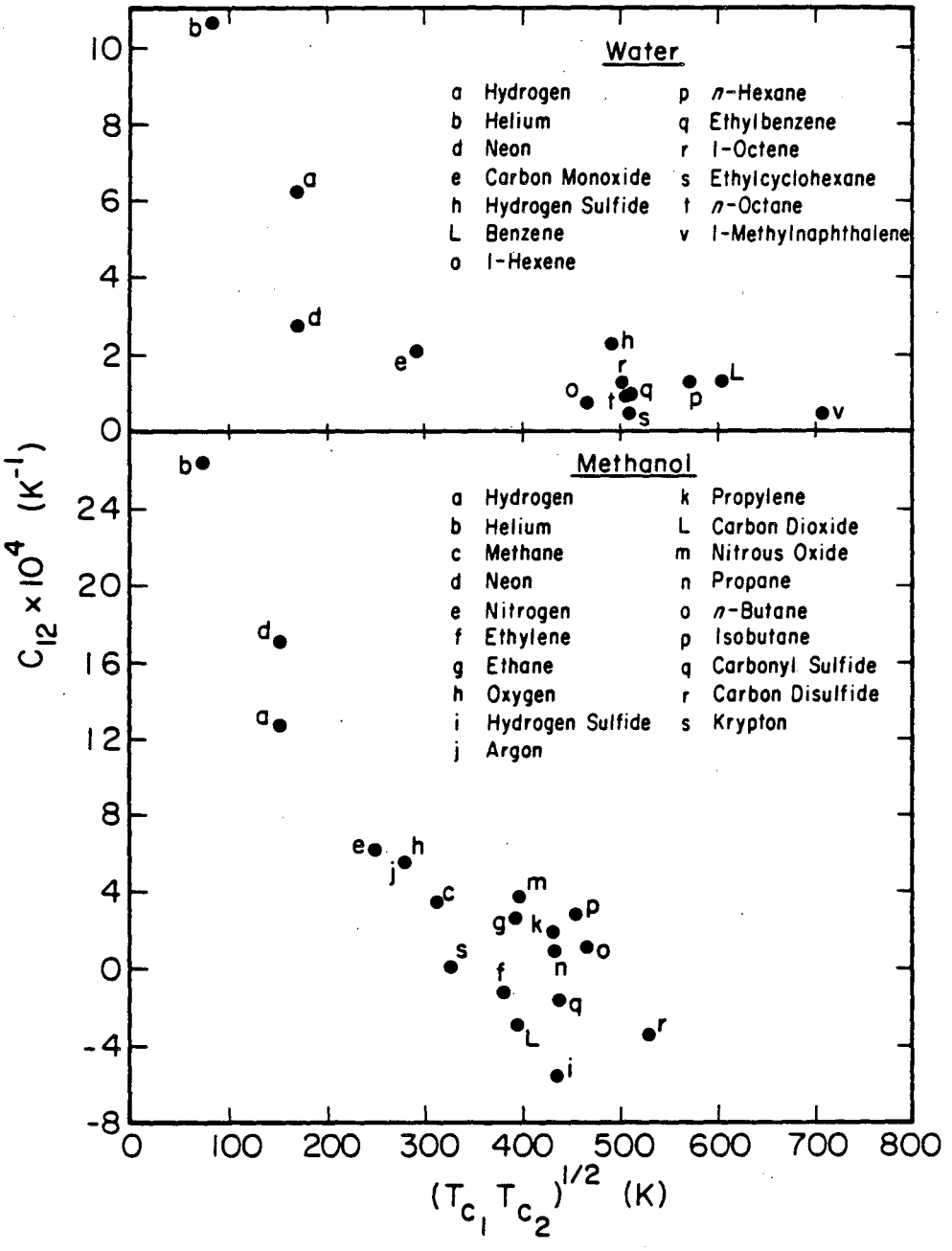
Figure 4



Generalized van der Waals Interaction Parameter for Nonpolar Solutes in Methanol at 300 K

XBL 841-537

Figure 5



Secondary Effect of Temperature on Binary Parameters a_{12} $(a_{12} = \tilde{A}_{12} A^*_{12} [1 + C_{12}(T-300)])$ for Nonpolar Solutes in Water and in Methanol

XBL 841-535

Figure 6

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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