density, lb. mass/cu. ft.
= surface tension, dynes/cm.
= parameter in proposed pressure drop correlation

Subscripts

G = gas
G_{am} = gas-arithmetic mean
L = liquid
S = slip
TP = two phase
1 = point of inlet to section
2 = point of outlet to section

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A Thermodynamic Correlation of Gas Solubilities

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Low-pressure solubility data have been correlated for eleven gases in nine solvents over a wide temperature range by considering the dissolution process in two steps. First the gas is condensed isothermally to a hypothetical liquid at 1 atm. pressure, and then this hypothetical liquid is dissolved in the solvent. The free energy of the first step depends only on the properties of the solute, which in the case of nonpolar gases can be adequately described by the theorem of corresponding states. The second step depends on the properties of both solute and solvent and, in the case of nonpolar systems, can be described by the theory of regular solutions. The correlation depends on three solute parameters: the solubility parameter, the molar volume, and the fugacity of the hypothetical liquid; the last of these has been plotted as a generalized function for the reduced temperature range of 0.7 to 3.2. A separate plot is given for hydrogen. These parameters may be used to make good estimates of low-pressure gas solubilities (or K values) in nonpolar solvents over a wide range of temperature.

A semiempirical method for correlating the solubilities of gases in polar solvents is also described and illustrated for several cases.

Since the correlation presented in this paper covers a wide temperature range, it is possible to make estimates of the heats of solution of gases in liquids. These may be useful in enthalpy-balance calculations as required in certain phase-separation operations.

The chemical literature contains many data on the solubility of gases in liquids, but a critical evaluation of these data points to two serious deficiencies. First, many data are of doubtful accuracy as is evidenced by the fact that for the same system under identical conditions, two or more authors frequently report very widely differing results. Second, the vast majority of the data were obtained at 25°C., and data at less than 0°C. and higher than 60°C. are very scarce. It therefore appeared desirable to take reliable gas solubilities and correlate them as well as possible within a simple but useful thermodynamic framework with the aim that the correlation might be used to predict solubilities for systems not previously studied and for temperatures other than those near 25°C.

THERMODYNAMIC FRAMEWORK

A rigorous method for the prediction of gas solubilities requires a valid theory of solutions. Such a theory is, unfortunately, not available, but for a semiempirical description of nonpolar systems the theory of regular solutions can serve as the basis of a correlating scheme. Previous attempts to use regular solution theory for gas-liquid solutions *(4, 11, 28, 32, 33)* have been quite successful. However these earlier studies were concerned either with a particular class of solutions (such as hydrocarbons), or were limited to a particular temperature, or were chiefly interested in the theoretical aspects of the problem. In this work however the theory is used in as general a way as

Table 1. Liquid Volumes and Solubility Parameters for Gaseous Solutes

Gas	v^L, $\frac{\text{cc.}}{\text{gmole}}$	$\delta, \left(\frac{\text{cal.}}{\text{cc.}}\right)^{1/2}$	Source of data and their temperature range	°K.
N_2	32.4	2.58	*1, 15, 18, 20, 25, 28, 30*	253.3 → 455
CO	32.1	3.13	*13, 20, 28*	253.3 → 333.3
O_2	33.0	4.0	*18, 20, 25, 28*	273 → 333
A	57.1	5.33	*5, 13, 16, 28, 29, 36*	287 → 313.3
CH_4	52.0	5.68	*18, 20, 25, 35*	253.2 → 444
CO_2	55.0	6.0	*14, 41*	193 → 307.2
Kr	65.0	6.4	*5*	289 → 313.6
C_2H_4	65.0	6.6	*20, 43*	273 → 398
C_2H_6	70.0	6.6	*16, 20, 23, 24, 25*	255.2 → 421.9
Rn	70.0	6.83	*39*	273 → 313
Cl_2	74.0	8.7	*38, 39*	273 → 363

possible. First, nonpolar systems are considered, and then some suggestions are made for the correlation of gas solubilities in polar solvents.

Consider a gaseous component at unit fugacity being dissolved isothermally in a liquid not near its critical temperature. The dissolution process is accompanied by a change in enthalpy and in entropy, just as occurs when two liquids are mixed. However in addition the dissolution process for the gas is accompanied by a large decrease in volume, since the volume of the solute in the condensed phase is much smaller than that in the gas phase. It is this large decrease in volume which distinguishes the dissolution of a gas from the dissolution of a liquid or a solid. In order to apply regular solution theory (which assumes no volume change) it is therefore necessary first to condense the gas to a volume close to the partial molar volume which it has as a solute in a liquid solvent. The isothermal dissolution process is then considered in two steps:

$$\Delta G = \Delta G_I + \Delta G_{II} \qquad (1)$$

$$\Delta G_I = RT \ln f_2^L/f_2^\circ \qquad (2)$$

$$\Delta G_{II} = RT \ln \gamma_2 x_2 \qquad (3)$$

The first step isothermally condenses the gas to a hypothetical state having a liquidlike volume. The second step dissolves the hypothetical liquidlike fluid into the solvent. Since the solute in the liquid solution is in equilibrium with the gas at unit fugacity, the equation of equilibrium is

$$\Delta G = 0 \qquad (4)$$

The regular solution equation gives the activity coefficient for the gaseous solute:

$$RT \ln \gamma_2 = V_2^L\,(\delta_1 - \delta_2)^2\,\phi_1^2 \qquad (5)$$

Substitution of Equations (1), (2), (3), and (5) into Equation (4) gives the solubility at 1 atm. partial pressure:

$$\frac{1}{x_2} = \frac{f_2^L}{f_2^\circ} \exp \frac{V_2^L(\delta_1 - \delta_2)^2\,\phi_1^2}{RT} \qquad (6)$$

[A more detailed justification of Equations (1) to (6) is given in Appendix I.]

This correlating scheme, then, involves three parameters for the gaseous component as a hypothetical liquid: the fugacity, the volume, and the solubility parameter. These parameters are all temperature dependent; however the theory of regular solutions assumes that at constant composition

$$\ln \gamma_2 \propto 1/T \qquad (7)$$

and therefore the quantity $V_2^L(\delta_1 - \delta_2)^2\,\phi_1^2$ is not temperature dependent. Accordingly any convenient temperature may be used to specify V_2^L and δ_2 provided the same temperature is used for δ_1 and V_1. (The most convenient temperature, of course, and the one used in this work, is 25°C.). The fugacity of the hypothetical liquid however must be treated as a function of temperature.

Previously a method has been given for evaluating the solute parameters from the properties of the gas alone (32), but this method is not for quantitative work. In the tion presented here the three p eters for the gaseous solute were tained from reliable gas-solubility in nonpolar solvents. Therefore results of this work are much easier to use than those previously reported.

The partial molar volume of a gas in liquid solution is of course not exactly the same in all nonpolar solvents. Hence even after the gaseous component is condensed to a specified liquidlike volume, it will upon dissolution in at least some solvents experience a further small volume change. However this volume change is very much smaller than that corresponding to step I. It has been shown by Scott (37) that because of a cancellation effect small changes in volume do not significantly affect the free energy of solution. Therefore the small effect of solvent on V_2^L need not be considered for the purposes of this work.

REDUCTION OF EXPERIMENTAL SOLUBILITY DATA

The fugacity of the hypothetical liquid solute at a pressure of 1 atm. depends only on the temperature and properties of the solute; it is independent of the properties of the solvent. It is possible therefore to apply the theorem of corresponding states and to show that the reduced fugacity of the hypothetical liquid solute is a universal function of the reduced temperature (see Appendix II). For the reduced temperature range 0.7 to 0.8 vapor-pressure data for liquefied gases (such as chlorine, radon, carbon dioxide) were used to obtain a plot of f^L/P_c vs. T/T_c. For reduced temperatures larger than 0.8 however it was necessary to use gas solubility data in order to obtain simultaneously values of the three solute parameters f_2^L, δ_2 and V_2^L.

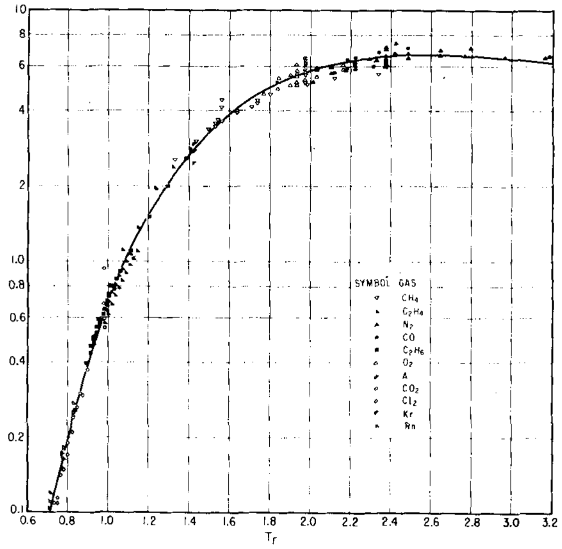

Fig. 1. Fugacity of hypothetical liquid at pressure of 1 atm.

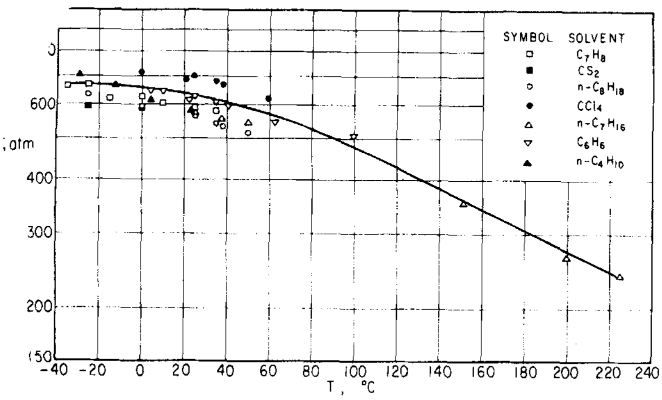

Fig. 2. Fugacity of hypothetical liquid hydrogen at 1-atm. pressure.

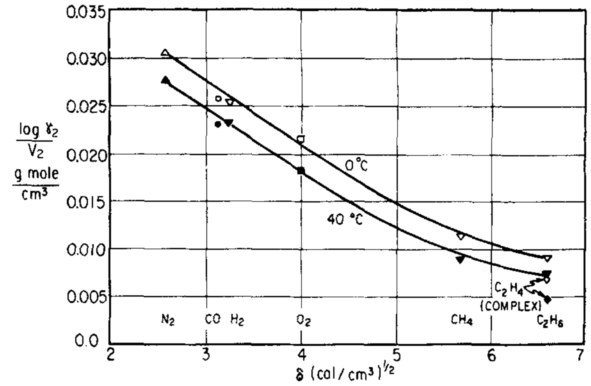

Fig. 3. Solubility of gases in acetone.

First, solubility data for the heavier gases (radon, krypton, chlorine, carbon dioxide, ethane, and ethylene) were examined. A first estimate of V_2^L at 25°C. was made with a previously presented correlation (32) for the partial molar volumes of gaseous solutes in liquid solutions. By using solubility data for any one gas in at least two solvents a value of δ_2 was computed such that the corresponding value of f_2^L would give a smooth continuation of the previously determined plot of ln f_2^L/P_c vs. reduced temperature. Slight adjustments in V_2^L and δ_2^L were then made in such a way as to account for all the reliable solubility data in as many solvents and at as many temperatures for which data were available and so as to minimize the scatter on the corresponding states fugacity plot. This procedure was followed for solubility data for the heavier gases up to a reduced temperature of 1.4.

For the higher reduced temperature region ($1.4 < T_r < 3.2$) solubility data for somewhat lighter gases (methane, oxygen, argon, carbon monoxide, and nitrogen) were used; values of δ_2 and V_2^L were again chosen in such a way as to correlate the available solubility data while at the same time minimizing the scatter on the plot of ln f^L/P_c vs. T/T_c.

RESULTS

The corresponding states plot for the fugacity of the hypothetical liquid is shown in Figure 1. The curve increases with reduced temperature as expected but shows a maximum near the Boyle point. The plot shown is in good agreement with the correlation of Curl and Pitzer (*9*) in the lower reduced-temperature region and with that of Chao and Seader (*4*).

In the past it has been common practice to compute hypothetical liquid fugacities by extrapolating a straight line on a semilogarithmic plot of vapor pressure vs. reciprocal temperature. When the data in Figure 1 are replotted in this manner, a straight line is obtained up to a reduced temperature of about 2, but at higher reduced temperatures the straight-line extrapolation is no longer valid.

Table 1 gives the parameters V_2^L and δ_2 for the gaseous solutes as well as the sources and temperature ranges of the solubility data used in obtaining the correlation. The parameters for the solvent V_1 and δ_1 may be obtained from volumetric data and calorimetric data for the solvent; these parameters are listed in reference *19*.

The fugacities given in Figure 1, together with the parameters given in Table 1, may now be used to estimate the solubility of any of the gases listed in Table 1 in any nonpolar solvent. The solubility at a partial gas pressure of 1 atm. can be calculated with reasonable confidence anywhere in the large temperature range 0.7 T_c to 3.2 T_c (where T_c is the critical temperature of the gaseous solute). The solubility is given by Equation (6); this equation is not explicit in x_2, since ϕ_1 also depends on x_2. However at a partial pressure of 1 atm. the mole fraction of solute in the liquid is usually much less than unity, and hence it is satisfactory to let $\phi_1 = 1$. In those few cases where x_2 is not very much smaller than unity, successive approximations must be used; two or three approximations always lead to convergence. A numerical example is given in Appendix III.

SOLUBILITY DATA FOR HYDROGEN

The very light gases hydrogen, helium, and neon are not included in the correlation given in Figure 1 and Table 1. Solubility data for helium and neon in nonpolar solvents are scarce, and hence no attempt was made to include them in any correlation; solubility data for hydrogen are more plentiful, but because of the extremely low value of the critical temperature of hydrogen these data were not used to extend the generalized fugacity diagram in Figure 1. The available reliable data for hydrogen solubility were however analyzed separately; values of δ_2, V_2^L, and f_2^L for hydrogen were determined in such a way as to reproduce the solubility data with minimum scatter and with a smooth variation of f_2^L with temperature. Fugacities of hypothetical liquid hydrogen at 1 atm. pressure are shown in Figure 2. The values of δ_2 and V_2^L

TABLE 2. SOLUBILITY DATA FOR HYDROGEN

Solvent	Reference
n-C_4H_{10}	*2, 31*
n-C_7H_{16}	*6, 27*
n-C_8H_{18}	*6, 27*
CCl_4	*6*
C_7H_8	*6*
C_6H_6	*6, 22*
CS_2	

δ_2 = 3.25 (cal./cc.)$^{1/2}$
V_2^L = 31.0 cc./gmole

TABLE 3. CALCULATED AND OBSERVED GAS SOLUBILITIES AT 1 ATM. PARTIAL PRESSURE

Gas	Solvent	Temp., °C.	Solubility × 10^4 $x_{calc.}$	$x_{obs.}$	Reference
N_2	Carbon disulfide	6.2	1.92	1.94	*25*
CO	Carbon tetrachloride	25	9.04	8.66	*28*
O_2	iso-Octane	25	23.4	25.3	*28*
O_2	iso-Octane	30.2	23.3	27.83	*25*
A	Benzene	37	9.02	9.00	*29*
CO_2	Benzene	60	65.5	79.4	*40*
N_2	Ethanol	25	3.37	3.48	*3*
A	Acetone	25	7.70	9.10	*28*
C_2H_6	n-Heptanol	25	152	159	*3*
H_2	Ethanol	25	2.2	2.1	*41*

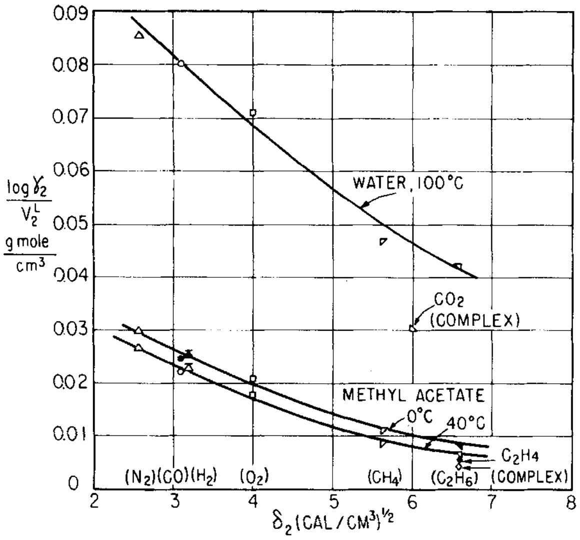

Fig. 4. Solubility of gases in water and in methyl acetate.

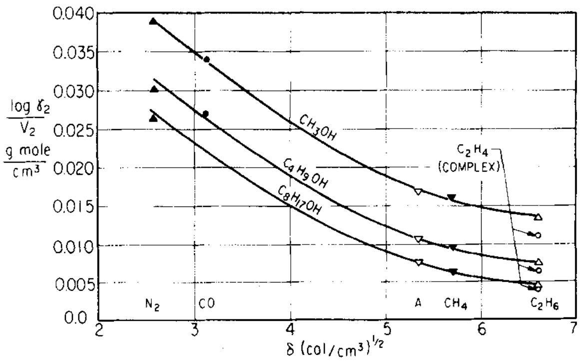

Fig. 5. Solubility of gases in normal alcohols at 25°C.

as well as the sources of solubility data are given in Table 2.

The regular solution relation does not correlate the available solubility data for hydrogen nearly as well as it correlates the solubility data for other gases. However even the approximate correlation indicated by Figure 2 makes it possible, with the use of Equation (6), to predict hydrogen solubilities in nonpolar solvents to about ± 15%. The relatively poor performance of the regular solution equation for hydrogen solutions can be understood if one remembers that one of the assumptions of this equation states that the intermolecular force between solute and solvent is given by the geometric mean of the forces in the pure solvent and those in the pure solute. Such an assumption becomes increasingly poor as the difference in size between solute molecules and solvent molecules increases; in the case of hydrogen, dissolved in common solvents, this difference is very large. In addition the regular solution equation does not allow for quantum corrections, which in the case of hydrogen are probably not negligible.

MIXED SOLVENTS

While this correlation is based on data for binary systems, it is applicable also to predicting the solubility of a gas in a mixed solvent. This extension follows directly from regular solution theory (*19*); for a mixed solvent Equation (6) becomes

$$\frac{1}{x_2} = \frac{f_2^L}{f_2^\circ} \exp \frac{V_2^L(\delta_2 - \bar{\delta})^2}{RT} \tag{8}$$

where $\bar{\delta}$ is an average solubility parameter defined by

$$\bar{\delta} = \sum_i \phi_i \, \delta_i \tag{9}$$

where the summation is over all components including the solute.

Table 3 compares predicted and observed gas solubilities for several systems which were not used in obtaining the correlating parameters. The agreement is good.

POLAR SOLVENTS

The regular solution equation is valid only for nonpolar systems, and therefore it cannot be used directly to correlate gas solubilities in nonpolar solvents. However the treatment above used for the correlation of gas solubilities in nonpolar solvents suggests a useful empirical method which may be used for polar solvents.

For a fixed polar solvent at a fixed temperature a plot of gas solubility vs. some gas property (for example force constants or critical temperature) will usually not result in a smooth correlation. This failure is due to the fact that gas solubilities depend not only on the interaction between solute and solvent but also on the fugacity of the pure solute in a condensed state; it is therefore unlikely that a single parameter for the gaseous component will be sufficient to produce a correlation. Rather than correlate solubilities directly it is more successful to correlate activity coefficients which are referred to the hypothetical liquid solute. The fugacities given in Figures 1 and 2 depend only on solute properties, and since they are independent of the solvent, it is permissible to use them in the calculation of activity coefficients for solutes in polar as well as nonpolar solvents. The solubility at a partial pressure of 1 atm. is related to the activity coefficient by

$$\frac{1}{x_2} = \frac{f_2^L}{f_2^\circ} \gamma_2 \tag{10}$$

TABLE 4. SOLUBILITY DATA IN POLAR SOLVENTS

Solvent	Reference
Methyl alcohol	*3, 12, 17, 26, 29*
Ethyl alcohol	*3, 41*
n-Butyl alcohol	*3, 17, 26*
n-Heptyl alcohol	*3*
n-Octyl alcohol	*3*
Acetone	*20*
Methyl acetate	*20*
Ethyl ether	*20*
Water	*7, 8, 10, 21, 34, 42*

For a nonpolar gas in a polar solvent the activity coefficient of the gas may be expected to depend on its volume and solubility parameter according to a function of the form

$$\ln \gamma_2 = V_2^L \, F(T, \delta_2, \text{properties of solvent}) \tag{11}$$

The parameters V_2^L and δ_2 depend only on solute properties, and hence they too, like the fugacity f_2^L, may be used with polar solvents. Equation (11) suggests that gas solubility data in a polar solvent could be correlated by plotting isotherms of $(\ln \gamma_2)/V_2^L$ vs. δ_2. Such plots are shown in Figures 3, 4, and 5 for gas solubility data in acetone, methyl acetate, water, and three alcohols. The sources of data are given in Table 4.

Figures 3, 4, and 5 show that, as expected, the activity coefficient of solute falls with rising solubility parameter. These plots also show how specific chemical interactions can enhance the solubility of a gas beyond that predicted by a strictly physical correlation. The low activity coefficient of ethylene (and hence its increased solubility) is due to the fact that olefins may act as electron donors and therefore form loose charge-transfer complexes with acidic polar components which can act as electron acceptors. Such complexing behavior may be expected of any solute possessing highly polarizable pi electrons, and therefore ethylene is considerably more soluble in electron-accepting polar solvents than ethane.

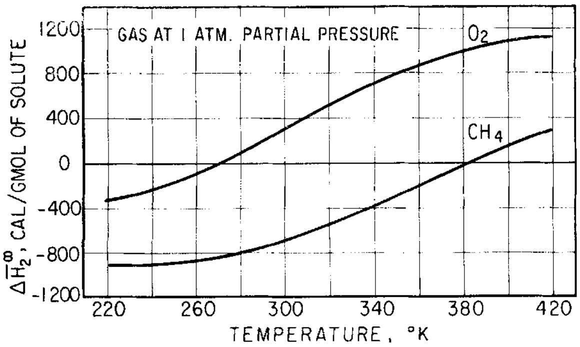

Fig. 6. Heat of solution of two gases at infinite dilution in carbon disulfide.

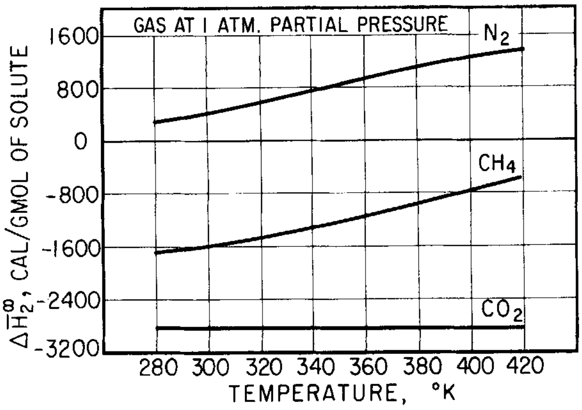

Fig. 7. Heat of solution of three gases at infinite dilution in *n*-pentane.

The solubility of carbon dioxide in water is larger than would be predicted on the basis of physical forces alone, since carbon dioxide and water have a slight tendency to form carbonic acid. Water is a particularly difficult solvent for thermodynamic correlations because of its structural features which, at lower temperatures, give rise to hydrates. Figure 4 shows that a correlation of gas solubility data in water can be obtained at 100°C., but the data at lower temperatures could not be correlated in this way.

HEAT OF SOLUTION OF GASES IN LIQUIDS

The thermodynamic analysis given above for gas solubility in liquids for nonpolar systems can also be used to estimate the enthalpy change which occurs when a gas at 1 atm. partial pressure dissolves in a liquid. At this low pressure Henry's law may be expected to hold, and the heat of solution is given by the change of solubility with temperature:

$$-\frac{R\,d\ln x_2}{d\,1/T} = \Delta\bar{H}_2^\infty = \bar{H}_2^L - H_2^G \qquad (12)$$

The solubility however is uniquely determined by the reference state fugacity and by the activity coefficient. Therefore Equation (12) can be rewritten as the sum of two parts:

$$\Delta\bar{H}_2^\infty = \Delta H_{2(I)} + \Delta H_{2(II)} \qquad (13)$$

where

$$\Delta H_{2(I)} = \frac{RT_c\,d\ln f^L/P_c}{d\,1/T_r} \qquad (14)$$

$$\Delta H_{2(II)} = V_2(\delta_1 - \delta_2)^2 \qquad (15)$$

Equation (14) gives the enthalpy change experienced by the gas as it goes isothermally from the gaseous state at 1 atm. to the hypothetical pure liquid state. This heat effect does not depend on the solvent; it is determined only by the slope of the curve shown in Figure 1.

Equation (15) gives the enthalpy change which accompanies the dissolution of hypothetical liquid in a very large amount of solvent such that the final concentration of solute is infinitely small. This heat effect is given by the regular solution equation.

To illustrate the use of Equations (13), (14), and (15) Figures 6 and 7 show the computed heats of solution of several gases in two solvents as a function of temperature. Since these results depend on the slope of the curve in Figure 1, they are probably not of very high accuracy; however these computations provide useful estimates. A meaningful comparison between calculated and observed heats of solution for gases in liquids cannot be made because of paucity of data. The curves in Figures 6 and 7 show that heats of solution may be either exothermic or endothermic depending on the temperature and on the nature of the gas and of the solvent. A few generalizations however are apparent. $\Delta H_{2(II)}$ is always positive (endothermic), and $\Delta H_{2(I)}$ is almost always larger than $\Delta H_{2(II)}$; therefore heats of solution of the heavier gases at normal temperatures will be exothermic. However for very light gases such as helium, hydrogen, and neon $\Delta H_{2(I)}$ and $\Delta H_{2(II)}$ will both be positive, and hence these gases will dissolve with endothermic heats of solution. Gases of intermediate force constants (for example nitrogen, argon, oxygen) will usually have small heats of solution which tend to be exothermic at lower temperatures and endothermic at higher temperatures.

These techniques for estimating solubilities and enthalpies of gaseous solutes in liquids may find useful application in the design of separation processes.

ACKNOWLEDGMENT

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NOTATION

F = a function
f^L = fugacity of hypothetical liquid at 1 atm.
f^o = fugacity of pure gas at initial conditions taken as 1 atm. in this work
G = Gibbs free energy
H = enthalpy
P^S = saturation pressure
P_c = critical pressure
π = isometric mixing pressure
R = gas constant
T = absolute temperature
V = molar volume
x = mole fraction in liquid phase
δ = solubility parameter
ϕ = volume fraction
γ = activity coefficient

Subscripts

1 = solvent
2 = gaseous solute
I = step I
II = step II
c = critical
i = component
r = reduced

Superscripts

G = gas
L = liquid
∞ = corresponding to infinite dilution
o = initial
S = saturation

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APPENDIX I

Hypothetical Liquid Equivalence

Considering the dissolution of a gas into a liquid as a two-step process is a simplification which can be shown to be equivalent to the three-step process used earlier (*32*). The three-step process is an isothermal cycle as follows:

a. Compress gas from 1 atm. to the isometric mixing pressure π at which the gas has reached a liquidlike volume V^L. The free energy for this change is

$$\Delta G_{2(a)} = RT \ln \frac{f(\pi)}{f^o(1)} \qquad \text{(I-1)}$$

Also compress the liquid to pressure π.

b. Mix isometrically and isobarically the compressed gas with the compressed liquid. The free energy change for the solute is

$$\Delta \overline{G}_{2(b)} = RT \ln \gamma_2 x_2 \qquad \text{(I-2)}$$

c. Expand the solution to 1 atm. total pressure. The free energy change for the solute is

$$\Delta \overline{G}_{2(c)} = \int_\pi^1 v^L \, dp \qquad \text{(I-3)}$$

The solubility x_2 is chosen such that the solution is in equilibrium with the gas at partial pressure of 1 atm. and the solvent is considered to be nonvolatile.

Then

$$\Delta G_{2(a)} + \Delta \overline{G}_{2(b)} + \Delta \overline{G}_{2(c)} = 0 \qquad \text{(1-4)}$$

Algebraic rearrangement of Equations (I-1) to (I-4) gives

$$\frac{1}{x_2} = \frac{f(\pi)}{f^o} \exp \frac{\int_\pi^1 V^L \, dP}{RT} \qquad \text{(I-5)}$$

It is now convenient to combine steps a and c into one equivalent step, namely that of condensing gas at 1 atm. to hypothetical liquid. That is steps a and c correspond to step I, and the fugacity of hypothetical liquid is given by

$$f^L = f(\pi) \exp \frac{\int_\pi^1 v^L \, dP}{RT} \qquad \text{(I-6)}$$

Step b corresponds to step 2, and hence the activity coefficient in Equations (5) and (I-2) refer to the pressure π.

APPENDIX II

Application of the Law of Corresponding States

The reduced fugacity of a saturated liquid at saturation pressure P^S is given by

$$\frac{f^L(P^S, T)}{P_c} = \frac{P^S}{P_c} \mu \qquad \text{(II-I)}$$

where P^S/P_c is the reduced vapor pressure which for small nonpolar molecules is a function only of the reduced temperature. μ is the fugacity coefficient which is given by

$$\mu = \exp \int_o^{P^S} (z\text{-}1) \frac{dP}{P} \qquad \text{(II-2)}$$

In the extension of the liquid range to the hypothetical liquid state the saturation pressure is replaced by the isometric mixing pressure π which is the equilibrium pressure corresponding to temperature T and liquidlike volume V^L. Therefore the reduced fugacity of the compressed fluid at the liquidlike volume V^L is given by

$$\frac{f(\pi, T)}{P_c} = \frac{\pi}{P_c} \exp \frac{\int_o^\pi (z\text{-}1) \, dP}{P} \qquad \text{(II-3)}$$

It was shown in Appendix I that the fugacity of the hypothetical liquid at 1 atm. is related to the fugacity of the compressed gas by

$$f^L(1, T) = f(\pi, T) \exp \frac{\int_\pi^1 V^L \, dP}{RT} \qquad \text{(II-4)}$$

Substituting Equation (3) into Equation (4) and noting that $V^g = zRT/P$ one gets

$$\frac{f^L}{P_c} = \frac{\pi}{P_c} \exp \int_o^\pi \left(\frac{V^o - V^L}{RT} - \frac{1}{P} \right) dP \qquad \text{(II-5)}$$

where it has been assumed that $z = 1$ for pressures up to 1 atm.

The reduced saturation pressure π/P_c, by analogy to the reduced vapor pressure, is a function only of the reduced temperature for small molecules obeying the simple law of corresponding states. The exponential term may also be considered to be a function only of the reduced temperature; this term is not at all sensitive to the (large) value of π, since the integrand vanishes at high pressures. Accordingly, to a good approximation the reduced fugacity of hypothetical liquid at 1 atm pressure is a function only of reduced temperature.

APPENDIX III

Sample Calculation

Compute the solubility of oxygen at a partial pressure of 1 atm. in iso-octane at 30.2°C. Subscript 1 refers to iso-octane and subscript 2 refers to oxygen.

From standard reference obtain the critical temperature and pressure of oxygen:

$$T_{c_2} = 154.2°\text{K.}, P_{c_2} = 49.7 \text{ atm.}$$

The reduced temperature is $(273.2 + 30.2)/154.2 = 1.966$

From Figure 1 obtain $f^L/P_c = 5.55$.

Therefore $f^L = (5.55)(49.7) = 275.8$ atm.

From Table 1 obtain the solute parameters V_2 and δ_2 for oxygen:

$$V_2 = 33.3 \text{ cc./gmole}, \delta_2 = 4.0 \text{ (cal./cc.)}$$

From reference *19* the solubility parameter δ_1 at 25°C. = 6.85 (cal./cc.)$^{1/2}$

The solubility is now calculated from Equation (6) with $f^o{}_2 = 1$ atm. In this case the solubility is so small that $\phi_2^2 = 1$. The constant R is 1.987 cal./gmole, °K. Substitution in Equation (6) gives

$$x_2 = 23.3 \times 10^{-4}$$

(This small value justifies the assumption that $\phi_2^2 = 1$.) The observed value is

$$x_2 = 25.3 \times 10^{-4}$$