Prediction of Gas Solubility in Nonpolar Liquids

S. K. LACHOWICZ[1] **and K. E. WEALE**
Department of Chemical Engineering, Imperial College of Science and Technology, London, England

Hildebrand (*14*) has given a general treatment of the solubility of nonelectrolytes. For solutions of sparingly soluble gases in nonpolar liquids he obtains (*8*) a simplified equation relating the logarithm of gas solubility at atmospheric pressure to the partial molal volumes and the partial molal energies of mixing. This has the form

$$-\log x_2 = -\log x_2{}^i + \log \bar{v}_2/V_1 + (1 - \bar{v}_2/V_1)/2.303 + \Delta\bar{E}^M{}_2/2.303\,RT \qquad (1)$$

in which

x_2 = mole fraction of gas in solution
$x_2{}^i$ = "ideal solubility" of the solute, equal to $1/p_2{}^i$ where $p_2{}^i$ is the "vapor pressure" of the gas at the equilibrium temperature
$\bar{v}_2$ = partial molal volume of gas in solution
V_1 = molar volume of the solvent
$\Delta\bar{E}^M{}_2$ = partial molal energy of mixing of the gas

In the derivation of the equation the small change of volume on mixing is neglected and $\Delta\bar{E}^M{}_2$ replaces the partial molal heat of mixing $\Delta\bar{H}^M{}_2$ (*14*, p. 139). For a sparingly soluble gas it is permissible to neglect the interactions between the dissolved gas molecules, and Hildebrand (*14*, pp. 246–7) obtains an expression for $\Delta\bar{E}^M{}_2$

$$\Delta\bar{E}^M{}_2 = \bar{v}_2\,\delta_1{}^2 - \Phi_{12}/V_1 \qquad (2)$$

where δ_1 is the square root of the "internal pressure" $(\partial E/\partial V)_T$ of the solvent and Φ_{12} represents the solvent-solute interactions. Substitution for $\overline{\Delta E}^M{}_2$ in Equation 1 gives

$$-\log x_2 = -\log x_2{}^i + \log \bar{v}_2/V_1 + (1 - \bar{v}_2/V_1)/2.303 + (\bar{v}_2\,\delta_1{}^2 - \Phi_{12}/V_1)/2.303\,RT \qquad (3)$$

which is used with one modification for the present correlation. The modification is introduced because values of the partial molal volume, $\bar{v}_2$, of gas in solution, which is lowest for solvents of high internal pressure (*13*), have been determined experimentally for very few gas-liquid systems. The authors therefore, in the ensuing calculations, replace $\bar{v}_2$ by the gas molar volume, $V_2{}^*$, at a pressure equal to the internal pressure of the solvent. Equation 2 then becomes

$$\Delta\bar{E}^M{}_2 = V_2{}^*\,\delta_1{}^2 - \Phi_{12}/V_1 \qquad (4)$$

and Equation 3 becomes

$$-\log x_2 = -\log x_2{}^i + \log V_2{}^*/V_1 + (1 - V_2{}^*/V_1)/2.303 + (V_2{}^*\,\delta_1{}^2 - \Phi_{12}/V_1)/2.303\,RT \qquad (5)$$

When the solute is a slightly soluble gas well above its critical temperature, $x_2{}^i$ has no physical meaning. The term $-\log x_2{}^i = \log p_2{}^i$ may, however, be estimated by straight-line extrapolation of the log p vs. $1/T$ relationship for the pure liquid solute into the region above the critical temperature, and $p^i{}_2$ is often called the hypothetical vapor pressure.

For most organic solvents V_1 and δ_1 are known and if the solubility of the gas in the liquid, x_2, has been found experimentally, the only unknown in Equation 5 is the parameter Φ_{12}, which may therefore be calculated. Equation 4 can be rewritten $\Delta\bar{E}^M{}_2$ in the form

$$\Phi_{12}/2.303\,RT = V_1(V_2{}^*\,\delta_1{}^2 - \Delta\bar{E}^M{}_2)/2.303\,RT \qquad (6)$$

The term $\Phi_{12}/2.303\,RT$ represents the solvent-solute interactions and, for the same gas at the same temperature in a variety of solvents it can be expected to be principally a function of the molecular parameters of the solvent. This expectation has been confirmed by plotting $\Phi_{12}/2.303\,RT$ vs. V_1 for solutions of the same gas in a number of solvents. The linear relationships which result permit in turn the calculation of the solubility of gases in solvents for which no experimental data are available.

APPLICATION OF EQUATIONS TO EXISTING DATA

The relation between Φ_{12} and V_1 has been determined for hydrogen at 0°, 25°, and 50°C. and for nitrogen, carbon monoxide, oxygen, and argon at 25°C. by calculating the values of $\Phi_{1,}/2.303\,RT$ from Equation 6, for nonpolar solvents in which the solubility of the gas is known. The lack of high pressure *P-V-T* data and scarcity of solubility measurements prevented extension of the calculations to helium and neon.

The molar volumes of the liquids (Table I) were calculated from densities collected by Timmermans (*31*) except for those of the fluorocarbons (*6,10*).

Table II gives the normal volumes of gases used to calculate $V_2{}^*$, at pressures equal to the internal pressures of various solvents, from the empirical equations fitted by the various authors to their high pressure *P-V-T* data. In all cases, with the exception of nitrogen, extrapolation of the experimental curves was necessary as the internal pressures range up to 4200 atm., and the high pressure measurements extend only to 3000 atm. The logarithm of the hypothetical vapor pressure of each gas, log $p^i{}_2$, was calculated from the respective vapor pressure equations (*3,5,15,24,27*) to two decimal places. The value of log $p^i{}_2$ for hydrogen should vary slightly with temperature, but the differences are smaller than the uncertainty of extrapolation and so the same value was used at 0°, 25°, and 50°C.

The data contained or referred to in Tables I and II, together with the solubility measurements reported in the literature, thus permit the calculation of $V_2{}^*$, of $\Phi_{12}/2.303\,RT$ (from Equation 5), and of $\Delta\bar{E}^M{}_2$ (from Equation 2). The values of $\Phi_{12}/2.303\,RT$ plotted against V_1 obey linear relationships, examples of which are shown in Figure 1. Table III gives the constants of the best straight lines through the experimental points, calculated by the method of least squares, together with the fiducial limits, correlational coefficient, and probability significance level for each correlation.

---

[1] Present address, Research and Development Department, The Distillers Co., Ltd., Epsom, Surrey, England.

Table I. Molar Volumes and Internal Pressures of Solvents

Solvent	Dipole Moment, $u \times 10^{18}$	0°C.			25°C.			50°C.		
		V_1, cc./mole	$(\partial E/\partial V)_T$, atm.	$\left(\delta_1, \frac{\text{cal.}}{\text{cc.}}\right)^{\frac{1}{2}}$	V_1, cc./mole	$(\partial E/\partial V)_T$, atm.	$\left(\delta_1, \frac{\text{cal.}}{\text{cc.}}\right)^{\frac{1}{2}}$	V_1, cc./mole	$(\partial E/\partial V)_T$, atm.	$\left(\delta_1, \frac{\text{cal.}}{\text{cc.}}\right)^{\frac{1}{2}}$ [a]
n-C_7F_{16}	0	217.4	1610	6.25 (*4*)	225.8	1440	5.9 (*4*)	234.3	1340	5.7
$C_6F_{11} \cdot CH_3$					196.0	1490	6.0 (*8*)			
$C_6F_{10} \cdot (CH_3)_2$					217.4	1540	6.1 (*8*)			
Iso-octane		161.7	2080	7.1 (*4*)	166.1	1940	6.85 (*14*)	171.3	1800	6.6
n-Hexane	0				131.6	2200	7.3 (*14*)			
Diethyl ether	1.1				104.7	2260	7.4 (*14*)			
n-Heptane	0	143.1	2450	7.7 (*4*)	147.5	2290	7.45 (*14*)	152.3	2140	7.2
n-Octane	0	159.3	2510	7.8 (*4*)	163.5	2350	7.55 (*14*)	168.5	2200	7.3
Methylcyclohexane	0				128.3	2540	7.85 (*14*)			
Cyclohexane	0				108.7	2780	8.2 (*14*)			
CCl_4	0	94.3	3270	8.9 (*4*)	97.1	3050	8.6 (*14*)	100.1	2810	8.25
Ethylbenzene	0.6				123.1	3200	8.8 (*14*)			
m-Xylene	0.5				123.5	3200	8.8 (*14*)			
Mesitylene	0.2				139.6	3200	8.8 (*14*)			
Toluene	0.4	104.2	3495	9.2 (*4*)	106.8	3270	8.9 (*14*)	109.8	3055	8.6
Benzene	0				89.4	3460	9.15 (*14*)	92.3	3195	8.8
Chloroform	1.1				80.7	3570	9.3 (*14*)			
Acetone	2.8				74.0	3570	9.3 (*7*)			
Methylacetate	1.7				79.9	3690	9.45 (*14*)			
Chlorobenzene	1.6				102.2	3730	9.5 (*14*)			
CS_2	0	59.0	4380	10.3 (*4*)	60.6	4090	9.95 (*4*)			
Dioxane	0				85.7	4130	10.0 (*14*)			

[a] Extrapolated from data in (*4*).

n-C_7F_{16} = n-perfluoroheptane; $C_6F_{11} \cdot CF_3$ = perfluoromethylcyclohexane; $C_6F_{10} \cdot (CF_3)_2$ = perfluorodimethylcyclohexane; iso-octane = 2,2,4-trimethyl pentane.

Table II. Gas Parameters

Gas	Molar Volume, at 0°C., 1 Atm., Cc.	Log $p^i_2 = -\text{Log } x^i_2$ at 25°C.	P-V-T Data
H_2	22,428	3.00 (*15*)	(*23*)
N_2	22,404	2.90 (*5*)	(*25*)
CO	22,404	2.90 (*27*)	(*26*)
O_2	22,393	2.80 (*5*)	(*1*)
A	22,393	2.80 (*3,24*)	(*28*)

Table III. Constants, for Various Gases, of Correlation Equation $\Phi_{12}/2.303\ RT = bV_1 + a$

Gas	Temp., °C.	b	95% Fiducial Limits in b	a	95% Fiducial Limits in a	Correl. Coeff.	P,%
H_2	0	0.4936	±0.0646	− 0.8320	± 9.220	0.993	0.1
H_2	25	0.5237	±0.0406	− 6.748	± 5.411	0.994	0.1
H_2	50	0.6061	±0.1116	−20.151	±17.210	0.987	0.1
N_2	25	1.0427	±0.0937	+31.936	±13.876	0.992	0.1
CO	25	1.0036	±0.1600	+53.583	±21.121	0.990	0.1
O_2	25	0.8631	±0.1325	+30.971	±17.555	0.985	0.1
A	25	0.7997	±0.0876	+43.576	± 8.950	0.999	0.1

In all cases the correlation is highly significant, although it varies slightly with temperature and from gas to gas.

Table IV. Experimental and Calculated Solubilities of Hydrogen at 1 Atm.

Solvent	V_2^*, Cc./Mole	$x_2 \times 10^4$, (Obsd.)	$\Phi_{12}/2.303\ RT$	$\Delta \log x_2$, Obsd.-Calcd.
		t = 0°C.		
n-C_7F_{16}	29.5	11.804 (*4*)	109.3	−0.013
Iso-C_8H_{18} [a]	26.1	6.783 (*4*)	73.7	+0.033
n-C_7H_{16}	24.2	5.902 (*4*)	72.8	−0.021
n-C_8H_{18}	24.0	5.867 (*4*)	76.9	+0.005
CCl_4	21.5	2.596 (*4*)	44.3	+0.015
Toluene	20.9	2.617 (*5*)	50.3	+0.003
CS_2	19.0	1.260 (*4*)	30.4	−0.035
		t = 25°C.		
n-C_7F_{16}	32.7	14.000 (*4*)	115.6	−0.019
Iso-C_8H_{18} [a]	28.1	7.812 (*4*)	74.6	+0.034
n-C_6H_{14}	26.4	6.51 (*11*)	65.1	−0.023
n-C_7H_{16}	25.9	6.882 (*4*)	72.9	−0.016
n-C_8H_{18}	25.6	6.830 (*4*)	76.2	+0.016
Cyclohexane	23.7	3.80 (*11*)	46.3	+0.036
CCl_4	22.8	3.196 (*4*)	43.1	+0.010
Toluene	22.1	3.163 (*4*)	47.3	+0.017
C_6H_6	21.6	2.579 (*4*)	40.1	−0.001
CS_2	20.2	1.600 (*4*)	29.2	−0.070
Dioxane	20.1	1.93 (*11*)	39.5	−0.017
		t = 50°C.		
n-C_7F_{16}	35.6	16.35 (*4*)	128.2	−0.027
Iso-C_8H_{18} [a]	30.3	8.88 (*4*)	76.4	+0.043
n-C_7H_{16}	27.7	7.92 (*4*)	73.9	−0.012
n-C_8H_{18}	27.3	7.85 (*4*)	76.2	+0.034
CCl_4	24.4	3.84 (*4*)	42.2	−0.017
Toluene	23.5	3.75 (*4*)	46.3	+0.001
C_6H_6	23.0	3.15 (*4*)	39.2	−0.037

[a] 2,2,4-Trimethylpentane.

The established correlations may be used to predict the solubility of one of the gases in a particular solvent by reversing the procedure. The value of $\Phi_{12}/2.303\ RT$ for the solvent is calculated by using the constants of Table III, inserted in Equation 5, and the logarithm of the solubility, $\log x_2$, is computed, the values of the other terms being obtained as described above. Tables IV and V include the experimental gas solubilities and the values of V_2^* and $\Phi_{12}/2.303\ RT$ which were used to establish the correlations; and also show $\Delta \log x_2$, the difference between the logarithms of the experimental solubilities and those calculated using the constants of Table III.

DISCUSSION

In view of the assumptions involved in the derivation of Equation 1 and in the substitution of V_2^* for $\bar{v}_2$ the agreement between the experimental and the calculated values of $-\log x_2$ in the correlation discussed in this paper is remarkably good, although it varies from gas to gas. The best agreement is found in the case of hydrogen at 0°C. and argon at 25°C. where the maximum difference between the observed and the calculated value of $-\log x_2$ for any solvent is 0.035 (0.9%) and 0.009 (0.3%), respectively. The greatest scatter of points is observed in the case of oxygen at 25°C. The agreement between the experimental and the calculated solubilities is diminished by the logarithmic relationship of Equations 1 and 5, but not all the differences are attributable to this or to the approximations made in deriving the correlation. The data reported in the literature are sometimes inaccurate, because of the experimental diffi-

Table V. Experimental and Calculated Solubilities of Nitrogen, Carbon Monoxide, Oxygen, and Argon at 1 Atm., 25° C.

Solvent	V_2*, Cc./Mole	$x_2 \times 10^4$, Obsd.	$\Phi_{12}/2.303\ RT$	$\Delta \log x_2$, Obsd.-Calcd.
		Nitrogen		
n-C_7F_{14}	42.7	39.1 (*8*)	273.4	−0.027
$CF_3 \cdot C_6F_{11}$[a]	42.3	31.8 (*8*)	233.9	+0.011
m-$(CF_3)_2C_6F_{10}$[b]	41.8	33.0 (*8*)	259.6	−0.005
Iso-octane[c]	38.9	15.3 (*19*)	186.9	+0.109
n-C_6H_{14}	37.5	14.0 (*8*)	175.1	−0.046
n-C_7H_{16}	37.0	13.5 (*2*)	185.8	+0.001
Cyclo-C_6H_{12}	35.1	7.55 (*8*)	142.6	+0.023
CCl_4	34.3	6.42 (*16*)	135.6	−0.027
m-Xylene	33.8	6.14 (*18*)	168.0	−0.060
Toluene	33.6	5.39 (*18*)	147.3	−0.039
C_6H_6	33.2	4.48 (*8*)	127.7	−0.030
		4.24 (*18*)	125.6	−0.006
		4.11 (*20*)	124.1	+0.010
CS_2	31.9	2.23 (*8*)	90.3	+0.182
		Carbon Monoxide		
n-C_7F_{16}	43.1	38.8 (*7*)	275.7	+0.020
n-C_7H_{16}	37.4	17.3 (*7*)	197.9	+0.024
CCl_4	34.6	8.66 (*16*)	149.2	+0.019
m-Xylene	34.1	8.95 (*18*)	190.6	−0.106
Toluene	33.9	7.90 (*18*)	167.0	−0.058
C_6H_6	33.5	6.65 (*16*)	145.2	−0.021
		6.24 (*18*)	142.7	+0.007
CS_2	32.2	3.60 (*7*)	104.4	+0.166
		Oxygen		
n-C_7F_{16}	36.3	55.3 (*7*)	234.7	−0.043
Iso-octane	33.2	25.3 (*19*)	164.0	+0.050
n-C_6H_{14}	32.0	19.3 (*11*)	138.8	+0.036
n-C_7H_{16}	30.8	19.7 (*11*)	149.1	+0.056
Cyclohexane	29.9	12.3 (*11*)	120.4	+0.022
CCl_4	29.2	12.1 (*16*)	121.2	−0.076
C_6H_6	28.3	8.16 (*16*)	111.4	−0.047
CS_2	27.1	4.42 (*7*)	78.4	+0.066
Dioxane	27.0	5.38 (*11*)	112.6	−0.101
		Argon		
$C_6H_{11}(CH_3)$[d]	30.7	17.7 (*30*)	146.7	−0.005
Cyclohexane	29.9	14.6 (*30*)	130.2	+0.009
		14.8 (*21*)	129.6	+0.003
C_6H_6	28.3	8.85 (*21*)	114.5	+0.004
Acetone	28.2	9.06 (*21*)	103.4	−0.007

[a] Perfluoromethylcyclohexane.
[b] Perfluorodimethylcyclohexane.
[c] 2,2,4-Trimethylpentane.
[d] Methylcyclohexane.

culty of determining the small solubilities of permanent gases in liquids, and the values given by various investigators often differ by several per cent.

The agreement between the observed and the calculated values of $-\log x_2$ is better for some solvents than for others. The results for normal paraffins, benzene, and toluene show smaller differences than those for iso-octane and carbon disulfide. The fact that the shape factor has been neglected in the derivation (*14*, p. 109) of the entropy terms in Equation 1 may account for this, as indicated by the increased deviations on passing from normal to iso-octane (2,2,4-trimethylpentane).

For hydrogen the differences, $\Delta \log x_2$ (Table IV), are smallest at 0° and greatest at 50°C. At least part of this increase is due to the fact that some solubilities and solubility parameters, δ_1, at 50°C. had to be obtained by extrapolation of the data available for temperatures up to 35°C. There is also no experimental point for carbon disulfide (boiling point, 46.3°C.) at 50°C., and in consequence the slope of the Φ_{12} *vs.* V_1 isotherm is probably greater than if that point were available. Figure 1 shows the correlation lines for five gases at 25°C., with the experimental points used to obtain them. The solvents can be identified by their molar volumes, V_1.

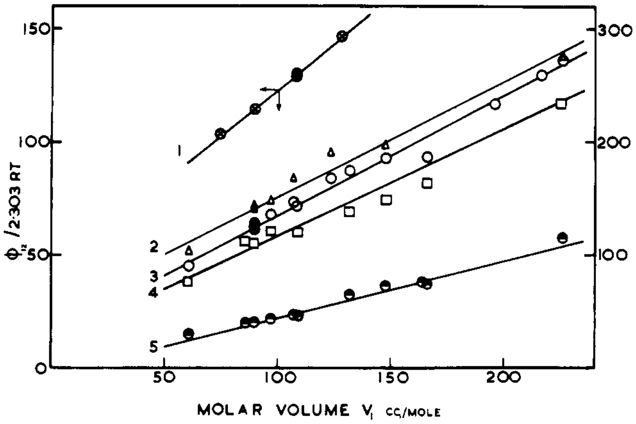

Figure 1. Linear relationship for solubilities of gases at 25° C. in some nonpolar solvents

1. Argon
2. Carbon monoxide
3. Nitrogen
4. Oxygen
5. Hydrogen

Solvents are identified in Table I. Left-hand ordinate applies to argon only

For strongly polar solvents the scatter of points is much greater than in Figure 1, presumably because Equations 1 and 3 do not apply to polar solvents and probably also because some of the points were obtained by extrapolation of solubilities determined at high pressure (*17*), which are only of moderate accuracy.

The solubility of gases in a given solvent increases in the order hydrogen, nitrogen, carbon monoxide, oxygen, and argon. The single exception to this rule among the available data is the solubility of carbon monoxide in *n*-perfluoroheptane, which is lower than the solubility of nitrogen. This might be due to a specific interaction between the gas and the solvent or may indicate an experimental error.

In the case of oxygen, Amagat's (*1*) compressibility measurements were used, for want of more recent data, and were extrapolated from 0° and 15° to 25°C. In view of this and because the *P-V-T* data for other gases are known with a much greater degree of accuracy, the values of V_2* for oxygen are subject to a greater uncertainty.

The correlation for argon is based on solubilities in three nonpolar liquids only and acetone, although a solvent of fairly high dipole moment, has been included to provide one more experimental point and extend somewhat the range of solvent molar volumes.

It is possible to check on the values of $-\log x_2^i$ and V_2* used in the correlation by comparing the partial molal heats of mixing, $\Delta \overline{H}_2^M$, calculated from the partial molal energies of mixing, $\Delta \overline{E}^M_2$, with the partial molal heats obtained from the solubility measurements at several temperatures according to the approximate relation

$$\partial \ln x_2 / \partial (1/T) = -\Delta \overline{H}_2^M / R \qquad (7)$$

The energy term $\Delta \overline{E}^M_2$ in solubility Equation 1 is not directly comparable with $\Delta \overline{H}^M_2$, but has to be multiplied by the correction factor $(1 + \alpha_0 T)$, where α_0 is the coefficient of thermal expansion, in order to obtain $\Delta \overline{H}_2^M$ (correction terms higher than first order neglected) (*14*, p. 139). Tables VI and VII give the values of $\Delta \overline{H}_2^M$ calculated from the slope of the ln x_2 *vs.* $1/T$ curve for the solubility of hydrogen and nitrogen in solvents for which solubility data exist at three or more temperatures in the neighborhood of 25°C.

Table VI. Approximate Heats of Solution of Hydrogen in Nonpolar Solvents at 25°C.

Solvent	$\alpha_1 \times 10^3$ Deg. C^{-1}	$1 + \alpha_1 T$	$\Delta \bar{E}^M{}_2(1 + \alpha_1 T)$, Cal./Mole Equation 1	$\Delta \bar{E}^M{}_2(1 + \alpha_1 T)$, Cal./Mole Equation 4	$\Delta \bar{H}^M{}_2$, Cal./Mole Equation 7
n-C_7F_{16}	1.711	1.510	660	695	1210 (*4*)
Iso-Octane	1.185	1.353	955	890	1030 (*4*)
n-Octane	1.188	1.354	1120	1080	1080 (*4*)
n-Heptane	1.236	1.368	1045	1075	1080 (*4*)
CCl_4	1.212	1.361	1470	1450	1410 (*4*)
Toluene	1.067	1.318	1510	1480	1280 (*4*)
Benzene	1.213	1.362	1625	1625	1580 (*4*)
CS_2	1.197	1.357	1820	1950	1530 (*4*)

Table VII. Approximate Heats of Solution of Nitrogen in Nonpolar Solvents at 25°C.

Solvent	$\Delta \bar{E}^M{}_2(1 + \alpha_1 T)$, Cal./Mole Equation 1	$\Delta \bar{E}^M{}_2(1 + \alpha_1 T)$, Cal./Mole Equation 4	$\Delta \bar{H}^M{}_2$, Cal./Mole Equation 7
n-C_7F_{16}	−250	−195	−185 (*8*)
CCl_4	850	910	630 (*16*)
C_6H_6	1170	1190	1030 (*16*)
Iso-Octane	390	190	190 (*19*)

They also contain values of $\Delta \bar{H}_2{}^M$ calculated from the relation $\Delta \bar{H}_2{}^M = (1 + \alpha_1 T) \Delta \bar{E}_2{}^M$ using for α_1 (instead of α_0), the mean coefficient of thermal expansion of the solvent between 20° and 30°C. obtained from densities given by Timmermans (*31*), and for $\Delta \bar{E}_2{}^M$ the values obtained from the solubility Equations 1 to 5 and from Dodge and Davis (*5*). In the case of hydrogen (Table VI) the agreement is very good in the solvents *n*-heptane, *n*-octane, carbon tetrachloride, and benzene, and much poorer in iso-octane and carbon disulfide. For *n*-perfluoroheptane the difference is much greater than could be accounted for by the approximate methods of calculating $\Delta \bar{H}_2{}^M$ and $\Delta \bar{E}_2{}^M$ $(1 + \alpha_1 T)$. Nevertheless, the degree of agreement between $\Delta \bar{E}_2{}^M$ $(1 + \alpha_1 T)$ calculated from Equations 1 to 5 and $\Delta \bar{H}_2{}^M$ suggests that the constant $\log x_2{}^i$ and the entropy terms depending on $V_2{}^*$ are close to the correct value. Some values of partial molal heats of solution of nitrogen in Table VII also agree, but the data are too meager to warrant drawing any conclusions.

COMPARISON WITH PREVIOUS SOLUBILITY CORRELATIONS

The method presented here seems more satisfactory than previous attempts to correlate gas solubilities with solvent properties, which have made use of the solubility parameter of the gas, $\delta_2 = (\partial \epsilon_2/\partial V)_T^{\frac{1}{2}}$. Above the critical temperature δ_2 has no physical meaning and also needs adjustment to fit experimental data. Thus δ_2 for hydrogen at its boiling point, 20.4°K., is 2.5 (cal./cc.)$^{0.5}$ (*14*, p. 434) but Gonikberg (*9*) uses the value 2.1, Gjaldbaek (*7*) the value 5.1, and Cook (*4*) the value 3.7, at 25°C., to obtain agreement between experiment and expressions based on Hildebrand's equations (*14*, p. 139, 456).

Uhlig (*32*) has derived an expression for the solubility of a gas by assuming that when a gas molecule of radius *r* enters the solvent a spherical cavity is produced of the same radius. The corresponding energy change consists of two terms, one given by the area of the cavity multiplied by the surface tension of the solvent, $4\pi r^2 \sigma$, and the other, *E*, arising from the interaction of solvent and solute molecules. On this hypothesis the Ostwald solubility coefficient is given by

$$\gamma = (-4\pi r^2 \sigma + E)\, kT \qquad (8)$$

where *k* is Boltzmann's constant.

The interaction term, which is nearly constant for each gas, is obtained from the plot of experimental $\log \gamma$ against σ, which is approximately a straight line. This equation neglects the influence of the ratio of the molecular volumes of the solvent and the solute, as well as the interactions between the solute molecules in solution, and takes account only of the internal pressure of the solvent, to which the surface tension is related.

Uhlig does not discuss how well the experimental data fit his straight lines, but the values of the molecular radii of several gases calculated by him differ from the values obtained by other methods by 0 to 23%.

During this work Hildebrand (*12*) has published an interim note on a simple correlation between the logarithms of the solubilities of gases (moles per liter of solvent) and the solubility parameters of the solvents. The lines obtained for various gases, with the exception of hydrogen, are almost parallel to each other, and their displacements are related to the relative vapor pressures of gases in the liquid state. By means of this correlation the solubilities of gases are related also to the molar volumes and the internal pressures of solvents, but the theoretical implications of the relation need clarification, and the scatter of the experimental points or the accuracy of the predicted solubilities is not recorded.

CONCLUSION

The correlation presented here provides a fairly simple method for calculating the solubility of permanent gases in nonpolar and slightly polar liquids with good accuracy. It also shows the existence of a relationship between the internal pressure of nonpolar solvents and the partial molal volumes, $\bar{v}_2$, of gases dissolved in them. The relationship appears to be of the same type as that between the molar volume, $V_2{}^*$, of a gas and pressure in the region 1400 to 4400 atm. While the authors have assumed that $\bar{v}_2 = V_2{}^*$ at pressures equal to the internal pressures of the solvents, it is more likely that $\bar{v}_2$ is a simple function of $V_2{}^*$, which could be found by experimental measurement. The fragmentary evidence available at present (*14*, pp. 246–7) indicates that $\bar{v}_2$ is generally greater than $V_2{}^*$ by about 35%. The use of the larger values in Equations 4 and 5 would result in a decrease of the absolute values of the entropy correction term in Equation 5. This would require a corresponding adjustment of the constant $-\log x_2{}^i$ (by about 0.10 to 0.15) in order to obtain partial molal energies of mixing comparable with those calculated from solubilities at several temperatures (Equation 7, and Tables VI and VII).

The correlation is limited to permanent gases, as their solubilities in liquids are small. For greater solubilities, it is no longer possible to neglect the interaction between the gas molecules in solution, and the correlation cannot be expected to hold for solubilities, x_2, of the order of 10^{-2}, and greater. The other limitation concerns strongly polar liquids. The equations have been derived on the assumption of the nonpolarity of both components, but it has been found—e.g., for toluene and *m*-xylene—that the solubilities of gases in slightly polar solvents may also be correlated successfully. It may eventually be possible to extend the correlation to include polar solvents by correcting the solubility equations for the polarity of the solvent as more accurate and extensive experimental results become available.

Since this article was written, argon solubilities in other nonpolar solvents at 25°C. have been published (*29*), so that constants for argon given in Table III could be revised. With the constants given, the values of $\Delta \log x_2$ (Obsd.-Calcd.) for perfluorocyclohexane, carbon tetrachloride, toluene, and carbon disulfide are, respectively, + 0.001, + 0.100, + 0.066, and + 0.114 (Table V).

LITERATURE CITED

(1) Amagat, E. H., *Ann. Chim. et phys.* **29**, 68 (1893).

(2) Boomer, E. H., Johnson, C. A., Piercey, A. G., *Can. J. Research* **16B**, 396 (1938).

(3) Clark, A. M., Din, F., Robb, J., *Physica* **17**, 876 (1951).

(4) Cook, M. W., thesis, University of California Radiation Laboratory, January 1954.

(5) Dodge, B. F., Davis, H. N., *J. Am. Chem. Soc.* **49**, 410 (1927).

(6) Fowler, R., Hamilton, J. M., Kasper, J. S., Weber, C. E., Burford, W. B. III, Anderson, H. C., *Ind. Eng. Chem.* **39**, 375 (1947).
(7) Gjaldbaek, J. Chr., *Acta Chem. Scand.* **6**, 623 (1952).
(8) Gjaldbaek, J. Chr., Hildebrand, J. H., *J. Am. Chem. Soc.* **71**, 3147 (1949).
(9) Gonikberg, M. G., *J. Phys. Chem.* (*U.S.S.R.*) **14**, 582 (1940).
(10) Grosse, A., Cady, G., *Ind. Eng. Chem.* **39**, 367 (1947).
(11) Guerry, D., Jr., thesis, Vanderbilt University, 1944.
(12) Hildebrand, J. H., *J. Phys. Chem.* **58**, 671 (1954).
(13) Hildebrand, J. H., Gjaldbaek, J. Chr., *J. Am. Chem. Soc.* **72**, 1077 (1950).
(14) Hildebrand, J. H., Scott, R. L., "Solubility of Non-Electrolytes," Reinhold, New York, 1950.
(15) Hoge, H. J., Arnold, R. D., U. S., *J. Research Natl. Bur. Standards* **RP2228/9** (1951).
(16) Horiuti, J., *Sci. Papers, Inst. Phys. Chem. Research* (*Tokyo*) **17**, 125 (1931).
(17) Ipatiev, V. V., Levina, M. L., *J. Phys. Chem.* (*U.S.S.R.*) **6**, 633 (1935).
(18) Just, G., *Z. physik. Chem.* **37**, 342 (1902).
(19) Kretschmer, C. B., Nowakowska, J., Wiebe, R., *Ind. Eng. Chem.* **38**, 506 (1946).
(20) Krichevskii, I. R., Efremova, G. D., *J. Phys. Chem.* (*U.S.S.R.*) **25**, 577 (1951).
(21) Lannung, A., *J. Am. Chem. Soc.* **52**, 68 (1934).
(22) Maxted, E. B., Moon, C. H., *Trans. Faraday Soc.* **32**, 769 (1936).
(23) Michels, A., Goudeket, M., *Physica* **8**, 347 (1941).
(24) Michels, A., Lunbeck, R. J., Wolkers, G. J., *Appl. Sci. Research* **A2**, 345 (1950).
(25) Michels, A., Lunbeck, R. J., Wolkers, G. J., *Physica* **17**, 801 (1951).
(26) Michels, A., Lupton, J., Wassenaar, T., Graaff, W. de, *Ibid.*, **18**, 121 (1952).
(27) Michels, A., Wassenaar, T., Zwietering, T., *Ibid.*, **18**, 160 (1952).
(28) Michels, A., Wijker, Hub., Wijker, Hk., *Ibid.*, **15**, 627 (1949).
(29) Reeves, L. W., Hildebrand, J. H., *J. Am. Chem. Soc.* **79**, 1313 (1957).
(30) Susskind, B., Kasarnovskiĭ, I., *J. Phys. Chem.* (*U.S.S.R.*) **4**, 683 (1933).
(31) Timmermans, J., "Physico-Chemical Constants," Elsevier, London, 1950.
(32) Uhlig, H. H., *J. Phys. Chem.* **41**, 1215 (1937).

Received for review October 20, 1956. Accepted May 6, 1957.

C_9 and C_{10} Alkylbenzenes and Aromatic Olefins in the Products of the Thermal Aromatization of Naphtha

E. GIL-AV, J. SHABTÁI, I. MICHAELI, R. SCHNURMANN,[1] and E. KENDRICK[1]
The Weizmann Institute of Science, Rehovoth, Israel

In a series of papers published in 1951 Weizmann and others (*12*) discussed the composition of products and the mechanism of thermal aromatizing of hydrocarbon oils by the Catarole process. At that time some fractions had been studied in detail, whereas others had not yet been investigated. The present results concern the composition of a cut distilling between 150° and 190°C.

The yield of this fraction depends on the nature of the charge stock (*11*) and amounts to between 5 and 8% for the type of raw material from which the cut considered in this study was obtained. Its proportion of aromatic olefins (indene, methylindenes, and alkylstyrenes) adds up to a total of 30 to 40%. Other constituents are C_9 and C_{10} alkylbenzenes, indane, and about 10% of naphthenes and paraffins. However, only the composition of the aromatic portion is considered here. The study of the aromatic olefins is of particular interest because very few data on the occurrence of this class of compounds in cracking products are found in the literature, and, from the more practical angle, because they are the raw material for the production of a valuable resin.

Aromatics can be separated by adsorption on silica gel (*6*) from their mixtures with naphthenes and paraffins. The alkylbenzenes of this range can be analyzed accurately by combining infrared spectrophotometry with fractional distillation.

The separation and identification of the aromatic olefins present certain difficulties: They cannot be separated by silica gel chromatography and tend to polymerize when heated over long periods during distillation.

For this reason the individual olefins were determined by an indirect method, using mild catalytic hydrogenation, which without affecting the aromatic rings in the molecules, converted the olefins to the corresponding alkylbenzenes and hydrindenes. The difference of the concentration of alkylbenzenes in the hydrogenated material and in a sample freed of its olefins by polymerization, was then determined. This difference is a measure of the amount of aromatic olefins present in the original cut.

MATERIALS

Two plant products of boiling range 150° to 190°C. were made available to the authors by Petrochemicals, Ltd., Manchester, England. These products had been obtained by cracking of a Middle East naphtha of 150° to 210°C. boiling range, containing 10% of naphthenes and 20% of aromatics. The cracking took place at 680° to 700°C., 30 pounds per square inch of pressure and in about 30 seconds of contact time.

The first product, A, contained 80% of material boiling between 150° and 190°C. It was obtained by atmospheric distillation of the crude cracking product and had lost part of its original olefinic constituents by the heat polymerization which occurred in the still. Hence, the results refer to the composition of the distillate and not to that of the crude material. The bromine number of A was 49, corresponding to about 37% of olefins.

The second product, B, was obtained from A after elimination of the major part of the aromatic olefins by clay polymerization. It amounted to 60% of the original distillation cut and contained essentially all the components of A with saturated side chains. This treatment was carried out at the plant of Petrochemicals, Ltd., in the course of the production of a resin used in the paint industry. The temperature for this process lies slightly above room temperature, and as these conditions are mild, it is assumed that no change other than polymerization of the olefins occurs. This is borne out by the fact that the amount of resin formed approached within a few percent the yield expected from the bromine number of the crude cut. A small amount of unpolymerized olefins, however, always

---

[1] Present address, Manchester Oil Refinery, Ltd., Manchester, England.