

## A test of Pierotti's theory for the solubility of gases in liquids, by means of literature data on solubility and entropy of solution

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**Abstract**—Pierotti's theory for the solubility of gases in liquids is tested by means of a large amount of literature data on solubility and entropy of solution. The involved solutes comprise the noble gases, mercury vapour, inorganic gases and hydrocarbons up to propane. The involved solvents comprise alkanes, cycloalkanes, nitromethane, polythene, aromatics, dimethylsulfoxide and perfluoromethylcyclohexane.

It appears, that this theory describes the solubilities satisfactory. The description of the entropies of solution is less good.

The enhanced solubilities of  $\text{BF}_3$ ,  $\text{CO}_2$ ,  $\text{Cl}_2$  and  $\text{C}_2\text{H}_2$  in some solvents are ascribed to electron donor-acceptor interaction. The association constants for donor-acceptor complex formation are tabulated.

### INTRODUCTION

THE SOLUBILITY of gases in liquids is both practically important in the most diverse fields of technology and science and theoretically interesting, e.g. because the gas molecules can be considered as probes measuring the intermolecular force field in the solution.

A satisfactory theory of solution for gases in liquids is much harder to construct than one for liquids or solids in liquids, the latter components differing from one another far less in significant properties such as molar volumes and intermolecular attractive forces.

The various theoretical concepts have been reviewed recently by Battino and Clever[1] and the pioneer of the regular solution theory, Hildebrand, has given a personal account of the present state of knowledge in the field[2].

An interesting contribution to the interpretation of gas solubilities has been made by Pierotti [3]. This theory is claimed on one hand, to give a good description of solubilities, entropies and enthalpies of solution and partial molar volumes of the dissolved gases and on the other, to be

applicable both to nonpolar solvents and to solvents as polar as water[4]. It even appeared to give a fair description of the solubilities and an excellent description of the entropies of solution in water of alkanes up to octadecane and octane respectively[5].

However, whereas the applicability of the theory to the solvent water has been investigated rather thoroughly, the applicability to nonpolar solvents has been claimed on the basis of a very limited number of data in the solvents argon, benzene and carbon tetrachloride only.

Therefore we thought it worthwhile to investigate the validity of Pierotti's theory for nonpolar solvents more thoroughly, and also for some polar solvents, using a large amount of accurate literature data.

### THEORY

Pierotti considers the solution process to consist of two steps: (1) the creation of a cavity in the solvent of a suitable size to accommodate the solute molecule and (2) the introduction into

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Table 1. Literature values

Solvent*	He	Ne	Ar	Kr	Xe	Rn	Hg <sup>b</sup>	H <sub>2</sub>	N <sub>2</sub>	CO
hexane	2.180	6.471 <sup>7</sup>	6.301 <sup>7</sup>	5.478 <sup>7</sup>	5.051 <sup>7</sup>	4.476 <sup>23</sup>	4.016 <sup>41</sup>	3.346	6.067 <sup>19</sup>	5.735 <sup>11</sup>
heptane	1.660	6.485 <sup>7</sup>	6.339 <sup>7</sup>	5.483 <sup>7</sup>	5.026 <sup>7</sup>			3.278	6.043 <sup>15</sup>	5.750 <sup>15</sup>
octane	1.145	6.497 <sup>7</sup>	6.327 <sup>7</sup>	5.492 <sup>7</sup>	5.032 <sup>7</sup>			3.223	6.046 <sup>15</sup>	5.764 <sup>15</sup>
nonane	0.643	6.499 <sup>7</sup>	6.337 <sup>7</sup>	5.492 <sup>7</sup>	5.031 <sup>7</sup>				6.040 <sup>15</sup>	5.774 <sup>15</sup>
decane	0.161	6.502 <sup>7</sup>	6.328 <sup>7</sup>	5.486 <sup>7</sup>	5.022 <sup>7</sup>					
dodecane		6.531 <sup>7</sup>	6.370 <sup>7</sup>	5.474 <sup>7</sup>	4.997 <sup>7</sup>	4.398 <sup>23</sup>				
tetradecane		6.527 <sup>7</sup>	6.370 <sup>7</sup>	5.468 <sup>7</sup>	4.988 <sup>7</sup>					
polythene <sup>24</sup>		5.086		4.173					4.557	4.371
hydropol <sup>24</sup>		4.110		3.309					3.514	3.462
3-methylheptane	1.291	6.485 <sup>7</sup>	6.317 <sup>7</sup>	5.483 <sup>7</sup>	5.025 <sup>7</sup>					
2,3-dimethylhexane	1.369	6.488 <sup>7</sup>	6.317 <sup>7</sup>	5.486 <sup>7</sup>	5.033 <sup>7</sup>					
2,4-dimethylhexane	1.482	6.446 <sup>7</sup>	6.280 <sup>7</sup>	5.454 <sup>7</sup>	5.016 <sup>7</sup>					
2,2,4-trimethylpentane	1.693	6.389 <sup>7</sup>	6.217 <sup>7</sup>	5.417 <sup>7</sup>	4.984 <sup>7</sup>					
cyclohexane	4.581	6.791 <sup>7</sup>	6.640 <sup>7</sup>	5.708 <sup>7</sup>	5.211 <sup>7</sup>	4.598 <sup>23</sup>	3.144	5.988 <sup>15</sup>	5.696 <sup>25</sup>	6.003 <sup>11</sup>
methylcyclohexane	3.836	6.682 <sup>21</sup>	6.532 <sup>21</sup>	5.612 <sup>21</sup>	5.120 <sup>21</sup>	4.519 <sup>21</sup>		6.266 <sup>27</sup>		
perfluoromethylcyclohexane	4.700	5.999 <sup>21</sup>	5.829 <sup>21</sup>	5.218 <sup>21</sup>	4.959 <sup>21</sup>	4.652 <sup>21</sup>				5.378 <sup>11</sup>
benzene		6.985 <sup>7</sup>	6.851 <sup>7</sup>	5.938 <sup>7</sup>	5.445 <sup>7</sup>	4.835 <sup>23</sup>	4.288 <sup>8</sup>	3.239	6.470 <sup>15</sup>	6.230 <sup>11</sup>
toluene		6.890 <sup>29</sup>	6.734 <sup>29</sup>	5.841 <sup>29</sup>	5.353 <sup>29</sup>	4.720 <sup>29</sup>	4.205 <sup>41</sup>	3.158	6.380 <sup>15</sup>	5.970 <sup>40</sup>
nitrobenzene		7.305 <sup>29</sup>	7.171 <sup>29</sup>	6.237 <sup>29</sup>	5.729 <sup>29</sup>	5.112 <sup>29</sup>			6.688 <sup>19</sup>	6.310 <sup>40</sup>
fluorobenzene		6.818 <sup>29</sup>	6.698 <sup>29</sup>	5.821 <sup>29</sup>	5.356 <sup>29</sup>	4.775 <sup>29</sup>				
chlorobenzene		7.040 <sup>29</sup>	6.887 <sup>29</sup>	5.951 <sup>29</sup>	5.442 <sup>29</sup>	4.851 <sup>29</sup>			6.471 <sup>17</sup>	6.241 <sup>17</sup>
bromobenzene		7.140 <sup>29</sup>	6.994 <sup>29</sup>	6.051 <sup>29</sup>	5.521 <sup>29</sup>	4.857 <sup>29</sup>				6.083 <sup>17</sup>
iodobenzene		7.295 <sup>29</sup>	7.149 <sup>29</sup>	6.184 <sup>29</sup>	5.650 <sup>29</sup>	4.931 <sup>29</sup>				
nitromethane <sup>43</sup>		7.294	7.148	6.376	5.958	5.481				6.578
dimethylsulfoxide <sup>44</sup>		7.428	7.315	6.693	6.231	5.650		6.999	6.960	

\*The data on the vapour pressures of the solvents are from [6].

the cavity of a solute molecule which interacts with the solvent.

Pierotti showed that for extremely dilute solutions:

$$RT \ln p/x = \Delta \bar{G}^0 \quad (1)$$

$$\Delta \bar{G}^0 = \bar{G}_c + \bar{G}_i + RT \ln (31,390 RT/V_1) \quad (2)$$

$$\Delta \bar{H}^0 = \bar{H}_c + \bar{H}_i - RT + \alpha_p RT^2 \quad (3)$$

$$\Delta \bar{S}^0 = \bar{S}_c + \bar{S}_i - R + \alpha_p RT - R \ln (31,390 RT/V_1). \quad (4)$$

The thermodynamic data for cavity formation can be written as follows:

$$\bar{G}_c, \bar{H}_c, \bar{S}_c = K_0 + K_1 \sigma_{12} + K_2 \sigma_{12}^2 \quad (5)$$

where the  $K$ 's are known functions of the temperature and the molar volume  $V_1$  and hard sphere diameter  $\sigma_1$  of the solvent and  $\sigma_{12}$  is the radius of a sphere around a solute molecule

which excludes the centers of the solvent molecules.  $\sigma_{12}$  is equal to:

$$\sigma_{12} = (\sigma_1 + \sigma_2)/2 \quad (6)$$

where  $\sigma_2$  is the hard sphere diameter of the solute.

Pierotti assumed that  $\bar{S}_i$  is zero and that  $\bar{G}_i(-\bar{H}_i)$  is equal to the molar interaction energy which in the case of a nonpolar solute molecule can be described in terms of dispersion, inductive and repulsive interactions. These are approximated by a Lennard-Jones (6-12) pairwise additive potential.

The result is:

$$\bar{G}_i = -\frac{R\pi\rho}{6k\sigma_{12}^3} (5.333C_{\text{disp}} + 8C_{\text{ind}}). \quad (7)$$

Equation (7) gives with:

$$C_{\text{disp}} = 4\epsilon_{12}\sigma_{12}^6 = 4(\epsilon_1\epsilon_2)^{1/2} \left(\frac{\sigma_1 + \sigma_2}{2}\right)^6 \quad (8)$$

of  $\log p_{mm}/x$  at 25°

O <sub>2</sub>	NO	CF <sub>4</sub>	BF <sub>3</sub>	CO <sub>2</sub>	SF <sub>6</sub>	N <sub>2</sub> O	Cl <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	c-C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub> <sup>14</sup>
5.595 <sup>10</sup>								5.175 <sup>30</sup>				3.696 <sup>13</sup>	3.829
5.546 <sup>18</sup>		5.551 <sup>18</sup>		4.801 <sup>19</sup>	4.878 <sup>20</sup>	4.622 <sup>21</sup>		5.365 <sup>22</sup>			4.368 <sup>18</sup>		
5.562 <sup>18</sup>											4.359 <sup>16</sup>		3.814
5.554 <sup>18</sup>											4.360 <sup>16</sup>		
								5.615 <sup>22</sup>					
4.294				3.590	3.953			3.899			3.278		
3.337				3.005	3.167			3.120			2.933		
5.479 <sup>25</sup>					4.695 <sup>28</sup>	4.553 <sup>21</sup>					4.414 <sup>26</sup>		
5.791 <sup>10</sup>	5.580 <sup>28</sup>	5.866 <sup>29</sup>		4.999 <sup>19</sup>	5.149 <sup>29</sup>		4.137 <sup>28</sup>	5.368 <sup>30</sup>			4.508 <sup>44</sup>		3.736 <sup>44</sup>
		4.858 <sup>32</sup>			5.035 <sup>29</sup>								
5.970 <sup>17</sup>		6.121 <sup>18</sup>	5.493 <sup>36</sup>	4.898 <sup>19</sup>	5.459 <sup>29</sup>	4.750 <sup>21</sup>	3.578 <sup>34</sup>	5.562 <sup>30</sup>	4.646 <sup>35</sup>	4.791 <sup>17</sup>	4.710 <sup>17</sup>	3.813 <sup>13</sup>	4.137
			5.432 <sup>38</sup>	4.863 <sup>40</sup>	5.350 <sup>29</sup>			5.823 <sup>22</sup>	4.616 <sup>35</sup>				
			4.274 <sup>42</sup>	4.881 <sup>40</sup>									
5.945 <sup>17</sup>				4.892 <sup>40</sup>		4.764 <sup>17</sup>	3.674 <sup>32</sup>	5.580 <sup>30</sup>	4.717 <sup>17</sup>		4.540 <sup>17</sup>		
					5.961								
6.685				4.923				6.294	3.916 <sup>33</sup>		5.630		

and:

$$C_{ind} = \mu_1^2 \alpha_2 \quad (9)$$

$$\bar{G}_i = \bar{G}_{disp} + \bar{G}_{ind} = -3.556 R \pi \rho \sigma_{12}^3 \epsilon_{12} / k - 1.333 N \pi \rho \frac{\mu_1^2 \alpha_2}{\sigma_{12}^3} \quad (10)$$

It appears, that a plot of  $\epsilon_2/k$  or  $\alpha_2$  vs.  $\sigma_2$  for the noble gases extrapolates to  $\epsilon_2/k = \alpha_2 = 0$  for  $\sigma_2 = 2.58 \text{ \AA}$ .

So, a plot of  $\Delta \bar{G}^0$  vs.  $\sigma_2$  for the noble gases extrapolates to  $\Delta \bar{G}^0 = \bar{G}_c + RT \ln (31,390 RT/V_1)$  for  $\sigma_2 = 2.58 \text{ \AA}$ . From such a plot and Eqs. (5) and (6),  $\sigma_1$  can be found.  $\sigma_1$  may thus be treated as an adjustable parameter [4], and this is done in the present investigation. Likewise,  $\epsilon_1/k$  may be [4]—and is here—treated as an adjustable parameter.  $\alpha_1, \mu_1, \epsilon_2/k, \alpha_2$  and  $\mu_2$  should be (and generally are) known.

### SOLUBILITIES

#### (1) Solubility data

The data used are assembled in Table 1. They

comprise data on globular, elongated, giant, apolar, moderately and strongly polar aprotic solvent molecules. Included are data on the vapour-liquid equilibria of the pure solvents (regarded as ideal solutions of mole fraction  $x = 1$ ).

#### (2) Physical data on the solutes

For polyatomic gases data on  $\epsilon/k$  and  $\sigma$ , derived from viscosities, are more abundant than data, derived from second virial coefficients. For the sake of consistency we used only data, derived from viscosities, in our calculations. Data on  $\sigma$  for a particular gas from different authors usually agree very well with each other and with the diameter that can be calculated from the Van der Waals volume  $V_W$  according to:

$$\sigma^3 = 6V_W/\pi N. \quad (11)$$

We estimate the accuracy of  $\sigma$  at a few hundredths of an  $\text{\AA}$ . Data on  $\epsilon/k$ , however, show considerable scatter, as appears from the 90 per cent

probability intervals of the mean values\* given in Table 2.

### (3) Physical data on the solvents

The data needed for the calculations are assembled in the 2nd–4th columns of Table 3. Also shown are the values of  $V_w$  (5th column).

### (4) Discussion

4.1 *The values of  $\sigma_1$ .*  $\sigma_1$  values were calculated from the solubilities of hard-sphere solutes of diameter  $\sigma_2 = 2.58 \text{ \AA}$ , found by extrapolation as described in the theoretical section. They are assembled in the 6th column of Table 3. The volumes of the corresponding spheres,  $\frac{1}{6} \pi N \sigma_1^3$ , are given in the 7th column of this table and are compared with the Van der Waals volumes [47] in Fig. 1.

The correspondence between  $\frac{1}{6} \pi N \sigma_1^3$  and  $V_w$ , even for such elongated molecules as tetradecane, is striking. Only three solvents, perfluoromethylcyclohexane and the high molecular weight solvents polythene and hydrocol ( $M = 10^4$  and  $10^5$ , respectively) deviate seriously from the linear relationship:

$$\frac{1}{6} \pi N \sigma_1^3 = -10 + 1.13 V_w. \quad (15)$$

\*For each gas, an estimate  $s$  of the standard deviation of a determination of  $\epsilon/k$  between different investigators was made from the available literature data. The values of  $s$  for different gases appeared to increase as  $\epsilon/k$  increases. In the calculation of the functional relationship between  $s$  and  $\epsilon/k$ , the statistical weight of the  $s$  values, i.e. their accuracies, should be taken into account. According to Davies [12], the standard deviation  $\sigma_s$  of  $s$  is equal to:

$$\sigma_s = s/\sqrt{2\varphi} \quad (12)$$

where  $\varphi$  is the number of degrees of freedom ( $\varphi + 1$  is the number of investigators). So:

$$\sigma_{\log s} = \sigma_s \frac{d \log s}{ds} = 0.43/\sqrt{2\varphi}. \quad (13)$$

So, the statistical weights of the values of  $\log s$  are simply proportional to the corresponding values of  $\varphi$ . We found the relationship:

$$\log s = 0.51 + 0.0037 \epsilon/k \quad (14)$$

from which the standard deviations of the individual and mean values of  $\epsilon/k$  can be calculated easily. To calculate their probability intervals, we estimated the number of degrees of freedom of the  $s$  values, calculated from (14), to be  $\Sigma\varphi/4 = 5$  for He, Ne, H<sub>2</sub>, Rn and Cl<sub>2</sub> (i.e. the lightest and the heaviest gases) and to be  $\Sigma\varphi/2 = 10$  for the other ones.

4.2 *The values of  $\epsilon_1/k$ .*  $\epsilon_1/k$  values of alkanes up to decane and of cycloalkanes were calculated from the vapour pressures of the pure solvents, by applying Eqs. (1–10). For dodecane, tetradecane, polythene and hydrocol, the vapour pressure of which is not known at 25° and for the aromatic and polar solvents  $\epsilon_1/k$  was calculated from the solubility of Ar, assuming  $\epsilon_2/k$  for Ar to be 113°K as found for alkanes and cycloalkanes (see Table 4). The resulting values are given in the last column of Table 3.

To judge if the so calculated values of  $\epsilon_1/k$  are realistic, we reasoned that for the n-alkanes it can be expected that the values of  $\epsilon/k$  are a simple function of the Van der Waals surface area  $A_w$ . For the lower members of the series a linear relationship can be expected whereas for the higher members the effective surface area for intermolecular interaction will be smaller than the total surface area, due to coiling of the molecules.

In Fig. 2 the  $\epsilon_1/k$  values of the n-alkane solvents and the values of  $\epsilon_2/k$  of the n-alkane solutes, calculated from solubilities in aliphatic and aromatic solvents by applying Eqs. (1–10), and also the literature values [37] are compared with the Van der Waals surface areas [47]. The calculated  $\epsilon/k$  values do show the expected relationship with  $A_w$ . The literature values, however, show a considerable scatter and deviate strongly from a linear relationship.

In our opinion, from propane onwards  $\epsilon/k$  values calculated from solubilities or vapour pressures in the above described way are more reliable than values calculated from viscosities or second virial coefficients.

If the deviation of the graph from linearity, for higher n-alkanes, is indeed due to a decrease of the effective surface area for intermolecular interaction by coiling, one would expect the branched alkanes to deviate still stronger from a linear relationship. Figure 2 shows that this is indeed the case.

So, it appears that Pierotti's theory holds even for such large and elongated molecules as those of tetradecane, as far as solubilities or free enthalpies of solution are concerned.

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Table 2. Physical data of the investigated solutes\*

Monatomic	Hard sphere	He	Ne	Ar	Kr	Xe	Rn <sup>46</sup>	Hg			
	$\epsilon_2/k$	0	10.2 ± 7.1	61.6 ± 7.8	120 ± 11	190 ± 29	229 ± 41	290 ± 76	851		
$10^8\sigma_2$	2.58	2.58	2.82	3.44	3.60	4.06	4.36	2.90			
$10^{24}\alpha_2$	0	0.204	0.393	1.63	2.46	4.00	5.86	5.04			
Polyatomic inorganic	H <sub>2</sub>	N <sub>2</sub>	CO	O <sub>2</sub>	NO	CF <sub>4</sub>	BF <sub>3</sub>	CO <sub>2</sub>	SF <sub>6</sub>	N <sub>2</sub> O	Cl <sub>2</sub>
	$\epsilon_2/k$	35.6 ± 6.2	85.6 ± 8.5	99.0 ± 9.6	100 ± 10	105 ± 10	152 ± 21	178 ± 26	198 ± 18	207 ± 24	228 ± 28
$10^8\sigma_2$	2.94	3.71	3.65	3.65	3.53	4.70	4.22	3.97	5.23	3.85	4.26
$10^{24}\alpha_2$	0.802	1.74	1.93	1.57	1.70	2.45 <sup>49</sup>	2.5†	2.59	4.0†	2.92	4.50
Hydrocarbons	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	c-C <sub>3</sub> H <sub>6</sub> <sup>50</sup>	C <sub>3</sub> H <sub>8</sub>					
	$\epsilon_2/k$	142 ± 10	199 ± 22	217 ± 26	233 ± 30	210 ± 35	230 ± 27				
$10^8\sigma_2$	3.81	4.16	4.15	4.40	6.84	5.06					
$10^{24}\alpha_2$	2.70	3.19	3.70	4.33		6.16					

\*Values of  $\epsilon_2/k$  (in deg) and  $\sigma_2$  (in cm) are from [37] (unless stated otherwise), values of  $\alpha_2$  (in cm<sup>3</sup> mole<sup>-1</sup>) are from [38].

†Estimated.

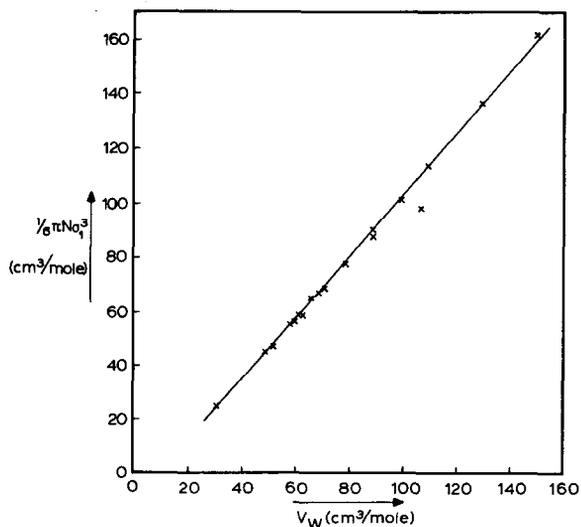
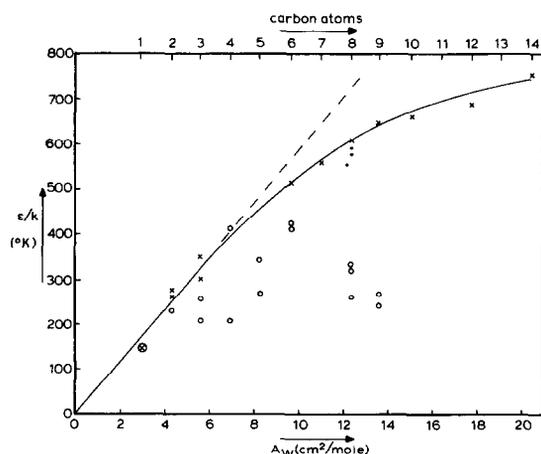
Table 3. Physical data of the solvents and parameters calculated from the solubility data of Table 1\*

Solvent	Physical data			Parameters		
	$V_1$	$10^{18}\mu_1$	$V_w$	$10^8\sigma_1$	$\frac{1}{2}\pi N\sigma_1^3$	$\epsilon_1/k$
hexane	131.60		68.28	5.97	67.10	512
heptane	147.44		78.49	6.27	77.74	556
octane	163.54		88.72	6.58	89.84	606
nonane	179.67		98.95	6.85	101.37	649
decane	195.95		109.18	7.11	113.35	659
dodecane	228.60		129.64	7.56	136.27	685
tetradecane	261.30		150.10	8.00	161.47	750
polythene	11710		10 <sup>4</sup>	69.89	11.10 <sup>4</sup>	1180
hydropol	117100		10 <sup>5</sup>	152.40	11.10 <sup>5</sup>	884
3-methylheptane	162.77		88.72	6.55	88.62	592
2,3-dimethylhexane	161.32		88.72	6.54	88.22	590
2,4-dimethylhexane	164.08		88.72	6.55	88.62	576
2,2,4-trimethylpentane	166.08		88.72	6.53	87.81	552
cyclohexane	108.76		60.24	5.63	56.28	535
methylcyclohexane	128.32		70.47	6.00	68.12	562
perfluoromethylcyclohexane	196.00		106.31	6.78	98.29	503
benzene	89.41		48.36	5.25	45.64	474
toluene	106.84	0.37	59.51	5.65	56.88	535
nitrobenzene	102.74	3.98	62.64	5.71	58.71	571
fluorobenzene	94.29	1.59	51.64	5.30	46.95	454
chlorobenzene	112.56	1.73	57.84	5.60	55.38	548
bromobenzene	157.02	1.71	60.96	5.71	58.71	562
iodobenzene	111.91	1.70	65.48	5.91	65.10	610
nitromethane	53.98	3.54	30.47	4.31	25.25	323
dimethylsulfoxide	71.34	4.3 <sup>52</sup>		4.91	37.33	315

\*Values of  $V_1$ <sup>46</sup>, and  $V_w$ <sup>47</sup> are in cm<sup>3</sup>.mole<sup>-1</sup>, values of  $\mu_1$ <sup>51</sup> are in e.s.u., values of  $\sigma_1$  are in cm, values of  $\epsilon_1/k$  are in deg.

Table 4.  $\epsilon_2/k$  values (deg), calculated from solubilities, and their 90 per cent probability intervals

Solute	Alkanes, cycloalkanes, nitromethane				Polythene ( $M = 10^4$ )		Hydropol ( $M = 10^5$ )		Aromatics	Nitrobenzene	Dimethylsulfoxide	Perfluoromethylcyclohexane
He	1.5 ± 0.7											5
Ne	13 ± 1											21
Ar	113 ± 1											111
Kr	178 ± 2											154
Xe	270 ± 3										301	211
Rn	348 ± 8											
Hg	547 ± 36											
H <sub>2</sub>					36 ± 1			40 ± 2			41	98
N <sub>2</sub>					96 ± 2			100 ± 3			105	
CO					104 ± 4			113 ± 2				
O <sub>2</sub>					113 ± 2			125 ± 3			131	
NO					130 ± 4							
CF <sub>4</sub>	143 ± 4							147 ± 5			209	188
SF <sub>6</sub>	221 ± 4	378			346			224 ± 5				
M <sub>2</sub> O	245 ± 6							284 ± 6				
CH <sub>4</sub>	148 ± 3	195			192			180 ± 3			193	
C <sub>2</sub> H <sub>4</sub>								279 ± 8				
C <sub>2</sub> H <sub>6</sub>	278 ± 4	420			297			303 ± 6			319	
C-C <sub>3</sub> H <sub>6</sub>	313 ± 5							334 ± 7				
C <sub>3</sub> H <sub>8</sub>	351 ± 6	608			405			350 ± 8				
BF <sub>3</sub>								197 ± 4	349			
CO <sub>2</sub>	215 ± 5	279			226			267 ± 3	267		429	
Cl <sub>2</sub>	327 ± 12							453 ± 9				
C <sub>2</sub> H <sub>2</sub>								302 ± 4			627	

Fig. 1. Values of  $\frac{1}{8} \pi N \sigma_1^3$  as a function of the Van der Waals volume  $V_W$ .Fig. 2.  $\epsilon/k$  values as a function of the Van der Waals surface area  $A_W$ . x calculated from solubilities in aliphatic and aromatic solvents, or from vapour pressures; n-alkanes; ●, calculated from vapour pressures; branched octanes; ○, literature data; n-alkanes.

4.3 *The values of  $\epsilon_2/k$ .*  $\epsilon_2/k$  values were calculated from solubilities by applying Eqs. (1–10). They are given in Table 4, together with their 90 per cent probability intervals which were calculated in the same way as described above for the literature values of  $\epsilon/k$ .

It appears from Table 4 that the solubilities in the very divergent solute–solvent systems can not be described by a single set of  $\epsilon_2/k$  values. The following sets appear to be required.

(1) The solvent perfluoromethylcyclohexane requires a separate set of  $\epsilon_2/k$  values. The same holds for dimethylsulfoxide for all but the lightest solutes

(2) The solubilities of monatomic solutes in the other solvents can be described by a single set of  $\epsilon_2/k$  values

(3) For diatomic solutes, two sets of  $\epsilon_2/k$  values are required: one for alkanes, cycloalkanes, nitromethane, polythene and hydropol and one for aromatics

(4) For polyatomic solutes, enhanced  $\epsilon_2/k$  values are required for the high molecular weight solvents polythene and hydropol. However, it is only remarkable that Pierotti's theory does not break down completely for this extreme case, as it is based on the model of a solvent, consisting of spherical molecules obeying to the Lennard–Jones potential

(5) When a solute can give electron donor–acceptor interaction with the solvent, enhanced  $\epsilon_2/k$  values are found. This concerns  $\text{Cl}_2$  and  $\text{C}_2\text{H}_2$  in aromatics,  $\text{BF}_3$  in nitrobenzene (but not in other aromatics) and  $\text{CO}_2$  and  $\text{C}_2\text{H}_2$  in dimethylsulfoxide.

This gives the interesting possibility to calculate the equilibrium constant for electron donor–acceptor complex formation from solubility (see below).

4.4 *Accuracy of the prediction of solubilities.* The standard deviation  $s$  of a single value of  $\epsilon_2/k$  holding in a particular solvent, from the mean value of  $\epsilon_2/k$  holding in alkanes or cycloalkanes and aromatics, respectively (given in Table 4) appeared to be given by:

$$\log s = 0.17 + 0.0022 \epsilon_2/k. \quad (16)$$

From this it follows that when the solubility of a gas in an alkane, cycloalkane or aromatic solvent is calculated by means of Eqs. (1–10) from the mean value of  $\epsilon_2/k$  given in Table 4, the standard deviation of the calculated solubility ranges from 15 per cent for light gases like Ne to 30 per cent for heavy gases like Xe.

4.5 *Electron donor–acceptor complex formation.* In Fig. 3 the  $\epsilon_2/k$  values, holding for aromatic solvents, are compared with the literature data. The points for the  $\text{C}_3$ -solutes have been omitted from this figure, as we think the literature values of  $\epsilon/k$  for these compounds to be unreliable (see discussion of Fig. 2). It appears that most of the points can be described by the relationship  $\epsilon_2/k$  (from solubility) =  $\epsilon_2/k$  (from literature). However, the points for  $\text{BF}_3$  in nitrobenzene,  $\text{Cl}_2$  and  $\text{C}_2\text{H}_2$  deviate from this relationship, and we ascribe this to donor–acceptor interaction with the solvents.

Figure 4 shows that with dimethylsulfoxide even  $\text{CO}_2$  and again  $\text{C}_2\text{H}_2$  give donor–acceptor interaction.

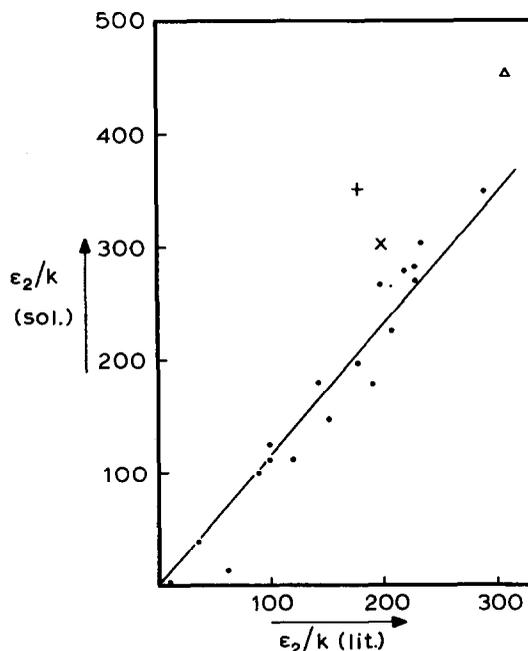


Fig. 3. Comparison of  $\epsilon_2/k$  values (deg), calculated from solubility in aromatic solvents, with literature data. +,  $\text{BF}_3$  in nitrobenzene;  $\Delta$ ,  $\text{Cl}_2$ ; x,  $\text{C}_2\text{H}_2$ .

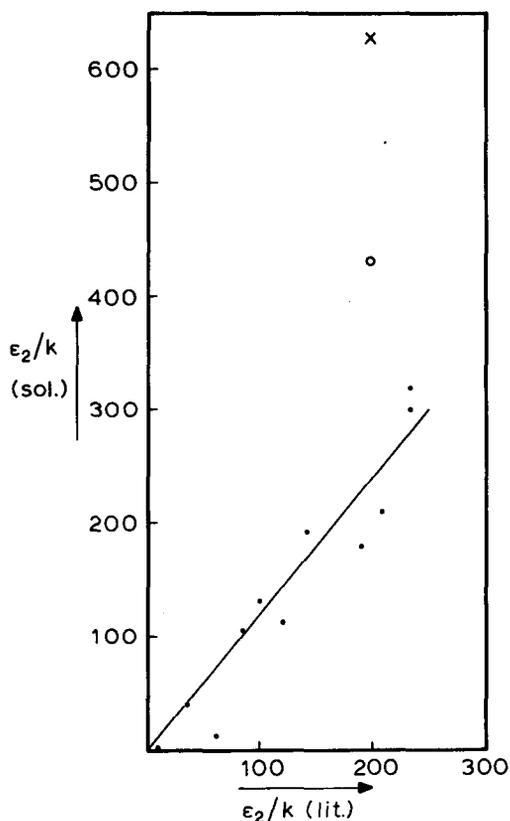


Fig. 4. Comparison of  $\epsilon_2/k$  values (deg), calculated from solubility in dimethylsulfoxide, with literature data. O, CO<sub>2</sub>; x, C<sub>2</sub>H<sub>2</sub>.

Table 5. Association constant for electron-acceptor complex formation, calculated from gas solubility (on the mole fraction scale)

Gas	Solvent	K
Cl <sub>2</sub>	benzene	3
C <sub>2</sub> H <sub>2</sub>	benzene	3
BF <sub>3</sub>	nitrobenzene	17
CO <sub>2</sub>	dimethylsulfoxide	14
C <sub>2</sub> H <sub>2</sub>	dimethylsulfoxide	180

The complex formation of C<sub>2</sub>H<sub>2</sub> with benzene and of CO<sub>2</sub> with dimethylsulfoxide was not detected by earlier investigators, applying the regular solution theory to their solubility data. As far as we are aware this is the first time that electron donor-acceptor complex formation for CO<sub>2</sub> is reported.

BF<sub>3</sub> does not form complexes with either benzene or toluene. As the nitro group decreases the electron density of the benzene ring, BF<sub>3</sub> is probably not coordinated to the ring but to the nitro oxygens, in its complex with nitrobenzene.

From u.v. spectroscopy, the association constant of the complex of Cl<sub>2</sub> with benzene, at 25° in carbon tetrachloride solution, is calculated to be 0.33 [54], an order of magnitude smaller than found by us. However, the authors themselves express their doubt about the accuracy of this value, in view of the smallness of the association constant and the molar extinction coefficient  $\epsilon_c$  of the complex. Further it is doubtful if the assumptions made in analysing the spectroscopic data, i.e. that  $\epsilon_c$  and the ratio of the activity coefficient of the complex and of the product of the activity coefficients of the free solute and benzene remain constant from  $x_1 = 1$  to  $x_1 \approx 0.1$  are correct. Last but not least, association constants of electron donor-acceptor complexes in the solvents benzene and carbon tetrachloride may differ an order of magnitude [33].

The association constant  $K$  of the resulting complex can be calculated as follows.

The mole fraction of the uncomplexed solute  $x_{2,\text{free}}$  can be calculated from Eqs. (1-10) where, in Eq. (8),  $\epsilon_2/k$  is set equal to the value, expected for aromatic solvents or dimethylsulfoxide on the basis of Figs. 3 or 4, respectively.  $K$  is equal to:

$$K = \frac{x_{2,\text{complexed}}}{x_1 x_{2,\text{free}}} = \frac{x_{2,\text{complexed}}}{x_{2,\text{free}}} \\ = \frac{x_{2,\text{complexed}} + x_{2,\text{free}}}{x_{2,\text{free}}} - 1 = \frac{x_{2,\text{found}}}{x_{2,\text{free}}} - 1. \quad (17)$$

The resulting data are given in Table 5. Some comments are as follows.

#### ENTROPIES OF SOLUTION

Figure 5 shows that the standard entropies of solution of a particular gas in different solvents

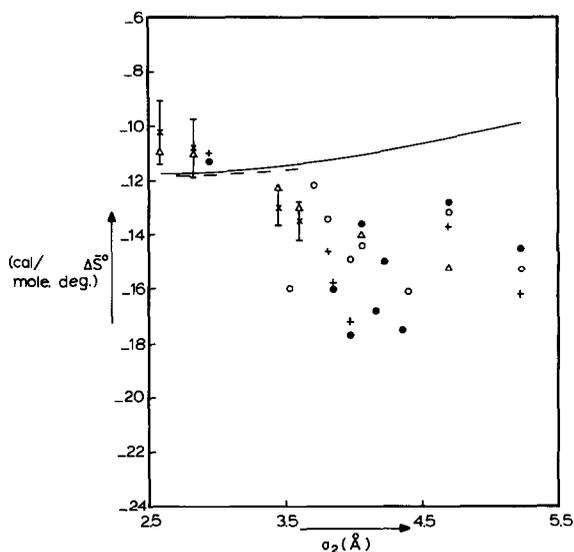


Fig. 5. Comparison of calculated and experimental values of the standard entropy of solution of gases. x, entropy of solution in various hydrocarbon solvents (including heptane, tetradecane, cyclohexane and benzene)[7]. Also shown is the 90 per cent probability interval. +, entropy of solution in the solvent heptane[15, 19, 21, 29, 30]. o, cyclohexane[29, 30, 44]. ●, benzene[15, 19, 21, 29, 35, 36]. Δ, perfluoromethylcyclohexane[31, 32]. —, heptane (calculated). ---, tetradecane (calculated).

are equal within the rather large experimental error (with an exception for the high-molecular weight solvents polythene and hydropol). They range from about  $-10$  cal/mole. degree for He to about  $-16$  cal/mole. degree for heavy gases.

This figure also shows that Eqs. (4–10) do not describe adequately  $\Delta\bar{S}^0$  as a function of  $\sigma_2$ .

### CONCLUSIONS

(1) Pierotti's theory gives a good description of gas solubilities in solvents consisting of globular, elongated, giant, apolar, moderately and strongly polar aprotic molecules. It even holds for the vapour–liquid equilibria of the pure solvents. Solubilities in alkane, cycloalkane and aromatic solvents can be predicted with an accuracy ranging from 15 per cent for light gases to 30 per cent for heavy ones.

(2) The hard-sphere diameter  $\sigma_1$  and the energy parameter  $\epsilon_1/k$  of the solvent molecules, occurring in the theoretical expressions, should

be treated as adjustable parameters. The values of the former are slightly different from the Van der Waals diameter, the values of the latter are probably more accurate than values deduced from vapour viscosities or second virial coefficients.

(3) Several slightly differing sets of  $\epsilon_2/k$  values of the solute gases are required to describe the experimental solubilities in the various solvent classes.

(4) The enhanced solubilities of  $\text{BF}_3$ ,  $\text{CO}_2$ ,  $\text{Cl}_2$  and  $\text{C}_2\text{H}_2$  in some solvents are due to electron donor–acceptor interaction.

(5) Pierotti's theory does not describe adequately the entropy of solution as a function of  $\sigma_2$ .

### NOTATION

$A_W$	Van der Waals surface area ( $\text{cm}^2 \text{mole}^{-1}$ )
$C_{\text{disp}}, C_{\text{ind}}$	constants, characterizing the dispersion and the inductive energy respectively ( $\text{erg cm}^6$ )
$\Delta\bar{G}^0, \Delta\bar{H}^0, \Delta\bar{S}^0$	standard partial molar free enthalpy, enthalpy and entropy of solution, respectively ( $\text{cal mole}^{-1}$ ) and ( $\text{cal mole}^{-1} \text{deg}^{-1}$ ) respectively
$\bar{G}_c, \bar{H}_c, \bar{S}_c$	partial molar free enthalpy, enthalpy and entropy of cavity formation respectively ( $\text{cal mole}^{-1}$ ) and ( $\text{cal mole}^{-1} \text{deg}^{-1}$ ) respectively
$\bar{G}_i, \bar{H}_i, \bar{S}_i$	partial molar free enthalpy, enthalpy and entropy of interaction respectively ( $\text{cal mole}^{-1}$ ) and ( $\text{cal mole}^{-1} \text{deg}^{-1}$ ) respectively
$K$	equilibrium constant
$K_0, K_1, K_2$	constants, characterizing the thermodynamic data for cavity formation
$k$	Boltzmann's constant ( $\text{erg deg}^{-1}$ )
$M$	molecular weight ( $\text{g mole}^{-1}$ )
$N$	Avogadro's number ( $\text{mole}^{-1}$ )

$p$	partial vapour pressure of a solute (mm Hg)	of the solvent (deg <sup>-1</sup> )
$R$	gas constant (cal mole <sup>-1</sup> deg <sup>-1</sup> )	$\epsilon$ molecular energy parameter (erg)
$s$	estimate of a standard deviation	$\mu$ dipole moment (e.s.u.)
$T$	temperature (deg)	$\rho$ number density of the solvent molecules (cm <sup>-3</sup> )
$V$	molar volume (cm <sup>3</sup> mole <sup>-1</sup> )	$\sigma$ molecular diameter (cm)
$V_w$	Van der Waals volume (cm <sup>3</sup> mole <sup>-1</sup> )	$\sigma_s$ standard deviation of $s$
$x$	mole fraction of a solute	$\varphi$ number of degrees of freedom

*Greek symbols*

$\alpha$	polarizability (cm <sup>3</sup> mole <sup>-1</sup> )
$\alpha_p$	thermal expansion coefficient

*Subscripts*

1, 2	denote solvent and solute respectively.
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**Résumé**— Les auteurs testent la théorie de Pierotti relative à la solubilité de gaz dans des liquides à l'aide de nombreuses données de la littérature sur la solubilité et l'entropie de solution. Les solutés concernés comprennent les gaz nobles, la vapeur de mercure, les gaz inorganiques et les hydrocarbures jusqu'au propane. Les solvants concernés comprennent les alcanes, les cycloalcanes, le nitrométhane, le polyéthylène, les aromatiques, le diméthylsulfinone et le perfluorométhylcyclohexane.

Il apparaît que cette théorie décrit avec satisfaction les solubilités. La description des entropies de solution est cependant moins bonne. Les solubilités augmentées de  $\text{BF}_3$ ,  $\text{CO}_2$ ,  $\text{Cl}_2$  et  $\text{C}_2\text{H}_2$  dans certains solvants semblent être dues à une interaction du donneur et du receveur d'électrons. Les constantes d'association de la formation du complexe donneur-receveur sont rapportées dans un tableau.

**Zusammenfassung**— Die Theorie von Pierotti in Bezug auf die Löslichkeit von Gasen in Flüssigkeiten wird mit Hilfe einer grossen Menge von Daten aus der Literatur über Löslichkeit und Lösungsentropie geprüft. Die betreffenden Solute umfassen die Edelgase, Quecksilberdampf, anorganische Gase und Kohlenwasserstoffe bis zu Propan. Die in Frage stehenden Lösungsmittel umfassen Alkane, Cycloalkane, Nitromethan, Polyäthylen, aromatische Kohlenwasserstoffe, Dimethylsulphoxyd und Perfluormethylcyclohexan.

Es scheint, dass diese Theorie die Löslichkeiten befriedigend beschreibt. Die Beschreibungen der Lösungsentropien sind weniger gut.

Die erhöhten Löslichkeiten von  $\text{BF}_3$ ,  $\text{CO}_2$ ,  $\text{Cl}_2$  und  $\text{C}_2\text{H}_2$  in manchen Lösungsmitteln werden einer Elektronen-Donor-Akzeptor-Wechselwirkung zugeschrieben. Die Assoziationskonstanten für Donor-Akzeptor-Komplexbildung werden in Tabellenform gebracht.