# The Solubility of Hydrogen, Oxygen, and Carbon Monoxide in Some Non-Polar Solvents

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In a previous paper 1 dealing with the solubility of nitrogen in a number of non-polar liquids it was shown that the solubility can be calculated with satisfactory accuracy from the equation:

In this equation  $x_2$  denotes the solubility in mole fraction,  $x_2^i$  the "ideal" solubility (see later),  $\overline{V}_2$  the partial molal volume of nitrogen in the saturated solution,  $V_1$  the molal volume of the solvent,  $\delta_1$  the "solubility parameter" of the solvent defined as the square root of the energy of vapourization per ml  $(\delta_1 = (\Delta E_1/V_1)^{1/2})$ ,  $\delta_2$  the "solubility parameter" of the gas (see later) and T the absolute temperature. With regard to the derivation of equation (I) reference should be made to Hildebrand and Scott <sup>2</sup>.

When the values  $x_2^i = 16 \times 10^{-4}$ ,  $\overline{V}_2 = 53$  ml, and  $\delta_2 = 5.2$  are substituted, equation (I) will express the solubility of nitrogen in all the non-polar solvents examined from perfluoro-n-heptane,  $n\text{-C}_7F_{16}$ , which has a particularly low solubility parameter ( $\delta_1 = 5.85$ ) to carbon disulphide which has a particularly high solubility parameter ( $\delta_1 = 10.0$ ).

It is the aim of the present work to ascertain whether equation (I) with the same accuracy can express the solubility of other gases with low solubility.

The solubility of oxygen was examined because the derived constants together with those previously found for nitrogen makes it possible to calculate the solubility of atmospheric air in non-polar liquids. Hydrogen was chosen as an example of a gas of particularly low solubility. Carbon monoxide was chosen because the author has previously <sup>3,4</sup> determined the solubility of this gas in a considerable number of alcohols.

# APPARATUS, PROCEDURE, AND MATERIALS

The apparatus used for the solubility determinations was as that described by Lannung <sup>5</sup> in whose paper an illustration and a description in greater detail may be found. The volume of the gas burette was about 8 ml and that of the flask about 90 ml. The volume of the gas was read with an accuracy of  $\pm$  0.005 ml, and the pressure of the gas with an accuracy of  $\pm$  0.2 mm Hg. The volume of the solution was in all cases determined with an accuracy exceeding 0.1 per cent. The temperature in the air thermostat was constant within 0.03° C in the case of experiments made at temperatures about 25° C and at temperatures about 50° C it was constant within 0.1° C.

The procedure was as described in the paper by Lannung quoted above. The errors involved in the solubility determinations were in most cases within 1 per cent.

Hydrogen from a cylinder was freed from oxygen by being passed through several glass-spiral washing bottles containing alkaline solution of pyrogallol and was dried by being passed through concentrated sulphuric acid. Following this purification the hydrogen proved by combustion analysis in a gas analysis apparatus as devised by Christiansen to contain 99.5 per cent hydrogen and 0.5 per cent nitrogen.

Oxygen was prepared by heating potassium permanganate placed in a refractory test tube the mouth of which has been drawn out to form a gas siphon. By absorption analysis in alkaline dithionite the composition was found to be: 99.7 per cent oxygen and 0.3 per cent nitrogen.

The carbon monoxide employed was prepared according to a method described in a previous paper <sup>7</sup> and contained 99.5 per cent carbon monoxide and 0.5 per cent nitrogen.

For the solvents used, which were all purified by fractionation in a wire-gauze column, the following physical constants were determined:

n-Heptane (pure grade) from Phillips Pet. Co., boiling point 98.3—98.4° C (760 mm) and  $n_{\rm D}$  (25° C) 1.3855.

Benzene ("analytical reagent", Merck), boiling point 80.28° C (760 mm) and melting point 5.43° C.

Carbon disulphide ("analytical reagent", Merck), boiling point 46.21-46.26° C (760 mm).

The perfluoro-n-heptane used was of the same origin and purity as the substance described in a previous paper  $^{1}$ .

It is necessary to know the vapour pressure of the solvent in order to be able to calculate the solubility of the gas at a partial pressure of 1 at. The vapour pressures at 25° C employed are summarized in Table 1. For the conversion from Bunsen's absorption coefficient (a) to mole fraction the specific gravities of the solvents, also included in Table 1, have been used.

Table 1. Vapour pressures and densities of the solvents at 25° C.

	$n ext{-}\mathrm{C}_{7}\mathrm{F}_{16}^{1}$	n-C <sub>7</sub> H <sub>16</sub> <sup>8</sup>	C <sub>6</sub> H <sub>6</sub> <sup>8</sup>	CS <sub>2</sub> <sup>9</sup>
$p \hspace{0.1cm}  ext{mm} \hspace{0.1cm}  ext{Hg}$	80.0	45.7	94.2	357
d 25/4	1.7208	0.6795	0.8737	1.255

# EXPERIMENTAL RESULTS

The results of the solubility determinations have been reproduced in Table 2, expressed as Bunsen's absorption coefficient (a), *i.e.* the number of ml of the gas reduced to  $0^{\circ}$  C and 1 at. which can be dissolved in 1 ml solvent at the temperature concerned when the partial pressure of the gas is 1 at.

Table 2. Solubility of hydrogen, oxygen and carbon monoxide. Experimental values expressed in Bunsen's absorption coefficient ( $\alpha$ ) at  $t^{\circ}$  C.

~ .	Hyd	rogen	Oxygen		Carbon monoxide	
Solvent	t.	α	t	α	t	α
	24.80	0.140	25.00	0.548	24.91	0.385
G. 17	48.30	0.166	24.96	0.544	24.90	0.385
$n ext{-} ext{C}_{f 7} ext{F}_{f 16}$	24.73	0.141			25.00	0.380
	48.75	0.166				
C II					24.88	0.263
<i>n</i> -C <sub>7</sub> H <sub>16</sub>					24.93	0.262
					25.03	0.1692
$C_{f 6}H_{f 6}$					24.95	0.1691
					24.98	0.1695
$\mathrm{CS}_2$	24.82	0.0606	25.00	0.162	24.90	0.133
<i></i> 2	24.86	0.0607	24.82	0.164	24.90	0.132

Table 3. Solubility of carbon monoxide and hydrogen expressed in Bunsen's absorption coefficient at 25° C. Comparison with older measurements.

	Just 10	Skirrow <sup>11</sup>	Horiuti <sup>12</sup>	Present investigation
CO in C <sub>6</sub> H <sub>6</sub>	0.156	0.160	0.167	0.169
CO in CS <sub>2</sub>	0.0761	0.0879; 0.0761		0.133
$H_2$ in $CS_2$ ,	0.0343			0.0607

It appears from Table 3, which includes the solubilities found by other investigators, that for the solubilities of carbon monoxide and hydrogen the

values found are higher than those stated by Just and Skirrow, while the solubility of carbon monoxide in benzene shows good agreement with the result obtained by Horiuti. In a previous paper <sup>1</sup> on the solubility of nitrogen the results also showed good agreement with those of Horiuti's while there were considerable discrepancies between the author's figures and those found by Just.

#### CORRELATION WITH THEORY

1. Calculations of the solubility of oxygen and carbon monoxide. According to Dolezalek <sup>13</sup> and Hildebrand <sup>2</sup> the "ideal solubility" of a gas can be determined on the following basis. Assume the liquefied gas to have a vapour pressure  $p_2^{\circ}$  at at  $t^{\circ}$  C. As the solubility in an ideal solvent at  $t^{\circ}$  C is equivalent to the concentration to which the liquefied gas must be diluted — under ideal conditions — in order to obtain a partial pressure of the gas equal to 1 at., the ideal solubility expressed in mole fraction  $x_2^{i}$  can be calculated by means of Raoult's law from the equation:

$$x_2^i = 1/p_2^{\circ} \tag{II}$$

For gases which at a temperature of  $t^{\circ}$  C is above their critical temperature a fictitious value of  $p_2^{\circ}$  is obtained by extrapolation of the measured vapour pressures  $(p_2)$  of the gas to the temperature  $t^{\circ}$  C. The extrapolation is performed by plotting  $\log p_2$  against 1/T.

It was, however, found through the more detailed investigation of the solubility of nitrogen in non-polar liquids that the value  $(p_2^{\circ} = 1000 \text{ at.})$  found by extrapolation resulted in such a value of  $x_2^{i}$  (10<sup>-3</sup>) that the solubilities in the fluorocarbons could not be represented by equation (I). When using, however, a value for  $x_2^{i}$  calculated from:

$$-\log x_2^i = \frac{\Delta H}{4.575} \left( \frac{1}{T_b} - \frac{1}{T} \right) \tag{III)}$$

where  $\Delta H$  is the heat of vapourization (1333 cal. per mole, Giauque and Clayton <sup>14</sup>) determined experimentally at the boiling point of nitrogen ( $T_b = 77.3^{\circ}$ K), we have, at  $T = 298.1^{\circ}$  C,  $x_2^i = 16 \times 10^{-4}$ . With this value of  $x_2^i$  the solubilities could be expressed by equation (I). The same procedure has been used in this paper for the calculation of  $x_2^i$  for oxygen and carbon monoxide.

For oxygen  $x_2^i$  is found from equation (III) to be equal to  $17.6 \times 10^{-4}$ ,  $\Delta H$  being equal to 1630 cal/mole at  $T_b = 90.2^\circ$  K according to Clusius and Konnertz <sup>15</sup>. For carbon monoxide  $x_2^i$  is found to be equal to  $15.5 \times 10^{-4}$  when substituting  $\Delta H = 1444$  cal/mole at  $T_b = 81.6^\circ$  K according to Clayton and Giauque <sup>16</sup>.

In the following a calculation of  $\delta_2$  for oxygen and carbon monoxide is performed by means of equation (I). The values of the partial molal volumes of the gases are calculated on the basis of Horiuti's experiments  $^{12}$  on the expansion displayed by the solvent when a gas is dissolved. The values are only to a slight extent dependent on the solvent, and the value chosen for  $\overline{V}_2$  is the average of the values for  $\overline{V}_2$  in benzene and carbon tetrachloride. The calculation gives for oxygen  $\overline{V}_2 = 46$  ml and for carbon monoxide  $\overline{V}_2 = 52$  ml. The values for the solubility parameters of the solvents,  $\delta_1$ , have been taken from Hildebrand and Scott  $^{2}$ , Appendix  $^{1}$ . For normal heptane the value 8.1 has been used, cf. Hildebrand  $^{17}$ . The values used will appear from Table 4.

Table 4. Solubility of oxygen and carbon monoxide in mole fraction  $(x_2)$  at 25° C. Comparison of experimental and calculated values.

			Oxygen				Carbon monoxide				
Solvent		$V_1$	$\delta_1$	$x_2 \cdot 10^4$	_	– log a		$x_2 \cdot 10^4$	$-\log x_2$		
				exp.	exp.	calc.	Δ	exp.	exp.	calc.	Δ
$n ext{-}\mathrm{C_7F_{16}}$		227	5.85	55.3	2.26	2.41	+0.15	38.8	2.41	2.50	+0.09
$n ext{-} ext{C}_6 ext{H}_{14}$	a)	132	7.3	19.3	2.71	2.67	-0.04				
$n ext{-} ext{C}_7 ext{H}_{16}$		147	8.1	19.7 a)	2.71	2.74	+0.03	17.3	2.76	2.84	+0.08
$c ext{-}\mathrm{C_6H_{12}}$	a)	109	8.2	12.3	2.91	2.84	-0.07				
$CCl_4$	b)	97.1	8.6	12.1	2.92	2.94	+0.02	8.66	3.06	3.04	-0.02
$\mathbf{C_6H_6}$		89.3	9.15	8.16 b)	3.09	3.08	-0.01	6.74	3.17	3.18	+0.01
1,4-dioxane	a)	86.1	10.0	5.38	3.27	3.31	-0.04		i		ŀ
$\text{CS}_2$		60.6	10.0	4.42	3.36	3.37	+0.01	i l	3.44	3.48	+0.04
CS <sub>2</sub>	c)							2.06	3.69	3.48	-0.21
$\mathrm{C_6H_5CH_3}$	d)	107	8.9					7.98	3.10	3.08	-0.02
$(C_2H_5)_2O$	b)	105	7.4	19.8	2.70	2.74	+0.04		2.77	2.82	+0.05
$CHCl_3$	d)	80.7	9.3	10.0	2.70	2.1 <del>1</del>	70.01	6.86	3.16	3.24	+0.08
$C_6H_5Cl$	b)	102	9.5	8.62	3.06	3.13	+0.07	1	3.20	3.25	+0.05
$C_6H_5OI$ $C_6H_5NH_2$	d)		11.2 e)	1 3	3.00	0.10	.0.07	1.99	3.70	3.86	+0.16
$C_5H_5N$	a)		10.7	4.58	3.34	3.54	+0.20		5.10	5.00	, 0.10
$(CH_3)_2CO$	b)		9.3 e)	1 1	3.07	3.15	+0.20	1	3.11	3.25	+0.14
$C_6H_5NO_2$			11.0 e)	, ,	5.01	0.10	7 0.00	3.90	3.41	3.76	+0.35
C6H5NO2	d)	103	11.06)	<u> </u>			]]	3.90	3.41	3.70	+0.30

a) Guerry <sup>18</sup>, b) Horiuti <sup>12</sup>, c) Just <sup>10</sup>, d) Skirrow <sup>11</sup>, e) calculated according to the "Hildebrand rule" <sup>2</sup>, p. <sup>427</sup>.

Calculations have subsequently been performed for oxygen and carbon monoxide by means of equation (I) to find the values of  $\delta_2$  which show the closest agreement with the experimental values of the solubilities in the non-polar solvents. For oxygen  $\delta_2$  was found to be 5.7 and for carbon monoxide  $\delta_2$  was found to be 5.8. The extent to which the constants thus calculated agree with the experimentally determined solubilities will appear from the upper half of Table 4.

It will be seen that the values of the solubilities in perfluoro-n-heptane found by calculation are somewhat lower than those determined experimentally — a difference which was also found to exist in the case of nitrogen. It will further be seen that the value found in the present investigation for the solubility of carbon monoxide in carbon disulphide agrees well with the theory.

In the lower half of Table 4 the solubilities of oxygen and carbon monoxide in a number of polar solvents have been summarized. The experimental values have been taken from Skirrow 11 and Horiuti 12. The calculation has been performed by means of equation (I) which does not allow for polar attraction. It will be seen that in toluene, which among the polar solvents applied is the one with the lowest dielectric constant ( $\varepsilon = 2.4$ ), the solubility can be calculated with the same accuracy as in the non-polar solvents. With regard to the other polar solvents it applies that the experimentally determined solubility is larger than the solubility calculated on the basis of equation (I). In the slightly polar solvents, ether, chloroform and chlorobenzene ( $\varepsilon = 4.3, 5.1, \text{ and } 5.9,$ respectively) the difference between the experimental and calculated values for the solubility is small. The difference is somewhat larger in the more polar liquids as aniline, pyridine and acetone ( $\varepsilon = 7, 12, \text{ and } 21, \text{ respectively}$ ) and greatest in nitrobenzene which is the most polar solvent among those used ( $\varepsilon = 36$ ). This phenomenon may be explained by assuming the molecules of the solvents to induce moments in the molecules of the solute gas, the consequent increased attraction will result in a higher solubility.

Skirrow <sup>11</sup> has made a series of determinations of the solubility of carbon monoxide in mixtures of benzene and naphtalene and has found that the solubility of carbon monoxide decreases with increasing naphtalene concentration. It will be shown in the following that this decrease in the solubility is in conformity with the theory. For mixtures of benzene and naphtalene molal volumes  $(V_1)$  and solubility parameters  $(\delta_1)$  have been calculated according to the equations <sup>2</sup>, <sup>p. 201</sup>

$$V_1 = \Phi_n V_n + \Phi_b V_b$$

$$\delta_1 = \Phi_n \delta_n + \Phi_b \delta_b$$

where  $\Phi$  denotes volume fractions and the subscripts n and b naphtalene and benzene, respectively. For naphtalene the values  $V_n = 123$  and  $\delta_n = 9.9$  have been used. Table 5 gives the calculated values of  $V_1$  and  $\delta_1$  together with the values for the solubility of carbon monoxide calculated on the basis of equation (I). It will be seen that this equation with good approximation represents the variation in the experimental values which, however, must all be assumed to be 3—6 per cent too low,  $c_f$ . Table 3. Skirrow found the solubility of carbon monoxide in pure benzene to be 13 per cent higher than in benzene containing 23.72 mole per cent naphtalene, while when applying equation (I) we find that the solubility should be 10 per cent higher.

Table 5. Calculation of the solubility of carbon monoxide in solutions of naphtalene in benzene at 25° C. Experimental values from Skirrow <sup>11</sup> expressed in Ostwald's absorption coefficient  $(\lambda)$ .

Mole %	V <sub>1</sub>		2	$x_2 \cdot 10^4$		
naphtalene		$o_1$	λ	exp.	calc.	
0	89.3	9.15	0.174	6.37	6.55	
7.35	92.4	9.22	0.164	6.15	6.35	
16.14	96.1	9.31	0.149	5.76	6.14	
23.72	$\boldsymbol{99.2}$	9.38	0.141	5.61	<b>5.94</b>	

In two previous papers 3,4 the author has determined the solubility of carbon monoxide in a number of monohydric alcohols. As equation (I) is derived on the condition that the molecules are non-polar and not associated, this equation cannot be used straight away for the calculation of the solubilities of carbon monoxide in alcohols. However, on the basis of the solubility experiments and by means of equation (I) it is possible empirically to determine a solubility parameter for each of the alcohols. The result of such a calculation is given in Table 6, column 5. From the heat of vapourization at the boiling point of these alcohols (column 3) the heat of vapourization at 25° C has been calculated, and from this value  $\delta_1 = (\Delta E/V)^{\frac{1}{2}}$  has further been calculated (column 6). For the calculation of the heat of vapourization at 25° C the specific heat difference  $C_{p}$  (liquid) —  $C_{p}$  (vapour) = 0.142 cal/g has been used for all the alcohols. It will be seen from the two last columns of the table that the difference between  $\delta_1$ , as calculated from the solubility experiments, and  $\delta_1$ , as calculated from  $\Delta H$  (25°C) is greatest in the case of the alcohols with the highest dielectric constants. It should be noticed that all the alcohols have nearly the same dipole moment (about 1.8 Debye).

alcohol	α	ΔH	$V_1$	$\delta_1$ at 25° C calculated from		Δδ	
alconor	at 25° C	at B.p.	at 25° C	the solubility measurement	ΔH	210	ε
CH <sub>3</sub> OH	0.207	8413	40.6	9.85	14.05	4.20	33
C <sub>2</sub> H <sub>5</sub> OH	0.186	9410	58.7	9.45	12.50	3.05	26
n-C <sub>3</sub> H <sub>7</sub> OH		9876	75.2	9.30	11.50	2.20	22
iso-C <sub>3</sub> H <sub>7</sub> OH		<b>9574</b>	77.0	9.15	11.10	1.95	26
n-C <sub>4</sub> H <sub>9</sub> OH	0.153	10460	91.9	9.25	10.85	1.60	18
iso-C <sub>4</sub> H <sub>9</sub> OH	0.161	10230	92.8	9.15	10.65	1.50	19
sec.C <sub>4</sub> H <sub>9</sub> OH	0.154	9959	92.2	9.20	10.45	1.25	16
tert.C4H9OH	0.175	9667	95.0	9.00	10.10	1.10	11

Table 6. Calculation of the solubility parameter  $(\delta_1)$  for some alcohols.

The solubility parameters for the alcohols given in Table 6, column 5 may in connection with equation (I) be used for the calculation of the solubility of other gases of low solubility in the alcohols concerned. The result of such a calculation has been given in Table 7.

Table 7. Solubility of some gases in methyl and ethyl alcohol at 25° C. Comparison of experimental and calculated values.

Solvent	$\begin{array}{c c} \text{Hydrogen} \\ -\log  x_2 \end{array}$			$\begin{array}{c} \text{Nitrogen} \\ -\log\ x_2 \end{array}$			$\begin{array}{c} \text{Oxygen} \\ -\log\ x_2 \end{array}$		
	exp.	calc.	Δ	exp.	calc.	Δ	exp.	calc.	Δ
CH <sub>3</sub> OH	3.80 a)	3.87	+0.07	3.63 a)	3.61	-0.02	3.40 c)	3.33	-0.07
				3.56 c)	3.61	+0.05			
$\mathrm{C_2H_5OH}$	3.69 b)	3.73	+0.04	3.46 a)	3.50	+0.04	3.25 d)	3.12	-0.13

a) Just <sup>10</sup>, b) Maxted a. Moon <sup>19</sup>, c) Levi <sup>20</sup>, d) Timofejew <sup>21</sup>.

2. Solubility calculations for hydrogen. Gonikberg <sup>22</sup> has on the basis of experiments by Just and Horiuti shown that the solubility of hydrogen in

 $<sup>\</sup>alpha$  = Bunsen's absorption coefficient for carbon monoxide in the alcohols,

 $<sup>\</sup>Delta H = {
m heat}$  of vapourization,  $V_1 = {
m molal}$  volume and  $\varepsilon = {
m dielectric}$  constantal.

ether, m-xylene, carbon tetrachloride, toluene and benzene can be represented with satisfactory accuracy by the equation,

$$-\log x_2 = -\log x_2^i + \overline{V}_2 (\delta_1 - \delta_2)^2 / 4.575 T$$
 (IV)

This equation is obtained from (I) by omitting the correction for the entropy of mixing. For his calculations (20 °C) Gonikberg used  $x_2^i = 24.6 \times 10^{-4}$  and  $\overline{V}_2 = 28.6$  ml (the molal volume of hydrogen at the boiling point 20.4° K). Only in carbon disulphide did the solubility of hydrogen display any considerable deviation from equation (IV) for which reason Gonikberg considered this experiment to have been subject to errors. A redetermination of the solubility of hydrogen actually gave a result which was about 75 per cent higher than that found by Just (Table 3), and this new value shows, as will appear from Table 8, better agreement with the theory.

Table 8. Solubility of hydrogen in mole fraction  $(x_2)$  at 25° C. Comparison of experimental and calculated values.

$$x_2^i = 5.5 \cdot 10^{-4}; \quad \overline{V}_2 = 37 \text{ ml}; \quad \delta_2 = 5.1$$

Solvent		T7 \$	$x_2 \cdot 10^4$	$-\log x_2$			
Solvent		$V_{1}$	$\delta_1$	exp.	exp.	calc.	Δ
G.F.		005	- 0-	14.0	0.05	0.05	0.00
n-C <sub>7</sub> F <sub>16</sub>		227	5.85	14.2	2.85	2.85	0.00
n-C <sub>6</sub> H <sub>14</sub>	a)	130	7.30	6.51	3.19	3.16	-0.03
n-C <sub>7</sub> H <sub>16</sub>	a)	147	8.10	6.63	3.18	3.23	+0.05
c-C <sub>6</sub> H <sub>12</sub>	a)	109	8.20	3.80	3.42	3.34	- 0.08
CCl <sub>4</sub>	b)	97.1	8.60	3.26	3.49	3.44	- 0.05
$C_6H_6$	<b>b</b> )	89.3	9.15	2.62	3.58	3.58	0.00
1,4-dioxane	a)	86.1	10.0	1.93	3.71	3.79	+ 0.08
$CS_2$		60.6	10.0	1.64	3.79	3.86	+ 0.07
CS <sub>2</sub>	<b>c</b> )			0.93	4.03	3.86	- 0.17
	İ						
$m\text{-}\mathrm{C_6H_4(CH_3)_2}$	c)	123	8.8	4.12	3.39	3.41	-0.02
$C_6H_5CH_3$	c)	107	8.9	3.82	3.42	3.47	-0.05
$(C_2H_5)_2O$	b)	105	7.45	6.25	3.20	3.24	+ 0.04
CHCl <sub>3</sub>	<b>d</b> )	80.7	9.3	2.20	3.66	3.63	- 0.03
$C_6H_5Cl$	b)	102	9.5	2.57	3.50	3.62	+ 0.12
$C_6H_5NH_2$	<b>c</b> )	91.5	11.2	1.065	3.97	4.13	+ 0.16
$(CH_3)_2CO$	b)	74.0	9.3	3.02	3.52	3.65	+ 0.13
$C_6H_5NO_2$	c)	103	11.0	1.56	3.81	4.04	+ 0.23

a) Guerry <sup>18</sup>, b) Horiuti <sup>12</sup>; the experimental value for the solubility in benzene is with variations which are within 2 per cent in agreement with a value reported by Maxted and Moon <sup>19</sup>. c) Just <sup>10</sup>, d) Maxted and Moon <sup>19</sup>.

It should be emphasized that the calculation of the ideal solubility of hydrogen is rather inaccurate, the reason being the low boiling point of hydrogen. Hildebrand 2, p. 243 has on the basis of determinations of the vapour pressure of liquid hydrogen (values from International Critical Tables) by extrapolation calculated  $x_2^i$  to be equal to  $8 \times 10^{-4}$ . When using vapour pressure measurements by Grilly 23, extrapolation provides the value  $x_2^i =$  $25 \times 10^{-4}$ , and if  $x_2^i$  is calculated on the basis of the heat of vapourization, 219 cal/mole <sup>24</sup> at the boiling point 20.4° K, the result obtained is  $65 \times 10^{-4}$ . As these values for the ideal solubility show such great discrepancies the procedure adopted for hydrogen has been to chose the set of values of  $x_2^i$  and  $\delta_2$  which on the basis of equation (I) shows the closest agreement with the experimental results. For hydrogen the value  $\overline{V}_2 = 37$  ml was calculated on the basis of experiments made by Horiuti<sup>12</sup>. Hence the values  $x_2^i = 5.5 \times 10^{-4}$  and  $\delta_2 = 5.1$ . The accuracy with which the constants determined in this way represent the experiments will appear from the upper half of Table 8. The lower half of Table 8 summarizes a calculation of the solubility of hydrogen in polar liquids. It will be seen that the comments made on the solubility of oxygen and carbon monoxide in polar liquids will also apply to hydrogen.

## SUMMARY

- 1. Determinations of the solubility of hydrogen, oxygen, and carbon monoxide in a number of non-polar liquids have been made. Expressed as Bunsen's absorption coefficient the values found were: *Hydrogen* in perfluoro-n-heptane 0.0141 (25° C), and 0.0167 (50° C), in carbon disulphide 0.0607 (25° C); oxygen (25° C) in perfluoro-n-heptane 0.546 and in carbon disulphide 0.163; carbon monoxide (25° C) in perfluoro-n-heptane 0.383, in n-heptane 0.263, in benzene 0.169 and in carbon disulphide 0.133.
- 2. The above data combined with existing data on the solubility in other solvents are used for the determination of the solubility parameters  $(\delta_2)$  for the gases concerned. It is shown (Tables 4 and 8) that the experimental values agree fairly well with the results obtained from equation (I) when using the following values for  $\delta_2$ ,  $x_2^i$  (ideal solubility), and  $\overline{V}_2$  (the partial molal volume of the gas):

	$x_2' \times 10^4$	$\overline{V}_{2}$	$\delta_{2}$
hydrogen	5.5	37	5.1
oxygen	17.6	46	5.7
carbon monoxide	15.5	<b>52</b>	5.8

It has further been shown that when equation (I) is used for the calculation of solubility in polar solvents, there will be certain discrepancies between the

calculated and the experimentally determined results. The deviations are greatest for the solvents which have the highest dielectric constants.

- 3. Skirrow has shown by experiments that the solubility of carbon monoxide in benzene falls off when a substance, as e.g. naphtalene, is dissolved in the benzene. It is shown that it is possible on the basis of equation (I) to calculate this reduction in the solubility (Table 5).
- 4. The solubility parameters for a number of monohydric alcohols are calculated on the basis of experiments on the solubility of carbon monoxide in the alcohols concerned (Table 6). It is shown (Table 7) that the solubilities calculated for hydrogen, nitrogen, and oxygen in methyl alcohol and ethyl alcohol show fairly good agreement with the experimental determinations found in the literature.

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