

SOLUBILITY OF GASES IN NORMAL-ALKANES

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Solubilities of a number of gases were determined in members of the n-pentane — n-hexadecane series. Relationships between gas solubilities and physico-chemical properties of members of the series were studied,

It was found that gas solubilities varied linearly in the function of reciprocal parachor values of the solvents, and the slopes of the lines were proportional to the sizes and mean polarizabilities of the gases dissolved,

An equation was derived to calculate solubilities of apolar and moderately polar gases in n-alkanes. The equation is not applicable for polar gases, because the interactions between the gas and liquid molecules cannot be neglected in such cases.

It is well known that members of homologous series in organic chemistry display certain regularities - frequently characterized by mathematical relationships - as far as some of their physico-chemical properties are concerned. The relationship describing the change of a certain property of the homologous series is generally not a simple, linear, but more complicated - though formulatable - relationship. Because the solubility of a given gas

depends on both the gas and the solvent, the hypothesis stating the existence of a relationship between the solubility values obtained in a homologous series and the carbon number of the members of the series seemed reasonable. This hypothesis is supported by the work of SEYMOUR and SOSA [1], who stated that the solubility parameters defined by HILDEBRAND and SCOTT [2, 3], known in the literature as cohesive energy density (CED), are linear functions of the logarithms of the carbon numbers.

Some of the regularities found in the course of studies on the solubility of gases in members of the normal-alkane homologous series are presented here.

## 1. EXPERIMENTAL

There are only a very limited number of gas solubility data measured in normal-alkanes available in literature. Therefore, solubilities of 15 gases in 12 members of the normal-alkane series were determined. The first member of the series was n-pentane, the last one n-hexadecane ( $C_5$  through  $C_{16}$ ). Measurements were carried out at a constant 25 °C temperature. (Later on, solubility values were also obtained at 40 °C to check the validity of the relationships derived at 25 °C.)

Gas solubility measurements were carried out - as usual - in the saturation apparatuses [4]. Partial pressure of the component to be dissolved was always kept at 760 torr in the equilibrium mixture, so the gas solubility values are reported as Ostwald coefficients. Analytical grade reagents of Hungarian and foreign origin were used (both liquids and gases). In those few cases where literature data were available, the measured values agreed to them within  $\pm 4\%$ . An absolute error of  $\pm 3\%$  was calculated for the measurements made.

## 2. DISCUSSION

Studying the solubility data two general conclusions can be made:

- solubility of a given gas (expressed either as Ostwald or Bunsen coefficient) decreases with the increasing carbon number
- solubility of apolar gases in a given n-hydrocarbon increases with increasing molecular size of the gas (a similar tendency can also be noted with polar gases).

Parachors of the members were used to take into consideration the properties of the homologous series. There are a number of factors compounded in the parachor value, each of which are significantly influence solubility; it can be used over a wide temperature range, its values are sums of increments and so the value is easily calculated.

Solubilities of the gases studied were plotted as functions of the reciprocal parachors of the n-alkanes (Figure 1a and 1b). The following conclusions were drawn:

- There is a linear relationship between the gas solubilities and the reciprocal parachors of the members of the n-alkane series - except for the value of ammonia. Extrapolated lines of the apolar gases meet in the origin. Lines of the moderately polar gases also tend to here, at least within the limits of experimental error. Lines of the strongly polar gases have positive interception values. (It follows that in the case of apolar and moderately polar gases, zero gas solubility would be found in n-hydrocarbons containing an infinitely large number of carbon atoms, while even in this case there would be some solubility for the strongly polar gases, such as  $\text{SO}_2$  and  $\text{H}_2\text{S}$ .)
- Slopes of the gas solubility lines are different for each gas, the bigger or more polarizable the gas molecules, the bigger the slope values.

There are two significant consequences of the above two observations:

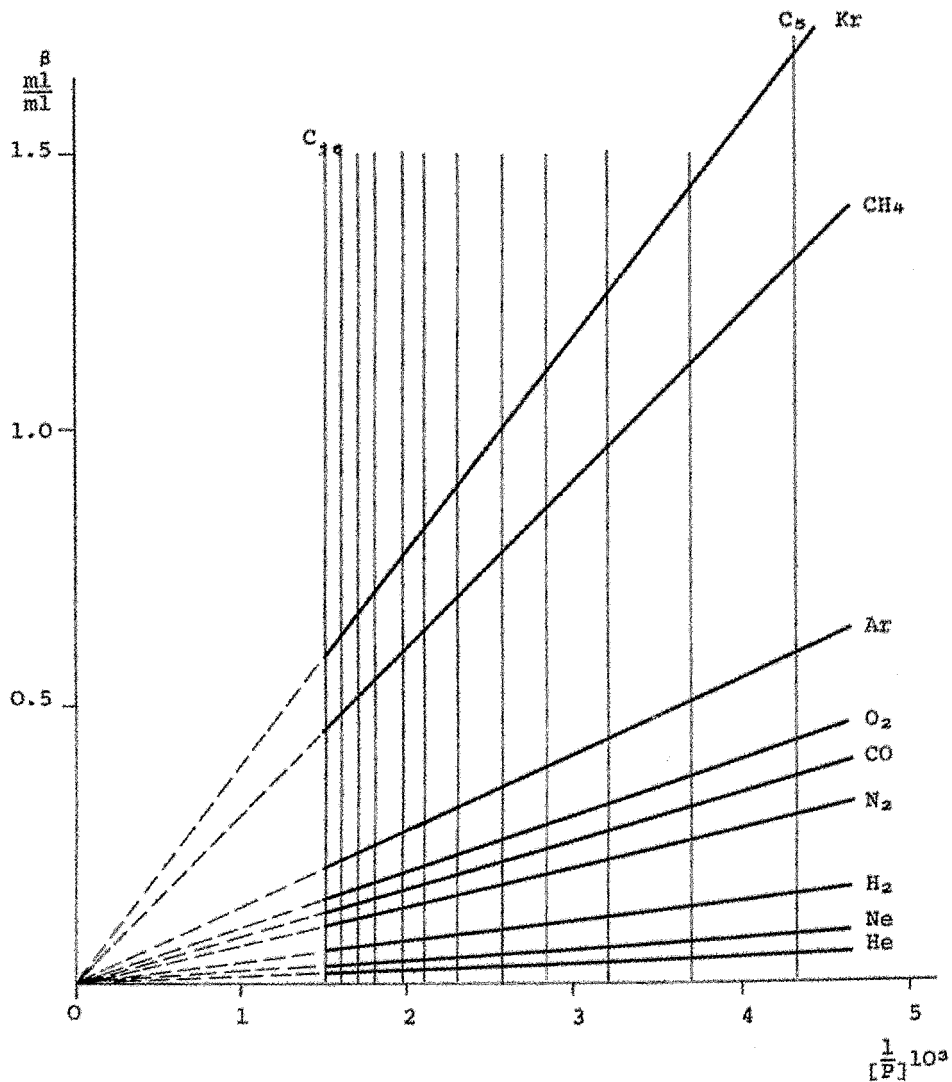


Fig. 1a. Relationship of Gas Solubility and Parachors of n-Alkanes

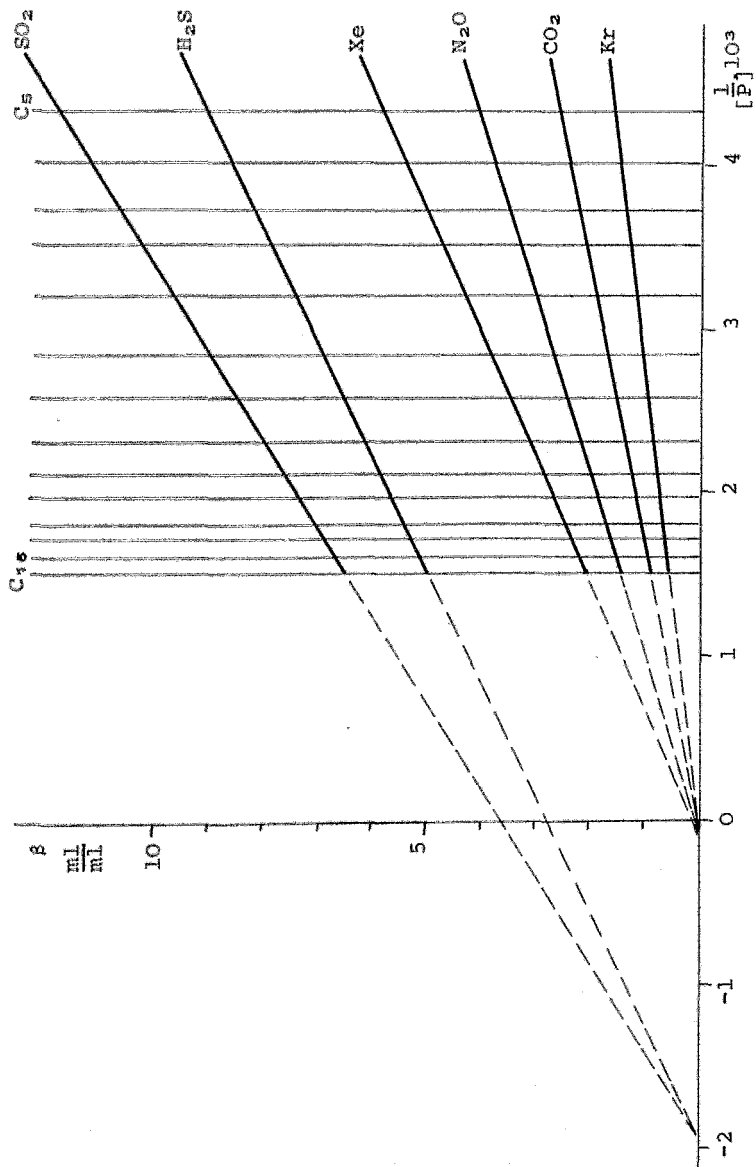


Fig. 1b. Relationship of Gas Solubility and Parachors of n-Alkanes

- a) The following relationship holds for the solubility of apolar gases measured in the n-alkane series:

$$\beta_n [P]_n = \text{constant}$$

where:

$\beta_n$  is the solubility of the apolar or moderately polar gas in the  $n^{\text{th}}$  member of the series,

$[P]_n$  is the parachor value of the n-alkane proper.

The relationship for the more polar gases can only be formulated if the intercepts are known:

$$(\beta-b)[P] = \text{constant}$$

where:

b is the intercept of the line.

- b) The practical value of the relationship mentioned in a). is that once the solubility of an apolar or moderately polar gas is known in any member of the series, the solubility found in the remainder can be calculated. (The same value for polar gases can only be calculated from two known data.)

As it was previously mentioned, slopes of the lines increase with increasing polarizability, therefore the relationship between the mean polarizability and the slope value was studied. (Because parachors are expressed as functions of the solvent molar volumes,  $[P] = V\sigma^{1/4}$ , the mean polarizability referring to one mole gas was used. The following simple relationship was graphically obtained between the slope (A) and mean polarizability data ( $\bar{\alpha}$ ):

$$\lg A = k\bar{\alpha}N - 2$$

(where N is the Avogadro number, k is a proportionality constant). This is graphically shown in Figure 2.

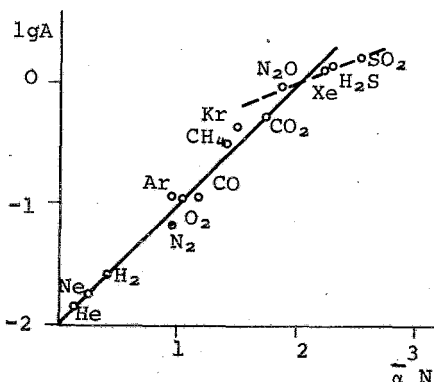


Fig. 2. Relationship of slopes and mean gas polarizabilities

Dimensional analysis was used to show that  $k$  was no dimensionless, but had the dimension of  $(\text{dyn/cm})^{\frac{1}{2}}$ , i.e. it could be derived from interfacial tension. Thus the interfacial tension measured between the gas and its liquid form was taken at the  $1/4$ -th power and substituted into the equation, which took the following final form:

$$\lg \beta = 1 + \sigma_g^{\frac{1}{4}} \bar{\alpha}_g N - \lg [P]_1$$

Using the above equation the Ostwald coefficients were calculated and compared to the ones measured. Deviation was expressed as a relative error in the usual manner:

$$\% \text{ Rel. error} = \frac{\beta_{\text{measured}} - \beta_{\text{computed}}}{\beta_{\text{measured}}} \times 100$$

(Parachor values were taken from ALTENBURG's paper [6], while the mean polarizability values were obtained from the book of HIRSCHFELDER et al [5]. Interfacial tension values for gases were obtained from handbooks or if not available, they were calculated by an approximative method [9].

Data measured and obtained by the derived equation are shown in Table 1. Relative deviations are also shown.

Using the co-ordinates given in Figure 1, solubilities of apolar and moderately polar gases are given by the following equation:

$$\beta = \frac{A}{[P]} 10^3$$

As  $\lg A = k\bar{\alpha}N - 2$ , the above equation can be rearranged:

$$\lg \beta = 1 + k\bar{\alpha}N - \lg [P]$$

Dimensional analysis was used

to show that  $k$  was no dimen-

sionless, but had the dimension of  $(\text{dyn/cm})^{\frac{1}{2}}$ , i.e. it could be derived from interfacial tension. Thus the interfacial tension measured between the gas and its liquid form was taken at the  $1/4$ -th power and substituted into the equation, which took the following final form:

Table 1. Solubility of gases in n-alkanes at 25 °C

Gas solvent	He			Ne			Ar			Kr		
	$\beta$ meas.	$\beta$ calc.	Rel.de- viation	$\beta$ meas.	$\beta$ calc.	Rel.de- viation	$\beta$ meas.	$\beta$ calc.	Rel.de- viation	$\beta$ meas.	$\beta$ calc.	Rel.de- viation
C5	0,055	0,0498	9,38	0,087	0,0853	1,95	0,600	0,5814	3,10	1,668	1,670	0,13
C6	0,044	0,0425	3,29	0,076	0,0728	4,21	0,477	0,4964	-4,07	1,411	1,425	-0,97
C7	0,044	0,0362	17,72	0,069	0,0634	8,11	0,418	0,4322	-3,35	1,229	1,241	-0,98
C8	0,037	0,0328	11,32	0,057	0,0562	1,40	0,373	0,3827	-2,60	1,095	1,099	-0,42
C9	0,028	0,0295	- 5,50	0,047	0,0506	-7,65	0,338	0,3446	-1,95	0,988	0,990	-0,11
C10	0,025	0,0268	- 7,16	0,045	0,0458	-1,77	0,305	0,3126	-2,49	0,886	0,898	-1,32
C11	0,022	0,0245	-11,27	0,043	0,0419	2,55	0,296	0,2856	3,51	0,825	0,821	0,57
C12	0,022	0,0226	- 2,64	0,040	0,0386	3,50	0,263	0,2635	-0,19	0,756	0,757	-0,07
C13	0,019	0,0209	-10,11	0,036	0,0358	0,55	0,247	0,2440	1,21	0,700	0,701	-0,20
C14	0,017	0,0195	-14,59	0,033	0,0330	0,00	0,230	0,2273	1,17	0,657	0,653	0,62
C15	0,016	0,0182	-14,06	0,031	0,0312	0,64	0,218	0,2130	2,29	0,625	0,612	0,99
C16	0,015	0,0172	-14,53	0,027	0,0291	7,77	0,206	0,2004	2,81	0,583	0,576	1,22
Xe												
C5	5,916	5,906	0,16	0,142	0,156	-9,85	0,306	0,299	2,25	0,432	0,428	0,97
C6	5,065	5,042	0,45	0,120	0,134	-11,66	0,262	0,252	2,56	0,368	0,365	0,76
C7	4,432	4,390	0,94	0,109	0,116	-6,42	0,229	0,222	2,93	0,322	0,318	1,21
C8	3,897	3,888	0,22	0,096	0,103	-7,29	0,199	0,197	1,06	0,284	0,282	0,85
C9	3,493	3,501	-0,23	0,088	0,093	-5,68	0,178	0,177	0,39	0,258	0,254	1,71
C10	3,165	3,175	-0,30	0,081	0,084	-3,70	0,156	0,161	-3,08	0,231	0,230	0,43
C11	2,914	2,901	0,46	0,079	0,077	2,53	0,146	0,147	-0,62	0,211	0,210	0,38
C12	2,685	2,676	0,34	0,078	0,071	8,84	0,132	0,136	-2,65	0,199	0,194	2,56
C13	2,478	2,479	-0,05	0,074	0,065	12,16	0,124	0,126	-0,81	0,179	0,180	-0,39
C14	2,314	2,310	0,17	0,064	0,061	4,68	0,116	0,117	-0,88	0,170	0,167	1,67
C15	2,150	2,265	-5,33	0,062	0,067	8,06	0,111	0,109	1,35	0,152	0,157	-3,09
C16	2,019	2,036	-0,83	0,060	0,054	10,00	0,102	0,103	-1,08	0,145	0,148	-1,72
Oa												



Table 1. (continued)

Gas sol- vent	CH <sub>4</sub>			CO <sub>2</sub>			H <sub>2</sub> S
	$\beta$ meas.	$\beta$ calc.	Rel. de- viation	$\beta$ meas.	$\beta$ calc.	Rel. de- viation	$\beta$ meas.
C <sub>5</sub>	1,279	1,282	-0,24	2,685	2,599	3,20	9,147
C <sub>6</sub>	1,146	1,095	4,46	2,270	2,236	1,50	8,230
C <sub>7</sub>	0,956	0,953	0,28	1,976	1,947	1,47	7,520
C <sub>8</sub>	0,849	0,844	0,58	1,746	1,724	1,26	6,986
C <sub>9</sub>	0,762	0,760	0,20	1,550	1,552	-0,01	6,560
C <sub>10</sub>	0,693	0,690	0,52	1,397	1,408	-0,79	6,232
C <sub>11</sub>	0,633	0,630	0,47	1,227	1,287	-0,78	5,949
C <sub>12</sub>	0,586	0,581	0,84	1,179	1,188	-0,76	5,698
C <sub>13</sub>	0,541	0,538	0,55	1,091	1,099	-0,73	5,501
C <sub>14</sub>	0,508	0,502	1,18	1,015	1,024	-0,90	5,305
C <sub>15</sub>	0,474	0,470	0,82	0,950	0,959	-0,95	5,152
C <sub>16</sub>	0,448	0,442	1,18	0,895	0,903	-0,89	4,999
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Gas sol- vent	CO			N <sub>2</sub> O			SO <sub>2</sub>
	$\beta$ meas.	$\beta$ calc.	Rel. de- viation	$\beta$ meas.	$\beta$ calc.	Rel. de- viation	$\beta$ meas.
C <sub>5</sub>	0,395	0,354	10,51	4,093	4,582	-11,94	11,876
C <sub>6</sub>	0,329	0,302	8,27	3,471	3,568	-2,79	10,876
C <sub>7</sub>	0,282	0,263	6,81	3,034	3,106	-7,20	9,790
C <sub>8</sub>	0,234	0,233	0,56	2,729	2,751	-0,81	9,092
C <sub>9</sub>	0,217	0,210	3,41	2,478	2,477	-0,01	8,558
C <sub>10</sub>	0,191	0,190	0,47	2,270	2,247	1,01	8,110
C <sub>11</sub>	0,177	0,174	1,86	2,063	2,053	0,48	7,826
C <sub>12</sub>	0,166	0,160	3,49	1,877	1,894	-0,91	7,444
C <sub>13</sub>	0,151	0,148	1,72	1,779	1,754	1,41	7,182
C <sub>14</sub>	0,136	0,138	-1,62	1,637	1,634	0,18	6,942
C <sub>15</sub>	0,128	0,129	-1,17	1,550	1,530	1,29	6,735
C <sub>16</sub>	0,120	0,122	-1,50	1,484	1,440	2,96	6,571

Table 2. Solubility of gases in n-alkanes at 40 °C

Gas solvent	Ar			N <sub>2</sub>			O <sub>2</sub>		
	$\beta_{meas.}$	calc.	Rel. deviation	$\beta_{meas.}$	calc.	Rel. deviation	$\beta_{meas.}$	calc.	Rel. deviation
C <sub>5</sub>	0.462	0.433	1.34	0.266	0.241	9.40	0.362	0.339	6.35
C <sub>6</sub>	0.390	0.370	5.13	0.223	0.206	7.62	0.291	0.289	0.69
C <sub>7</sub>	0.333	0.322	3.30	0.180	0.179	0.55	0.264	0.251	4.92
C <sub>8</sub>	0.292	0.285	2.40	0.161	0.159	1.24	0.229	0.223	2.62
C <sub>9</sub>	0.265	0.257	3.02	0.145	0.143	1.38	0.200	0.201	-0.5
C <sub>10</sub>	0.231	0.233	-0.87	0.131	0.130	0.76	0.183	0.182	0.55
C <sub>11</sub>	0.214	0.213	0.47	0.122	0.119	2.46	0.165	0.163	1.21
C <sub>12</sub>	0.196	0.196	-	0.105	0.109	-3.81	0.153	0.153	-
C <sub>13</sub>	0.181	0.182	-0.55	0.100	0.101	-1.00	0.144	0.142	1.39
C <sub>14</sub>	0.169	0.169	-	0.092	0.092	-	0.131	0.132	-0.76
C <sub>15</sub>	0.160	0.158	1.25	0.085	0.088	3.53	0.126	0.124	1.59
C <sub>16</sub>	0.143	0.149	-4.20	0.081	0.082	1.23	0.119	0.116	2.52
							$\beta_{meas.}$	$\beta_{SO_2}$	$\beta_{meas.}$
C <sub>5</sub>	2.175	2.140	1.61	3.688	3.642	1.24	6.93	8.90	
C <sub>6</sub>	1.859	1.827	1.67	3.146	3.109	1.18	6.23	8.02	
C <sub>7</sub>	1.602	1.555	2.98	2.712	2.707	0.18	5.69	7.34	
C <sub>8</sub>	1.420	1.409	0.77	2.415	2.398	0.73	5.28	6.82	
C <sub>9</sub>	1.275	1.266	0.71	2.153	2.159	-0.28	4.96	6.40	
C <sub>10</sub>	1.151	1.150	0.09	1.952	1.958	-0.31	4.71	6.08	
C <sub>11</sub>	1.051	1.051	-	1.803	1.789	0.77	4.50	5.81	
C <sub>12</sub>	0.969	0.970	-0.1	1.655	1.651	0.24	4.31	5.56	
C <sub>13</sub>	0.892	0.899	-0.78	1.528	1.529	0.07	4.15	5.36	
C <sub>14</sub>	0.835	0.837	0.24	1.421	1.391	2.11	4.02	5.18	
C <sub>15</sub>	0.782	0.784	0.26	1.323	1.334	-0.83	3.89	5.04	
C <sub>16</sub>	0.733	0.736	0.68	1.255	1.255	-	3.80	4.90	

It can be seen that there is a rather good agreement between the measured and calculated values in the case of apolar and moderately polar gases. This is especially true for the gases with accurately known parameters, such as  $\text{CO}_2$ ,  $\text{CH}_4$ , Xe, Kr and  $\text{O}_2$ . The greatest deviation occurs in the cases where the interfacial tension was obtained from approximations and where the other constants required for the calculation were rather uncertain. Such gases were helium and neon. Solubilities of two polar gases were not calculated ( $\text{H}_2\text{S}$  and  $\text{SO}_2$ ), because these gases had positive interceptions and further research is needed to determine their meaning and true numerical values. It is worth noting that other gas solubility measurements of the authors - such as those obtained with n-alcohols - proved that the interactions must not be neglected in the case of apolar - polar and polar -polar gas -liquid systems.

As mentioned earlier, further measurements were made at  $40^\circ\text{C}$  to check the validity of the relationships obtained. Calculated values were compared to those measured. It was found that the appropriately derived equation also described the solubilities at  $40^\circ\text{C}$ . There was only a slight deviation between the calculated and measured data, shown in Table 2. Again no calculations were made in the case of  $\text{H}_2\text{S}$  and  $\text{SO}_2$  because to do so would involve the interception values. This problem will be reviewed in a later paper.

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## REZÜME

Экспериментальным путем определялась растворимость многих газов в членах гомологического ряда нормальный пентан - нормальный гексан, исследовалось, какая зависимость имеется между растворимостью и химическими свойствами жидкостей данного гомологи - ческого ряда.

Установлено, что в зависимости от обратного числа парахорных значений растворителей растворимость газов изменяется линейно и тангенс таких полученных прямых пропорционален размеру растворимой молекулы и ее средней полярности.

Из рассмотренных систем газ - жидкость для типа неполярных - полярных и слабо полярных - неполярных выведено уравнение, с помощью которого может быть рассчитана растворимость газов в нормальных алканах. Это уравнение для полярных газов неприменимо по скольку в таком случае взаимодействие между молекулами газа и жидкости уже нельзя отбросить.

Авторы приводят в виде таблиц результаты, полученные экспериментальным и расчетным путем.