difficulty and irregularities which are liable to be encountered because of the variation in the quality of the adsorbent.

TABLE II

RESULTS WITH SECOND IRON OXIDE SAMPLE

Compound adsorbed	Adsorbed by Sample No. 1, %	Adsorbed by Sample No. 2, %
Piperidine	25.2	19.6
Nicotine	0.2	2.7
Arginine	34.2	15
Quinoline	1	22.9
Glutamic acid	81.6	15.53
Aspartic acid	87.5	14.9

Further experimentation on the effects of different factors on adsorption of organic compounds is contemplated for the future.

Summary

The extent to which eighteen pure organic compounds are adsorbed from 0.01 *M* solutions on the hydrous oxides of silicon, aluminum and iron and on fuller's earth has been determined. It is found that the extent of adsorption on silica of the compounds used is roughly proportional to their basic strengths, and roughly proportional to their acidic strengths in the case of adsorption on alumina. Adsorption by hydrous iron oxide was very irregular, possibly due to impurities on the adsorbent. The extent of adsorption by fuller's earth was somewhat similar to the adsorption by silica, but in a few cases there was no parallel.

EUGENE, OREGON

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF STANFORD UNIVERSITY]

THE INTERNAL PRESSURE OF LIQUID CARBON DIOXIDE FROM SOLUBILITY MEASUREMENTS

BY ELTON L. QUINN[1]

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In a previous paper[2] on the surface tension of liquid carbon dioxide it was found that carbon dioxide had an internal pressure much the same as carbon tetrachloride, toluene and chloroform. This was determined by comparing the total energy of surface formation with the values found for these compounds, according to the method of Hildebrand.[3] It seemed desirable to check these results with the solubility data of liquid carbon dioxide but it was found that the few determinations[4,5] of a quantitative

[1] On sabbatical leave from the University of Utah.

[2] Quinn, THIS JOURNAL, **49**, 2704 (1927).

[3] Hildebrand, "Solubility," Chemical Catalog Company, New York, **1924**, p. 111.

[4] Thiel and Schulte, *Z. physik. Chem.*, **96**, 328 (1920).

[5] Büchner, *ibid.*, **54**, 665 (1906).

nature available did not lend themselves readily to a calculation of this kind. It was thought best, therefore, to make a series of determinations using naphthalene and iodine as solutes and if possible to apply the method of Hildebrand[6] in calculating the relative internal pressure of the solvent.

Experimental Procedure

Fig. 1 is a drawing of the reaction tube in which the solubility determinations were made. It will be noted that this type of reaction tube is essentially the same as that ordinarily used for liquid ammonia, the slight modifications being made to increase the strength and to facilitate handling in the thermostat. These tubes were made of soft glass tubing having an internal diameter of about 8 mm. and a 2mm. wall. The connecting tube between the measuring and reaction tubes had an internal diameter of about 4 mm. It was found that a smaller tube at this point did not work satisfactorily as it prevented the free passage of the liquid from one tube to the other. The tube was carefully cleaned with a boiling solution of sulfuric and nitric acids, then washed and dried. A plug of glass wool was placed in the end of the leg designed for the solute and the proper quantity of solute introduced. Both legs were then sealed, great care being taken to keep the flame away from the open ends. The measuring tube was then graduated, the graduation marks being etched into the glass with a solution of hydrofluoric acid.

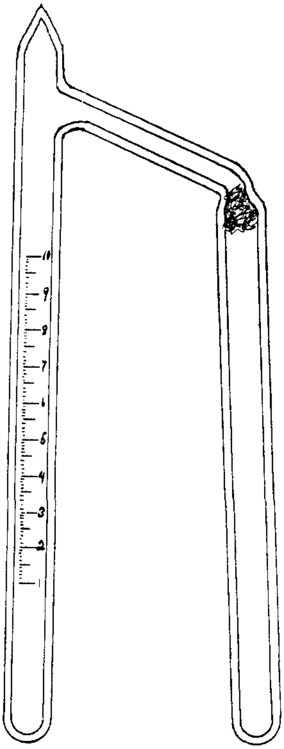

Fig. 1.

The method of introducing the liquid carbon dioxide into the tubes was essentially the same as that described in connection with the surface tension measurements.[2] In this case, however, the calcium chloride drying tower was made from an iron pipe 6.4 cm. in diameter by 56 cm. high. A safety valve fitted to the top of the tower made it possible to admit the gas to the reaction tube under any pressure up to the saturation pressure of liquid carbon dioxide.

Equilibrium between the solution and the solute was obtained by pouring the liquid carbon dioxide into the reaction tube and causing it to flow backwards and forwards over the solute for six to eight hours while it was kept at constant temperature in a thermostat. The thermostat was provided with a mechanical arrangement which kept the contents

[6] Hildebrand, *Proc. Nat. Acad. Sci.*, **13**, No. 5, 267 (1927).

of the tubes agitated during the time required to reach equilibrium. It was found in preliminary tests that tubes agitated one, two or three hours gave practically the same solubility; it was therefore assumed that a run of six or seven hours would be sufficient to reach equilibrium in all cases.

The naphthalene solution was, of course, colorless but the iodine solution was of a beautiful violet color. This latter fact is of some importance as it indicates the absence of solvation in the iodine solutions and places carbon dioxide in the class with "regular" solvents.

A few minutes before the end of each run the solubility tube, which had been hanging with the reaction leg below, was turned over so that the measuring leg came underneath and the agitation was continued until all of the solution had run into this part of the apparatus. Rubber gloves were worn whenever any of the tubes were handled in order to protect the hands in case one exploded and also to prevent any temperature change in the solutions. When the tube was removed from the thermostat the height of the liquid was quickly read and it was then placed in a freezing mixture and allowed to remain until the solution had frozen to a solid mass. A small hole was then melted in the top of the measuring tube and it was allowed to remain in the freezing mixture until the whole system had reached room temperature, which usually took from twenty-four to thirty-six hours depending upon the amount of solid carbon dioxide in the freezing mixture. When the tube was removed from the ether-bath the solute was found in beautiful crystals in the bottom of the measuring leg. The measuring tube was then sealed off from the rest of the apparatus and preserved until a convenient time for analysis.

The amount of naphthalene in each solution was determined by weighing the solid left after the solvent had evaporated. The iodine was determined by washing it out of the measuring tube with a strong solution of potassium iodide and titrating with a standard solution of sodium thiosulfate. The solution volume was found by filling the tube with water to the mark reached by the solution and weighing. From the weight of water the volume of the solution was calculated.

The operations described above gave the weight of solute and the volume of the solution. This was, of course, not sufficient to calculate the solubility of these substances in terms of their mole fractions. The densities of the solutions were determined by means of the special type of pycnometer shown in Fig. 2. In this tube was placed a definite quantity of the solute just sufficient to saturate the solution and leave a slight excess at the highest temperature at which readings were to be made. Liquid carbon dioxide was then admitted and the amount carefully adjusted so that it would nearly fill the tube at the highest temperature of the laboratory. It was very important that the liquid did not completely fill the tube as this condition always resulted in an explosion. After weighing the pycnometer and its contents, it was placed in a thermostat and the height of the meniscus determined at several temperatures. The solution was then frozen and the tube opened by melting a very small hole in the tip. After the solvent had evaporated at a low temperature, the tube was weighed. The difference between this weight and the weight of the tube plus contents gave the weight of the carbon dioxide in the liquid and gaseous state. The solute was then washed out and the tube again weighed after drying. The difference between this and the previous weight gave the weight of the solute. The tube was then calibrated to the marks reached at the various temperatures. Subtracting from the total weight of carbon dioxide the weight of the vapor, which was calculated by means of Amagat's[7] values, and correcting for the small amount of undissolved solute, the weight of the solution was obtained. In this manner it was possible to determine the density of the solution over a range of about eight degrees. It was not possible to make these determinations much below the temperature of the laboratory on account of the difficulty of keeping the temperature of the tube below the danger point during the weighing operation.

The question arose as to whether the density tubes had the same volume when filled with liquid carbon dioxide, exerting a pressure of 50 to 60 atmospheres on the inside, that they had after the carbon dioxide had been removed. In order to test this point a side tube was sealed onto a test-tube and then bent into a shape something like the letter S. This was filled with distilled water until it overflowed through the side tube. The pycnometer filled with carbon dioxide was then carefully lowered to the bottom of the test-tube and the water overflowing through the side tube was collected in a weighing bottle and weighed. This was repeated several times and the carbon dioxide was then discharged and several more readings were taken sometimes several days apart in order to give the glass time to regain its former condition. In no case could a difference greater than the experimental error be detected, and as the volume of the tube could be determined within less than 0.1% the change in the tube, if any, must be smaller than this and could, of course, be neglected in this work.

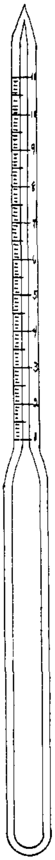

Fig. 2.

The densities of the solutions at lower temperatures were determined in the following manner. First, the solubility curve was constructed by plotting the weight of solute obtained from a definite volume of solution against the temperature and extrapolating to zero concentration. This gave the point where the density of the solution became the same as the

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[7] Amagat, *Ann. chim. phys.*, [6] **29**, [68] (1893).

pure solvent. Then on large scale cross section paper the density curve of the pure solvent was constructed using the density values of Behn[8] and Jenkin.[9] The experimental densities of the solutions were plotted beside this curve for the pure solvent and curves constructed which cut this solvent curve at the temperature where the concentration of the solute became zero. These solution curves came so close to the curve of the pure solvent that no great accuracy was necessary at the junction point. The values read from these curves are shown in Table I.

TABLE I

VALUES READ FROM THE CURVES

Temp., °C.	Density, pure solvent	Density, naphthalene solution	Density, iodine solution
25	0.710	0.740	0.720
20	.770	.790	.775
15	.816	.833	.822
10	.858	.872	.863
5	.896	.906	.898
0	.927	.938	.929
− 5	.955	.967	.957
−10	.981	.993	.982
−15	1.005	1.018	1.006
−20	1.031	1.040	1.031

Purification of Material

The carbon dioxide used in these determinations was obtained from commercial cylinders of the liquefied gas manufactured by the Pure Carbonic Company of Berkeley, California. The analysis of the gas showed a purity of 99.85% of carbon dioxide with a trace of water vapor when the sample was taken from the top of the cylinder. Although oil was found when the gas was taken from an inverted tank, no evidence of it was ever found when the sample was taken from the top of the cylinder.

The naphthalene used was Baker's Analyzed, Lot No. 4425, with a melting point of 79°. This was fractionally distilled several times, the middle fraction only being collected from each distillation. This was crystallized from redistilled alcohol twice and dried in a desiccator for several weeks. The freezing point of the purified naphthalene was then determined by taking the cooling curve of a large sample in a test-tube. Several determinations gave values between 79.9 and 80.2° with an average of 80°. The iodine used was also Baker's Analyzed. This was resublimed once in the presence of potassium iodide before it was used.

The results obtained from these solubility determinations are shown in Tables II and III.

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[8] Behn, *Ann. Physik,* [4] **3,** 733 (1900).

[9] Jenkin, *Proc. Roy. Soc.* (*London*), **98A,** 170 (1920).

TABLE II

SOLUBILITY OF NAPHTHALENE IN LIQUID CARBON DIOXIDE AT VARIOUS TEMPERATURES

Det. no.	Temp., °C.	Vol. of CO_2 soln., cc.	Wt. of CO_2, g.	Wt. of $C_{10}H_8$ found, g.	Wt. of $C_{10}H_8$ per mole of CO_2, g.	Av. weight, g.	Mole frac.	Log N
1	25	3.387	2.456	0.0502	0.8993			
2	25	4.044	2.932	.0600	.9004			
3	25	6.822	4.946	.1016	.9038	0.901	0.00698	−2.156
4	20	4.851	3.760	.0722	.8449			
5	20	4.935	3.823	.0748	.8609			
6	20	6.054	4.691	.0913	.8563	.854	.00662	−2.179
7	10	2.481	2.131	.0316	.6525			
8	10	5.817	4.996	.0758	.6675			
9	10	3.105	2.667	.0397	.6549	.658	.00511	−2.292
10	0	6.726	6.241	.0678	.4780			
11	0	4.918	4.563	.0501	.4831			
12	0	4.672	4.335	.0469	.4760	.479	.00372	−2.429
13	−21	4.631	4.809	.0255	.2333			
14	−21	3.038	3.156	.0165	.2300			
15	−21	5.379	5.586	.0291	.2292	.231	.00180	−2.745

TABLE III

SOLUBILITY OF IODINE IN LIQUID CARBON DIOXIDE AT VARIOUS TEMPERATURES[a]

Det. no.	Temp., °C.	Vol. of CO_2 soln., cc.	Wt. of CO_2, g.	Wt. of I_2 found, g.	Wt. of I_2 per mole of CO_2, g.	Av. weight, g.	Mole frac.	Log N
1	25	5.140	3.700	0.0075	0.0900			
2	25	3.860	2.779	.0058	.0931	0.0915	0.000361	−3.442
3	20	5.002	3.876	.0068	.0772			
4	20	8.229	6.377	.0112	.0777	.0774	.000305	−3.515
5	10	4.273	3.688	.0044	.0520			
6	10	4.106	3.543	.0043	.0533	.0526	.000207	−3.683
7	0	5.451	5.064	.0039	.0343			
8	0	4.561	4.237	.0033	.0350	.0347	.000136	−3.864
9	−11.4	3.360	3.322	.0014	.0191	.0191	.0000753	−4.123
10	−21	3.493	3.615	.00089	.0105			
11	−21	4.715	4.880	.00111	.0100	.0102	.0000405	−4.392

[a] This is the second set of iodine determinations made. The agreement between the averages in the two sets was quite satisfactory but the agreement between the individual measurements in the first set was not.

Discussion of Results

The relation between the internal pressure of a solvent and the deviation of its solutions from Raoult's law has been discussed in detail by Hildebrand.[10] He points out that one of the most important methods of estimating internal pressure differences between various solvents is to plot their solubility curves for the same solute (log N_2 against $1/T$) with the curve of the ideal solvent. The displacement of these curves from

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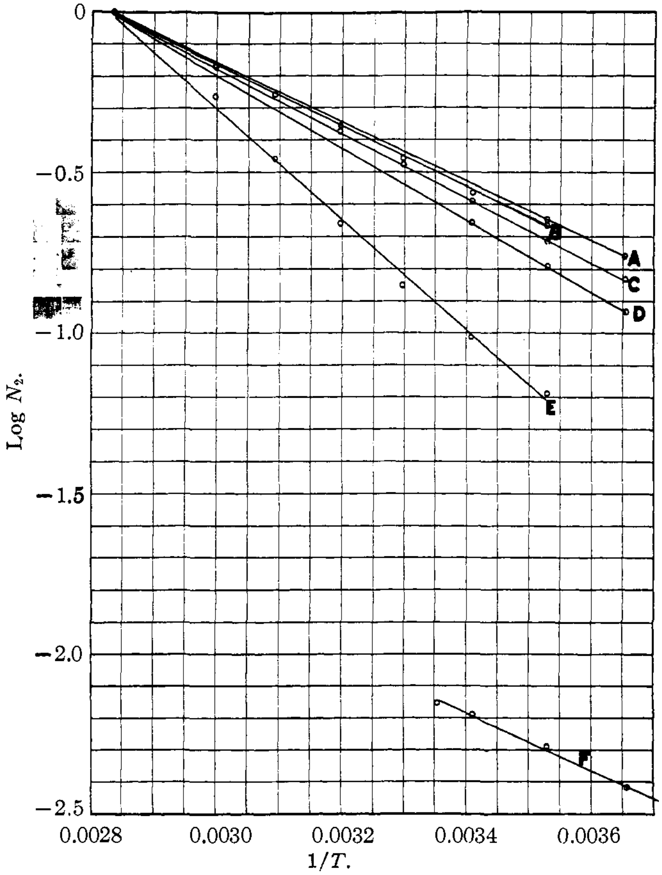
[10] Ref. 3, p. 115.

that of the ideal solution is a measure of their internal pressure differences and from such a plot it is possible to arrange the solvents in an internal pressure series. This method has the disadvantage of requiring the plotting of the curves before the position of any solvent in the series can be assured and in addition lacks quantitative significance. Recently Hildebrand[6] developed an equation by means of which this deviation can be calculated quantitatively for what he calls regular solvents and which has the added advantage that the approximate internal pressure factor can be calculated from a single solubility measurement.

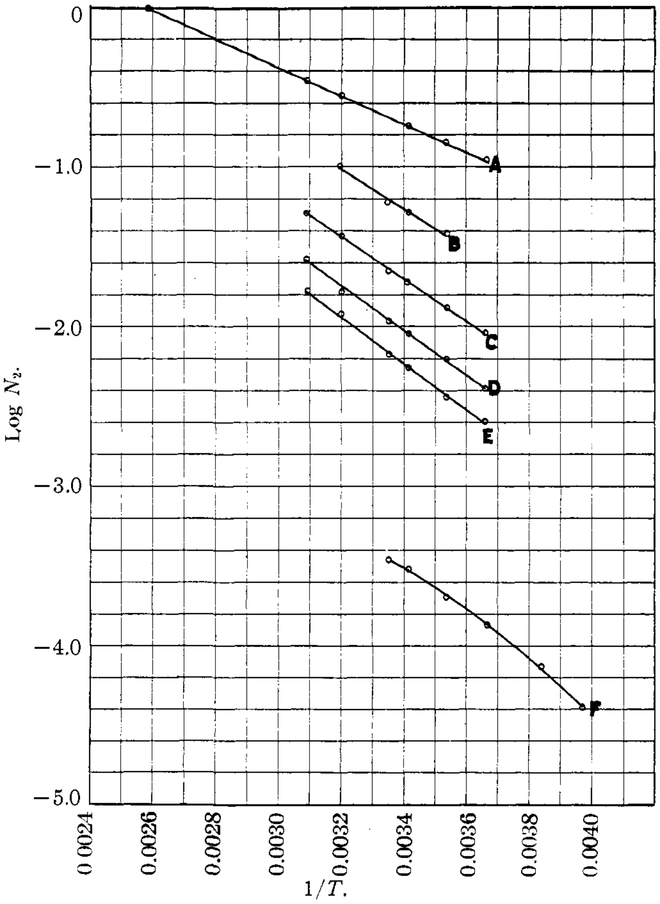


A, ideal; B, C_6H_5Cl; C, C_6H_6; D, CCl_4; E, C_6H_{14}; F, CO_2.

Fig. 3.—Solubilities of naphthalene.

The Hildebrand equation may be written in the following form, $\ln N_2^R/N_2 = bN_1^2/RT$, in which N_2^R and N_2 are mole fractions of the ideal and experimental solubilities of a solute, respectively, at the absolute temperature T, while N_1 is the mole fraction of the solvent, b is a constant which is related to the difference in internal pressure for the two components and R the usual gas constant or 1.99. The ideal solubility of N_2^R can be calculated from the heat of fusion and melting point of the solute.

Ward[11] has made solubility determinations of naphthalene in a number of solvents and Fig. 3 shows a few curves plotted from his data together with the curve for the solubility of naphthalene in carbon dioxide. This gives a clear idea of the relation of carbon dioxide as a solvent to the more common solvents and indicates that the internal pressure of liquid carbon dioxide is very low. Fig. 4 plotted in the same manner from data given by Hildebrand shows the solubility of iodine in various solvents. This also indicates that carbon dioxide has a very low internal pressure.



A, ideal; B, $CHBr_3$; C, $CHCl_3$; D, CCl_4; E, C_7H_{16}; F, CO_2.

Fig. 4.—Solubilities of iodine.

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[11] Ward, *J. Phys. Chem.*, **30**, 1327 (1926).

If we write the Hildebrand equation as $(T \log N_2/N_2^R)/N_1^2 = k$ and calculate the value of k for the solutions of naphthalene and iodine in liquid carbon dioxide at different temperatures, we obtain the results indicated in Tables IV and V.

TABLE IV

DATA FOR NAPHTHALENE

Log N_2^R	Log N_2	N_2	T	k
−0.490	−2.156	0.00698	298	499
− .542	−2.179	.00662	293	485
− .647	−2.292	.00511	283	469
− .764	−2.429	.00372	273	458
−1.033	−2.745	.00180	252	433
			Average	469

TABLE V

DATA FOR IODINE

Log N_2^R	Log N_2	N_2	T	k
−0.673	−3.442	0.000361	298	827
− .723	−3.515	.000305	293	820
− .829	−3.683	.000207	283	807
− .942	−3.864	.000136	273	800
−1.075	−4.123	.0000753	262	800
−1.200	−4.392	.0000405	252	805
			Average	810

In order to show the relation of these values of k to the average value obtained for other solvents, Table VI has been arranged, in which the solvents have been placed in the increasing order of their internal pressures. The data from which these values of k were calculated were taken from the determinations made by Ward and the tables published by Hildebrand. In the series of solvents of naphthalene the value of k was calculated at five degree intervals over a range of temperature from 0 to 25°, while the series of solvents for iodine were calculated at ten degree intervals from 0 to 50°.

TABLE VI

INTERNAL PRESSURE SERIES

Naphthalene as solute		Iodine as solute	
Solvent	k	Solvent	k
Carbon dioxide	469	Carbon dioxide	810
Carbon tetrachloride	57	Heptane	450
Toluene	30	Carbon tetrachloride	393
Benzene	26	Chloroform	302
Chlorobenzene	8	Bromoform	178
Nitrobenzene	23		
Acetone	74		
Aniline	122		

Internal Pressure from Surface Tension Measurements

When an attempt was made to evaluate the internal pressure of carbon dioxide from the surface tension measurements there was much doubt as to the best way to accomplish this. The total energy of surface formation was calculated by means of the Thomson equation and a value of 62 was obtained. This indicated that carbon dioxide had an internal pressure much the same as carbon tetrachloride, toluene and chloroform. In the light of these solubility determinations it is readily seen that this comparison is very misleading, as carbon dioxide has a very much lower internal pressure than any of these compounds. It is now clear that some other unit of comparison should have been used and if we calculate the value of $\gamma/V^{1/3}$ at 20° we obtain a value of 0.35, which places carbon dioxide in the internal pressure series in a position more nearly in accord with that obtained from solubility determinations. A more exact comparison at this time is not feasible.

Summary

1. A method has been described for determining the solubility of solids in liquefied gases, which can be applied to liquids having very high vapor pressures.

2. The solubility of naphthalene and iodine in liquid carbon dioxide has been determined over a range of temperature from 25 to $-21°$.

3. The position of liquid carbon dioxide in the internal pressure series has been determined. This indicated that this compound has an internal pressure much less than those liquids commonly used as solvents.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

THE STANDARDIZATION OF SILVER NITRATE SOLUTIONS USED IN CHEMICAL STUDIES OF SEA WATERS[1]

BY THOMAS G. THOMPSON

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The advantages of the use of standard sea water prepared by the Hydrographic Laboratories of Copenhagen have been pointed out by Knudsen.[2] This standard water has been used for over a quarter of a century for the evaluation of silver nitrate solutions employed in oceanographic investigations and is obtainable only from the Hydrographic Laboratories. However, Bertrand, Freundler and Ménager,[3] Ménager[4] and Giral[5] have recently criticized this standard and the two latter authors have recommended the use of sodium chloride.

[1] Presented before the Division of Water, Sewage and Sanitation at the 74th meeting of the American Chemical Society, Detroit, Michigan.

[2] Knudsen, *Publications de circonstance*, No. 2 (1903); No. 87 (1925).

[3] Bertrand, Freundler and Ménager, *Compt. rend.*, **174**, 1251–1253 (1922).

[4] Ménager, *ibid.*, **179**, 195–198 (1924).

[5] Giral, *Publications de circonstance*, No. 90 (1926).