SOLUBILITY OF CO_2 AND N_2O IN CERTAIN SOLVENTS.

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SYNOPSIS.

Solubility of CO_2 and N_2O in Twelve Solvents, 18° to 36° C.—Since according to the Lewis-Langmuir theory these two gases have similar molecular structures, it is of interest to compare their solubilities in various liquids. In the method adopted, the air was thoroughly removed from the solvent by boiling and then the gas to be tested, having been carefully purified with the help of liquid air, was admitted and shaken up with the solvent until no further solution took place. Observations accurate to better than one per cent. were made for *water, acetone, acetic acid, methyl alcohol, pyridine, ethyl alcohol, benzaldehyde, aniline, amyl acetate, ethylene bromide, isoamyl alcohol, and chloroform.* Taken in this order, the ratio of the solubility of CO_2 to that of N_2O decreases regularly from 1.34 (20°) for water to 0.66 for chloroform. This range of variation is small, and moreover the ratio is nearly constant for each solvent, changing less than one per cent. for six solvents, and not more than three per cent. for the others except chloroform and acetone. Also, the temperature coefficient (ds/sdT) is in most cases nearly the same for the two gases. It is always negative, the solubility decreasing with increasing temperature.

Discussion of Suggested Solubility Relations, for Gases in Liquids.—*Raoult's law* does not hold for the solubility of gases in liquids. It is also shown that there is little, if any, relation between solubility and the difference between the internal or *cohesion pressures* of solvent and solute. However, the ratio of the solubilities of CO_2 and N_2O varies regularly with the *dielectric constant* of the solvent, and since this constant may be taken as an index of the *polarity* of the solvent and since CO_2 is more active chemically and therefore has stronger polarity than N_2O, this result suggests that polarity may be an important factor in determining the relative solubility of gases in liquids.

INTRODUCTION.

IN view of the great interest in molecular structure at this time and in view of the possible relation between it and solubility it has seemed of interest and importance to get more complete and more accurate data on certain types of solubility than have hitherto been available.

In the work which is here to be described the solubility of carbon dioxide and of nitrous oxide in twelve different liquids was determined over a range of 18° C. These gases were used because according to recent theories of molecular structure[1] they have the same number and arrangement of electrons. They should therefore exhibit little if any difference in solubility, if the latter depends only on the number and arrangement of electrons. If they do show difference then, according to these theories, it must be due to other properties and the magnitude of the difference should be of interest for any theory of solubility.

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[1] Kossell, Ann. der Physik, 49, p. 229 (1916). Lewis, Jour. of Amer. Chem. Soc., 38, p. 762 (1916). Langmuir, Jour. of Amer. Chem. Soc., 41, p. 868 (1919). Thomson, Phil. Mag., 37, p. 419 (1919).

Apparatus.

The apparatus used for this work was very much like that used by McDaniel.[1] The chief part of it is shown in figure 1. It consists of a gas burette A (vol. 120 c.c.) which is graduated to 0.5 c.c. and can be read to 0.1 c.c., and an absorption pipette B (vol. 31.3 c.c.) connected by a glass capillary C. The whole forms one solid piece of glass and is clamped to a wooden frame (not shown in the figure) which is held in an upright position on an iron rod near the burette. With this rod as a pivot the apparatus can be very thoroughly shaken when solution of the gas in the solvent is to take place in the pipette.

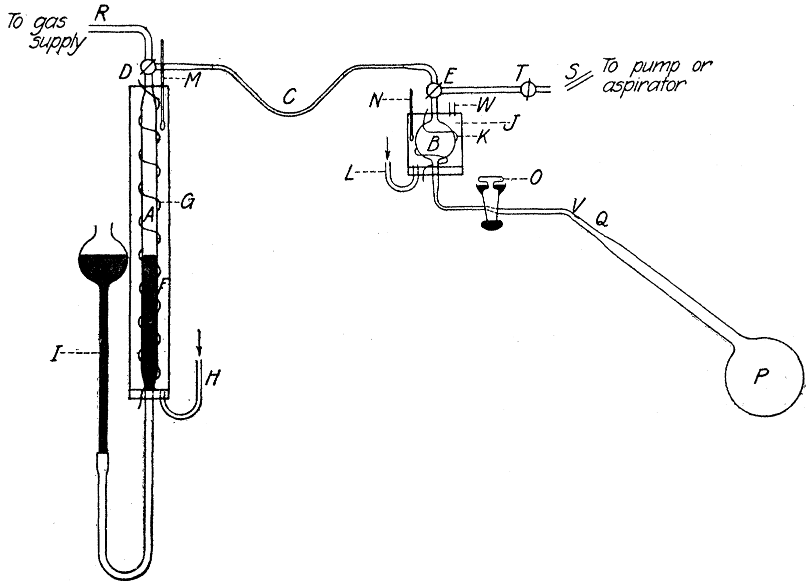

Fig. 1.

At each end of the capillary there is a three-way stopcock (D, E). The burette is provided with a water jacket F, an electric heating coil G, and a compressed-air inlet H. The reservoir I connected with burette A by a rubber tube and containing mercury makes it possible to keep the gas in A at atmospheric pressure. The pipette is likewise provided with a water jacket J, an electric heating coil K, and a compressed-air inlet L. The coils G and K are of Chromel A wire and either one may be used alone or they may be connected in series. They are so adjusted in length that the resistances are to each other as the respective radiating surfaces of the two water jackets. This insures an equal rate of temperature increase in the two vessels when the coils are in series.

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[1] McDaniel, Jour. of Phys. Chem., 15, p. 587 (1911).

Two thermometers *M* and *N* can be read to 0.1° C. and are used to indicate the temperature of the gas in the burette and pipette respectively. *O* is a mercury-seal stopcock, and *P* is a boiler of pyrex glass. *W* is an exit for the air which has been bubbled through the water in *J*. Compressed air is also bubbled through *F* to stir the water and hence assure the same temperature at top and bottom. Stopcock *E* is carefully ground to prevent leakage, and graphite is used as a lubricant on it and also on the mercury-seal stopcock *O*. Grease could be used on neither *E* nor *O* because of the organic solvents used in this work.

ORDER OF PROCEDURE.

In making any determination the burette *A* is filled with mercury except that a few drops of the solvent to be used are put in at the top. After the air has all been pumped out of the tube *RE* and it has been washed out with the pure gas which is to be used in this work, cock *D* is so adjusted as to allow the pure gas to displace the mercury in the burette. Part of the solvent placed in the burette evaporates and thus saturates the gas with the vapor of the solvent. This arrangement makes it unnecessary, as will appear later, to know the vapor pressure of the solvent at any temperature, a quantity which had to be allowed for in Just's work.[1] It is probably for this reason that Just's results on the solubility of CO_2 in liquids do not check very accurately those obtained here. The air is completely removed from the solvent in *P* by boiling for five minutes under reduced pressure and then applying a strong aspirator pump usually for upwards of half an hour more. During this time the solvent in *P* decreases by one fourth or one fifth of its volume. While this is being done *Q* is connected to *S*. Then *Q* is closed by the use of a rubber tube and clip, and forthwith connected to *V*. When the air has next been pumped out of *B* with a good vacuum pump, the boiler *P* is raised above the level of *B* and sufficient air-free solvent is run into *B* by gravity to approximately half fill *B*. To make sure that the last trace of air has been removed from the capillary *C*, this tube is in each case washed out twice with pure gas before a solubility determination is made. A short stub of pressure tubing is used to connect *V* and *Q*. Through this the liquid runs from *P* into *B*. Since this takes only a moment and since the liquids here used have little if any affect on rubber, this proceeding is not objectionable. The solvent is thus at no time exposed to air after once the air has been removed.

The air is then pumped out of the capillary *C* and after stopcock *T* has been closed and *A*, *C*, and *ET* allowed to communicate with each

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[1] Just, Z. S. für Phys. Chemie, 37, p. 342 (1901).

other, the height of gas in *A* at atmospheric pressure is carefully read. The mercury reservoir *I* can be raised or lowered to secure atmospheric pressure in *A*. Next *E* is turned so as to bring *B* and *A* into communication, *B* is then shaken to hasten solution and the mercury in *A* rises indicating the volume of gas dissolved. When further shaking causes no more decrease in the volume of the gas in *A* the solution is assumed to be saturated. This takes only a few minutes of thorough agitation of *B*. This apparatus can be shaken more vigorously than that of other investigators and hence solution is hastened. Since the burette is close to the pivot of the apparatus the mercury in it is little agitated when the pipette is vigorously shaken. In consequence of this there was no emulsion between the mercury and the layer of solvent in the burette above the mercury.

Before solution takes place the temperature is made the same in the two jackets *A* and *B* either by the use of ice water or the electric heating coils. After the reading has again been taken on the burette the temperature is raised simultaneously in both burette and pipette by means of coils *G* and *K*. During this time the shaking is continued, and at the proper time readings are repeated on the burette at intervals of 2° up to 36°. At a temperature much below that of the room it is difficult to keep the two jackets constant and at the same temperature because of radiation.

When the reading for the temperature at 36° has been taken the solvent in *B* is measured in a small graduate calibrated to 0.2 c.c. Dividing the volume of gas which disappears into the solvent by the volume of solvent used gives the solubility at any one temperature. In order to determine the solubility at the other temperatures correction for temperature change has to be applied to the volume of the solvent and also for the expansion of the gas when saturated with the vapor of the solvent as it is in burette *A*. The expansion coefficient of the latter is determined separately in the ordinary way either before or after a regular run. Every determination on solubility is repeated at least once, and recorded results are accurate to within about 1 per cent.

The nitrous oxide for this work was obtained from a steel cylinder of the gas purchased from the S. S. White Dental Company. It was rated as 99.7 per cent. pure, and to further insure its purity it was frozen with ethyl alcohol and liquid air, and while it was in that state all the gases were pumped off. When the frozen nitrous oxide had been thus sublimed it was passed over P_2O_5 and thus freed from possible traces of moisture. Its density was then determined and found to be 1.968 grams per liter at standard temperature and pressure.

With the exception of a short stub of pressure tubing connecting the steel cylinder with the glass system, the entire apparatus containing the purified gas was one piece of solid glass. This insures the continued purity of the gas when it has once been obtained in pure form, and as it is always under pressure a leak would mean a loss of gas rather than a contamination and would be registered on the attached manometer.

The carbon dioxide was made by heating $NaHCO_3$; and after the gas had passed through a long $CaCl_2$ tube to free it from the water, it was treated in the same way as was the nitrous oxide.

The solvents were obtained from standard chemical companies, and tests for boiling point and density were found to be in accord with the tables.

RESULTS.

Table I. shows the solubilities of CO_2 and of N_2O in each one of the twelve liquids used, at intervals of 2° from 18°–36°. The solubility is expressed in c.c. of the gas under existing barometric pressure and at the temperature specified, per c.c. of solvent under the same conditions. It will be noticed that the solubility decreases as the temperature increases, also that the solubilities of CO_2 and of N_2O in any one solvent at a given temperature are very much alike.

Table II. represents the coefficient of temperature change of solubility times 10^2, *i.e.*, $(ds/s \cdot dt)$ at the temperatures indicated. In each case the solubility decreases with increase of temperature.

In Table III. the second column contains the number of molecules of the solvent (M_{solvent}) for each molecule of CO_2 (M_{CO_2}) in a saturated solution at 20° C. The last column contains the corresponding number of molecules of solvent for each molecule of N_2O.

ATTEMPTS AT THE PREDICTION OF SOLUBILITY BY RAOULT'S LAW.

There are two general principles which have been used in the endeavor to predict solubility and it will be of interest to see how these fare in the interpretation of the foregoing results.

The first one to use Raoult's Law in an attempt to predict solubility seems to have been Dolezalek.[1] As used by him this law means that the partial vapor pressure of one component divided by its vapor pressure when pure and in the liquid state is equal to its number of molecules divided by the total number of molecules in the solution. It is an empirical law giving, for a very limited number of substances,[2] a linear relationship between concentration and vapor pressure.

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[1] Dolezalek, Z. S. für Physik Chemie, 64, p. 727 (1908) and p. 1919 (110).

[2] Dolezalek, Z. S. für Physik Chemie, 64, p. 728 (1908).

TABLE I.

	Water.		Acetone.		Acetic Acid.		Pyridine.		Methyl Alcohol.		Ethyl Alcohol.		Benzal-dehyde.		Aniline.		Amyl Acetate.		Ethylene Bromide.		Isoamyl Alcohol.		Chloro-form.	
	CO_2.	N_2O.	CO_2.	N_2O.	CO_2.	N_2O.	CO_2.	N_2O.	CO_2.	N_2O	CO_2.	N_2O.	CO_2.	N_2O.	CO_2.	N_2O.	CO_2.	N_2O.	CO_2.	N_2O.	CO_2.	N_2O.	CO_2.	N_2O.
18°	....	0.703	....	6.30	5.40	5.00	3.95	....	3.63	3.38	2.95	3.07	3.06	3.23	....	1.50	4.79	5.24	2.32	2.87	....	2.52	3.83	5.70
20	0.900	0.675	6.98	6.03	5.23	4.85	3.85	3.58	3.57	3.32	2.87	2.99	2.98	3.15	1.38	1.48	4.65	5.14	2.27	2.81	1.91	2.47	3.71	5.60
22	0.872	0.638	6.76	5.78	5.07	4.70	3.75	3.50	3.51	3.27	2.80	2.91	2.90	3.07	1.35	1.45	4.55	5.05	2.22	2.75	1.88	2.43	3.60	5.51
24	0.836	0.617	6.55	5.50	4.91	4.55	3.63	3.45	3.44	3.23	2.73	2.85	2.80	3.00	1.32	1.42	4.44	4.93	2.16	2.69	1.85	2.37	3.50	5.26
26	0.800	0.587	6.22	5.21	4.73	4.39	3.53	3.34	3.37	3.19	2.66	2.77	2.73	2.93	1.29	1.40	4.35	4.83	2.12	2.64	1.81	2.32	3.39	5.07
28	0.765	0.561	5.88	4.84	4.57	4.25	3.45	3.25	3.28	3.07	2.58	2.68	2.66	2.85	1.25	1.37	4.24	4.71	2.07	2.58	1.76	2.27	3.26	4.83
30	0.729	0.530	5.49	4.46	4.41	4.11	3.33	3.17	3.19	2.98	2.48	2.61	2.58	2.78	1.22	1.35	4.14	4.60	2.03	2.52	1.72	2.24	3.11	4.57
32	0.693	0.513	5.08	4.07	4.25	3.98	3.25	3.10	3.09	2.88	2.41	2.52	2.52	2.72	1.21	1.32	4.10	4.49	1.97	2.46	1.69	2.19	2.94	4.29
34	0.656	0.478	4.66	3.66	4.12	3.84	3.13	3.02	2.97	....	2.31	2.43	2.46	2.65	1.19	1.31	4.02	4.39	1.92	2.42	1.67	2.16	2.81	4.03
36	....	0.449	....	3.23	4.00	3.75	3.03	2.94	....	....	....	2.33	2.39	2.59	1.17	1.28	....	4.30	1.86	2.37	....	2.12	2.68	3.70

By assuming that gases are completely miscible in liquids, Dolezalek has, however, attempted to apply this law to the computation of the mol-fraction of a gas which under a given pressure is soluble in various solvents.

TABLE II.

Temperature Coefficient of Solubility × 10^2.

Solvents.	Solutes.	18°.	20°.	22°.	24°.	26°.	28°.	30°.	32°.	34°.	36°.
Water	CO_2	1.78	1.88	2.00	2.12	2.23	2.35	2.47	2.58	2.70	2.80
	N_2O	2.03	2.10	2.18	2.27	2.35	2.43	2.52	2.60	2.68	2.76
Acetone	CO_2	0.84	1.27	1.73	2.20	2.66	3.14	3.60	4.13	4.62	5.12
	N_2O	1.50	1.96	2.44	2.94	3.42	3.93	4.40	4.92	5.40	5.90
Acetic acid	CO_2	1.60	1.63	1.65	1.66	1.68	1.70	1.72	1.75	1.76	1.78
	N_2O	1.60	1.62	1.63	1.63	1.64	1.64	1.65	1.65	1.65	1.66
Methyl alcohol	CO_2	0.60	0.76	0.93	1.10	1.26	1.44	1.60	1.77	1.95	2.10
	N_2O	0.40	0.58	0.77	0.97	1.18	1.38	1.57	1.77	1.97	2.17
Pyridine	CO_2	1.28	1.32	1.37	1.41	1.46	1.49	1.53	1.57	1.61	1.66
	N_2O	1.08	1.11	1.14	1.17	1.20	1.23	1.26	1.29	1.32	1.36
Ethyl alcohol	CO_2	1.16	1.23	1.32	1.40	1.48	1.57	1.67	1.74	1.84	1.90
	N_2O	1.16	1.23	1.32	1.40	1.48	1.57	1.67	1.74	1.84	1.90
Benzaldehyde	CO_2	1.32	1.33	1.34	1.34	1.35	1.36	1.37	1.38	1.39	1.39
	N_2O	1.26	1.26	1.25	1.25	1.25	1.26	1.26	1.26	1.26	1.26
Aniline	CO_2	1.12	1.10	1.07	1.05	1.03	1.02	1.00	0.98	0.97	0.95
	N_2O	0.83	0.84	0.85	0.87	0.89	0.90	0.91	0.93	0.94	0.96
Amyl acetate	CO_2	1.35	1.30	1.24	1.19	1.16	1.10	1.03	0.98	0.93	0.88
	N_2O	1.03	1.04	1.05	1.06	1.07	1.09	1.10	1.11	1.12	1.13
Ethylene bromide	CO_2	1.07	1.10	1.13	1.16	1.18	1.21	1.24	1.26	1.29	1.32
	N_2O	1.06	1.06	1.07	1.08	1.09	1.10	1.11	1.12	1.13	1.14
Isoamyl alcohol	CO_2	1.00	0.98	0.97	0.96	0.96	0.95	0.95	0.94	0.94	0.93
	N_2O	1.00	0.98	0.97	0.96	0.96	0.95	0.95	0.94	0.94	0.93
Chloroform	CO_2	1.10	1.30	1.53	1.77	2.00	2.20	2.43	2.66	2.90	3.10
	N_2O	0.66	1.03	1.40	1.80	2.20	2.58	2.98	3.35	3.70	4.07

If Dolezalek's assumption of the validity of Raoult's Law, thus defined, for mixtures of gases in liquids is correct, then obviously the solubility of gases in liquids can be completely predicted if we mean by solubility[1] the mol-fraction of one substance which will be mixed with the other under a given condition of temperature and external pressure. In Dolezalek's paper in which he attempts to test this assumption, he obtains results which are in accord with the theory. However, when the same method is applied to other data wide deviations are found even with the constant he uses.

To see how well we fare in this work in predicting solubilities of gases in liquids by the use of Raoult's Law, let us turn to the first two columns

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[1] This use of the word "solubility" is somewhat confusing since it differs from the usual acceptation of the term. This confusion might be reduced by replacing the word "solubility" in its ordinary usage by the word "miscibility."

Table III.

	M_{solvent} M_{CO_2}.	M_{solvent} M_{N_2O}.
Water	1350	1800
Acetone	46	53
Acetic acid	73	79
Methyl alcohol	155	167
Pyridine	72	77
Ethyl alcohol	131	126
Benzaldehyde	73	69
Aniline	174	162
Amyl acetate	32	29
Ethylene bromide	111	90
Isoamyl alcohol	106	82
Chloroform	74	49

in Table IV. Here are shown the solubilities of CO_2 and of N_2O in terms of mol-fractions in the twelve different solvents used. In the first column of Table V. are shown the solubilities of CO_2 in terms of mol-fractions in twenty different solvents as found by Just. For CO_2 under ordinary conditions the mol-fraction according to Raoult's Law would be 0.0178 = (1/56.3 atm.). This should be the same for all

Table IV.

Solvents.	Solubility in Mol-fractions $\times 10^4$ at 20°.		Internal Pressures at 0° C. in Atmospheres.		
	CO_2.	N_2O.	*A*.	*B*.	*C*.
Amyl acetate	283	312	1,500	—	—
Acetone	211	185	2,230	2,600	4,440
Pyridine	129	120	2,460	—	—
Benzaldehyde	125	134	2,440	—	—
Acetic acid	124	115	2,100	5,960	7,140
Chloroform	121	182	2,030	2,430	3,030
Isoamyl alcohol	87	111	2,400	—	—
Ethylene bromide	82	100	2,200	1,980	4,400
Ethyl alcohol	69	72	3,720	3,760	3,120
Methyl alcohol	60	53	4,730	6,360	4,030
Aniline	53	56	2,740	3,300	—
Water	7	5	11,600	17,300	—
CO_2			985	1,510	—
N_2O			980	1,440	—

solvents. From Tables IV. and V. here given we see that the mol-fractions are not what this theory predicts at all and that they are by no means alike. Thus it becomes apparent that this law rarely, if ever, holds for gases dissolved in liquids. This is in accord with the conclusion arrived at by Hildebrand.[1] It means that the procedure of Dolezalek is utterly worthless for predicting solubility of gases in liquids.

TABLE V.

Solvents.	Solubility of CO_2 in Mol-fractions $\times 10^4$ at 20°.	Internal Pressures at 0° C. in Atmospheres.		
		A.	*B.*	*C.*
Amyl acetate	270	1,500	—	—
Acetone	209	2,230	2,600	4,440
Pyridine	129	2,460	—	—
Benzaldehyde	128	2,440	—	—
Ethylene chloride	125	2,070	2,730	4,500
Chloroform	123	2,030	2,430	3,030
Acetic acid	121	2,100	5,960	7,140
Nitrobenzene	113	2,340	—	—
Toluene	107	1,710	2,210	3,570
Meta xylene	102	1,670	2,100	—
Carbon tetrachloride	100	1,685	2,030	3,220
Benzene	91	1,870	2,240	3,900
Ethylene bromide	82	2,200	1,980	4,400
Propyl alcohol	77	2,970	3,020	2,480
Methyl alcohol	71	4,730	6,360	4,030
Ethyl alcohol	70	3,720	3,760	3,120
O – toluidine	66	2,280	—	—
Aniline	55	2,740	3,300	—
Carbon disulphide	22	3,000	3,220	3,800
Water	7	11,600	17,300	—

ATTEMPTS AT THE PREDICTION OF SOLUBILITY FROM COHESION PRESSURES.

The real problem of predicting solubility comes where the components are not completely miscible. The method here to be discussed has been used by Traube,[2] Walden,[2] Hildebrand,[2] and Bradford,[2] and consists essentially in the assumption that two substances will be more nearly soluble in one another in proportion as the internal pressures (Laplace's cohesion constants) of the two substances approach one another. The fundamental idea underlying this theory appears to be that if two

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[1] Hildebrand, Jour. of Amer. Chem. Soc., 38, p. 1454 (1916).

[2] Traube, Verh. der d. Physik Gesell, 10, p. 880 (1908). Walden, Z. S. fur Phys. Chemie, 66, p. 409 (1909). Hildebrand, Jour. of Amer. Chem. Soc., 38, p. 1452 (1916). Bradford, Phil. Mag., 38, p. 696 (1919).

substances A and B have the same cohesion pressures when in the liquid state, then the molecules of substance A will exert the same sort of forces upon the molecules of substance B as the molecules of A (or of B) exert upon one another. In other words, if A's molecules have a certain attraction for one another as measured by cohesion pressure and B's molecules have the same attraction, then the two substances will readily mix, but if the cohesion pressure of either one is greater than that of the other then the one will draw itself away from the other just as would be expected if there were no such thing as selectivity among molecular forces. This idea is perhaps most definitely expressed in an equation set up by Bradford and written in the form

$$f = \frac{M_A^2}{r_A^4} - \frac{2M_AM_B}{r_{AB}^4} + \frac{M_B^2}{r_B^4}\,.$$

The f in this expression is what he calls the force opposing solution, the term M_A^2/r_A^4 is the term which in his theory is proportional to the internal pressure of substance A, whereas the term M_B^2/r_B^4 is proportional to the internal pressure of substance B. The attraction between molecules of substance A is assumed to be electrical in origin and the term M in Bradford's theory is what he calls the electrical "moments of the atomic doublets in each molecule." He assumes, following the proofs given by J. J. Thomson[1] and by Sutherland,[2] that with such forces the molecular attraction will be inversely proportional to the fourth power of the distance between molecules. Hence he gets the form of the cohesion term M^2/r^4. The force drawing molecules A and B together is then of the form $2M_AM_B/r_{AB}^4$, so that the force opposing solution is the difference between this term and the sum of the other two terms which express the cohesion of the molecules for each other respectively.

From this point of view we should be able to calculate the value of the solubility of one component in another if we have given their internal pressures. These I have calculated by three different methods and listed under headings A, B, and C in Tables IV. and V. for the solvents found in column one in each case. Under A are found the internal pressures obtained by Stefan's method,[3] under B the Laplacian cohesion constant obtained from the expression $K = a(v_1/v_2)^2$, and under C are the internal pressures obtained by use of the expression[4] $K = \alpha T/\beta$ where α is the expansion and β the compressibility coefficient. The data required for the calculation of internal pressures were obtained from the Landolt-Börnstein Tables.

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[1] Thomson, Phil. Mag., 27, p. 757 (1914).

[2] Sutherland, Phil. Mag. (5), 39, p. 1 (1895).

[3] Stefan, Wied. Ann., 29, p. 655 (1886).

[4] Kleeman, Kinetic Theory of Gases and Liquids, p. 71.

To show how the theory of internal pressures works out when applied to the data here obtained we need to refer again to Table IV. where the solvents are arranged in decreasing order of the solubility of CO_2, but the order would be very nearly the same if arranged according to N_2O. The cohesion pressure theory requires that the solubility should decrease as the difference of internal pressures between solvent and solute increases. The fact that the solubilities are those at 20° C. and the internal pressures are at 0° C., makes little if any difference in the relative order of solvent and internal pressure. It will be evident from Table IV. that there is no correlation there which is sufficiently good even as evidence that this theory is in its main features correct. It will also be noticed that as far as the reliability of the theory is concerned it is immaterial which of the three methods of calculating internal pressures is used. It is true that some of the solvents are probably associated. But the situation is not improved even by omitting entirely those solvents which we feel confident are associated.

Bradford has used this method for the prediction of solubility with some apparent success, as is shown in the table he cites. But the agreement which is there shown is accidental, I think, and due to the relatively few cases chosen.

Hildebrand[1] also sets up a similar table and draws the conclusion that Bradford does. In my opinion a critical study of his table yields no evidence which justifies a conclusion of this kind, and when this table is extended to more solvents as is done in Table V. above, where the solubilities are those by Just on CO_2 and are listed in decreasing order of magnitude, the conclusion Hildebrand draws is very obviously not warranted. When a comparison is made with the theory the departures will be seen to be just as great as in Table IV. So far, therefore, as these data are concerned, this method must be considered practically useless.

Again it should follow from the point of view of this theory that:

1. Substances which have the same internal pressures should all be completely miscible.

2. All substances which are completely miscible should have the same internal pressures.

3. The order of miscibility should be the order of difference in internal pressures.

As to the third point we note from the tables given above that it does not hold at all.

Under the second point should be mentioned many combinations of

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[1] Hildebrand, Jour. of Amer. Chem. Soc., 38, p. 1467 (1916).

non-associated liquids miscible in all proportions, the internal pressures of whose components are widely different. These are not in accordance with the theory. Among these may be mentioned ether and benzaldehyde, ether and chloroform, ethylene bromide and ether, ethylene chloride and ether, carbon disulphide and ether. According to the theory these should not be completely miscible. It should be said that Hildebrand also recognizes a difficulty of this sort.

Under the first point above mentioned there are only a few cases to be considered because very few substances have the same or very nearly the same internal pressure. The combinations cited by Hildebrand should be noted. They are benzene and carbon tetrachloride, benzene and chlorobenzene, benzene and chloroform, benzene and ethylene chloride, chlorobenzene and toluene. They have nearly equal internal pressures and are miscible in all proportions. But methyl alcohol should be completely miscible in carbon disulphide, for according to one method at least their internal pressures are nearly alike. The polarity of methyl alcohol is given as the cause of this discrepancy. This suggests that polarity as a factor in solubility may be worthy of further study. But the conclusion of the studies in this field would appear to be that present theories of miscibility, though perhaps of some little value as indices, can scarcely be said to have gained any very notable successes.

POLARITY.

If we now turn to Table VI. where are listed the ratios of solubilities of CO_2 to N_2O in the twelve solvents here used, it seems worthy

TABLE VI.

Ratio of Solubility of CO_2 to that of N_2O.

Solvents.	18°.	20°.	22°.	24°.	26°.	28°.	30°.	32°.	34°.	36°.
Water	....	1.333	1.366	1.354	1.363	1.364	1.372	1.350	1.370	....
Acetone	....	1.157	1.170	1.191	1.194	1.215	1.230	1.248	1.272	....
Acetic acid	1.080	1.078	1.078	1.078	1.076	1.075	1.072	1.067	1.072	1.066
Methyl alcohol	1.073	1.075	1.073	1.065	1.056	1.068	1.070	1.072	....	....
Pyridine	....	1.075	1.070	1.052	1.057	1.060	1.050	1.048	1.035	1.030
Ethyl alcohol	0.961	0.960	0.963	0.958	0.960	0.963	0.950	0.957	0.950	....
Benzaldehyde	0.048	0.946	0.945	0.933	0.932	0.933	0.928	0.927	0.928	0.923
Aniline	....	0.932	0.931	0.930	0.922	0.912	0.904	0.917	0.908	0.914
Amyl acetate	0.914	0.905	0.902	0.902	0.900	0.901	0.901	0.913	0.916	....
Ethylene bromide	0.808	0.807	0.807	0.803	0.803	0.803	0.805	0.801	0.793	0.785
Isoamyl alcohol	....	0.773	0.774	0.781	0.780	0.776	0.768	0.772	0.773	....
Chloroform	0.672	0.663	0.653	0.666	0.668	0.674	0.680	0.685	0.697	0.724

of note that CO_2, which is considered more polar than N_2O, is also in general more soluble than N_2O in the solvents considered polar, namely: water, acetone, acetic acid, methyl and ethyl alcohol. CO_2 and N_2O are so completely alike in so many ways that it is perhaps difficult to differentiate them on the basis of polarity. The dielectric constant which is usually considered a criterion of polarity is the same in the two cases, but chemical reactivity is also a sign of polarity and in this respect CO_2 differs from N_2O, being more active than the latter. For the solvents here mentioned we can apply the criterion of the dielectric constant and order their polarities on the basis of this property.

At present there exists little definite quantitative data on the effect of polar substances upon each other and upon non-polar substances in their neighborhood; but so far as the present table goes its indications are that the solubility of gases in liquids is connected with polarity rather than with Raoult's law or with internal pressures.

The indications of the present work then are that the most hopeful lines of attack for the problem of the prediction of solubility must be looked for in the study of chemical properties rather than of physical properties such as internal pressures.

In conclusion the writer wishes to acknowledge his indebtedness to Prof. R. A. Millikan for suggesting the subject, for his kindly interest in this work, and for his continuous friendly advice and help, and to Prof. A. J. Dempster for occasional assistance.

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September [illegible], 1921.