[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

SOLUBILITY. VIII. SOLUBILITY RELATIONS OF CERTAIN GASES

BY NELSON W. TAYLOR AND JOEL H. HILDEBRAND

Received December 9, 1922

Introduction

The present study was undertaken in order to shed further light on the truth of the theory of solubility that has been advocated in a series of papers from this Laboratory during the past 6 years.[1] The broad outlines of this theory are given in the first paper published in 1916. Frequent reference will be made to it as well as to the revised table of internal pressures which is given in the third paper of the series. The reader is also referred particularly to the recent summary in the *Physical Review.*

Solubility of Chlorine

Chlorine gas is of peculiar theoretical interest as a solute on account of the fact that liquid chlorine finds a place near the middle of the Table of Internal Pressures.[2] It might, therefore, be expected to show a different order of solubility from that shown by the gases considered in our first paper by having a maximum solubility in the adjacent liquids, such as carbon tetrachloride, and lower solubilities in those liquids at the top and bottom of the table. Pure liquid chlorine has but slight polarity, having a dielectric constant of 1.7 and an entropy of vaporization 2 × 13.9.[3] It is, however, sufficiently polar to react with many organic liquids. For this reason we have used as solvents only silicon tetrachloride, carbon tetrachloride, ethylene dibromide and heptane. Other liquids such as benzene, bromoform and chloroform would have been of interest, but these react with chlorine, giving benzene hexachloride in the first case and free hydrogen chloride in the last two cases.

Experimental Procedure

Our method consisted in bubbling chlorine gas slowly through the solvent and, after equilibrium had been reached, determining the dissolved chlorine by titration. Chlorine from an electrolytic supply was first condensed in a bulb of about 25 mm. diameter using carbon dioxide and ether, or liquid air, as the refrigerant. A steady, easily controllable stream of gas could then be obtained by lowering the Dewar vessel so that the liquid chlorine was vaporized by the warm air of the laboratory. The chlorine contained a negligible amount of free acid, less than 0.1%.

---

[1] (a) Hildebrand, THIS JOURNAL, **38**, 1452 (1916); (b) **39**, 2297 (1917); (c) **41**, 1067 (1919). (d) Hildebrand and Jenks, *ibid.*, **42**, 2180 (1920). (e) Hildebrand and Buehrer, *ibid.*, **42**, 2213 (1920). (f) Hildebrand, *ibid.*, **43**, 500 (1921). (g) Hildebrand and Jenks, *ibid.*, **43**, 2172 (1921). (h) Hildebrand, *Phys. Rev.*, **20**, 52 (1923).

[2] See the condensed table, VI, of this paper.

[3] Hildebrand, THIS JOURNAL, **37**, 920 (1915).

The saturator tube used was of the type described by Bichowsky and Storch.[4] This device has several advantages. The pressure head of the incoming gas is reduced to a minimum. The liquid is kept in circulation by the bubbling gas and thus equilibrium is reached quite rapidly. Very little liquid is lost as spray.

The saturator tube was first filled with the solvent and then sealed with de Khotinsky cement to the tube containing the liquid chlorine. The saturator was immersed in a small thermostat which was equipped with a motor-driven stirrer. The temperature was held constant to 0.1° by hand control. More accurate control than this was unnecessary since a change of 0.1° produces a variation in solubility no greater than that between duplicate determinations in a single run. The chlorine was allowed to bubble through the solvent for about 1$^1/_2$ hours. At the end of the run, the de Khotinsky joint was broken, the saturator bulb removed from the bath and samples were immediately obtained by inverting the bulb and allowing the solution to run into glass-stoppered Erlenmeyer flasks which had previously been weighed with an aqueous solution of 10 g. of potassium iodide. Iodine formed at once and no chlorine was lost. The flask and contents were then reweighed to give the gain due to the weight of the saturated solution. The liberated iodine was determined by titration of standard sodium thiosulfate solution, 1 cc. of which equalled 0.01615 g. of chlorine.

From the weight of chlorine per gram of saturated solution, its mole fraction at the partial pressure, p, was readily obtained. N'_{Cl_2} = moles Cl_2/(moles Cl_2 + moles solvent). To find the value of N_{Cl_2} when p equals 1 atmosphere, we use Henry's law in the form $N_{Cl_2} = N'_{Cl_2} \times (760/p)$. A typical calculation is given below.

Solubility of Chlorine in Carbon Tetrachloride at 0°

One g. of saturated solution contains 0.156 g. of chlorine or 0.0022 moles, and 0.844 g. of carbon tetrachloride or 0.0055 moles. Mole fraction $Cl_2 = N'_{Cl_2} = 0.0022/0.0077 = 0.286$. Mole fraction $CCl_4 = 1 - 0.286 = 0.714$.

Vapor-pressure of CCl_4 at 0° = 33 mm.[5] Hence, assuming Raoult's law,[6] partial pressure of $CCl_4 = 0.714 \times 33 = 24$ mm. Barometric pressure = 753 mm. Therefore partial pressure of $Cl_2 = 753 - 24 = 729$ mm.

Hence, mole fraction of Cl_2 at a partial pressure of 1 atmosphere = $(760/729) \times 0.286 = 0.298$, or 29.8%.

The measurements are given in Table I. The eighth column gives the mole per cent. of chlorine at its partial pressure in the experiment, while the last column gives the calculated values of N_{Cl_2} assuming 1 atmosphere partial pressure.

[4] Bichowsky and Storch, THIS JOURNAL, **37**, 2695 (1915).

[5] The vapor-pressure data on CCl_4 are from Young, *J. Chem. Soc.*, **59**, 911 (1891). The data on the remaining liquids were taken from Landolt-Börnstein Tabellen.

[6] Theoretically, we are not justified in assuming Raoult's law in such a calculation as this because we have no knowledge of the partial pressure-composition curves for these various liquids when Cl_2 is present. However, in view of the fact that the partial pressure of the solvent is small, the error introduced by the above assumption is probably not great. At higher temperatures, where the solvent has a greater vapor pressure, the system deviates less from Raoult's law and so the error is probably no greater than before. This method of calculating gas solubilities to a partial pressure of 1 atmosphere from a measurement at a total pressure of 1 atmosphere has been used for most of the gas-solubility data in the literature. Our calculation is therefore open to no greater objection than any previous work on the subject. It may be mentioned that if the system shows a positive deviation from Raoult's law the gas solubility values under 1 atmosphere partial pressure would be somewhat greater if a correction were made for the deviation.

Table I

Chlorine Solubilities

Solvent	Temp. ° C.	Partial press. Cl_2 Mm.	Cl_2 per g. of solution G.	G.	G.	Av. G.	Mole % Cl_2 In expt.	At 1 atm. P. p.
Heptane	0	750	0.196	0.205	0.210	0.2036	26.5	27.0
$SiCl_4$	0	681	0.130	0.132	....	0.131	26.6	28.8
CCl_4	0	729	0.156	0.157	0.155 0.156	0.156	28.6	29.8
CCl_4	19	680	0.0846	0.0848	0.0848	0.0848	16.3	18.7
CCl_4	20	760	(By interpolation from 0°, 19°, 40°)			....	...	18.2
$C_2H_4Br_2$	20	752	0.0812	0.0805	0.0824	....	...	...
	..	...	0.0805	0.0820	....	0.0813	19.0	19.2
CCl_4	40	557	0.0436	0.0430	0.0425	....	...	...
	..	...	0.0440	0.0438	0.0431	0.0433	8.91	12.15
$C_2H_4Br_2$	40	736	0.0466	0.0472	0.0465	....	...	...
	..	...	0.0476	0.0470	0.0465	0.0469	11.51	11.9

In the case of heptane, values at 20° and 40° were erratic on account of reaction with the chlorine. The same was true for silicon tetrachloride because of occlusion of iodine by the colloidal silica. No measurement was possible on ethylene dibromide at 0°, since the freezing point of this liquid is 9.5°.

The ideal mole fraction of a dissolved gas at any temperature is given by Raoult's law as $N=p/p°$, where p is the partial pressure of the dissolved gas (usually 1 atmosphere) and $p°$ is the vapor pressure of the liquefied gas at this temperature. An approximate value for the latter may have to be gotten by extrapolation above the critical temperature, most satisfactorily by the use of a plot of log $p°$ against $1/T$. Since vapors do not obey the gas laws very strictly it is preferable to substitute the escaping tendencies or fugacities of the gas, f and $f°$, for p and $p°$, respectively, writing Raoult's law as $N=f/f°$, and in the case of chlorine there is sufficient deviation from the gas laws to make the calculation of $f/f°$ worth while. Lewis and Randall[7] have given the following relation between fugacity and pressure; $\ln f/p=\alpha p/RT$, where $\alpha=RT/p-V$, and V is the volume of 1 mole of the gas under 1 atmosphere pressure.

Table II

Ideal Chlorine Solubilities

Temp. ° C.	Press.[8] $p°$ Atm.	Fugacity When $p=1$ Atm.	Fugacity When $p=p°$ Atm.	Mole per cent. calc. from $1/p°=N$	from $f/f°=N$
0	3.66	0.984	3.44	27.3	28.6
20	6.62	0.986	6.04	15.1	16.34
40	11.50	0.989	10.1	8.7	9.79

---

[7] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances." McGraw-Hill Book Co., **1923**.

[8] Vapor-pressure data are taken from Knietsch, *Wied. Ann.*, **259**, 124 (1890). His measurements are in good agreement with those of Johnson and McIntosh, This Journal, **31**, 1140 (1909).

Taking the weight of 1 liter of chlorine at 0° and at 100° as 3.220 g. and 2.329 g., respectively, we calculate α to be 380 cc. and 160 cc., respectively. Interpolation gives for α 335 cc. at 20° and 290 cc. at 40°. From these values we have prepared the preceding table.

It will be noticed that these "ideal" values do not differ much from those actually obtained. That Raoult's law is obeyed closely in very dilute chlorine solutions in carbon tetrachloride at 0° is shown by the vapor pressure measurements of Jakowkin.[9] A comparison of our calculated f/f° with his observed values of N is given below.

N_{Cl_2}	0.00086	0.00225	0.00423	0.00718
p/p°	0.00092	0.00208	0.00410	0.00673
f/f°	0.00098	0.00221	0.00436	0.00716

Reference to Table VI shows that the liquids heptane, silicon tetrachloride, carbon tetrachloride, chlorine and ethylene dibromide have increasing internal pressures in the order named. Our measurements show as predicted, that increase in solubility runs parallel with decreasing internal pressure differences. Thus, chlorine, which falls between carbon tetrachloride and ethylene dibromide in the table of internal pressures, shows approximately equal solubilities in these two solvents, being slightly more soluble in carbon tetrachloride at 40° and slightly less at 20°. Further, heptane which is least like chlorine as regards internal pressure, shows the poorest solvent power. Silicon tetrachloride also falls in the expected position.

Liquid Chlorine as a Solvent

Waentig and McIntosh[10] have studied the behavior of liquid chlorine as a solvent. They give some interesting data on the depression of the freezing point of chlorine due to the solution of small amounts of various substances. Their measurements seem to be accurate to 0.001°. The table below gives the depressions in solutions of mole fraction $N = 0.01$. These values were obtained by a careful plot of the original data and interpolation at the point $N = 0.01$. The solutes are listed in order of increasing values of $-\Delta T$.

TABLE III

FREEZING-POINT DEPRESSIONS OF CHLORINE

Solute	$-\Delta T$ °C.	Solute	$-\Delta T$ °C.
Acetone	0.190	CCl_4	0.210
Ethyl acetate	0.199	Toluene	0.215
Ether	0.204	$CHCl_3$	0.222
$SnCl_4$	0.208		

---

[9] Compare Ref. 1a, p. 1466.

[10] Waentig and McIntosh, *Proc. Roy. Soc. Canada*, [3] **9**, 207 (1915).

The theoretical value for the freezing-point depression of chlorine based on Estreicher's determination of the heat of fusion is $-\Delta T = 0.27°$ when $N = 0.01$. This is high in comparison to the measurements of Waentig and McIntosh. We were unable to examine the accuracy of Estreicher's experimental data as we had access only to the abstract.[11] The fact that the vapor-pressure measurements in solutions in carbon tetrachloride agree rather closely with Raoult's law indicates that the theoretical depression of the freezing point should be about 0.22° instead of 0.27°, and that the above value of the heat of fusion is too small.

The well-known expression, based upon Raoult's law, for the depression of the freezing point of a liquid X_2 by the addition of n_1 moles of X_1 is

$$-\Delta T = \frac{RT^2}{\Delta H_F} \cdot \frac{n_1}{n_1 + n_2} \tag{1}$$

Here the liquid phase consists of n_1 moles of X_1 and n_2 moles of X_2, and the solid phase is pure X_2. This equation assumes that the heat necessary to dissolve X_2 is equal to its heat of fusion ΔH_F. This, however, is true only in the ideal case. In the more general case, the heat of solution of solid X_2 is determined by two factors; first, its heat of fusion, ΔH_F, and second, *the heat of mixing of this liquefied X_2 with the solution*. If, therefore, we let ΔH_m be the heat of mixing, Equation 1 becomes

$$-\Delta T = \frac{RT^2}{\Delta H_F + \Delta H_m} \cdot \frac{n_1}{n_1 + n_2} \tag{2}$$

It is evident from a comparison of Equations 1 and 2 that the greater the magnitude of ΔH_m, the greater will the actual freezing-point depression, ΔT, deviate from the value required by Raoult's law. G. N. Lewis[12] has shown that when Raoult's law is obeyed at all temperatures the heat of mixing is zero.

Our theory of solubility indicates that for normal non-polar liquids the heat of mixing will be roughly proportional to the difference, $\Delta \Pi$, between the internal pressures of the two components. The experimental values of ΔT will thus become smaller and smaller as $\Delta \Pi$ increases. We find strong evidence in support of this idea when we examine the solubility-temperature curves for solids[1d,1g] in various liquids. We find that equal molal quantities of various liquids do not lower the freezing point of the solute to the same extent, but that $-\Delta T$ is greater when $\Delta \pi$ is small and *vice versa*.

Let us now examine Table III. Of the substances listed, acetone is highly polar and ethyl acetate is slightly polar, so these were not included in the table of internal pressures given in the third paper of this series, but the order of increasing ΔT for the remaining solutes is exactly that given in that paper. Moreover, the high polarity of acetone and the low

---

[11] *Chem. Zentr.*, **1910**, II, 1737.

[12] Compare Ref. 1f, p. 50.

internal pressure and appreciable polarity of ethyl acetate accord well with their positions in Table II.

It will be noted that the solubility data both for chlorine gas and for solid chlorine (freezing-point depression) are in harmony with the position originally assigned to chlorine in the internal pressure table, and show a different order from that found with gases such as nitrogen, hydrogen and carbon monoxide, which are most soluble in liquids at the top of the table.

The results are also interesting in that they show that critical pressure is not a perfect criterion for solubility. Van Laar,[13] for example, points out that we should expect deviations from Raoult's law even when both liquids are normal, provided their critical pressures are different. As has been stated in an earlier paper, there is undoubtedly considerable justification for this statement since, in terms of the van der Waals theory, critical pressure is given by $8a/27b^2$, while internal pressure is a/V^2, and b and v are closely related. Nevertheless, it is unlikely that 2 liquids having equal critical pressures at vastly different critical temperatures should have equal internal pressures at all other temperatures. For example, the critical pressure for argon is 52.9 atmospheres at —117°, and the corresponding value for aniline is 52.3 atmospheres at 426°. But argon and aniline do not possess equal internal pressures at all temperatures, for at 20° one is a liquid and the other is a permanent gas of low density. Carbon tetrachloride has a critical pressure of 45 atmospheres, chloroform 55, ethylene dibromide 71 and chlorine 89 atmospheres. These pressures vary greatly and do not indicate that chlorine should show, as it does, nearly equal solubilities in carbon tetrachloride and ethylene dibromide. Our results, however, are in harmony with the internal pressure series.

Solubilities of Phosgene

Some solubilities of phosgene, $COCl_2$, have been published during the last 2 years which serve as additional tests of the theory. The measurements of Atkinson, Heycock and Pope[14] have been recalculated to mole-fraction units. Some of their measurements were made at temperatures

TABLE IV

MOLE FRACTION PHOSGENE

Atkinson, Heycock and Pope

Solvent	17°	24°	30°
m-Xylene	0.70	0.53	0.44
Toluene	0.70	0.53	0.445
Ideal $1/p°$	0.71	0.55	0.45
Chlorobenzene	0.70	0.54	0.48
α-Chloronaphthalene	0.63	..	..
Nitrobenzene (polar)	0.56	..	..

---

[13] Van Laar, *Z. physik. Chem.*, **72**, 723 (1910); **83**, 599 (1913).

[14] Atkinson, Heycock and Pope, *J. Chem. Soc.*, **117**, 1410 (1920).

differing by 0.1° or 0.2°, so for convenience of comparison we have made some small interpolations. The ideal solubilities have been calculated on the basis of their data on the pressures of the saturated phosgene vapor. The solvents are again tabulated in the order of increasing internal pressure. α-Chloronaphthalene was not listed in the table of internal pressures, but would undoubtedly occupy a place just below naphthalene, as chlorobenzene is just below benzene. It therefore follows chlorobenzene in the preceding table.

Baskerville and Cohen[15] also have published data on the solubility of phosgene. Their method, however, was not an accurate one, and gave results which, when converted to mole fractions, prove equal to only about 50 or 60% of the values listed in Table IV. Possibly their solutions were not saturated at the time of analysis. We have not included their data in this paper.

Inspection of these figures shows that phosgene dissolves equally readily in xylene, toluene and chlorobenzene. This would be expected on the basis of our theory if liquid phosgene has an internal pressure about the same as that of toluene. Let us see whether this is true. Any of the methods used in the third paper of this series for calculating internal pressures may be used here if the necessary physical constants are available. The value of the expression $\frac{5200 + 30\ t_b}{V_{20}}$ is 76.4 for phosgene and 80.0 for toluene. The difference is not great. The corresponding value for nitrobenzene is 113.0. This high value is in accordance with the fact that it gives low solubilities for phosgene. It has, however, a very high dielectric constant, 35, so that its polarity should greatly affect its solvent power.

Solubilities of Niton

We will now consider a very interesting test of the validity of this theory. Radium emanation,[16] or niton, is a chemically inert gas and its solubility behavior should be determined solely by its physical characteristics. Whatever results may be obtained, therefore, are not complicated by chemical factors and any differences in its solubility in different normal liquids may be attributed to internal pressures alone (including the increased internal pressure due to polarity in some cases).

The original solubility data on niton were recorded in terms of the Ostwald coefficient for gas solubility. These values have been recalculated to mole fractions, and are given in Table V. When the values are placed on a plot of log N against $1/T$, the curves obtained are almost straight lines, and interpolation is a simple matter. On such a plot the results of Remstedt at 18° are found to be in excellent agreement with those of

[15] Baskerville and Cohen, *J. Ind. Eng. Chem.*, **13**, 333 (1921).

[16] (a) Schulze, *Z. physik. Chem.*, **95**, 257 (1920). (b) Remstedt, *Le Radium*, **8**, 253 (1911).

Schulze at —18°, 0°, 15°, 25°, 30° and 40°. The table below gives values at 0°, 20° and 40°, the 20° values being interpolated graphically from the other measurements. The solvents are again listed in order of increasing internal pressure at 20°.

TABLE V

MOLE PER CENT. NITON

$N \times 10^2$

Solvent	0° (S)	20° (S)	40° (S)	18° (R)
Ideal[17]	11.36	6.92	4.55	7.41
Hexane	11.72	7.95	5.75	8.31
Ethyl ether	8.23	6.03	4.89	6.14
Ethyl acetate	3.84	2.75	2.15	2.78
Cyclohexane	..	7.80	..	8.14
m-Xylene	..	5.85	..	6.16
Toluene	7.86	5.20	3.60	5.60
Chloroform	6.21	4.68	3.60	4.80
Benzene	6.45	4.31	2.95	4.57
Carbon disulfide	8.06	5.56	4.29	5.84
Aniline	1.73	1.41	1.17	1.43

Inspection of these values shows that in the case of the truly normal liquids, hexane, cyclohexane, *m*-xylene, toluene and benzene, there is no discrepancy between the solubility series and the internal pressure series, as given in Table VI. Niton, like all the other permanent gases,[18] behaves as though its liquid form had low internal pressure. The influence of this factor on gas solubility is thus shown very clearly. The fairly close agreement of the solubilities at the top of the table with those calculated from Raoult's law illustrates the value of this law for predicting solubility. There is one liquid in Table V, however, which does not show the solvent power for niton that would be predicted from its place in the internal-pressure table. This liquid is carbon disulfide. At the time the table of internal pressures was compiled it was observed that the various methods used for locating the position of carbon disulfide in the table were not in harmony. Thus,[19] calculation of Π from heat of vaporization, from critical data, and from coefficient of expansion served to place carbon disulfide near aniline at the foot of the table while, on the contrary, the value of Π calculated from the ratio of the coefficient of expansion to that of compressibility was almost identical with the corresponding value for benzene. There is, then, some uncertainty with regard to the internal pressure of carbon disulfide. If we refer to Table VI we find that the very low solubilities of nitrogen, carbon monoxide and carbon dioxide in carbon disulfide indicate that it should possess a high internal pressure. The

---

[17] Vapor-pressure data on niton are taken from Ref. 16a.

[18] Ref. 1c, p. 1075.

[19] Ref. 1c, p. 1071, Table I.

solubilities of iodine, sulfur, phosphorus, *p*-dibromobenzene, phenanthrene and anthracene, recorded in previous papers, all confirm this conclusion. The fact that these 10 solutes, none of which reacts with carbon disulfide, should all be in agreement, gives one considerable confidence regarding the position of this liquid in the solubility series, and so it is rather surprising that niton alone should indicate a different position. If the experimental data cited are correct, some factor must be sought which can modify to a considerable extent the predictions based upon the internal-pressure series alone. Smaller discrepancies have already been noted.[1d,1g].

In this case, also, there is apparently a slight discrepancy with ether and cyclohexane. According to the criteria available the latter has a higher internal pressure, and should, therefore, be the poorer solvent for most non-polar gases. The slight polarity of ether may be responsible for the reversal in position shown in Table V.

Solubilities of Actinium Emanation

It is interesting at this point to mention the solubilities at room temperature of actinium[20] emanation. This gas is an isotope of radium emanation. Its half-life period is very short and, therefore, an indirect method for determining solubilities was used. The gas was bubbled slowly through various liquids and then passed on to an ionization chamber where the rate of discharge of an electroscope was measured. If the liquid was a poor solvent and absorbed only a small amount of the emanation the electroscope was rapidly discharged.

Listed in order of decreasing absorptive power for actinium emanation the liquids are as follows: carbon disulfide, "petroleum" (probably heptane, hexane, octane), toluene, benzene, benzaldehyde, acetone, amyl alcohol, ethyl alcohol, water. This series is the same as the Ostwald-coefficient series found by Schulze, using niton as the solute. Hence, if we could convert these results to mole-fraction units, the liquids would fall into the same order as they do for niton. Therefore, with the exception again of carbon disulfide, they appear to support our theory.

General Summary of Data

A large part of the available data upon the solubilities of gases of low polarity is summarized in Table VI, together with the dielectric constants of the solvents as rough indications of their polarities. An approximate figure for the ideal solubility at 1 atmosphere partial pressure is given for all gases except hydrogen, where the extrapolation of $p°$ to ordinary temperatures would have to be made over such a wide range as to rob the result of nearly all significance. The values for hydrogen, nitrogen, carbon monoxide and carbon dioxide are by Just,[21] for the hydrocarbons by

[20] V. Hevesy, *Physik. Z.*, **12**, 1214 (1911).

[21] Just, *Z. physik. Chem.*, **37**, 342 (1901).

McDaniel,[22] for oxygen by Fischer and Pfleiderer,[23] for nitrous oxide and some of the values for carbon dioxide by Kunerth.[24] The sources of the other data have been discussed previously.

The solvents have been listed in this table in the order of increasing internal pressure as given by various methods outlined in the third paper of this series, the polar solvents, however, being listed in the positions corresponding to their solvent powers for the non-polar gases as the solubility falls off from top to bottom of the table.

The methods for calculating relative internal pressures are not very significant when applied to highly polar substances, and do not agree very well as to the position of such liquids in the internal pressure series, though the agreement is better for a substance such as aniline, of which the polarity is not great, than it is for acetone and the alcohols. We may note that the liquids of low polarity in the table maintain the same order with other solutes, while the highly polar liquids do not. In other words, the solvent powers of the polar liquids are far more specific. Nevertheless, the regularity in the positions of the polar liquids in the table with respect to all the gases for which we have data, except niton, whose solubility is abnormally diminished by polarity, indicates that the series is of considerable value for predicting solubilities of other inert gases, or for filling in the gaps in the table. For example, we may predict values, such as hydrogen in chloroform, 0.03, oxygen in carbon disulfide 0.021, our confidence in the prediction being greater where the solvent is non-polar.

The most striking feature of this table is that the regular decrease in solubility from top to bottom is maintained with but slight irregularities for hydrogen, nitrogen, carbon monoxide, oxygen, methane, ethylene, in accord with the low internal pressures of the liquefied gases.[25]

Chlorine and phosgene with their higher internal pressures show a maximum of solubility lower down in the table, as previously noted. The parallelism between the values for the first 7 gases in the table corresponds to a useful generalization given by Just, that the ratio of the solubilities of 2 gases is constant for all solvents. The table makes it evident, however, that this is true only when the 2 gases show the maximum or ideal solubility in the same region of the table. Chlorine and nitrogen, for example, would not show this constant ratio.

The chemical behavior of carbon dioxide indicates that it has a very appreciable polarity. Its ready union with various oxides to form carbonates would indicate the possibility of its uniting more or less generally with polar compounds. On the other hand, the fact that it is by no means

---

[22] McDaniel, *J. phys. Chem.*, **15**, 587 (1911).

[23] Fischer and Pfleiderer, *Z. anorg. allgem. Chem.*, **124**, 61 (1922).

[24] Kunerth, *Phys. Rev.*, **19**, 519 (1922).

[25] Ref. 1c, p. 1073.

TABLE VI

GENERAL SUMMARY OF DATA

Solubility of various gases in mole per cent. N × 10²												Relative internal pressures of solvents at 20°				
Temp.	20°	20°	20°	16–20°	25°	20°	20°	0°	40°	24°	20°					
Solute	H_2	N_2	CO	O_2	CH_4	CO_2	N_2O	Cl_2	Cl_2	$COCl_2$	Niton	$293\alpha/\beta$	$\frac{5200 + 30t_b}{V_{20}}$	$\alpha/V^{1/3}$	$a/V^2 \cdot 10^8$	Dielect. const.
Raoult's law		0.10	0.11	0.16 (18°)	0.32	1.78	1.81	27.3	8.7	55	6.92					
Hexane	...	...	...	...	0.31	..	..	..	..	..	7.95	2920	55.6	3.80	290	1.9
Heptane	...	...	...	...	..	..	..	27.0	..	..	..	..	55.5	..	300	1.9
Ethyl ether	...	...	...	0.190 (20°)	..	..	..	..	..	..	6.03	2630	60.1	3.64	320	4.3
Silicon tetrachloride	...	...	...	...	..	..	..	28.8	..	..	..	..	61.0	3.42	390	2.4
Amyl acetate	0.046	0.094	0.13	...	..	..	..	..	..	..	..	..	64.4	4.55	...	4.8
Cyclohexane	...	...	...	...	..	..	..	..	..	..	7.80	..	73.0	5.61	396	2.1
Ethyl acetate	0.032	0.068	0.099	...	..	..	..	..	..	..	..	..	78.5	5.16	340	6.1
m-Xylene	0.040	0.061	0.089	0.093 (16°)	0.26	1.02	..	..	..	53	5.85	3690	76.2	5.64	400	2.3
Carbon tetrachloride	...	...	...	0.099 (18°)	..	1.00	..	29.6	12.15	..	..	3690	77.5	5.78	416	2.2
Toluene	0.037	0.053	0.077	0.082 (18°)	0.21	1.08	..	..	..	53	5.20	3830	80.0	6.06	428	2.3
Chloroform	...	0.043	0.063	0.073 (16°)	..	1.23	1.82	..	..	..	4.68	3880	87.5	6.20	454	5.1
Chlorine	...	...	...	...	..	..	..	..	..	..	..	..	84.0	..	460	1.9
Benzene	0.026	0.041	0.061	0.065 (19°)	0.18	0.94	..	..	..	..	4.31	4100	85.6	6.48	472	2.3
Chlorobenzene (polar)	...	...	...	...	..	..	..	..	..	54	..	..	90.2	7.05	488	11.0
Acetone (polar)	0.021	0.042	0.065	0.068 (19°)	..	2.11	..	..	..	..	..	..	94.0	5.5	510	22.0
Ethylene dibromide	...	...	...	...	..	0.82	1.00	..	11.9	..	..	4760	106	8.71	560	4.9
Nitrobenzene (polar)	0.015	0.026	0.039	0.032 (18°)	..	1.12	..	..	..	..	..	..	110	10	...	35.0
Carbon disulfide	...	0.013	0.020	...	..	0.23	..	..	..	..	5.56	3840	109	8.7	610	2.6
Aniline	0.012	0.011	0.019	...	..	0.55	0.56	..	..	..	1.41	..	117	10	635	7.3
Water (polar)	0.0015	0.0013	0.0019	0.0017 (20°)	0.024	0.07	0.05	0.75	0.31	..	0.02	..	450	28	3650	80

highly polar would tend to make it adhere to the same solubility series with liquids of low polarity as was shown by the more inert gases. It will be noted, accordingly, that the solvents in the table which have low dielectric constants, and from which very polar bonds are absent, show solvent powers for carbon dioxide falling off regularly, almost within the obviously considerable limit of error, as the bottom of the table is approached. Polarity in the solvent, however, causes an abnormally high solubility, as illustrated by amyl acetate, acetone, ethylene chloride, aniline and nitrobenzene, and to a lesser degree by the alcohols, chlorobenzene and chloroform. Thus, aniline, which was a slightly poorer solvent for nitrogen and carbon dioxide than was carbon disulfide, is a much better solvent for carbon dioxide, due to its polarity and its basic character. Doubly bound oxygen in the solvent seems to produce abnormally high solubilities.

The relative solvent powers of aniline, *o*-toluidine and pyridine, given separately in Table VII, seem to depend, as might be expected, upon their relative strengths as bases. The dissociation constants of these bases in water may be used to indicate their relative powers of attracting molecules of carbon dioxide. Table VII gives the values found in the literature, together with those for 2 xylidines.

TABLE VII

Bases	Dissociation constants $\times 10^{-10}$	Temp. ° C.	10^4 *N* for CO_2 at 20°
Aniline	3.2	15	55
o-Toluidine	2.9	15	66
1,3,4-Xylidine	6.3	15	...
1,2,4-Xylidine	9.6	20	...
Pyridine	16.0	18	129

Although the constant for toluidine is given as practically identical with that for aniline, the distinctly higher constants for the xylidines indicate that the basic character increases in the order given, which accords fully with the solvent powers for carbon dioxide in the last column.

Although the solvent power of water for carbon dioxide is small, despite its power to react with that gas, its solvent power must be regarded as abnormally high on this very account, as the following ratios will show.

Ratio	N_2	CO	O_2	CO_2
$\frac{\text{Sol. in } H_2O}{\text{Sol. in } C_6H_6}$	0.032	0.031	0.031	0.077
$\frac{\text{Sol. in } H_2O}{\text{Sol. in } CS_2}$	0.10	0.095	...	0.32

The chemical nature of nitrous oxide is less familiar than that of carbon dioxide, and the data available are less abundant, but its solubilities seem to follow rather closely if it is regarded as similar to carbon dioxide, but slightly less polar. It is, therefore, somewhat less soluble than is carbon dioxide in the more polar solvents, but distinctly more soluble in the non-polar solvents, both by reason of its smaller polarity and the larger value for the ideal solubility.[26]

Summary

1. Solubilities of chlorine have been measured in heptane, carbon tetrachloride, silicon tetrachloride and ethylene dibromide.

2. These data, together with other data upon freezing-point depressions in liquid chlorine, are discussed in the light of the theory of solubility previously outlined, and shown to be in accord with earlier predictions.

3. Solubility data for hydrogen, nitrogen, carbon monoxide, oxygen, methane, carbon dioxide, nitrous oxide, chlorine, phosgene, niton and actinium emanation are summarized and their theoretical relations discussed.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A COMPARISON OF THE ATOMIC WEIGHTS OF TERRESTRIAL AND METEORIC NICKEL. II. THE ANALYSIS OF NICKELOUS CHLORIDE

BY GREGORY PAUL BAXTER AND FRANK ARTHUR HILTON, JR.

Received December 12, 1922

In a recent investigation, Baxter and Parsons[1] compared nickel extracted from a meteorite with that contained in commercial nickel salt, by quantitative reduction of nickelous oxide. In this way the atomic weight of terrestrial nickel was found to be 58.70, and that of meteoric nickel 58.68. While the concordance of the results obtained with terrestrial material was satisfactory, the three results with the meteoric sample varied from 58.66 to 58.72. This variation was unquestionably due to the fact that the magnitude of a correction for occluded gases in the oxide was less certain in the latter case. Although there seemed to be no real indication of a difference in the two sorts of material, the subject was taken up anew with material from the same meteorite but by the less troublesome and more satisfactory method of analyzing the anhydrous chloride.

---

[26] Kunerth has used his own data and those of Just as a basis for a denial of any connection between solubility and internal pressure for gases. He has, however, neglected to make the distinction previously insisted upon by the present author between liquids of low and high polarity. The reader can see that if the more polar liquids are omitted from Table VI the solvent powers of the non-polar liquids for carbon dioxide fall in the same order, within the limits to be expected, as was found for the other gases.

[1] Baxter and Parsons, THIS JOURNAL, 43, 507 (1921).