[CONTRIBUTION FROM THE LABORATORY OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Solubilities of Hydrogen Chloride and Hydrogen Bromide in Carbon Tetrachloride and in Chloroform

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A need which arose in this Laboratory for a knowledge of the solubilities of hydrogen chloride and hydrogen bromide in carbon tetrachloride and in chloroform has led us to determine these values at 0, 15 and 25°.

The only measurements of any of these values which we have found in the literature are those of Bell[2] on the solubility of hydrogen chloride in carbon tetrachloride and in chloroform and those of Hamai[3] on the solubility of hydrogen chloride in carbon tetrachloride. Bell records only one determination for each solvent; Hamai's results show evidence of large error due to failure to attain equilibrium with respect to the partial pressure of the solvent vapor in the gas phase.

Our method of measurement has consisted of saturating the solvent in an absorption flask with the solute vapor under known partial pressure and then analyzing a weighed sample of the solution to determine the amount of dissolved gas. This method is superior to the common method of determining the amount of dissolved gas by means of a gas buret because its accuracy does not depend on a knowledge of the degree to which the solute gas in the connecting tubes and manometer is saturated with the solvent vapor. It has added convenience because it does not require thermostating of any part of the apparatus except the absorption vessel.

Experimental Procedure

Carbon Tetrachloride.—Merck technical grade carbon tetrachloride was dried with phosphorus pentoxide, decanted and distilled. It was collected in a flask containing dry air with no opening except through a calcium chloride tube. Care was taken to avoid contamination with moisture in transferring it to the absorption flask. Some solubility determinations made with untreated carbon tetrachloride indicated that these drying precautions did not significantly affect the results.

Chloroform.—Merck or Mallinckrodt reagent grade chloroform was washed three times each with concentrated sulfuric acid, with dilute sodium hydroxide and with water. It was then dried over phosphorus pentoxide, decanted and distilled into a flask containing dry nitrogen.

Hydrogen Chloride.—Hydrogen chloride was made by dropping concentrated sulfuric acid from a separatory funnel onto sodium chloride in a flask and passing the evolved gases through glass wool and calcium chloride.

Hydrogen Bromide.—Hydrogen bromide was prepared by bubbling tank hydrogen through liquid bromine and then passing the mixed gases, which contained excess hydrogen, over an electrically heated platinum wire spiral. After the gases passed over this hot wire (red glow) no bromine color was visible but they were then bubbled through mercury or freshly reduced copper gauze to remove residual bromine. The hydrogen bromide was then frozen out in a liquid-air trap and the excess hydrogen allowed to escape. All connections in the preparation system were of glass from the point where the hydrogen was admitted to the liquid-air trap. The middle fraction of the gas which distilled when the temperature of the hydrogen bromide was allowed to rise to the boiling point was used in the solubility determinations.

Apparatus and its Operation.—Solvent was introduced into the absorption flask F (Fig. 1) by disconnecting the pressure tubing joint at C, flushing the system with dry air or nitrogen, connecting the solvent storage flask at C and pushing the solvent from it into F with dry nitrogen. Then the system was degassed by connecting an aspirator at K and boiling the solvent. The three-way stopcock D prevented air from being trapped in the sample exit tube E, or the liquid from remaining in the tube up to the stopcock where it could not come in contact with the solute gas. The absorption flask was immersed up to the level of the stopcock in a water-bath G thermostated to ±0.05°.

During the degassing the mercury in the manometer I was adjusted to the level of the stopcock H. After the degassing the stopcocks H and J were turned to shut the line to the aspirator and allow a reading of the vapor pressure of the solvent in F. This vapor pressure value was used as the partial pressure of the solvent in the subsequent calculations. In no case did it vary by more than 2 mm. from the values given in "International Critical Tables."

For the purpose of introducing solute gas to the system the hydrogen chloride generator or the trap P containing liquid hydrogen bromide was connected to the system at O. When hydrogen bromide was used it was passed through reduced copper gauze in the tube N. Preceding admission of the gas to the manometer and absorption vessel it was bubbled through the metering flask L until the tubes P, N, M, K had been flushed out with several times their volume of the gas. Then stopcocks H and J were turned to introduce gas into the manometer and absorption vessel until the pressure reached the desired value. The absorption vessel was then shaken vigorously and the pressure was read immediately before taking a sample for analysis. About two minutes of shaking was found sufficient to assure solute-solvent equilibrium at the interface in the absorption flask, as indicated by the fact that further

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[2] Bell, *J. Chem. Soc.*, 1371 (1931).

[3] Hamai, *Bull. Chem. Soc. Jap.*, **10**, 5 (1935).

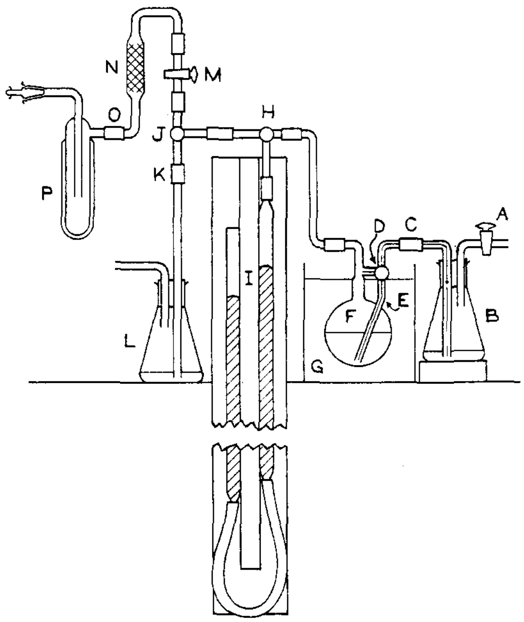

Fig. 1.

intermittent shaking and standing for periods as long as thirty minutes caused no further change (within 1 mm.) in the pressure reading on the manometer. The fact that no gradual increase in pressure was observed during this time indicates that diffusion of solvent vapor into the solute gas in the 6 mm. o. d. connecting tubing is a very slow process.

The sample flask B (including flask, rubber stopper, glass tubing, stopcock A and about 75 cc. of water) was weighed, connected at C, and partially evacuated by means of an aspirator to a pressure less than that in the absorption flask F. Then stopcock A was closed and stopcock D was opened for one to five seconds to allow solution to flow from the absorption flask F to the sample flask B. This gave a 10- to 20-g. sample which was weighed to 0.01 g. The flask was then set aside to be analyzed after several samples had been taken.

The rubber connections in the system, which were incorporated to allow vigorous shaking of the absorption vessel, were all of pressure tubing. Those which did not have to be detached were coated with beeswax and rosin. The absence of leaks was frequently reaffirmed by observing the manometer while the absorption system was at pressures below atmospheric.

Analysis.—The acid in each weighed sample of the solution from the absorption flask was determined by titration with standard sodium thiosulfate (0.01 to 0.1 *N*) after first adding excess potassium iodate and potassium iodide, using starch as indicator. Standardizations of the sodium thiosulfate against standard hydrochloric acid plus excess iodate and iodide were in agreement with standardizations against potassium dichromate. The results were not altered by the presence of technical grade carbon tetrachloride in the standardization flask. Normalities were determined to 0.1%. Titrations were reproducible to 0.2% even in 0.001 *N* solutions.

Calculations.—From the experimental data the mole fraction (N_{HX}) of the hydrogen halide in each sample, the partial pressure of the hydrogen halide in the gas phase (P_{HX}) and the solubility constant (K_S) were calculated with the aid of the following formulas

$$N_{HX} = \frac{\frac{cc. \times N}{1000} - a}{\frac{\text{wt. of sample} - b}{\text{mol. wt. of solvent}} + \frac{cc. \times N}{1000} - a}$$

$$P_{HX} = P - P_S\,(1 - N_{HX})$$

$$K_S = \frac{N_{HX}}{P_{HX}}$$

cc. = cubic centimeters of thiosulfate solution used for the titration; N = normality of the thiosulfate; a = moles of HX gas in the capillary tube E of Fig. 1; b = weight in grams of gas in the sample; P = total pressure in mm.; P_S = vapor pressure of pure solvent in mm.

Sources of Error.—The capillary exit tube E (0.35 cc.) contained solute gas which was pushed over with the sample. Correction was made for this on the assumption that equilibrium conditions of gas and solvent vapor prevailed in the tube. With no correction the error introduced in the solubility value would have been only 1%.

It was found that about 0.05 g. of water was evaporated from the sample flask when it was evacuated with the aspirator before taking a sample. A correction of 0.05 g. (less than 0.5%) was therefore added to the observed weight of the sample in each case. The evacuation procedure was carried out in the same manner each time. Several experimental checks of the correction factor agreed within 0.01 g.

Certain experiments, during which there was evidence of leakage of air into the system, gave abnormally low values of K_S. A few others, in which there was evidence of the presence of free bromine in the solute gas gave high results. These values were discarded.

Stopcock Grease.—The flow of carbon tetrachloride or chloroform through the stopcock D (Fig. 1) resulted in sufficient thinning of Cenco or Apiezon stopcock grease so that the stopcock could not be used for more than one or two samples without developing a leak which necessitated regreasing of the stopcock and repetition of the process of degassing the solvent. Further, the grease washed into the sample flask added an unknown mass (probably about 0.1 g.) to the sample.

In the latter part of the work these difficulties were avoided by using a lubricant made of dextrin, *d*-mannitol and glycerol.[4]

Results

Hamai's results[3] for hydrogen chloride in carbon tetrachloride at 25° together with the values of K_S which we have calculated from them are given in Table I. Our results for the same system are given in Table II and our results for the four systems which we have investigated are given in condensed[5] form in Table III.

The average deviation from the average for the K_S values is given after the average value.

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[4] Meloche and Frederick, THIS JOURNAL, **54**, 3264 (1932).

[5] The detailed experimental data are included in senior theses filed with the University of Wisconsin library by J. J. Howland, Jr., and D. R. Miller in 1940 and 1941, respectively.

TABLE I

HCl IN CCl_4, 25°; RESULTS OF HAMAI

p_{HCl}	N_{HCl}	$K_S \times 10^5$
433.5	0.00367	0.85
531.5	.00622	1.17
580.0	.00757	1.30
631.5	.00817	1.29
680.5	.00955	1.40
779.5	.01200	1.54

TABLE II

HCl IN CCl_4, 25°; OUR DETERMINATIONS

p_{HCl}	N_{HCl}	$K_S \times 10^5$
178.5	0.00379	2.12
379.5	.00803	2.11
425.0	.00922	2.16
548.5	.01190	2.17
662.5	.01415	2.14
		2.14 ± 0.02

TABLE III

System	Temp., °C.	No. of detns.	$K_S \times 10^5$	p_{HX} range, mm.
HCl in CCl_4	0	4	3.22 ± 0.01	269–667
	20	7	2.34 ± .03	123–695
	25	5	2.14 ± .02	178–662
HCl in $CHCl_3$	0	3	4.66 ± .03	308–581
	15	5	3.48 ± .02	171–587
	25	5	2.93 ± .02	194–610
HBr in CCl_4	0	2	8.26 ± .01	304–430
	15	3	5.95 ± .02	298–555
	25	2	5.03 ± .02	345–517
HBr in $CHCl_3$	0	3	9.92 ± .03	294–511
	15	5	7.17 ± .03	155–407
	25	8	5.97 ± .03	210–664

The limited number of determinations in certain cases, particularly for hydrogen bromide in carbon tetrachloride, reduces the significance of the estimation of the precision of the results.

Heats of Solution.—Plots of log K_S against $1/T$ show all of the points falling on a straight line (within 2%) in the case of each solution studied. The heats of solution calculated from these plots are given in Table IV. If all of the points were in error by 2% and if the errors were such as to amplify rather than cancel each other, the heat of solution values would be in error by 200 to 300 cal.

TABLE IV

HEATS OF SOLUTION

System	Heat of solution
HCl in CCl_4	2670 cal./mole
HCl in $CHCl_3$	3000
HBr in CCl_4	3230
HBr in $CHCl_3$	3260

Discussion

Previous Work.—Bell[2] made one measurement each on the solubilities of hydrogen chloride in carbon tetrachloride and in chloroform at 20°. His method consisted of bubbling the gas at atmospheric pressure through a known volume of the solvent until equilibrium was attained and then flushing the solute gas out of the solvent into a known amount of alkali for titration. We have calculated values of K_S of 2.38 for hydrogen chloride in carbon tetrachloride and 5.84 for hydrogen chloride in chloroform from his data. Seven experimental determinations which we have made on the carbon tetrachloride system at 20° give a value of 2.34 ± 0.03, in good agreement with Bell's results. Calculation of a value of K_S for the chloroform system at 20° from our data obtained at 0, 15 and 25° gives 3.19, which is considerably lower than Bell's. In the absence of an inhibitor chloroform produces phosgene when exposed to air. Phosgene hydrolyzes in aqueous solution to produce hydrochloric acid. It is probable that the oxidation and hydrolysis of this nature which must have occurred during the prolonged aeration used in Bell's experiment is responsible for the high result which he obtained. Such oxidation does not occur with carbon tetrachloride.

The value of 2670 cal./mole which we have calculated for the heat of solution of hydrogen chloride in carbon tetrachloride is in contrast to the value of 3680 cal./mole obtained from the direct colorimetric measurements of Noyes and Tully.[6] We have no satisfactory explanation for this discrepancy. Noyes and Tully note that their value is in close agreement with the heat of vaporization (3600 cal./mole) of hydrogen chloride at its boiling point.[7] Such correspondence is surprising since the heat of vaporization was determined at −84.3° and the heat of solution at 0°, and since the solution does not obey Raoult's law.

The results obtained by Hamai[3] on the solubility of hydrogen chloride in carbon tetrachloride at 25° (Table I) give values of K_S which increase with increasing pressure. His values for 20 and 15° show a similar variation.

Our values of K_S are consistently higher than these and do not vary with pressure. He obtains a value of 6000 cal./mole for the heat of solution as contrasted to our value of 2670 cal./mole.

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(6) Noyes and Tully, THIS JOURNAL, **47**, 1338 (1925).

(7) Estreicher and Schnerr, *Chem. Zentr.*, **81**, II, 1737 (1910).

Hamai used the conventional method for solubility determination which consists of bringing a known amount of solvent into contact with the solute gas and measuring the change in volume of the gas with a gas buret. This method is valid only if the partial pressure of the solvent vapor in all parts of the apparatus is known. It is usually assumed that in the absorption vessel itself and the parts of the apparatus directly connected to it this pressure is equal to the vapor pressure of the solvent. However, unless the gas as well as the liquid is thoroughly mixed, the composition of the gas phase will vary, since it depends on the slow diffusion of the solvent vapor against the incoming of HX gas. Failure to attain a definitely known partial pressure of the solvent vapor throughout the gas phase may lead to values of K_S which are either high or low depending upon the assumptions which are made with regard to the degree of saturation. If it is assumed that complete equilibrium is attained in the gas phase, when this is not the case, the results will be high. If solvent vapor diffuses further into the system than is assumed, the K_S values will be low.

The results of Hamai, which are low but which increase with pressure, indicate that the solvent vapor diffused further into his system than he assumed to be the case. As the pressure of the solute gas increases the vapor pressure of the solvent becomes relatively less important and it would be predicted that the K_S values would increase as he observed. Added weight is given to this interpretation of Hamai's results by the fact that he observed nearly constant K_S values for hydrogen chloride in ethylene bromide, a solvent which has a much lower pressure than carbon tetrachloride. The fact that his value for the heat of solution of hydrogen chloride in carbon tetrachloride is much larger than ours may be due to a fictitious decrease in his solubilities with rising temperature, resulting from the increasing vapor pressure of the solvent.

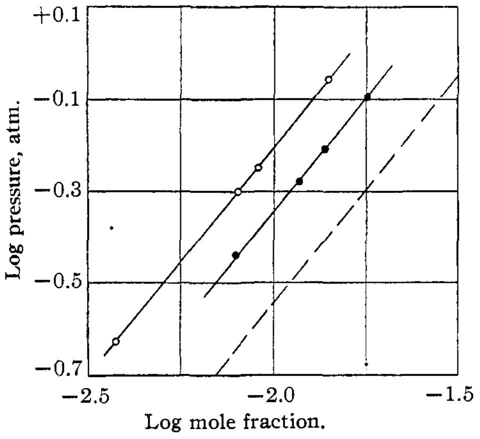

Fig. 2.—●, HCl in $CHCl_3$ at 25°; ○, HCl in CCl_4 at 25°. Broken line represents Raoult's law.

The method used in the work of the present paper avoids the need of concern with regard to the degree of saturation of the gas with the solvent vapor since only the total pressure of the gas and not its volume is measured. If the total pressure in the gas phase is greater than the vapor pressure of the solvent, the partial pressure of the solute at the liquid–gas interface will be equal to the total gas pressure minus the vapor pressure of the solvent from the solution.

The problem of attaining saturation of the liquid phase with the gaseous solute has received the attention of a number of workers. At one time[8] it was suggested that the shaking method, employed in the work of the present paper, might lead to supersaturation; but this has been disproved.[9] The shaking method has decided advantages in speed and simplicity over the magnetic stirring or gas bubbling methods and is much faster than the static method of attaining equilibrium used by Saylor.[10]

Agreement with the Laws of Henry and Raoult.—It is apparent from the data presented that the solutions in question obey Henry's law, *i. e.*, that the concentration of solute is proportional to the partial pressure. In order to determine whether these solutions obey Raoult's law, plots of the type of Fig. 2 have been made to allow comparison of the observed vapor pressure with the ideal vapor pressure, obtained by multiplying the fugacity of the pure liquid solute by the mole fraction in solution. The difference between the observed and ideal pressures is almost wholly due to the non-ideality of the solution since the deviation of the vapors from the gas laws at the low pressures in question is less than 1%, and hence the pressure may be considered as equal to the fugacity. Table V summarizes the Raoult's law comparisons. The deviation from the law is indicated by the values of the activity coefficient, γ, of the solute, given in columns 4 and 5 ($a = f/f_0$ where f is the observed partial pressure of solute and f_0 is the fugacity of the pure liquid

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[8] Cady, Elsey and Berger, This Journal, **44**, 1456 (1922).

[9] Livingston, Morgan and Ryne, *J. Phys. Chem.*, **34**, 1578 (1930).

[10] Saylor, This Journal, **59**, 1712 (1937).

solute. $\gamma = a/N = f/f_0N$ where N is the mole fraction of the solute).[11]

TABLE V

T, °C.	V. p. liq., atm.	Fugacity, liq., atm.	γ in CCl_4	γ in $CHCl_3$
		HCl		
0	25.5	19.5	2.12	1.39
15	37.0	25.4		1.48
20	41.6	26.9	2.09	1.57
25	46.2	28.7	2.19	1.57
		HBr		
0	12.3	11.1	1.44	1.19
15	18.1	16.2	1.36	1.12
25	23.0	20.2	1.29	1.10

The values for the fugacity of the pure liquid hydrogen chloride were estimated with the aid of vapor pressure and vapor density data,[12] and the approximate equation of Lewis and Randall for the fugacity.[13] Since vapor densities of saturated hydrogen bromide vapor were not available, van der Waals equation with the constants calculated from critical constant data[12] was used for estimating the molal volumes of this gas for use in the Lewis and Randall equation. That the fugacity values obtained are at best only rough approximations is emphasized by the fact that when the experimentally determined density[12] of saturated hydrogen chloride vapor at 25° is used in the computation a value of 28.6 atm. is obtained in contrast to the value of 33.8 based on van der Waals equation. The calculation of O'Brien and co-workers gave 30.3[14] atm. for this same quantity; and 18.3[15] atm. for the fugacity of saturated hydrogen bromide vapor at 25° in contrast to the value of 20.2 calculated with the aid of van der Waals equation.

It is evident from the values of Table V that all of the solutions investigated show positive deviations from Raoult's law. In this respect carbon tetrachloride and chloroform then fall into a class with the mono-halobenzenes.[16] References and discussion of attempts to correlate solubilities of compounds of the type dealt with in this paper with other physical properties of the solutions are given by the authors cited.[16]

Summary

1. The solubilities of hydrogen chloride and hydrogen bromide in carbon tetrachloride and in chloroform have been determined at 0, 15 and 25° at pressures below one atmosphere. The solubility in each case is proportional to the partial pressure of the solute. All of the solutions show positive deviations from Raoult's law.

2. The values for the solubility of hydrogen chloride in carbon tetrachloride given by Hamai are found to be too low and to show a false pressure dependence. A probable source of the error is suggested.

3. A solubility apparatus which offers certain advantages in the investigation of gaseous solutes which can be determined chemically is described.

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[11] Hildebrand, "Solubility," Reinhold Publishing Corp., New York, N. Y., 1936, p. 24.

[12] "International Critical Tables," Vol. III, p. 228.

[13] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Compounds," McGraw-Hill Book Co., New York, N. Y., 1923, p. 198.

[14] O'Brien, Kenny and Zuercher, THIS JOURNAL, **61**, 2504 (1939).

[15] O'Brien and Bobalek, *ibid.*, **62**, 3227 (1940).

[16] O'Brien and Byrne, *ibid.*, **62**, 2063 (1940).

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Conductance of Hydrochloric Acid in Aqueous Solutions from 5 to 65°

BY BENTON BROOKS OWEN AND FREDERICK HUMPHREY SWEETON[1]

The purpose of this study was to investigate the conductance of hydrochloric acid in water as a function of temperature over a very wide concentration range. The data in dilute solutions are useful in the study of weak electrolytes and the extrapolated limiting conductances supplement the series of values obtained by Owen and Waters[2] in dioxane–water mixtures at various temperatures. In the more concentrated solutions the data show a remarkable decrease in the effect of concentration upon both the conductance and its variation with temperature. At the highest concentrations the proton exchange mechanism, which explains the high mobility of the hydrogen ion, would be seriously affected by proton–chloride ion combination and possibly hindered by combination of the chloride ion with water. The meas-

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[1] This communication embodies part of the thesis presented by Frederick Humphrey Sweeton to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy (1941).

[2] B. B. Owen and G. W. Waters, THIS JOURNAL, **60**, 2371 (1938).