3. The values found for the solubility of sodium bicarbonate check very closely the best values given in the literature.
4. The values found for the solubility of potassium bicarbonate, especially at 25 and at 30°, are higher than the best values found in the literature.
5. The composition of the solutions found in the ternary system, and the absence of complicating double salts and solid solutions, indicate that the present study might be of value in the commercial separation of sodium and potassium carbonates.

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[CONTRIBUTION FROM THE PHYSIKALISCHES INSTITUT, LEIPZIG, AND THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

THE DETERMINATION OF THE SOLUBILITY OF SLIGHTLY SOLUBLE LIQUIDS IN WATER AND THE SOLUBILITIES OF THE DICHLORO-ETHANES AND -PROPANES

BY PAUL GROSS

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In order to make some measurements of the salting out effect of salts in water on the slightly soluble dichloro-ethanes and propanes, it became necessary to develop a method for determining their solubility in water and salt solutions. As this method is capable of considerable precision and as Hill[1] has pointed out that the methods for determining the solubility of liquids in liquids are in general very unsatisfactory, it is described here, together with the results of some solubility determinations made by its use.

The principle of the method is to prepare saturated solutions of the substance in water by shaking in a thermostat in the usual way. These solutions are then analyzed by the use of a liquid interferometer. The interferometer scale is calibrated by dissolving weighed amounts of the substance in weighed quantities of water.

Experimental

The instrument available was a Zeiss portable water interferometer with a glass comparison chamber 40 mm. in length with two cells, in one of which a sample of the solution to be analyzed was placed and in the other the comparison or reference liquid. The general procedure and precautions to be observed in the use of the interferometer have been described in a number of places,[2] so it is unnecessary to repeat them here.

The scale readings on the compensator drum of the interferometer are not directly proportional to the number of interference bands it is necessary to shift to return the displaced upper bands to zero setting. The relation of bands shifted to scale divisions for different parts of the range of the instrument (which has a total of 3000 scale di-

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[1] Hill, THIS JOURNAL, **45**, 1143 (1923).

[2] See, for example, L. H. Adams, *ibid.*, **37**, 1181 (1915).

visions) was therefore found. From these, using the procedure described by Gans and Bose,[3] the following equation was obtained

$$S = R - 0.00003762\,R^2 \qquad (1)$$

where R is the observed scale reading and S is the reading which would be observed if the scale readings were directly proportional to the number of bands shifted.

Standard solutions of the substance being investigated were prepared by dissolving weighed amounts of it in 500 or 1000 g. of water. These were made by dropping a vial with a ground-in stopper containing the liquid into the weighed sample of water contained in a bottle with a well ground-in glass stopper. The stopper of the vial was loosened, the vial dropped in and its stopper after it. The bottle was then stoppered as quickly as possible. The weight of the water in the bottle was so chosen that the free space in the bottle after the vial and liquid were in was not more than 10 cc. in the case of the bottles holding 1000 cc., and 5 cc. in the case of those holding 500 cc. By making this space small, appreciable loss of the liquid as vapor was thus avoided. These bottles were placed on a shaker and shaken until no more droplets of the liquid remained undissolved. This was quite easy to determine as these substances are heavier than water and have high refractive indices, so that even minute drops are readily visible. When solution was complete the scale reading R was found for a sample of the solution placed in the interferometer. Blank experiments made by shaking an empty vial in these bottles with 500 g. of water showed that no appreciable solution of the glass had taken place. The proper quantities of liquid to be used in making up the standard solutions can be found by a trial determination using about 0.2 g. of the substance per 1000 g. of water and from the value for the saturated solution made as described later.

From the observed readings R for these solutions the values of S were calculated by means of Equation 1. The values of S so obtained, when plotted, were found to be a linear function of the concentrations expressed as grams per 1000 g. of solution. This is illustrated by the data of Table I for 1,1-dichloro-ethane in water. The values of C are the concentrations in grams per 1000 g. of solution. The values of C' are those calculated from the equation

$$C' = 0.00507\,S \qquad (2)$$

where S is obtained as above.

TABLE I

DATA FOR 1,1-DICHLORO-ETHANE

S	C	C'	ΔC	% error
158	0.773	0.801	−0.028	3.5
345	1.711	1.750	− .039	2.2
475	2.443	2.408	+ .035	1.4
633	3.209	3.209	+ .000	0.0

Average error, 1.8%.

The direct proportionality of C and S was also established in another way, as follows. The saturated solutions of the substance were prepared by shaking 10–20 cc. of the liquid with about 500 g. of water in thin-walled cylindrical flasks in a large water thermostat regulated to 25 ± 0.01°.

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[3] Gans and Bose, *Z. Instrumentenkunde,* **36**, 137 (1916).

Samples were withdrawn and analyzed at intervals of several hours until constant readings on the interferometer were obtained. About five hours was usually sufficient to effect equilibrium. However, the shaking in all cases was continued for at least twenty-four hours, and in most cases forty-eight hours elapsed before the final samples for the solubility values were taken. The readings for the saturated solutions were very reproducible. After equilibrium had been attained, one or more samples weighing several hundred grams were siphoned out of the shaking flask in the thermostat and run beneath the surface (to prevent loss by vaporization) of a weighed amount of water contained in a weighed flask with a ground-in stopper. The flask was then stoppered and weighed, and thus the weight of the saturated solution added was found. From this the dilution of this solution as a fraction of the saturated solution was calculated. The interferometer readings for these solutions were then determined. As an illustration of the accuracy with which the direct proportionality between readings and the concentrations figured as fractions of the saturated solution holds, some data for 1,1-dichloro-ethane are given in Table II.

TABLE II

DATA FOR 1,1-DICHLORO-ETHANE

Fraction of saturated solution	1.000	0.6901	0.4187
S, observed	993	685	414
S, calculated	...	685	416

From the data of Table II and Equation 2 the value of the solubility is calculated to be 5.035 g. per 1000 g. of solution and 5.06 g. per 1000 g. of water.

The substances used were purified from the best obtainable commercial samples by fractional distillation, using an all-glass still with a column 150 cm. long of the type previously described.[4] Temperatures were determined on thermometers standardized by the Bureau of Standards and pressures were read on a precision barometer.

1,1-Dichloro-ethane.—A fraction of 414 g. boiling between 57.0 and 57.1° was used. I. C. T. gives 57.3°.

1,2-Dichloro-ethane.—A fraction containing 637 g. boiling from 83.6 to 83.8° was used. Timmermans[5] gives 83.69–83.71°.

1,2-Dichloropropane.—The commercial sample containing 1000 g. was fractionated three times and the constant-boiling fraction weighing 257 g. from the third fractionation was used. It boiled from 94.4 to 96.6°. I. C. T. gives 96.8°.

1,3-Dichloropropane.—A fraction of 507 g. boiling from 120.5 to 120.6° was used. Freund[6] gives a boiling point of 119.5° at 740 mm. This would correspond to a corrected boiling point of 120.3° if we assume that the value of C in Crafts' correction rule is C = 0.000100, the same as the value given by Crafts for propylene bromide.

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[4] Gross and Wright, *J. Ind. Eng. Chem.*, **13**, 701 (1921).

[5] Timmermans, *Bull. soc. chim. belg.*, **24**, 244 (1910).

[6] Freund, *Monatsh.*, **2**, 639 (1881).

The value 125° given in I. C. T., Vol. I, p. 183, is evidently too high by at least 3°. It is apparently the value of Herzfelder[7] for a sample of 1,3-dichloropropane which, as Herzfelder himself states, contained iodine. The other values in the literature all agree in placing the boiling point at about 120 to 120.5°.

Carbon Tetrachloride.—This was a sample of Kahlbaum's "sulphur-free reagent for analytical use." It was used without further purification. The results for this substance are only preliminary.

The two remaining isomers of dichloropropane had originally been prepared and it was proposed also to measure their solubility. On trial it was found that they were hydrolyzed by water, as shown by the failure to obtain constant saturation values. This was confirmed by testing for chlorides, which were shown to be present. In the case of each of the five substances used above, hydrolysis was carefully tested for and found absent.

The solubility data are given in Table III. The estimated errors of these solubility values are as follows: for 1,2-dichloro-ethane, 1%; for 1,1-dichloro-ethane, 2.0%; for the dichloropropanes, 2.5%. The error for the carbon tetrachloride is about 5%, as in this case the limit of the sensitivity of the interferometer with the 40-mm. chamber available was approached. This value must therefore be regarded as only preliminary. It is planned to repeat the measurements for this substance with a purer sample and with a longer (80-mm.) liquid chamber.

The sensitivity of the method can be appreciated when it is realized that an error of 2.0% in the solubility value of 1,1-dichloro-ethane represents an error of 0.01% on the total composition of the solution.

TABLE III

SOLUBILITY DATA

	Solubility in water at 25°, g. per 100 g. of H_2O	Moles per 1000 g. of H_2O
1,1-Dichloro-ethane	0.506	0.0511
1,2-Dichloro-ethane	.865	.0874
1,2-Dichloropropane	.280	.0248
1,3-Dichloropropane	.273	.0243
Carbon tetrachloride	.077	.0050

Rex[8] gives values for the solubility of three of these substances in water at 20 and 30°. From these the following values for the solubility in grams per 100 g. of water at 25° were interpolated: for 1,1-dichloro-ethane, 0.545; for 1,2-dichloro-ethane, 0.881; for carbon tetrachloride, 0.082. These values are consistently higher than those given above but this seems probable in view of the method used by Rex, which was to measure in a capillary the volume of liquid before and after saturating a known amount of water with it and determining the solubility from the difference in volume. Apparently no allowance was made for possible loss of the liquid which may have adhered to the walls of the larger vessel, containing the water,

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[7] Herzfelder, *Ber.*, **26**, 2434 (1893).

[8] Rex, *Z. physik. Chem.*, **55**, 365 (1906).

to which the capillary was sealed. This loss would result in a larger apparent solubility.

The method as outlined has also been used to determine the solubility of these substances in salt solutions, in particular in 0.5 *M* potassium chloride and 0.5 *M* magnesium sulfate. The procedure is in all particulars the same as for water. A large volume of the salt solution of the desired concentration is made up and used throughout for dilutions, standard solutions, comparison solutions in the interferometer, etc., in the place of distilled water. In general, there appears to be no reason why the method should not be applicable to solubility measurements in practically any colorless aqueous solutions for any type of substance. Measurements of solubilities in non-aqueous solvents are also possible but these would in many cases involve difficulties inherent in the construction of the interferometer itself, which is primarily designed for aqueous solutions.[9]

In conclusion I take this opportunity to thank Professor Peter Debye for placing facilities at my disposal at the Physikalisches Institut, Leipzig, with which part of the work was done, and for valuable suggestions and advice.

Summary

1. A method for the determination of the solubility of difficultly soluble liquids in water and aqueous solutions is described.

2. The solubilities of 1,1-dichloro-ethane, 1,2-dichloro-ethane, 1,2-dichloropropane and 1,3-dichloropropane are given. A preliminary value for the solubility of carbon tetrachloride is also given.

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THE ACTIVATION OF OXYGEN BY ELECTRON IMPACT

BY ROBERT H. DALTON

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Introduction

The purpose of this research was to study the chemical behavior of oxygen activated by electron impact and to measure the energy necessary for its activation. The general plan was to use an apparatus similar to that employed by Glockler, Baxter and Dalton[1] in the study of the reaction between copper oxide and active hydrogen.

The oxygen was introduced at pressures of 0.05–0.4 mm. of mercury into a four-electrode tube connected with a liquid-air trap and a Pirani pressure gage. A four-electrode tube was used in order that the energy loss of the

[9] In this connection see Cohen and Bruins, *Proc. Acad. Sci. Amsterdam*, **24**, 114 (1921).

[1] Glockler, Baxter and Dalton, THIS JOURNAL, **49**, 58 (1927).