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

# THE USE OF CALCIUM HYDRIDE FOR THE DETERMINATION OF THE SOLUBILITY OF WATER IN BENZENE, CARBON TETRACHLORIDE AND TOLUENE

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## Introduction

For the determination of small amounts of water, 0.1% or less, a gasometric method has the advantage of giving a relatively large volume of gas from a small amount of water. Various reagents have been used to react with water to evolve a gas the volume of which was measured. Calcium carbide was used by Roberts and Frazer[2] and other investigators. Sodium[3] and the Grignard reagent[4] have also been used.

The energetic reaction of calcium hydride with water to evolve hydrogen suggested its use for the determination of water. The hydride offers two advantages over calcium carbide: (1) in most reagents the hydrogen evolved is not as soluble as acetylene and (2) the experimental accuracy is greater since, according to the following equations, twice the volume of gas is evolved:

$$CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2$$
$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$

Calcium hydride has been used by Wirth[5] to determine water in ethyl alcohol using the reaction

$$CaH_2 + CO_2 + H_2O = CaCO_3 + 2H_2$$

His results, however, are of doubtful value because of the possible reaction of calcium hydride with the alcohol to evolve hydrogen.[6]

Since the completion of the work reported in this paper, an article has been published describing a method developed by Olav Notevarp,[7] who used calcium hydride to determine the water content of various solids and high-boiling liquids. The two methods, developed simultaneously and independently, are radically different since in Notevarp's method the hydride is suspended above the sample and does not mix with it. He found his apparatus to be impractical for determinations of water in low-boiling

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[1] Part 2 of a dissertation submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Roberts and Frazer, *J. Soc. Chem. Ind.*, **29**, 197 (1910).

[3] Graefe, *ibid.*, **25**, 1035 (1906).

[4] Zerewitinoff, *Z. anal. Chem.*, **50**, 680 (1911).

[5] Wirth, *Z. Deut. Öl-Fett-Ind.*, **41**, 147 (1921).

[6] Moissan, *Compt. rend.*, **127**, 29 (1898); B. von Lengyl, *Math. Nat. Ber. Ungarn.*, **14**, 180 (1898); Perkin and Pratt, *J. Chem. Soc.*, **95**, 161 (1909).

[7] Olav Notevarp, *Z. anal. Chem.*, **80**, 21 (1930).

organic solvents such as were used in the present investigation. Also, his analyses were concerned with various practical determinations in which larger percentages of water were present.

The present investigation was begun by studying the determination of water in benzene since the latter does not react[8] with the calcium hydride. The method developed was then extended to other solvents.

## Experimental

### Materials

The **benzene** was reagent grade, found free from thiophene, and had a boiling point 79.6° (corr.) and melting point 5.4° (corr.).

The **carbon tetrachloride** was found to be free from all impurities (boiling point 76.8° corr.).

The **toluene** was purified by standing over mercury, refluxing with phosphorus pentoxide and fractionating, the fraction distilling at 110.4–110.6° being used.

The **calcium hydride** was found to be about 97% pure. The chief impurity was about 2% calcium nitride as determined by acid titration of the ammonia evolved in the reaction with water. It contained about 0.2% of calcium carbide and possibly some metallic calcium and calcium oxide. None of these impurities interfered with the determinations, as will be shown later by the results in Table I.

**Apparatus.**—In the type of apparatus used by McNeil,[9] calcium carbide was dropped from a side arm into the sample contained in a flask connected with a gas buret. This gave inaccurate results when calcium hydride was used to determine water in benzene. The errors introduced by such an apparatus are as follows. (1) The largest error is due to adsorbed gases found present on the powdered calcium hydride. A considerable volume of gas was released when the hydride was heated in a tube or when the powder was dropped into a dry organic liquid. (2) A film of moisture remains on the reaction flask despite drying at 110° and is also adsorbed during the manipulations. (3) Any rubber present is attacked by the organic vapor with consequent leaks and introduction of impurities.

These errors are eliminated in the apparatus shown in Fig. 1, which is constructed as follows: a 150-cc. pyrex flask A is connected by the ground-glass stopcock B with the 50-cc. bulb C fitted with a ground-glass joint D. The ground-glass joint F is tightly held together by the rubber bands G stretched between wires encircling each half of the joint. The tube J is partly filled with calcium hydride to insure reaction of any water in the organic vapor with the hydride before it reaches the phosphorus pentoxide placed in the tube K. The rubber connection L is surrounded by a well of mercury M to prevent gas leakage. The 100-cc. gas buret N and the leveling tube P are filled with water. Constant temperature is maintained by pumping water at 30° from a thermostat through H, O, and the bath Q.

**Method.**—The apparatus was prepared for an actual water determination by the following preliminary treatment. About 5 g. of powdered calcium hydride was placed

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[8] Moissan, *Compt. rend.*, **127**, 29 (1898); Reich and Serpek, *Helv. Chim. Acta.*, **3** 138 (1920).

[9] McNeil, U. S. Dept. Agr., *Bur. Chem. Circ.* **97**, pp. 1–8.

in the flask A with about 15 cc. of the undried solvent being studied. The ground-glass joints were then lubricated by a special graphite paste made by mixing dry graphite powder (100 mesh) with just enough stopcock grease to give a thick paste. This special preparation was found necessary because the hot organic vapors dissolved the ordinary lubricants with consequent leakage. The flask A was then put in place as shown in Fig. 1 and was heated for several hours. This heating was conveniently accomplished by a small electric heating coil. After several hours the heating coil was removed from beneath A, the flask was allowed to cool and the thermostat Q was raised into place around A. After the system had come to equilibrium the gas volume was read. The barometric pressure was also recorded, since it was found that 1 mm. change in atmospheric pressure resulted in a change of 0.3 to 0.5 cc. in the gas volume (depending on the volume of gas present in the apparatus); this correction was always applied when any change in pressure occurred. The thermostat Q was then lowered and the heating of the flask continued for several hours. The heating coil was then removed from beneath A, Q was raised into place and a reading taken of gas volume and barometric pressure. The process of heating, cooling and taking readings was continued until no more hydrogen was evolved. This preliminary treatment served a three-fold purpose: (1) it checked the apparatus for leaks, (2) it removed any moisture in the apparatus, (3) it removed the adsorbed gases from the calcium hydride.

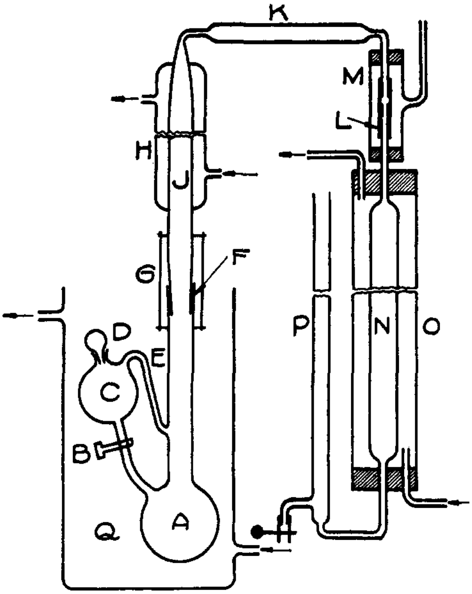

Fig. 1.—Apparatus for water determination.

After the above procedure the actual determination of water was carried out as follows. The organic solvent was first saturated by shaking with water in a flask at high temperature and then allowing the flask to cool in a thermostat to the desired temperature, with the resulting separation of excess water as shown by the turbidity. The solution was allowed to stand for a day or more to come to equilibrium before a sample was withdrawn for solubility measurements. The sample was then withdrawn with a 25-cc. pipet, the tip of which was guarded by a ground-glass cap and the upper end by a tube filled with calcium hydride to prevent absorption of moisture when not in use. The sample (25 or 50 cc.) was introduced into the bulb C through D after B had been closed. The joint D was then closed and the bath Q raised around A. After the system had come to equilibrium, the initial gas reading and barometric pressure were recorded. The bath Q was then lowered and B was opened to allow the sample to react with the calcium hydride already present with the dry solvent in A. Hydrogen was evolved rapidly at first and after the evolution slowed down, the flask was heated to expedite the reaction. The process of heating, cooling and taking readings was continued until it was found that no more gas was being evolved. In some cases the reactions were allowed to continue for three days before the last traces of gas were evolved, although it was found that the reaction was about 95% complete within the first ten hours.

After one determination was completed, another sample was added to the flask and successive analyses were carried out until the flask A was filled with the solvent.

**Results.**—The accuracy of the method was first established by adding a weighed amount of water from a weighing pipet to calcium hydride contained in benzene from which all water had been abstracted by boiling with the hydride until no more hydrogen was evolved. The results of these experiments are shown in Table I.

TABLE I

ACCURACY OF METHOD

| Experiment | 1 | 2 | 3 |
|---|---|---|---|
| Water taken, g. | 0.0387 | 0.0396 | 0.0406 |
| Hydrogen evolved (calcd. as water), g. | .0384 | .0396 | .0402 |

**Solubility of Water in Benzene, Carbon Tetrachloride and Toluene.**—The solubility of water in the above solvents was determined at various temperatures. The results are shown in Table II and are graphed in Fig. 2.

TABLE II

SOLUBILITY OF WATER IN BENZENE, CARBON TETRACHLORIDE AND TOLUENE

| | Grams of water per 100 g. of solvent | | |
|---|---|---|---|
| Temp., °C. | Benzene | Carbon tetrachloride | Toluene |
| 10 | 0.0451 | 0.00711 | 0.0335 |
| 20 | .0573 | .00844 | .0450 |
| 30 | .0746 | .0109 | .0600 |
| 40 | .0953 | .0152 | .0733 |
| 50 | .1271 | .0237 | .0953 |
| 60 | .1637 | .... | .... |

(a) **Solubility of Water in Benzene.**—The values given in the table are an average of two to four determinations of the solubility at each temperature. A typical example of the accuracy of the individual determinations is illustrated by values of 0.0962, 0.0953 and 0.0944 (average 0.0953) for the solubility of water in benzene at 40°.

These results for the solubility of water in benzene are higher than those obtained by Clifford[10] by absorbing the moisture from the benzene with calcium chloride. They are somewhat lower than the results of Groschuff[11] determined by the turbidity method and also lower than the results of Hill[12] determined by measuring the solubility of silver perchlorate in benzene–water solutions.

As a practical application of this method of analysis, the drying of benzene by distilling off and discarding the first 10% was tested. This method is recommended for the removal of water from benzene.[13] Ordinary tech-

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[10] Clifford, *Ind. Eng. Chem.*, **13**, 632 (1921).

[11] Groschuff, *Z. Elektrochem.*, **17**, 348 (1911).

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

[13] "Organic Syntheses," John Wiley and Sons, Inc., New York, **1924**, Vol. IV, p. 81.

nical benzene was used and in Table III the effect of distilling off 10% of Sample No. 1 was determined. Sample No. 2 was first saturated with water and 20% of the solution was distilled before the distillate came over unclouded, thus showing no more excess water.

TABLE III

THE REMOVAL OF WATER FROM BENZENE BY DISTILLATION

| Sample No. 1. 10% distilled | Sample No. 2. 20% distilled |
|---|---|
| Original sample 0.025% $H_2O$ | Original sample 0.0746% $H_2O$ |
| Residue contained 0.0147% $H_2O$ | Residue contained 0.0156% $H_2O$ |

(b) **Solubility of Water in Carbon Tetrachloride.**—The results given in Table II were obtained using 50-cc. samples and despite the very low solubility the method gave checks between individual determinations of 0.0004% $H_2O$. Clifford[10] using the calcium chloride method obtained values of 0.010% at 24° and 0.013% at 28.5°, the latter not agreeing with the present results.

The presence of carbon disulfide as an impurity in technical carbon tetrachloride was found to increase the solubility of water in the solvent by about 50%. As an example typical of several determinations, the solubility of water in carbon tetrachloride containing carbon disulfide was found to be 0.0170% instead of the value 0.0109% $H_2O$ in pure carbon tetrachloride.

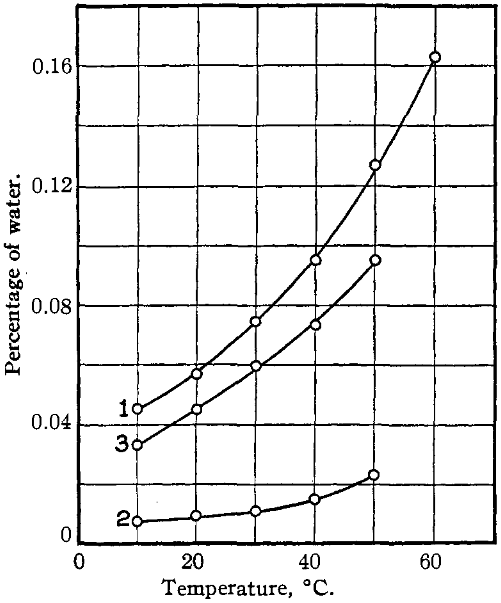

Fig. 2.—Solubility of water in organic solvents: Curve 1, benzene; Curve 2, carbon tetrachloride; Curve 3, toluene.

(c) **Solubility of Water in Toluene.**—The results given in Table II are average values obtained with 25- and 50-cc. samples of toluene.

## Discussion

The principal value of the present method is its extreme accuracy. As shown by the results in Table I and the individual solubility determinations, the method is accurate to about 0.001% $H_2O$ in determinations of less than 0.10% $H_2O$ present in organic solvents.

A possible practical application of the method besides its use in solubility studies is as follows. A dry organic solvent such as benzene could be used to extract the water from a solid sample by leaching or refluxing and the water present in the solvent could subsequently be determined.

The two chief objections to the calcium hydride method are the following. First, the method is limited to solvents which do not react with calcium hydride or otherwise react so slowly that necessary corrections can be applied; second, the method is not rapid, since the analyses are of one to three days' duration, although they do not require much actual time or care. The time required can be shortened for practical determinations since the reaction is about 95% complete in ten hours and the percentage of total moisture could then be estimated.

## Summary

1. A new improved apparatus and method have been developed for the gasometric determination of water in certain organic solvents.
2. Calcium hydride has been shown to be a good reagent for the quantitative determination of water, giving an accuracy of 0.001% $H_2O$ in determinations of about 0.1% $H_2O$.
3. The solubility of water in benzene, in carbon tetrachloride, and in toluene has been determined at various temperatures.
4. Benzene can be dried to a water content of 0.015% by distilling and discarding the first 10 to 20% of the liquid.

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# A STUDY OF THE PRODUCTS OBTAINED BY THE REDUCING ACTION OF METALS UPON SALTS IN LIQUID AMMONIA SOLUTION. III. THE ACTION OF SODIUM UPON SILVER IODIDE AND SILVER CHLORIDE[1]

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## Introduction

In the first paper of this series,[2] there was described a reaction in liquid ammonia between sodium and a salt, which resulted in the formation of a compound of sodium and the reduced metal. In the present paper a simpler case is presented where the reduced metal is obtained without further reaction.

Kraus and Kurtz[3] found that sodium reacted readily with silver cyanide

[1] This article is based upon the thesis presented to the Faculty of the Graduate School, University of Cincinnati, by Edward H. Smoker in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Burgess and Rose, THIS JOURNAL, **51**, 2127 (1929).

[3] Kraus and Kurtz, *ibid.*, **47**, 43 (1925).