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## INTENSIVELY DRIED CARBON TETRACHLORIDE

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Recently, in an extension of his work on intensively dried liquids, H. B. Baker<sup>1</sup> has reported vapor density measurements on eight liquids dried for from two to fifteen years which indicate an increase in molecular weight on drying.

Last year boiling-point determinations were carried out on benzene and carbon tetrachloride which showed no change in boiling point on prolonged drying.<sup>2</sup> The present paper describes some further measurements on intensively dried carbon tetrachloride.

Carbon tetrachloride was prepared in exactly the way described previously.<sup>2</sup> It was sealed up, as before, in specially prepared, capillary-free, hard glass tubes together with redistilled phosphorus pentoxide. The tube, which had an external diameter of 18 mm. with 2-mm. walls, was heated to softening before the introduction of the phosphorus pentoxide. The redistilled pentoxide was introduced into the dry tube by plunging a dry glass tube into the pentoxide and forcing it into the drying tube with a glass rod. This operation prevented the pentoxide from coming into contact with atmospheric moisture except possibly at the ends of the tube. The tube was sealed up on June 19, 1924. Care was taken to thicken the glass where the tube was sealed off. The tube was allowed to stand at room temperature.

This tube was opened on May 15, 1929; the drying time was five years. The boiling point of the dry carbon tetrachloride was measured in a platinum wire boiling-point apparatus<sup>3</sup> under conditions where there was less than 0.03° of superheating. The boiling point of the carbon tetrachloride, measured three minutes after the drying tube was opened, was 76.8° at 762.2 mm. No difference in temperature could be observed between the boiling liquid and the vapor 1-2 cm. above the liquid. The thermometer used had been compared with Bureau of Standards thermometer No. 35388.

The boiling point was then determined using the procedure adopted by Baker for his boiling-point measurements. The carbon tetrachloride from this boiling-point determination was placed with the same thermometer in a straight tube of 2-cm. diameter and heated in a Nujol-bath. The carbon tetrachloride did not begin to boil until the thermometer in the liquid registered 90°. Boiling was then not violent, but was quiet and regular and gave no indication of superheating other than the reading on the thermome-

<sup>1</sup> Baker, *J. Chem. Soc.*, 1051 (1928).

<sup>2</sup> Lenher and Daniels, *Proc. Nat. Acad. Sci.*, 14, 606 (1928).

<sup>3</sup> Mathews, *Trans. Am. Electrochem. Soc.*, 19, 81 (1911).

ter. The carbon tetrachloride was not entirely free of dust particles and of tiny bits of phosphorus pentoxide. This experiment shows clearly the difficulty of avoiding superheating when a boiling point is measured in this way.

The molecular weight of the intensively dried carbon tetrachloride was measured by the method of Victor Meyer. The familiar form of the Victor Meyer apparatus was used,<sup>4</sup> the only innovation being that mercury was used in the gas buret. The intensively dried carbon tetrachloride was introduced directly into small bulbets from the dry tube by dipping the open capillary end of the warmed bulbets into the liquid and allowing them to cool. The bulbets were weighed and the vapor density of the carbon tetrachloride was measured in the apparatus which had been previously evacuated for four hours at the boiling point of aniline. The measurements were carried out at the boiling point of aniline. The six measurements were made over a period of an hour and a half after the opening of the drying tube. The molecular weight of intensively dried carbon tetrachloride in six experiments was found to be 160.1, 149.9, 153.8, 152.1, 154.5, 154.9; the molecular weight of ordinary carbon tetrachloride is 153.8.

The phosphorus pentoxide in the drying tube was treated with water in a calorimeter to determine how much unused pentoxide remained after five years' contact with carbon tetrachloride. When the tube was opened the pentoxide was in a finely divided state, giving no sign of formation of phosphoric acid. This test showed that 3.5 g. of phosphorus pentoxide was still present when the tube was opened. This figure is at least 30% too low, because of the difficulty of transferring the pentoxide to the calorimeter without heat loss.

The criticism cannot be made that the drying time was insufficient to effect intensive drying for the writer's carbon tetrachloride which showed a normal boiling point and normal molecular weight by the vapor density method was dried for five years, while Baker<sup>1</sup> reports a molecular weight of 191 for carbon tetrachloride dried for three years and a molecular weight of 201 for the same substance dried for five years.

The writer<sup>5</sup> has been able to observe some of the phenomena described by Baker<sup>1</sup> for dried liquids and liquids subjected to electrical potential with ordinary liquids under as nearly as possible the same experimental conditions. These experiments which will be described elsewhere<sup>6</sup> will show that superheating is an important factor in Baker's experiments.

It may be remarked that Briscoe, Peel and Robinson<sup>7</sup> have recently measured with great care the density and surface tension of benzene dried

<sup>4</sup> Findlay, "Practical Physical Chemistry," Longmans, Green and Company, London, 1923, 4th ed., p. 43.

<sup>5</sup> Lenher, *Nature*, 123, 907 (1929).

<sup>6</sup> Lenher, *J. Phys. Chem.*, October (1929).

<sup>7</sup> Briscoe, Peel and Robinson, *J. Chem. Soc.*, 368 (1929).

for eighteen months and have found no change which would justify an assumption of a change in degree of association on drying.

### Summary

Carbon tetrachloride which has been in contact with pure phosphorus pentoxide in a sealed tube for five years at room temperature shows no change in boiling point or molecular weight, by the Victor Meyer vapor density method, which can be attributed to intensive drying and consequent change in degree of association.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## THE VISCOSITY OF AQUEOUS SOLUTIONS OF STRONG ELECTROLYTES WITH SPECIAL REFERENCE TO BARIUM CHLORIDE

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### Introduction

A number of related properties of barium chloride solutions have been determined with a high precision over a considerable range of concentration in the hope that a study of the data in the light of modern theories of solutions might reveal new relationships between the properties and new laws for the variation of the properties with the concentration. The first paper<sup>1</sup> of this series records the results of measurements of transference numbers by both the analytical- and electromotive-force methods which resulted in the discovery of a new and exact relationship between the transference number and the concentration. This, the second paper of the series, records measurements at 25° of the viscosity of barium chloride solutions relative to that of water, over the range 0.005 to 1.0 molal. This investigation has resulted in the discovery of a new exact relationship between the fluidity and the concentration. A later paper will give data on the conductivity of the same solutions.

**Historical Review.**—Poiseuille,<sup>2</sup> the great pioneer in research on viscosity, found that some salts increase the viscosity of water whereas others decrease the viscosity. Sprung<sup>3</sup> appears to have been the first to measure solutions of barium chloride and found that it increased the vis-

<sup>1</sup> Grinnell Jones and Malcolm Dole, *THIS JOURNAL*, 51, 1073 (1929). We regret that in this paper we implied that Washburn found it necessary to filter his solutions during his work on transference numbers [*THIS JOURNAL*, 31, 322 (1909)]. This implication is, however, misleading as Washburn actually avoided the filtration of his solutions.

<sup>2</sup> Poiseuille, *Ann. chim. phys.*, [3] 21, 76 (1847).

<sup>3</sup> Sprung, *Ann. Physik*, 159, 1 (1876).