

This was undoubtedly the air not originally removed by the pump and absorbed air liberated from the surface of the salt and of the glass by the heating. The original conclusion, that ammonium iodide in the state of saturated vapor is in part associated, is therefore undoubtedly correct.

Summary.

1. The vapor densities of the saturated vapor of phosphorus pentachloride were determined from 90° to 160° .
2. The degrees of dissociation calculated from the vapor densities show that the saturated vapor is somewhat associated at 90° , and dissociated to an approximately constant extent of about 4% from 110° to 160° .
3. The latent heat of vaporization was calculated to be 15.5 Kg. cal. per mol.
4. A note on the case of ammonium iodide, previously investigated, is appended.

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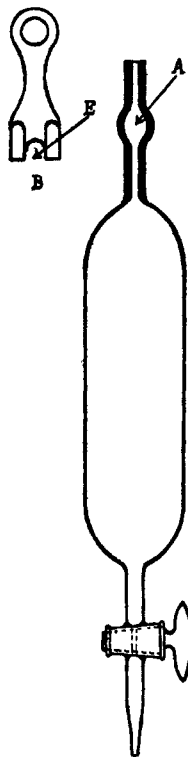


Fig. 1.

NOTES.

A Convenient Weighing Pipet.—Recent work of the author has made necessary the extensive use of a weighing pipet. One of the type suggested by Mertes¹ was first adopted, but was found to have the following disadvantages:

1. It is inconvenient to fill and difficult to clean.
2. The necessary size of the tubing for the neck, to permit of its being hung on the balance, makes the larger sizes too fragile.

To remove these defects the form shown in Fig. 1 was devised. It consists essentially of an ordinary pipet body fitted with a stopcock at the bottom, and a short neck of thick-walled narrow glass tubing with a bulb, A, blown in it. The purpose of this latter is two-fold: first, to serve as an overflow bulb when filling, and second, to serve as a means of support by preventing the neck from slipping through the supporting hook B, which hangs from the balance arm. The supporting hook is made out of some sheet metal, such as brass, about one millimeter thick. Two elevations of the latter, front B, and side C, are shown. The slot E is cut slightly wider than the diameter of the

¹ *J. Ind. Eng. Chem.*, 7, 236 (1915).

neck of the pipet so as to admit the latter freely, and yet not wide enough to allow the bulb A to slide through.

A series of such pipets of varying capacities, having the same sized neck, may be constructed and thus used with the same hook. For use with quantities less than their total capacity the larger pipets may be graduated to indicate every 5 cc. or so. For use with more volatile liquids ground glass caps may easily be fitted both to the top and bottom to prevent possible evaporation. Anyone having a little skill at glass-blowing can construct this type of pipet, and to make its construction still more simple it can be made from the body of an ordinary plain pipet.

The advantages of this form of pipet can readily be seen; it is easily filled and cleaned, and its compactness permits its being conveniently weighed on the ordinary analytical balance. Furthermore, its lack of fragility reduces the probability of breakage.

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Note on the Interpretation of Molecular Weight Results from Measurements on Solutions (with special reference to a paper by Beckmann and Maxim).—In a recent memoir,¹ Beckman and Maxim record some measurements of the molecular weight of phenol which were made in order to test the influence both of temperature and the nature of the solvent.

Two solvents were employed, carbon tetrachloride and bromoform, the former at four different temperatures, namely -23° , $+75.4^{\circ}$, $+66.3^{\circ}$ and $+54.1^{\circ}$, the latter only at its freezing point ($+8^{\circ}$).

In all cases, phenol was found to be associated, the degree of association increasing continuously over the whole range of concentration tested, being about 1.0 in very dilute solution and exceeding 3 in the strongest solutions in freezing carbon tetrachloride.

From the comparison of the degree of association at the same concentrations in carbon tetrachloride the conclusion was drawn that, at any rate between 75.4° and 54.1° , alteration of temperature has but little effect on the molecular weight of phenol. At -23° (freezing carbon tetrachloride) the degree of association is distinctly greater than at 75° , but, even so, variation of temperature was held to be much less effective in altering the molecular size than variation of concentration.

The interpretations given by Beckmann and Maxim of their results seem to the writer somewhat inadequate. It may be pointed out that, in the measurements of Beckmann and Maxim (as in all similar measurements), the actual effect of temperature cannot be ascertained until a second factor is accounted for, namely, the variation of the dielectric constant of the solvent with the temperature; for, the influence of the

¹ *Z. physik. Chem.*, 89, 411 (1915).

nature of the solvent can in a large measure be correlated with the magnitude of its dielectric constant,¹ the degree of association being greater the lower the dielectric constant.

Now as the dielectric constant diminishes with rise of temperature, the two factors, namely, increase of temperature (tending to produce dissociation) and decrease of dielectric constant (permitting an increased degree of association), serve in some measure to counterbalance one another. No measurement appears yet to have been made of the variation with temperature of the dielectric constant of carbon tetrachloride, so that the true effect of temperature in reducing the degree of association cannot be ascertained. It will, undoubtedly, be greater than Beckmann and Maxim conceive.

Although not indicated by Beckmann and Maxim, their results are in harmony with the rule that the higher the dielectric constant of the solvent the smaller the degree of association of the solute. The following figures illustrate this fact:

Solvent.	Dielectric constant.	Grams of phenol per 100 cc. solution.	Degree of association.
Carbon tetrachloride (23°)...	2.2518 ^{o2}	2.50	2.85 ⁴
Bromoform (+8°).....	4.5818 ^{o3}	2.50	1.16

The order is the same at other corresponding concentrations and is unchanged even if the results in boiling carbon tetrachloride be compared with those in freezing bromoform.

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An Allotropic Modification of Lead.—The existence of a gray allotropic modification of lead has recently been observed by Heller,⁵ who found that, when a piece of bright, pure lead was placed in a nitric acid solution of lead acetate, transition commenced at the end of two days and was complete at the end of about three weeks.

A similar phenomenon has been observed by the writer in an electrolysis experiment, which substantiates Heller's observation: The electrolyte employed in this experiment was nitric acid (sp. gr. 1.42), the cathode a piece of sheet lead 2 cm. wide, 2 mm. thick and 10 cm. long, and the anode a thin piece of platinum foil. A current of 2-3 amperes at 6 volts was passed through the electrolyte for eight hours, at the end of which time the current was stopped and the lead cathode removed immediately.

¹ Meldrum and Turner, *J. Chem. Soc.*, **93**, 876 (1908); **94**, 1605, 1805 (1910); Turner, *Ibid.*, **99**, 880 (1911); **101**, 1923 (1912); Turner and Pollard, *Ibid.*, **105**, 1751 (1914); Turner and Bissett, *Ibid.*, **105**, 1777 (1914); Turner, "Molecular Association," Longmans, 1915.

² B. B. Turner, *Z. physik. Chem.*, **35**, 385 (1900).

³ Canwood and W. E. S. Turner, *J. Chem. Soc.*, **104**, 276 (1915).

⁴ Determined graphically from Beckmann and Maxim's data.

⁵ H. Heller, *Z. physik. Chem.*, **89**, 761 (1915).

Examination showed that the portion of the lead cathode in the electrolyte had increased slightly in volume, and that it had lost its former malleability and firmness. Its bright color had changed to gray. On rubbing the lower part of the electrode between the fingers, it was found to have been completely transformed into small particles, which could be rubbed into a fine powder, or pressed together into a soft mass.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA.]

THE RATE OF CONVERSION OF CINCHONINE INTO CINCHOTOXINE.¹

(ON CATALYSES WITH WEAK ACIDS. VI.)

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i. Introduction.—The most carefully investigated cases of catalysis in aqueous solution are those reactions of hydrolysis in which the accelerating influence of an acid is largely determined by the concentration of the hydrogen ions. Such, for example, are the familiar inversion of cane sugar and the saponification of an ester in the presence of an acid. In the case of the remarkable conversion of the cinchona alkaloids into their poisonous isomers in the presence of weak organic acids we are, however, dealing with a catalysis of a different nature. In this catalysis, as has been previously shown, the speed of the reaction is apparently a direct function of the molecular concentration of the undissociated acid and an inverse function of the concentration of the hydrogen ion.

The rate of the conversion of cinchonine to cinchotoxine was measured by Biddle and Rosenstein² for the alkaloid in two concentrations of acetic acid. In the present paper is given a detailed study of this catalysis in the presence of various acids through a wide range of concentration of the several acids studied and in mixtures of acetic acid and hydrochloric acid presenting also a wide range in concentration of H⁺ ion. The data obtained in conjunction with like data from the study of the stereoisomeric cinchonidine and the two stereoisomers, quinine and quinidine, would, it was believed, afford a basis for a more thorough investigation of this extraordinary catalysis. Such data might naturally among other things be expected: first, to show with some greater degree of certainty not only what molecular species are involved in each reaction, but also

¹ Biddle, *Ber.*, 45, 526, 2832 (1912); *THIS JOURNAL*, 34, 500 (1912); 35, 273 (1913); 36, 84 (1914); Biddle and Rosenstein, *Ibid.*, 35, 418 (1913).

² *THIS JOURNAL*, 35, 418 (1913).