[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF STANFORD UNIVERSITY AND OF THE UNIVERSITY OF CALIFORNIA]

THE VAPOR DENSITY OF FORMIC ACID

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Papers on the vapor density of formic acid have been published recently by Wrewsky and Glagoleva[2] and by Coolidge.[3] In a paper entitled "The Ultraviolet Absorption Spectrum of Formic Acid," published by Ramsperger and Porter in May, 1926,[4] the vapor densities of formic acid at temperatures between 25 and 80° were reported. Since, in the title of this paper, no reference was made to vapor density, it was overlooked by Coolidge who credits Bineau and Pettersson and Ekstrand with the only earlier work in this field.

The purpose of this communication is to make a graphical comparison of all the data on this subject. Equilibrium constants for the reaction $(HCOOH)_2 = 2HCOOH$ have been calculated from the data of Pettersson and Ekstrand,[5] of Wrewsky and Glagoleva,[2] of Coolidge,[3] and of Ramsperger and Porter.[4] The equilibrium constant is given by the expression $K = p_m^2/p_b$, where p_m is the pressure in atmospheres, due to the unimolecular form, and p_b is the pressure of the bimolecular form.

In Fig. 1 $R \ln K$ is plotted against $1/T$. The line drawn approximately through the experimental points of Wrewsky and Glagoleva is the graph of an equation given by Willard Gibbs[6] which he found would fit the experimental values of Bineau[7] fairly well, and it is seen that it also fits most of the data of Wrewsky and Glagoleva. The recent, very accurate determinations of Coolidge do not fit this equation at all. Constants have not been calculated for all of the large number of experiments of Coolidge. We have selected those having about the same pressures at low temperatures as were used in our own work. At the higher temperatures his lowest pressures experiments were chosen so as to minimize errors due to deviations from the gas laws. The straight line drawn through his points is also the best straight line through the points obtained by Ramsperger and Porter. The slope of this line corresponds to a heat of dissociation of 14,100 cal. per mole, which is identical with the average value published by Ramsperger and Porter. The equation of Gibbs gives a heat of dissociation of 17,400 cal. per mole, and Pettersson and Ekstrand's data give 16,000 cal. per mole.

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[2] Wrewsky and Glagoleva, *Z. physik. Chem.*, **133**, 370 (1928).

[3] Coolidge, THIS JOURNAL, **50**, 2166 (1928).

[4] Ramsperger and Porter, *ibid.*, **48**, 1267 (1926).

[5] Pettersson and Ekstrand, *Ber.*, 13, 1194 (1880).

[6] Gibbs, *Am. J. Sci.*, **18**, 247 (1877).

[7] Bineau, *Ann. chim. phys.*, [3] **18**, 228 (1846).

Coolidge took very great precautions as to the purity of his formic acid. This is a matter of importance. In our early experimental work it was observed that considerably lower constants were obtained at low temperatures and at pressures approaching the saturation pressure than under other conditions. Adsorption on the glass walls could have been responsible for only a small part of this, since the addition of broken pieces of the same kind of glass gave only a small increase in density. An impurity such as a trace of stopcock grease greatly increased the apparent density. Our final results were obtained with a sample of Kahlbaum formic acid which was analytically pure. This was distilled in vacuum and was free from non-condensable gases. It was passed through glass wool which apparently helped to remove those impurities which favored incipient condensation on the walls. It seems very likely that traces of impurities were responsible for the lower constants of earlier investigators.

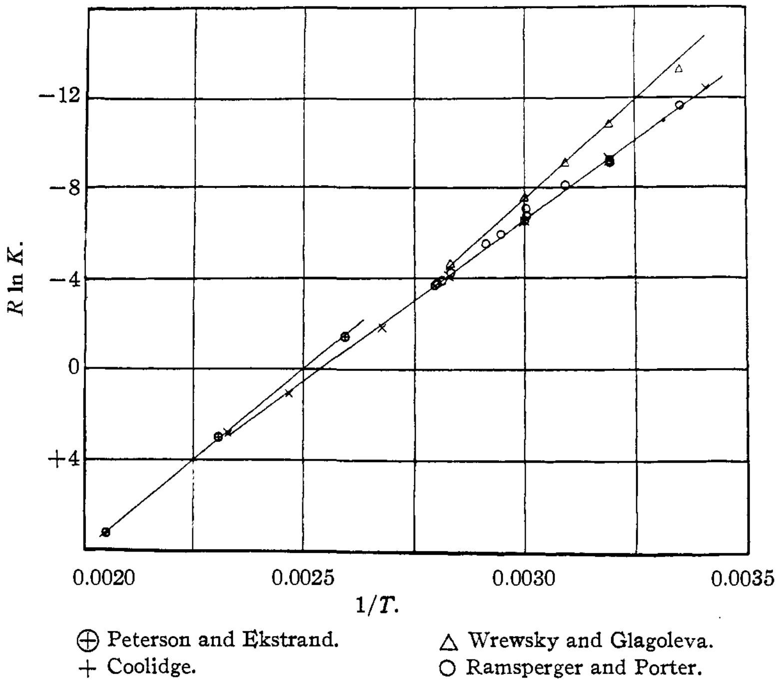

Fig. 1.

The experiments of Wrewsky and Glagoleva were made by a method in which the vapor density was determined by an analysis of air which had passed through liquid formic acid. The higher densities may have been due to small fog-like particles of liquid which were carried over with the vapor. Such particles are not easily eliminated.

Summary

A survey has been made of all existing data on the vapor density of formic acid. There is complete agreement between the measurements made by Coolidge and those of Ramsperger and Porter. Traces of impurities were probably responsible for the discordant results of the earlier investigators.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

SOME PROPERTIES AND TRANSFORMATIONS OF ORTHO-DICHLORO-4-NITROBENZENE[1,2]

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Introduction

Beilstein and Kurbatow[3] found that 4-nitro-*o*-dichlorobenzene formed in two modifications when *o*-dichlorobenzene was treated with fuming nitric acid. They describe a semi-fluid mixture from which the solid part settles out and can be crystallized from alcohol in long needles of m. p. 43° and b. p. of 255–256°. Holleman[4] has studied the nitration of the dichlorobenzenes and found that when the ortho compound is dropped into nitric acid cooled to 0 or 30° the 1,2-dichloro-4-nitrobenzene is the principal product along with small amounts of isomers. His work on its physical constants agrees with those of Beilstein and Kurbatoff but he makes no mention of a liquid form.

In connection with some work to prepare *o*-chloro-*p*-nitraniline, we found that the nitration of *o*-dichlorobenzene always gave us a mixture of the liquid and solid forms of *o*-chloro-4-nitrobenzene. Since Beilstein and Kurbatoff give no information regarding any changes of the one form into the other and since the literature records no other nitro-*o*-dichlorobenzenes as liquids we decided to make a study of some of the properties and transformations of *o*-dichloro-4-nitrobenzene.

Experimental

Purification and Nitration of *o*-Dichlorobenzene.—The *o*-dichlorobenzene used in this work was prepared from the commercial material supplied us by the Monsanto Chemical Works. It was first distilled to remove any mono- and trichlorobenzene, the fraction between 165 and 200° being retained. One liter of this fraction was then cooled to −15° so that any of the para compound present would crystallize out and could be

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[1] In memory of Ira Remsen.

[2] Presented before the Organic Chemistry Division of the American Chemical Society at the St. Louis Meeting, April, 1928.

[3] Beilstein and Kurbatow, *Ann.*, 176, 41 (1875).

[4] Holleman, *Rec. trav. chim.*, 23, 357 (1904).