Boiling Points of the System of Formic Acid and Water.

By Sorozi TAKAGI.

Papers related to the vapour pressure of pure formic acid are published by Richardson,[1] Kahlbaum,[2] Schmidt[3] and Coolidge,[4] and those related to the constant boiling point in the system of formic acid and water by Roscoe[5] and Jones.[6]

As these papers, however, give only descriptions of the azeotropic mixtures, they do not fit for the purpose of reference to obtain the concentrated acid.

Thus, the author repeated the measurements on the head article to fill up the lacking data of this system and to establish facts for practical use.

Experimental. Sample used was purified by repeated redistillation and the measurement of boiling point was carried out by ordinary dynamical method. About 500 c.c. of the original solution was taken for distillation and by using a short condenser, about 2 c.c. of the distillate of required constant boiling point was collected.

Accuracy of the data is 0.5 mm. Hg in pressure and 0.1°C. in temperature. The composition of the distillate is not of high accuracy as the distillate can not be seized completely.

As the data of azeotropic mixture, however, were obtained by carrying out the experiments to the coinsidence of constant boiling points starting from samples of higher and lower concentrations than the azeotropic mixture, the data are of considerable precision, i.e. the error is within ± 0.1°C. in temperature, and within ± 0.1% in composition.

Result. Boiling points of liquid and the compositions of liquid and the vapour phase in equilibrium are shown in the following table and figure.
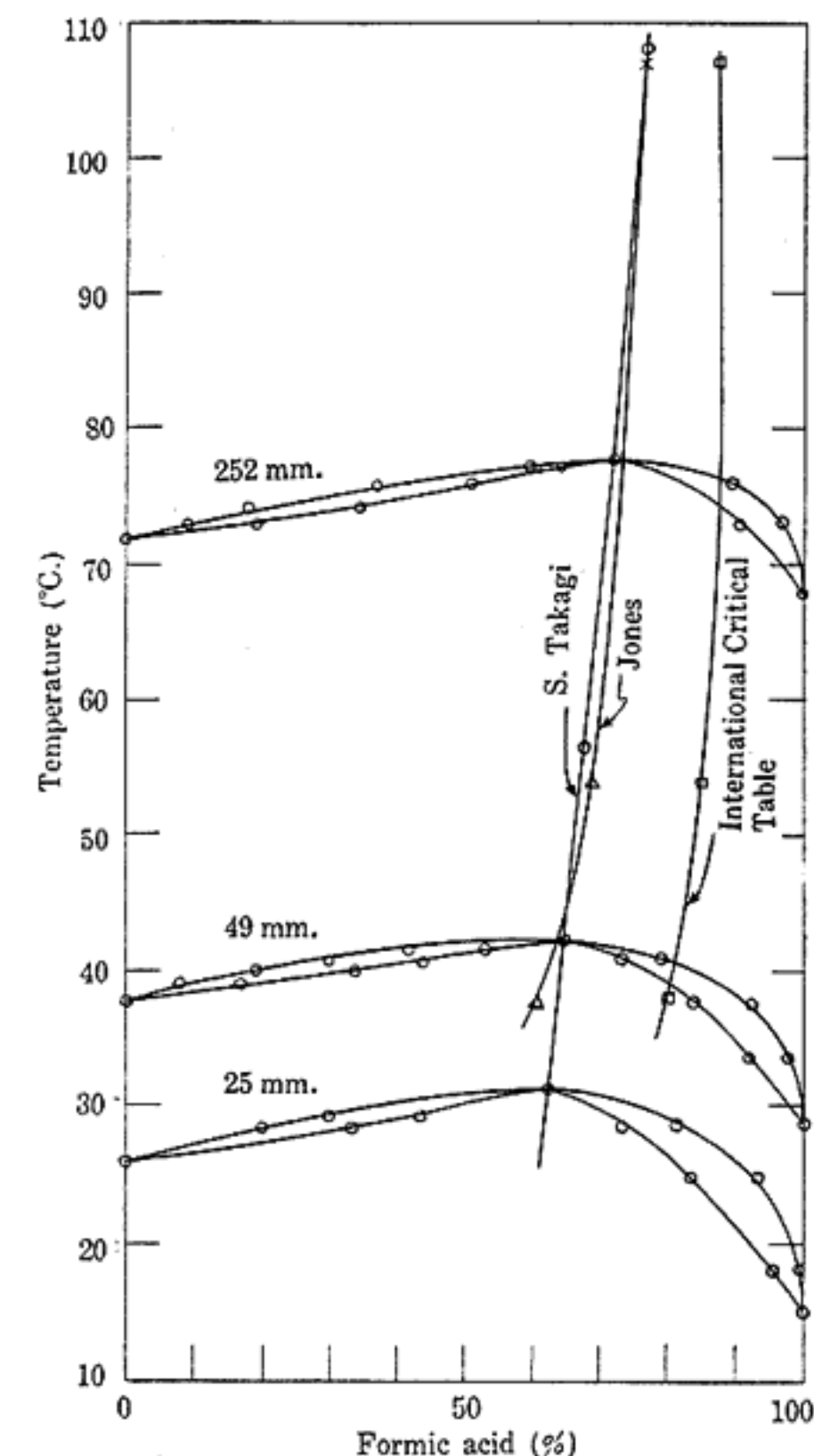
The data of Jones, Roscoe and International Critical Tables are approximate to the results of the author with the exception of the last ones which are perhaps due to error in transcribing the Roscoe's data.

From above table, the equation of vapour pressure of azeotropic point is obtained as follows:

$$p = 25 + 1.87715\,(t-31.4) + 0.017706\,(t-31.4)^2 + 0.00102904\,(t-31.4)^3$$

No.	Pressure (mm. Hg)	HCOOH (%) Liquid	HCOOH (%) Vapour	Temperature (°C.)
1	25	95.6	99.4	18.0
2	,,	83.5	93.6	24.3
3	,,	73.2	81.3	29.0
*4	,,	62.3	62.3	31.4
5	,,	43.6	30.1	29.2
6	,,	33.6	20.1	28.3
7	49	91.8	97.4	33.7
8	,,	83.4	92 4	37.7
9	,,	73.0	79.0	41.0
*10	,,	64.7	64.7	42.3
11	,,	58.0	52.9	41.5
12	,,	43.9	30.0	40.7
13	,,	33.7	19.1	40.1
14	,,	16.9	7.3	39.0
*15	100	67.4	67.4	56.6
16	252	90.7	96.8	73.0
17	,,	83.2	89.6	75.8
*18	,,	72.1	72.1	77.7
19	,,	64.5	59.5	77.2
20	,,	51.0	37.2	75.8
21	,,	34 3	18.0	74.0
22	,,	19.1	8.9	72.8
*23	774	76.8	76.8	108.1

* are azeotropic mixtures. Boiling points of pure formic acid are calculated from Coolidge's equation $\log p = 7.8584 - 1860/T.$.

△, × and □ are data by Jones, Roscoe and International Critical Tables (Vol. III, p. 364) respectively.

Summary.

Boiling points of liquid and the compositions of the liquid and the vapour phase in equilibrium in the system of formic acid and water were determined in wide range of composition and temperature, and from above data the equation of vapour pressure of azeotropic point was determined.

(1) Richardson, *J. Chem. Soc.*, **1886**, 761.
(2) Kahlbaum, *Ber.*, **16** (1883), 2480; *Ber.*, **27** (1894), R 459; *Z. physik. Chem.*, **26** (1898), 591.
(3) Schmidt, *Z. physik. Chem.*, **7** (1891), 433.
(4) Coolidge, *J. Am. Chem. Soc.*, **52** (1930), 1877.
(5) Roscoe, *J. Chem. Soc.*, **1862**, 270.
(6) Jones, *J. Soc. Chem. Ind.*, **1919**, 363.