

[CONTRIBUTION FROM BROOKLYN POLYTECHNIC INSTITUTE, BROOKLYN, N. Y.]

## Vapor Pressures of Saturated Aqueous Solutions. Monoammonium and Diammonium Acid Phosphates

BY EDWARD J. ROEHL

In connection with other current research work, the author has determined the vapor pressure curves for saturated aqueous solutions of monoammonium and diammonium acid phosphates over a temperature range.

A search of the literature failed to reveal data for the diammonium salt, and the only record for the monoammonium salt seems to be that of Edgar and Swan<sup>1</sup> over the limited temperature range of from 19 to 30°.

### Experimental Method

The isoteniscope of Smith and Menzies<sup>2</sup> was employed. The bulb of the isoteniscope had a capacity of about 15 ml., and was connected to a 10-liter bottle as reservoir. The manometer was of the closed end type described by Roehl<sup>3</sup> and was read by means of a cathetometer. The usual precautions as to temperature control, stirring, etc., were employed. A saturated solution of the salt was used as the confining liquid. The two ammonium phosphates were prepared by crystallizing commercial c. p. chemicals repeatedly from water. In all cases, duplicate determinations were made upon separate samples, and in several cases other duplicate determinations were made on samples which had been still further purified by recrystallization. The curves were checked for both falling and rising temperatures.

The experimental data for the monoammonium salt were found to fit the equation given over a range of temperature from 19–90°

$$\log P = -2240/T + 8.862$$

with a mean deviation of 0.8% in pressure. The data for the diammonium salt can be represented by the equation given from 19–55°

$$\log P = -2240/T + 8.807$$

with a mean deviation of 0.4% in pressure.

The only available data, those of Warren,<sup>4</sup> give the following values for the ammonia pressure of the solid salts, and which would correspond to the ammonia pressures for the saturated solutions.

### PRESSURES IN MM. OF MERCURY

	80.24°	100°	125°
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	....	0.00	0.05
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	1.36	5.0	30.0

This indicates that the ammonia pressure over the saturated solution has not reached an appreciable value for the monoammonium salt at 100° and for the diammonium salt at 55°.

It was found that the data for the two salts gave parallel straight lines when plotted as  $\log P$  against  $1/T$ , and that the two lines were parallel to the vapor pressure curve for water. A search of the literature was made and all the data possible to locate for saturated aqueous solutions plotted as  $\log P$  against  $1/T$ . It was found that all the curves were straight lines and all parallel to the water curve. Thus the data can be represented by the equation

$$\log P = -2240/T + B$$

and in Table I there are given the material, the temperature range, and the values for the constant  $B$ .

TABLE I

Material	Temperature range, °C.	Constant $B$
H <sub>2</sub> O <sup>5</sup>	20–100	8.895
Na <sub>2</sub> CO <sub>3</sub> <sup>6</sup>	30–100	8.800
NaCl <sup>6,7</sup>	20–95	8.760
Na <sub>2</sub> SO <sub>4</sub> <sup>6,7</sup>	20–100	8.835
KCl <sup>1,7</sup>	20–45	8.812
KClO <sub>3</sub> <sup>5</sup>	55–100	8.864
K <sub>2</sub> SO <sub>4</sub> <sup>7</sup>	20–55	8.880
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> <sup>7</sup>	20–50	8.885

The values obtained from the equations check the observed data with a mean deviation of 1%.

### Summary

The vapor pressures for the saturated aqueous solutions of monoammonium acid phosphate have been determined over a temperature range of from 19 to 90°; and for the diammonium acid phosphate from 19 to 55°. Empirical equations were derived to express the data.

On plotting the data and all the data possible to locate in the literature for saturated aqueous solu-

(1) Edgar and Swan, *THIS JOURNAL*, **44**, 570 (1922).(2) Smith and Menzies, *ibid.*, **32**, 1412 (1910).(3) Roehl, *ibid.*, **52**, 1020 (1932).(4) Warren, *ibid.*, **49**, 1904 (1927).

(5) "Int. Crit. Tables," Vol. III, p. 212.

(6) Landolt-Börnstein, Vol. II, p. 1392.

(7) Leopold and Johnston, *THIS JOURNAL*, **49**, 1974 (1927).

tions, as  $\log P$  against  $1/T$ , it was found that the curves were all straight lines and all parallel to the curve for water. At present there seems

to be no explanation for this unexpected result.

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## The Synthesis of 3-Hydroxy-2-(3)-benzofuranone and of 4-Hydroxymandelic Acid

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A number of hydroxy acids were recently investigated in regard to the treatment of urinary infections. Mandelic acid was the most effective of these,<sup>1</sup> and this was due in part to the fact that it was excreted unchanged in the urine. It seemed quite possible that the introduction of a phenolic hydroxyl group into this acid might increase its antiseptic action. 2-Hydroxymandelic acid appeared promising, since salicylic acid has been found to pass through the body into the urine largely unchanged,<sup>2</sup> and because it seemed possible that this hydroxymandelic acid might also be excreted partly unchanged. It was of further interest to determine the influence of the 4-hydroxy group in the bactericidal efficiency of the mandelic acid molecule.

There is but little information on 2-hydroxymandelic acid in the chemical literature. Plöschl<sup>3</sup> treated salicylaldehyde with hydrocyanic acid in solution. The crude 2-hydroxymandelonitrile was then treated with concentrated hydrochloric acid for hydrolysis to 2-hydroxymandelic acid. The acid product was a sirup, which like the nitrile was neither purified, nor analyzed. Later Baeyer and Fritsch<sup>4</sup> obtained crude 2-hydroxymandelic acid by reduction of 2-hydroxyphenylglyoxylic acid with sodium amalgam. They were unable to crystallize the crude sirupy acid, and finally converted it to the crystalline 2-hydroxyphenylacetic acid by further reduction with hydriodic acid. Rosenmund and Schindler<sup>5</sup> mentioned the reaction of 2-hydroxymandelic acid with acetyl chloride to give a diacetyl derivative of m. p. 68°, but gave neither the source nor a description of their 2-hydroxymandelic acid.

(1) Rosenheim, *Lancet*, **228**, 1032 (1935). See also, Lyon and Dunlop, *Brit. Med. J.*, No. 3909, 1096 (1935); Holling and Platt, *Lancet*, **230**, 769 (1936); Cubitt, *ibid.*, **230**, 922 (1936); *Proc. Staff Meetings of the Mayo Clinic*, **11**, 231 (1936).

(2) Sollmann, "Manual of Pharmacology," 4th ed., W. B. Saunders and Co., 1932, p. 626.

(3) Plöschl, *Ber.*, **14**, 1316 (1881).

(4) Baeyer and Fritsch, *ibid.*, **17**, 974 (1884).

(5) Rosenmund and Schindler, *Arch. pharm.*, **266**, 282 (1928).

Plöschl's preparation of 2-hydroxymandelic acid was repeated carefully several times. The result was always a very small yield of a colored sirup, which would not crystallize. According to Plöschl, the aqueous solution of the acid on evaporation yielded an oil which crystallized, but a description of the solid was not given. This solid, supposed to be the lactone of 2-hydroxymandelic acid (3-hydroxy-2-(3)-benzofuranone),<sup>6</sup> was obtained in these experiments, but in all cases, the products were so impure and unsatisfactory that a more detailed examination of the reactions was made.

2-Hydroxymandelonitrile was found to be an oil, which was stable for only about twelve hours at about 0°. Its distillation under high vacuum was hardly satisfactory due to decomposition. To convert certain nitriles to the acids, it has frequently been advantageous to proceed first to the imino ether hydrochloride, then to the ethyl ester and finally to the acid. Consequently, three experiments were made in which the nitrile was treated with dry hydrogen chloride and ethanol. At the ester stage, only one of the three products could be induced to crystallize partially. The analytical data indicated that the crystals were 3-hydroxy-2-(3)-benzofuranone, the lactone of 2-hydroxymandelic acid.

These results suggested that in the one case the reaction designated as A had proceeded to a greater extent than reaction B so that there was sufficient lactone present to crystallize and be isolated.

If this were true, then the lactone should be isolated without difficulty when ethanol was omitted from the reaction. This contention was verified by experiment, and this reaction has provided an excellent method of preparing the pure 3-hydroxy-2-(3)-benzofuranone.

(6) The International Rules numbering has been used for the benzofuran nomenclature.