XIX.—*The Vapour Pressure of Water over Sulphuric Acid–Water Mixtures at 25°.*

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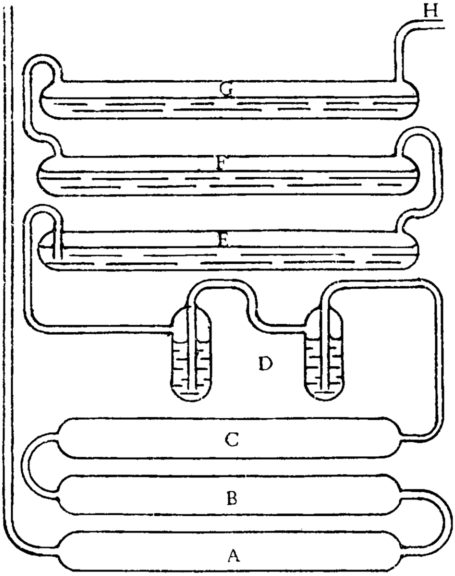
THE present investigation was carried out to test the accuracy of a method of measuring very small amounts of water vapour, present in air, employed by the author in another research. It was thought that this could be attained by measuring the vapour pressure of water over sulphuric acid–water mixtures of fairly high concentration. The results did not agree with the data relating to 25° given in the Landolt–Börnstein tables, but were in good agreement among themselves and with those of other workers. As sulphuric acid–water mixtures are frequently used for controlling the amount of water vapour present in air, the results may prove of interest.

The method of measuring small amounts of water vapour present in " permanent " gases has been described elsewhere (*J. Amer. Chem. Soc.*, 1926, **48**, 1143) and is briefly as follows. The water vapour from a known volume of air is frozen out, by means of liquid air, in a condensation tube of known volume to which a mercury manometer is attached. The air is then removed from the condensation tube, still maintained at the temperature of liquid air, by mercury-diffusion vacuum pumps. The temperature of the condensation tube is then raised until all the water frozen out has been converted into vapour. The pressure of this water vapour at a known volume is then read off; hence it is possible to calculate the mass of water present.

The system of saturators is shown in Fig. 1. The tube A was filled with soda-lime, B with phosphorus pentoxide, and C with a mixture of hydrated and anhydrous oxalic acid. The bubblers, D, and the tubes, E, F, and G, contained the sulphuric acid–water mixtures. H was connected to the condensation tube, which was in turn connected to an aspirator bottle and the necessary evacuating apparatus. The volume of the portion of the apparatus containing the sulphuric acid–water mixtures was 500 c.c., half of which was filled with the mixtures. The greater amount of the spray produced in the bubblers, D, would settle out in the tubes E, F, and G; also at rates of flow varying from 1 to 4 litres per hour no change in the value of the vapour pressure at any one concentration of the mixture was observed. For these reasons, the insertion of a spray filter at the end of the saturator was considered to be unnecessary. The portion of the apparatus shown in Fig. 1 was immersed in a water thermostat maintained at 25°.

At each concentration measurements were made both with and without the tube C in the saturating system; thus equilibrium was reached with air containing both a higher and a lower concentration of water vapour than that in equilibrium with the sulphuric acid–water mixtures. At the highest concentration of sulphuric acid, each successive determination was lower than the previous one. The value given for this concentration in the following table is the first one obtained and has a probable error of 0·01 mm. The explanation of this appears to be that, with mixtures at this concentration, there is an appreciable vapour pressure of sulphuric acid as well as water vapour in the gas phase. Consequently sulphuric acid as well as water vapour would collect in the condensation tube and the pressure measured would be too low. This accumulation of sulphuric acid will not be totally removed by the evacuating pumps, during the preliminary drying of the condensation

Fig. 1.



tube, hence each reading will be lower than the preceding one. This effect cannot be due to the presence of sulphur dioxide as an impurity in the sulphuric acid, as this would tend to give too high rather than too low a result.

Results.—The readings obtained in the series of measurements at 25° are in Table I.

TABLE I.

% H_2SO_4.	$T_{\text{asp.}}$.	V (c.c.).	p_b.	P_{H_2O}.	T_u.	p.	Vap. press. (mm. Hg).
65·9	15·5°	200	760·7	11·5	34·4°	15·90	1·803
65·9	15·6	275	754·5	11·5	41·0	22·15	1·789
76·0	16·3	400	747·5	12·5	17·8	5·00	0·301
76·0	17·0	600	748·4	11·0	17·8	7·33	0·295
76·0	16·3	1800	743·4	11·5	39·0	23·54	0·294
79·4	16·0	2000	745·3	12·0	31·1	13·74	0·158
83·5	17·5	5000	759·9	14·0	38·8	18·08	0·082

(The volume of the condensation tube was 23·73 c.c.)

The first column gives the proportion of sulphuric acid present in the mixtures; $T_{\text{asp.}}$ is the temperature of the aspirator; V, the number of c.c. of air passed through the apparatus; p_b, the barometric pressure; P_{H_2O}, the pressure of the water manometer attached to the aspirator; and T_u is the temperature of the condensation tube at which the pressure p, due to water vapour, was read. The last column gives the vapour pressure (in mm. Hg) calculated from the data by the expression

$$23{\cdot}73pB_{\text{sat.}}T_{\text{asp.}}/VT_uB_{\text{asp.}},$$

in which the temperatures are expressed as degrees absolute; $B_{\text{sat.}}$ is the pressure of the air within the saturator, *i.e.*, p_b corrected for P_{H_2O}; $B_{\text{asp.}}$ is the pressure of the air within the aspirator, *i.e.*, p_b corrected for P_{H_2O} and for the vapour pressure of water at the temperature $T_{\text{asp.}}$.

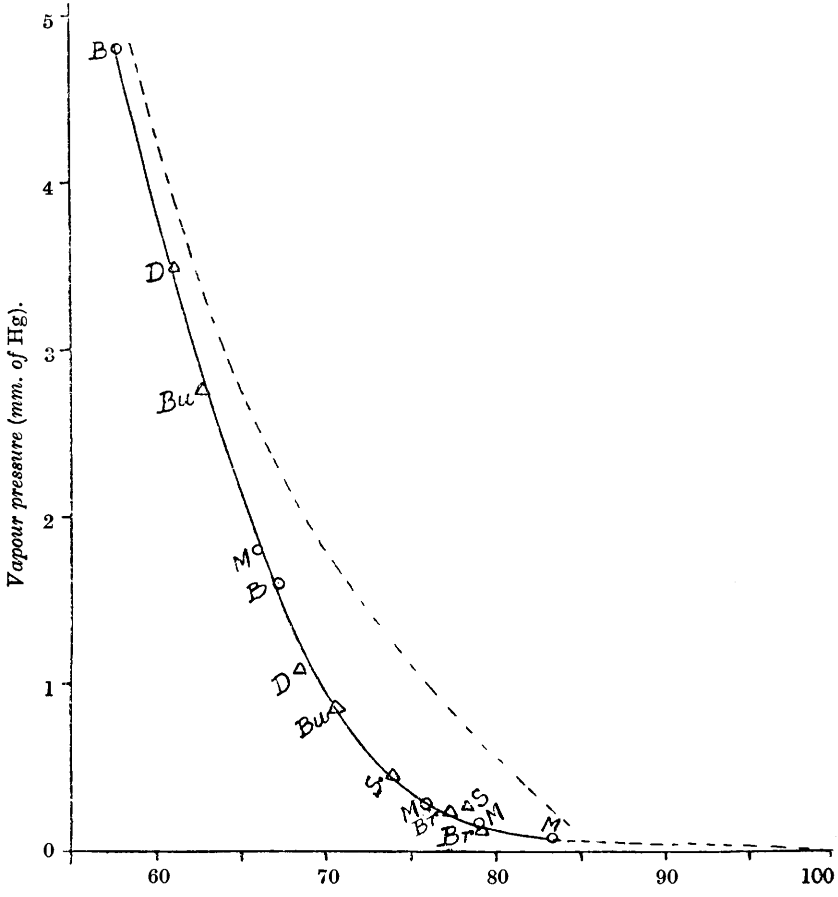
Brönsted (*Z. physikal. Chem.*, 1910, **68**, 708) (compare Lewis and Randall, "Thermodynamics," p. 331) has carried out similar measurements employing a modified tensimeter. The vapour pressures obtained by him, at the corresponding concentrations, are shown in Fig. 2.

Wilson (*Ind. Eng. Chem.*, 1921, **13**, 4, 326) has calculated the vapour pressures of these mixtures at 25° from the data of various workers obtained at 0° and 100°, by means of the equation

$$\log (r_2/r_1) = \Delta H_2(T_2 - T_1)/2{\cdot}3RT_1T_2,$$

where r_1 and r_2 are the ratios of the vapour pressures of the mixtures to those of pure water at the temperatures T_1 and T_2, and ΔH_2 is the heat absorbed when 1 mole of water is removed from the solution without change in concentration. The value of ΔH_2 used was always that for the mean between the particular T_1 and T_2 involved. These calculated values are shown in Fig. 2; the investigator upon whose data they were based is named. The values found in the present investigation are also shown. The values from the Landolt–Börnstein tables at 25° are represented by the broken curve. There is very good agreement between the calculated values of Wilson, the experimental values of Brönsted, and those of the present investigation. This would tend to show that the values obtained for the vapour pressure of water over sulphuric acid–water mixtures are

Fig. 2.



○ *Experimentally determined.* △ *Calculated by Wilson.*

B Brönsted; D Dieterici; Bu Burt; Br Briggs; S Sorel; M McHaffie.

correct, and also that the method of measuring small amounts of water vapour is trustworthy when the pressure of water vapour is as low as 0·08 mm.

Summary.

(1) The vapour pressure of water over sulphuric acid–water mixtures at 25° has been measured for mixtures containing from 66 to 84% of sulphuric acid.

(2) These results agree with the experimental values obtained by Brönsted and with those calculated by Wilson, but not with the data for 25° in the Landolt–Börnstein tables.

(3) The method employed in the present research for measuring small amounts of water present in air has been found trustworthy for pressures as low as 0·08 mm.

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