

# ON THE DENSITY OF THE WATER VAPOUR.<sup>(1)</sup>

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Received November 16, 1926.      Published February 28, 1927.

**Introduction.** On the molecular state of the water vapour many discussions were published. But they cannot be said decisive. Some<sup>(2)</sup> of them claim the existence of polymerised molecules such as  $(\text{H}_2\text{O})_n$  besides single molecules  $\text{H}_2\text{O}$  in the water vapour, while others<sup>(3)</sup> refute them. Most of these discussions are based on the data calculated indirectly, for example the density of the water vapour under the orthobaric state calculated from the vapour pressure and the heat of vaporization. In fact the data<sup>(4)</sup> of the density of the water vapour directly measured are so scarce that they are not sufficient to be used in this discussion. The data of Kornatz,<sup>(5)</sup> however, are somewhat sufficient, which were used by Bose<sup>(6)</sup> to conclude the existence of twice polymerized molecules  $(\text{H}_2\text{O})_2$  in equilibrium with single molecules. According to his formula we can obtain so much  $(\text{H}_2\text{O})_2$  molecules as to 8.9% at  $100^\circ$  under one atmosphere. But precisely examining his formula, it is found that it does not reproduce the data of Kornatz correctly. Therefore we must make more careful measurement of the density of the water vapour, which I have undertaken.

**Experimental.** The apparatus is shown in Fig. 1, which has been designed after that of Prof. Sameshima<sup>(6)</sup> with some modifications. A is a glass vessel, whose volume above the mark *b* is accurately measured filling mercury at several temperatures. The stopper of the vessel carries two pieces of platinum wire sealed in, to which is hanged a small glass bulb containing an accurately weighed sample. The small glass bulb is wound round by fine platinum wire as shown in the separate figure. Through this wire electric current is passed to break the bulb in order to set free the water vapour into vessel A. The vessel A is immersed in a thermostat, the temperature of which is kept constant within one tenth degree (or  $\pm \frac{1}{20}^\circ$ ).

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- (1) Translation of a paper published in the *Journal of the Chemical Society of Japan* (in Japanese), 44 (1923), 887.  
(2) Winkelmann, *Wied. Ann.*, 9 (1880), 208; Oddo, *Gaz. chim. ital.*, 45 (1915), 319; Bose, *Z. Elektrochem.*, 14 (1908), 269; Weber, *Comm. Phys. Lab. Leiden*, No. 150.  
(3) Kendall, *J. Am. Chem. Soc.*, 42 (1920), 2477; Menzies, *J. Am. Chem. Soc.*, 43 (1921), 851.  
(4) Regnault, *J. de chim. et de phys.*, 15 (1845), 129; Horstmann, *Liebig's Ann. Chem., Sup. Bd.*, 6 (1868), 64; Kornatz, *Inaug. Diss.*, Königsberg, 1908.  
(5) Sameshima, *J. Am. Chem. Soc.*, 40 (1918), 1482.

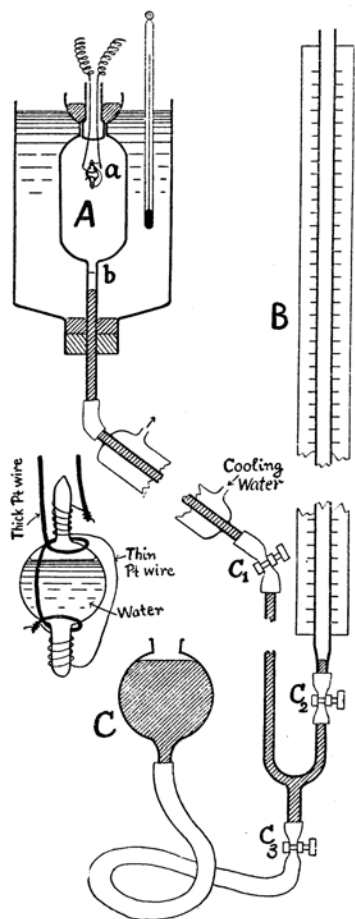


Fig. 1.

The liquid paraffine is used for the thermostat liquid, which is heated electrically. As the operating temperature lies so high as from 80° to 140°, the bath is carefully enveloped by thermal insulators, the electric current is continuously passed and only its small fraction is interrupted by means of a thermoregulator and a relay. The regulator is of ordinary type but the liquid filled is mercury only.

The measurement is carried out as follows. Raising the mercury reservoir C to fill the vessel A with mercury, we put the stopper fitted with the glass bulb already mentioned. Now lowering the reservoir, the vessel becomes to vacuum. This operation is repeated two or three times to get rid of any trace of gas occluded in the mercury or wall of the vessel. Adjusting the mercury level near the mark *b*, temperature of the thermostat is raised to the required temperature. Then adjusting the mercury level to the mark *b* accurately, the height of the mercury in the manometer B is noted. To make the change of the condition of the heated mercury column as small as possible, the connecting tube between A and B is covered with water jacket, and any moving of the heated part of mercury is avoided. For this purpose, in the case of breaking the glass bulb containing the

sample, the connecting tube is shut at *C*<sub>1</sub> by means of a pinchcock. After the break, the counterbalancing mercury level in manometer B is acquired on several trials of slightly releasing the pinchcock at *C*<sub>1</sub>.

The difference of the level in the manometer is reduced to the standard value with respect to temperature and gravity. This value (*P*) is the pressure exerted by the water vapour of *w* gr. The volume of the vapour *V* is that of the vessel subtracted by the net volume occupied by the glass of the sampling bulb, which always amounts to 0.03 c.c. And as the temperature of the bath (*T*) is known, we can calculate the apparent molecular weight (*M*) by the following equation

$$PV = \frac{w}{M} RT,$$

where *R* = 0.082068 litre-atmosphere.

Following table contains the obtained value of  $M$  besides its percentage deviations from the ideal value 18.016. Here we find that no deviation exceeds one percent, and also in Fig. 2 it is shown that these deviations are of order comparable to that expected from the equation of state of water vapour. The lines in Fig. 2 represent the differences of the ideal density of water vapour and the densities calculated by means of van der Waals' equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT,$$

where  $a = 0.01089$ ,  $b = 0.001362^{(1)}$ , while the circlets represent the differences of the ideal density and the observed ones.

Temp. $T - 273.09$	Volume of vapour ( $V$ ) c.c.	Weight of water ( $w$ ) gr.	Pressure ( $P$ ) mm. Hg	Observed mol. wt. $M = \frac{wRT}{PV}$	Deviation from 18.016 (%)
80.03	312.28	0.04115	161.05	18.021	0.03
80.00	312.28	0.07188	280.3	18.085	0.38
100.03	306.07	0.03070	129.3	18.053	0.21
100.02	297.54	0.05170	226.4	18.060	0.24
99.99	306.07	0.08087	340.2	18.073	0.32
99.98	297.54	0.10050	435.2	18.060	0.24
100.00	311.68	0.12405	512.4	18.075	0.33
120.00	297.74	0.04959	226.4	18.037	0.12
120.03	297.74	0.10190	464.6	18.062	0.26
119.98	297.74	0.11160	508.7	18.064	0.27
119.99	297.74	0.11285	515.1	18.041	0.14
140.05	297.94	0.10730	513.2	18.083	0.37
140.00	297.94	0.11440	548.2	18.046	0.17
140.00	297.94	0.11623	556.8	18.052	0.20

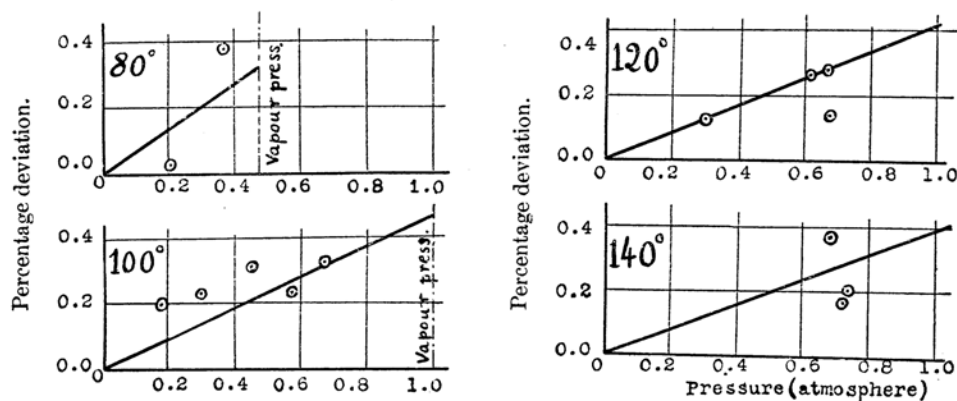


Fig. 2.

(1) Landolt-Börnstein, "Tabellen," 4th ed., p. 447.

Occasionally, however, irregularly higher values of deviation were obtained. In these cases either the vessel A was not clear or the quantity of water was too much that the pressure exerted by it was very near or exceeded the saturated vapour pressure at the temperature. Moreover, on strongly illuminating the vessel we could detect film glittering on the wall of the vessel. Therefore the higher deviation must be caused by such adsorption of water vapour on the stained wall. Now as to the higher deviations found in Kornatz's data, I do not know how to explain it, as I am not available of his original paper.

We can conclude, therefore, from the above measurements that the water vapour consists of single molecules only.

In conclusion the author wishes to express his best thanks to Prof. J. Sameshima for his kind guidance during the investigation.

March 1923.

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