

III. Summary.

1. The precipitation of iron by cupferron is quantitative in hydrochloric or sulfuric acid solutions containing as much as 20% by volume of either acid.

2. The cupferron precipitate of iron is not soluble in cold dil. hydrochloric acid (1:9) wash water.

3. Ammoniacal wash waters, which need be rarely employed, may cause losses. These are always indicated by the formation of turbid filtrates.

4. Crystal clear filtrates and washings are absolutely essential in accurate determinations of iron by the cupferron method.

5. Cupferron precipitates of iron occasionally exhibit the annoying tendency of creeping through the filter. Consequently when the filtrate or wash water is even opalescent the need of such corrective treatments as refiltration or digestion in the cold followed by refiltration is indicated.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY.]

THE MOLECULAR STATE OF WATER VAPOR.

BY ALAN W. C. MENZIES.

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In a recent article with the above title, Kendall¹ has directed attention to the unwarranted conclusions as to the ionization and the polymerization of water vapor drawn by Oddo² and by Bose³ from the values of the vapor density of water computed from Regnault's data⁴ and from the experimental values of Kornatz.⁵ Because of the fundamental importance of the subject in several fields of science, and because the conclusions of Oddo and of Bose continue to be taken seriously by modern chemists,⁶ certain considerations, not dealt with by Kendall, are here brought forward in regard especially to the data themselves upon which the questionable conclusions have been based; and, at the same time, the opportunity is taken to point out a notable discrepancy that requires explanation.

It may be said at the outset that, although Regnault made direct measurements of the vapor density of water, he regarded his results as abnormally high under conditions approaching saturation and suggested that this was caused either by a veritable condensation of the vapor itself, or else by a surface condensation of liquid water on the walls of the glass

¹ Kendall, *THIS JOURNAL*, **42**, 2477 (1920).

² Oddo, *Gazz. chim. ital.*, [1] **45**, 319 (1915).

³ Bose, *Z. Elektrochem.*, **14**, 269 (1908).

⁴ Cf. Landolt-Börnstein-Roth, "*Tabellen*," 1912, p. 369.

⁵ Kornatz, *Inaug.-Diss.*, Königsburg, 1908.

⁶ Cf. Rideal, "*Ozone*," 1920, p. 27; Tomkinson, *Chem. News*, **122**, 9 (1921).

balloons employed. The Regnault data used by Zeuner and, through him, by Oddo, are not, however, the vapor densities obtained by direct measurement, but the values computed by Zeuner by means of the Clausius-Clapeyron equation. In the application of this equation to compute the specific volumes of water vapor, no uncertain assumptions are involved, and the only difficulty lies in securing accurate values for the various factors required. Zeuner used Regnault's data for the values of dp/dt and for the latent heat of vaporization. From 100° , where these values are perhaps most reliable, downwards, the percentage error, especially in the pressure differential, tends to become the greater the lower the temperature, so that the diminishing values of the difference between the so-computed and the ideal density for water vapor become, as 0° is approached, increasingly illusory as a basis for arriving, for example, at the supposed degree of ionization of water vapor.¹ But the values due to Regnault, most excellent though they were, had long been superseded when Oddo wrote. It is, therefore, of interest to repeat the calculation using modern values for the various factors involved in the Clapeyron equation.

For purposes of comparison, the ideal value for the volume of one mole of 18.016 g. of water vapor as at 273.09° K. and 760 mm. pressure is here taken as 22.412 liters, corresponding to a value for R of 0.082068 liter-atmospheres per degree. This gives a normal specific volume (for 1 g. of water vapor) of 1.2440 liters; and a relative density to air of 0.62183, if the weight of a standard liter of air is taken as 1.29273 g. The reference to air, is, however, to be deprecated, because it injects an extraneous "constant" whose value is not constant with, nor in all cases specified by, the various writers using this mode of defining density. Thus, for the "theoretical" density of water vapor, Regnault² uses 0.6219, Griffiths³ 0.6206, Bose⁴ 0.6216, Perman⁵ 0.6227, and the Smithsonian Meteorological Tables (4th ed., 1918) 0.6221. By this usage, also, water vapor is permitted to partake of the same degree of gas imperfection as normal air.

The values here used for dp/dt were obtained by direct differentiation from the equation due to Marvin⁶ relating p and t for saturated water vapor. Following Cederberg's⁷ very successful modification of the single

¹ The difficulty at the lower temperatures, therefore, does not really reside, as has been supposed, in the experimental determination of the density of a rather rarified vapor.

² Regnault, *Ann. chim. phys.*, [3] 15, 149 (1845).

³ Griffiths, *Trans. Roy. Soc. (London)*, [A] 186, 325 (1895).

⁴ Bose, *loc. cit.*

⁵ Perman, *Proc. Roy. Soc. (London)*, 72, 72 (1903).

⁶ *Smithsonian Meteor. Tables*, 1918.

⁷ Cederberg's, *Physik. Z.*, 15, 694, 824 (1914).

constant of the van der Waals vapor pressure equation, Marvin is able to write a single equation covering the whole range of temperature from 0° to the critical temperature which not only unifies and reproduces with fidelity the experimental data, but serves to point to certain inconsistencies in them. The experimental data embraced include those of Scheel and Heuse,¹ Holborn and Henning² and Holborn and Baumann.³ The latent heat of vaporization of water is here stated in terms of the 15° calorie. For 30° and 80° , the values 579.6 and 550.85 cal. are used, which are the arithmetical means of the values of Henning⁴ (579.3, 551.1) and Griffiths⁵ (579.9, 550.6); for 100° , the mean, 538.4, of the values of Henning (538.7) and of Richards and Matthews⁶ (538.1); and for 180° the value of Henning (482.2 cal.), whose range ends at this point. The mechanical equivalent of heat is taken as 4.184×10^7 ergs,⁷ referring likewise to the 15° calorie; g as 980.66 dynes; and the density of mercury at 0° as 15.595.⁸

In Table I are compared at a few points of temperature the densities of saturated water vapor computed by means of the Clapeyron equation, on the one hand, by Zeuner from Regnault's data, and on the other by the writer from the more recent data to which reference has just been made. In each case the comparison is made with the ideal value for the density as defined above, and the differences only are tabulated, in terms of the percentage correction to be applied in order to obtain the ideal value.

TABLE I.—DEPARTURE IN PER CENT. FROM IDEAL DENSITY SHOWN BY WATER VAPOR.

Temp. ° C.	Calculated from Clapeyron eq.		Expt. values, K. I. and K.
	Zeuner.	Menziés.	
30	+0.04	-0.30
80	-2.0	-1.0
100	-2.9	-1.4	-1.5
180	-8.7	-7.4	-7.4

Because it is planned to deal with the general subject on another occasion, little need be said here of the direct experimental determinations of the density of saturated steam. The values of Knoblauch, Linde and Klebe,⁹ whose work is unfortunately neglected by others, are, however, added in Table I for 100° and 180° , which temperatures alone of those

¹ Scheel and Heuse, *Ann. Physik*, **31**, 715 (1910).

² Holborn and Henning, *ibid.*, **26**, 833 (1908).

³ Holborn and Baumann, *ibid.*, **31**, 945 (1910).

⁴ Henning, *Ann. Physik.*, [4] **29**, 441 (1909).

⁵ Griffiths, *loc. cit.*

⁶ Richards and Matthews, *THIS JOURNAL*, **33**, 863 (1911).

⁷ Cf. *Smithsonian Physical Tables*, 6th ed., p. 237.

⁸ Cf. Leduc, *Trav. Mem. Bur. Int. Poids Mes.*, **16**, 36 (1917).

⁹ Knoblauch, Linde and Klebe, *Z. Ver. deut. Ing.*, **49**, 1697 (1905).

tabulated fall within their experimental range.¹ These workers realized, in part at least, the influence of surface condensation, and took steps to minimize this source of error, which otherwise is so serious. An inspection of Table I is sufficient to show (1) that the experimental values of Knoblauch, Linde and Klebe are in good agreement with the values calculated by the Clapeyron equation using the modern data; (2) that the value of vapor density on which Oddo based his computed degree of association at 100° is, on these grounds, about 100% high; and (3) that the difference between ideal density and that calculated by the Clapeyron equation using modern data, does not change sign at a temperature somewhat above 30°, as Zeuner's values would indicate, but, so far as extrapolation is justifiable,² remains of the same sign down to 0°. Thus all foundation for supposed ionization of water vapor below 30° is removed, and by the identical type of evidence that was adduced in its favor.

In regard to polymerization at 30°, 100° and 180°, application of D. Berthelot's equation of state to the densities of even saturated steam as recalculated by the writer yields values for the molecular weight of water 0.19, 0.41 and 1.3% higher, respectively, than 18.016, if the critical data of Holborn and Baumann³ are utilized. Batelli's data⁴ for the critical constants yield in Berthelot's equation, a molecular weight of 0.34% above 18.016. Supposing them to be trustworthy in reporting such inconsiderable divergencies from a somewhat exacting standard of ideality,⁵ it will be observed that these figures based upon newer data, allow a yet narrower foothold for the polymerization hypothesis than do the figures derived from Regnault's data.

Because the application of the Clapeyron equation furnishes, at best, a rather indirect method of determining the densities of saturated vapors, and because of the experimental difficulties admittedly associated with the direct measurement of the vapor density of water especially at temperatures below 100°, it is of importance to look for confirmation to vapor density values obtainable by other methods. Such values are furnished by the exceptionally concordant measurements of two independent in-

¹ The dissertation of Kornatz is not available to the writer. Bose's quotation of his figures would show that, at 75°, he obtains for vapor at a pressure only 0.8 of the saturation pressure an excess of density 3.3% above his ideal value. This datum, viewed in the light of what is said below for the temperature 73°, may serve in the appraisal of the value of his work.

² The latent heat ranges of neither Griffiths nor Henning extend below 30°.

³ *Loc. cit.*

⁴ Batelli, *Mem. accad. Torino*, [2] 43, 1 (1892).

⁵ The fact that both nitrogen and carbon monoxide resemble acetylene in their inability to meet this standard is evidence toward the acetylenic type of union for the neon octets concerned, rather than toward the somewhat exceptional molecular structure postulated for these gases by Langmuir.

investigators, Perman¹ and Krauskopf,² who determined the vapor pressures of water by different forms of the gas-current-saturation method. When air is saturated with water vapor, it was assumed by these workers, following Dalton in part, that the partial pressure A of water vapor in it is related to the total pressure B of the air with its contained vapor in the same ratio as the normal volume C of this contained water vapor is to the normal volume D of the saturated air plus its contained vapor. To obtain C, each used the "theoretical" specific volume of water vapor, taken as 1.242 and 1.243 liters, respectively, multiplying these numbers by the weight of water collected in their absorption tubes. This product enters also as a term into D, which is equal to C plus the normal volume of air in the dry condition. The volumes concerned are, implicitly or explicitly, reduced to standard conditions by application of the simple gas laws. If the assumptions made are justifiable, it should be possible to measure the vapor pressure knowing the specific volume of water vapor, and also *vice versa*. Table II compares the vapor pressure results of Perman and Krauskopf, published in 1903 and 1910, respectively, with the vapor pressures given by the Marvin equation of 1918, which is based upon entirely different experimental work by other methods. The pressures are expressed in mm. of mercury at 0°. The numerals in brackets refer to the number of individual experiments averaged.

TABLE II.—COMPARISON OF VAPOR PRESSURE RESULTS FOR WATER.

Temp. ° C.	Marvin, 1918.	Perman 1903.	Krauskopf, 1910.
20.00	17.55	17.61 (4)
25.00	23.78	23.71 (7)
30.00	31.86	31.88 (4)	31.84 (5)
35.00	42.32	41.91 (7)
40.00	55.40	55.18 (5)
40.66	57.37	57.34 (5)
50.00	92.64	92.39 (4)	92.16 (4)
60.00	149.57	148.94 (5)	149.26 (5)
70.00	233.91	233.98 (6)	233.99 (11)
80.00	355.40	355.08 (6)
80.10	356.84	357.1 (9)
90.00	525.97	526.3 (4)

The additional independent values for 25° by the gas current saturation method obtained by Lincoln and Klein³ (23.76) and by Derby, Daniels and Gutsche⁴ (23.75) have already been cited elsewhere⁵ by the writer as evidence of the normal behavior of water vapor at this temperature. This alone is *prima facie* evidence against spontaneous ionization of water

¹ *Loc. cit.*

² Krauskopf, *J. Phys. Chem.*, **11**, 318 (1907).

³ Lincoln and Klein, *J. Phys. Chem.*, **11**, 318 (1907).

⁴ Derby, Daniels and Gutsche, *THIS JOURNAL*, **36**, 793 (1914).

⁵ Menzies, *THIS JOURNAL*, **42**, 978 (1920).

vapor at 25°. Perman explains that his results for the higher temperatures are the more reliable, and it is just these temperatures that are of greatest interest in the present connection, as being closest to 100°, where the factors for the Clapeyron equation are known with highest precision. The three highest temperature values of Krauskopf (60–80°) and the four highest of Perman (60–90°) have accordingly been utilized in computing an average value for the density of water vapor at a temperature which averages, from the unweighted data, close to 73°. In making the calculation, due allowance has, of course, been made for the different, low, specific volumes for ideal water vapor used by these workers, and also for the fact that specific volume enters into both numerator and denominator of the expression giving the vapor pressure. The Marvin equation is assumed to give the true pressure. The corrected average result gives the density of water vapor close to 73° as less than one part in 1000 above the ideal value. This result is based on the mean of some 46 individual experiments whose average divergence, in groups of about 6, from a mean value is only about 1.5 parts in 1000.

For 73°, the Clapeyron equation, with the average of the latent heat values of Henning and Griffiths and the other factors as explained above, yields a density for saturated water vapor that is 0.9% above the ideal density.

There is thus brought to light a discrepancy between these two values of almost 0.9%, an amount that can be explained only by the entrance of error of the systematic variety.

Comment will here be confined to the possibility of such error in the gas-current-saturation method. It will be noted that the supposed cause of error, while serious near 73°, must operate at 25° scarcely at all. Thus are excluded possible lowering of vapor pressure due to air gases dissolved especially in the surface layers of water,¹ as well as such minor influences as could be attributed to the uncertainty of the vacuum correction to be applied to water weighed in combination with its absorbent; for such factors would cause greater disturbances at the lower temperatures. The solution from the glass vessels of non-volatile impurities in sufficient quantity to account for much of the observed discrepancy is improbable on many grounds. The known departure of air from the behavior of a perfect gas is, of course, negligible for the differences of pressure and temperature here concerned, unless this be affected by the presence of water vapor, which, apparently, is not the case.² Among other possibilities, there remains the surface condensation error,³ which has not yet been studied near 73°, but which one would hardly expect to

¹ Cf. Campbell, *Trans. Faraday Soc.*, 10, 197 (1914).

² Cf. Galizine, *Ann. Physik*, 41, 588 (1890).

³ Cf. Menzies, *loc. cit.*

increase, as from 25° , to so high a value under the conditions of these experiments.

It is of interest to note that the density at 73° expected in accordance with the Berthelot equation, using the critical data of Holborn and Baumann, exceeds the ideal value by 0.46%, a figure which is sensibly one-half of 0.9%, the amount of the discrepancy referred to. If, therefore, we are willing to distribute the error equally between the two values derived above by the two different methods, we shall obtain a resulting density for saturated water vapor at 73° that is higher than the ideal value by precisely the amount anticipated by the application of D. Berthelot's equation of state. This would remove the last vestige of foundation for postulating polymerization of water vapor near this temperature.

Summary.

The density of saturated water vapor has been recalculated by means of the Clausius-Clapeyron equation for various temperatures using modern data for the several factors involved. Hence it is shown (1) that the density does not become less than the ideal value below 30° , and that there is therefore no foundation for the hypothesis of spontaneous ionization; and (2) that the excess density for 100° computed from Regnault's data is about 100% too large.

The numerous and remarkably concordant independent results of Perman and of Krauskopf for the vapor pressure of water at temperatures averaging 73° obtained by the gas-current-saturation method are shown to lead to a vapor density for saturated water vapor at that temperature that is less than 0.1% higher than the ideal value, while the value from the Clapeyron equation is 0.9% higher. This discrepancy requires investigation.

If D. Berthelot's equation of state is applied to the mean of these two results for 73° , the numerical basis remaining from which to postulate polymerization of water vapor at this temperature is precisely zero.