[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY. No. 345.]

THE MOLECULAR STATE OF WATER VAPOR.[1]

BY JAMES KENDALL.

Received April 27, 1920.

Up to a few years ago it was universally considered that water vapor at ordinary temperatures was, so far as could be deduced from vapor density determinations, entirely monomolecular H_2O and obeyed the gas laws within the limits of experimental error. Regnault's measurements gave 18.0 for the molecular weight, Gay-Lussac's 18.01 and Leduc's 18.1, while the formula H_2O requires the value 18.016.[2] In the derivation of equations for osmotic pressure, vapor pressure lowerings etc. in dilute aqueous solutions the assumption was accordingly made, without any question, that water vapor could be treated as a perfect gas. Some measurements by Winkelmann[3] appeared to indicate a tendency towards association at temperatures slightly above normal, but even as late as 1907, in a discussion at the Faraday Society,[4] the different results quoted for saturated vapor at 15° varied more among themselves than from the theoretical value, and the conclusion that the vapor behaved as a perfect gas was undisputed.

In 1908, however, some calculations were published by Bose,[5] based upon new vapor density determinations by Kornatz,[6] claiming that association in the saturated vapor was considerable even at ordinary temperatures. The equilibrium $(H_2O)_2 \rightleftarrows 2H_2O$ was assumed to exist in the vapor phase and an equation for the variation in the equilibrium constant with temperature was derived. This equation indicated for the saturated vapor at 0°, 6.6% association; at 50°, 8.2% association; at 100°, 8.9% association.

In 1915 Oddo,[7] evidently ignorant of the work of Bose, calculated from the tables of Landolt-Börnstein[8] (Regnault's data, reproduced from Zeuner's "Technische Thermodynamik") the molecular weight of saturated water vapor between —20° and 200°, obtaining values steadily increasing from 17.03 at —20° to 19.92 at 200°. Only at 32° did the experimental value agree with that required by monomolecular H_2O. The conclusion was drawn that at temperatures below 32° a *dissociation*

---

[1] Presented at the Buffalo Meeting of the American Chemical Society, April 10, 1919.

[2] Abegg, "Handbuch der anorganischen Chemie," [1] **2**, 67, (1908).

[3] Winkelmann, *Wied. Ann.*, **9**, 208 (1880).

[4] Wilsmore, *Trans. Faraday Soc.*, **3**, 85 (1907).

[5] Bose, *Z. Elektrochem.*, **14**, 269 (1908).

[6] Kornatz, *Inaug-Diss.*, Königsberg **1908**.

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

[8] "Tabellen," **1912**, p. 369.

equilibrium, $H_2O \rightleftharpoons H^+ + OH^-$, existed, and above 32° an *association* equilibrium: $(H_2O)_2 \rightleftharpoons 2H_2O$. At —20° the degree of "ionization" was calculated to be 5.79%; at 200° the "association" reached 19.11%. Great emphasis was laid upon the former phenomenon—*the spontaneous ionization of water vapor*—as opening up a new field in science, and in a second article[1] remarkable deductions were drawn therefrom upon such diverse topics as atmospheric electricity, the influence of temperature on vegetation, the respiratory processes of plants and animals, the electrolytic reactions in a monocellular organism, and the first experimental mechanism for the origin of life.

An adequate discussion of so many important questions cannot be entered into here, but since the molecular weight of water vapor is a matter of fundamental interest in a few minor fields (such as the modern theory of solutions and steam engineering practice) it has been thought profitable to subject the mutually contradictory conclusions of Bose and Oddo to a critical examination, particularly since these conclusions are now quoted without reserve in standard monographs.[2] The results below 32° may first be considered.

According to Oddo, saturated water vapor below 32° is partly dissociated into hydrogen and hydroxyl ions. At 0° the calculated degree of ionization is 2.6%, the vapor pressure being 4.6 mm. From these figures we can determine the concentration of hydrogen and hydroxyl ions in saturated vapor at 0°. The value obtained is 7×10^{-6} g. ions per liter, in other words, just 200 times as great as the corresponding concentration in pure liquid water[3] at 0°. Since the mobility of the ions in the vapor phase would certainly be enormously greater than in the liquid, owing to the diminished viscosity of the medium, it follows that the conductivity of saturated water vapor (or air saturated with water vapor) at 0° should be comparable with that of a fairly concentrated salt solution. Now this is admittedly not the case, hence Oddo's whole argument must be quite invalid.

The explanation is not far to seek. Regnault's data at temperatures below the normal (although smoothed off on a curve to render them consistent) are far too inaccurate to be employed as a basis for determinations of molecular weights to the second place of decimals. In fact, the density of the saturated vapor at pressures so low as 4.6 mm. becomes so small that it is impossible to measure it with anything approaching the above order of accuracy. Even the exceedingly careful determinations of Young[4] on the specific volumes of the saturated vapor of 30 organic liquids

---

[1] Oddo, *Gazz. chim. ital.*, [1] **45**, 395 (1915).

[2] See Turner, "Molecular Association," **1915**, p. 89.

[3] Kohlrausch and Heydweiller, *Z. physik. Chem.*, **14**, 317 (1894).

[4] Young, *Proc. Roy. Soc. Dublin*, **12**, 374 (1910).

are conceded to be uncertain at the lower temperatures investigated, for this same reason. Consequently, until more definite proof of this spontaneous ionization of water vapor is brought forward,[1] we cannot consider the molecular weight of water vapor to be appreciably diverted from the normal value as a consequence of such ionization.

It remains to examine the abnormally high vapor densities for temperatures above normal, upon which both Bose and Oddo postulate the equilibrium $(H_2O)_2 \rightleftarrows 2H_2O$. Bose's calculations are dependent entirely upon a series of 19 determinations at 13 different temperatures (T ranging from 50° to 182°, p ranging from 52.6 to 790 mm.) by Kornatz. It is true that a few isolated measurements of previous investigators are quoted, which are in fair agreement with these results, but of the many determinations which do not agree no mention is made.

While Kornatz's measurements certainly indicate a greater vapor density than the theoretical for monomolecular water throughout the whole series, yet examination shows that *at any one temperature* the observed variation in density with pressure is *systematically* different from that calculated by the use of Bose's equation for the equilibrium: $(H_2O)_2 \rightleftarrows 2H_2O$. The following table will illustrate this clearly. Densities are given relative to air; the theoretical ratio for monomolecular water is 0.6216.

T (abs.).	p (mm. Hg).	Density (obs.).	Variation with p.	Density (calc.).	Variation with p.
348	86.8	0.6324	0.0095	0.6307	0.0139
348	231.5	0.6419		0.6446	
353	71.0	0.6308	0.0063	0.6276	0.0144
353	249.0	0.6371		0.6420	
358	86.76	0.6307	0.0052	0.6278	0.0116
358	260.3	0.6359		0.6394	
363	52.6	0.6286	0.0061	0.6247	0.0119
363	263.0	0.6347		0.6366	
368	63.4	0.6282	0.0051	0.6247	0.0091
368	253.6	0.6333		0.6338	

It will be evident from the above table that the observed variation is approximately only 50% of the calculated. Bose remarks, in a passing comment on this fact, that it is possible that the experimental results are affected by systematic errors, which may be partially explained by assuming that the equilibrium $(H_2O)_2 \rightleftarrows 2H_2O$ in the vapor phase is only slowly established. It is extremely improbable that this assumption is correct, since even in liquid water no indication of anything but instantaneous equilibria between the different molecular species present has ever been obtained. If Kornatz's data *are* trustworthy, Bose's in-

---

[1] The dielectric constant of water vapor is so near to unity as to appear to preclude more than the merest trace of ionization (Bädeker, *Z. physik. Chem.*, 36, 305 (1901).

terpretation of them is not justified; if they are *not* trustworthy, no such interpretation should have been attempted.

We are consequently left to face the fact that, while vapor density measurements for temperatures above the ordinary give abnormally high results, these high results cannot be adequately explained by assuming association in the vapor phase. Indeed, other evidence renders it certain that such association is negligible even at 100°. Let us compare the abnormality in the density of saturated water vapor at this temperature with the abnormalities shown by the saturated vapors of other liquids at their boiling points. The data in the following table are taken from Washburn.[1]

Liquid.	Boiling point. ° C.	Vapor density $\left(\frac{\text{observed}}{\text{calculated}}\right)$.	Vapor density $\left(\frac{\text{observed}}{\text{corrected}}\right)$.
Benzene	80.1	1.024	0.990
Pentane	36.3	1.046	1.002
Heptane	98.4	1.055	1.007
Chlorobenzene	132.0	1.055	1.019
Nitrogen	—195.7	1.05	1.00
Helium	—268.5	1.09	.....
Water	100.0	1.028[a]	1.018[b]

[a] Value taken from Regnault's determinations; see Oddo, *Gazz. chim. ital.*, [1] 45, 328 (1915).

[b] Critical data employed were taken from Holborn and Baumann, *Ann. Physik.*, [4] 31, 945 (1910).

The ratios obtained in the third column show that *all* substances (even such generally accepted non-associated liquids as the saturated hydrocarbons and the inert gases) give saturated vapors of abnormally high density even at pressures as low as one atmosphere. As has been pointed out by Guye,[2] the assumption of the merest trace of association in the vapor phase involves extreme association in the more concentrated liquid phase, consequently if the above abnormalities are due to molecular complexity in the vapor state than even the so-called "normal" liquids are all exceedingly complex. While it would be going too far to state that we have *no* indications of association in the liquid state for the substances listed above,[3] yet their general physical properties show conclusively that any deviations from ideality are very slight.

To what, then, are the abnormalities due? To the simple fact that the saturated vapors under discussion do not exactly follow the gas laws, but require a correction according to the equation of state. When such a correction is applied (as has been done in the last column of the above table

---

[1] Washburn, "Principles of Physical Chemistry," 1915, p. 31.

[2] Guye, *Trans. Faraday Soc.*, 6, 84 (1910).

[3] Dolezalek has recently claimed (*Z. physik. Chem.*, 93, 585 (1919)), that liquid argon is slightly associated, but rightly notes that such association does not extend appreciably unto the vapor phase.

by means of Berthelot's modification of van der Waal's equation)[1] the abnormalities practically disappear.

It will be noticed that water vapor diverges *less* from the "theoretical" than the majority of substances listed. Have we any more reason to attribute the abnormalities here to the presence of dimolecular $(H_2O)_2$ than we have to postulate polymerization in pentane vapor or the existence of He_2 in helium gas? It is true that liquid water is highly associated, and that the vapors of certain similarly associated liquids such as acetic acid[2] show unmistakable association even at low temperatures, yet from the values obtained in the table above it is evident that, below 100° at least, association in water vapor can only be minute. While the observed vapor density is still slightly above the corrected theoretical value, yet the excess is not so great as in the case of chlorobenzene and may be accounted for in part by uncertainty in the critical data.[3] At temperatures approaching the critical, where the pressure is very high, association of the saturated vapor may become appreciable,[4] but the extensive association claimed by Bose and Oddo at temperatures below the boiling point is certainly an exaggeration of the facts.

In conclusion, it is necessary to record a protest against the optimistic habit, prevalent among writers of text books as well as of original articles, of treating all gases as perfect. In work on gaseous systems, it is rare to find any correction applied for "the equation of state," although frequently intricate calculations which presuppose considerable accuracy are carried out with the use of the observed densities. In technical processes (probably following Haber's "Thermodynamics of Technical Gas Reactions" and similar monographs) no regard at all is commonly paid to possible abnormalities, even when reactions under high pressures are considered. That the quantities of different gases introduced into the reaction vessels under such conditions are quite at variance from the correct proportions has been strikingly shown in recent work on the Haber process.[5] The extended discussion of this general question given by Lewis in several articles[6] does not appear to have attracted the attention which it deserves.

[1] See Washburn, *loc. cit.*, p. 33.

[2] Young, *loc. cit.*

[3] If association exists at the critical point, the critical data are not strictly applicable to the Berthelot equation.

[4] The experiments of Ramsay and Young (*Phil. Trans.*, 183, 107 (1892)), indicate a rapid increase in the ratio (obs./calc.) above 200°. At 270° the observed vapor density is more than 15% in excess of the corrected theoretical.

[5] "Physical and Chemical Data of Nitrogen Compounds," p. 5–6 (M. I. D. Research Laboratory, University College, London, 1918).

[6] G. N. Lewis, *Proc. Am. Acad.*, 37, 66 etc. (1901); 43, 262 (1907); THIS JOURNAL, 37, 2309 (1915).

For the same reason, vapor density determinations upon dissociating substances, such as phosphorus pentachloride and the ammonium halides,[1] will not furnish exact values for their dissociation unless correction is made for the appreciable divergence from the perfect gas laws of all of the substances concerned in the equilibrium. The possible error in functions derived from *variations* in the calculated degrees of dissociation (such as the heat of dissociation)[2] will naturally be much greater. To attempt to obtain quantitative values for the association of *liquid* water from uncorrected vapor density measurements, as has been done by Guye,[3] is obviously altogether futile.

In the standard Victor Meyer vapor-density experiment the textbooks on practical physical chemistry "allow" the student an error of "less than 5%," although the abnormalities in the vapor densities of many common liquids exceed that value. Since corrections of less than 1% (*e. g.*, for the water vapor content of the atmosphere)[4] have been proposed, it would evidently be well worth while to introduce the equation of state factor into the discussion. Otherwise, the accurate student and the conscientious instructor will inevitably clash, without prospect of reconciliation.

Summary.

The monomolecular nature of water vapor has recently been questioned, "spontaneous ionization" of H_2O into H^+ and OH^- at low temperatures and association into $(H_2O)_2$ at higher temperatures being postulated. It has been shown here that the evidence for the existence of the equilibria $H_2O \rightleftarrows H^+ + OH^-$ and $2H_2O \rightleftarrows (H_2O)_2$ is in each case entirely insufficient, that the abnormalities in the vapor densities of normal substances at their boiling points are similar to that in water vapor at 100°, and that such abnormalities practically vanish on applying the corrections for deviation from the perfect gas laws.

An "equation of state" correction is similarly necessary in gas reactions at high pressures, in calculations on dissociation in the vapor state and in Dumas or Victor Meyer vapor-density determinations.

NEW YORK, N. Y.

---

[1] Smith and Lombard, THIS JOURNAL, **37**, 38, 2055 (1915).

[2] Smith and Lombard, *loc. cit.*, p. 55.

[3] Guye, *Trans. Faraday Soc.*, **6**, 84 (1910).

[4] Evans, THIS JOURNAL, **35**, 958 (1913).