Intermolecular Attractions and Saturation Vapor Pressure[1]

J. E. McDonald

Institute of Atmospheric Physics, The University of Arizona

15 October 1962

In most meteorological applications, one deals with saturation water-vapor pressures and saturation densities in the presence of a large partial pressure of another gas, "dry air." Fortunately, the thermodynamic effects of the latter component are small by usual standards. Nevertheless they are not so minute but that they must be taken into account in such basic data-tabulations as those found in the *Smithsonian Meteorological Tables* (List, 1951). The purpose of the present note is to point out and to correct an interesting error that appears in the discussions accompanying the latter tabulations. Although the numerical magnitude of the error is not large, the underlying physics deserves the following clarification.

It will suffice to restrict attention here to saturated air under a total pressure of 1013.25 mb at the temperature of the triple-point for water substance. At the latter temperature, the saturation vapor pressure e_w in *absence* of air is 6.1114 mb according to the latest revision of the Goff-Gratch formulation (Goff, 1957). If we shift from a pure water system to the one specified above, i.e., if we now let into our system enough air to raise the total pressure on the water surface to one atmosphere, we find that after this two-component system has attained full equilibrium, the (saturation) vapor pressure has changed due to two distinct physical effects on the vapor tension of the liquid phase.

First, a small amount of air has become dissolved in the liquid phase, thereby *lowering* the vapor tension in accordance with Raoult's law. Since 29.2 cm^3 of air dissolves in one liter of water near 0C (Dorsey, 1940, p. 534) and since these gases will behave as nearly ideal solutes, we calculate a Raoult suppression of 1.4×10^{-4} mb.

Second, we find that the specified rise in total pressure exerted on the liquid phase has led to an *increase* of vapor tension as specified by the Poynting equation (Glasstone, 1947, p. 236). For our case, where the pressure increase is 1007.14 mb, we calculate a Poynting enhancement of 4.88×10^{-3} mb.

Thus the combined Raoult and Poynting effects lead to a net increase of vapor tension of 4.74×10^{-3} mb. At equilibrium the partial pressure of water vapor must exactly equal this vapor tension, whence the saturation vapor pressure e_w' of our moist air under the specified conditions becomes 6.1161 mb. It may be well to emphasize that even such slight alterations (in a quantity for which we are usually content with about two-digit accuracy in meteorological computations) are of more than casual academic interest: The distinction between the *ice point* and *triple point* depends entirely on the above two effects. By combining the cited values with the Clausius-Clapeyron equations for water and for ice, respectively, one deduces (see, for example, Sears, 1953) the 0.010C difference between ice point and triple point that enters into all discussions of precise thermometry.

Now, if, instead of going through the above analysis, one turns directly to the *Smithsonian Meteorological Tables* to determine the saturation vapor pressure of moist air, he finds an explicit expression for this purpose presented on p. 347, namely

$$e_w' = r_w p/(\epsilon + r_w) \qquad (1)$$

where r_w is the saturation mixing ratio, p is the total pressure, and $\epsilon=0.62197$ is the ratio of molecular weights of water and air. Reference to p. 340 of the

---

[1] Work supported by the Office of Naval Research.

Tables then yields the necessary auxiliary relation

$$r_w = \epsilon f_w e_w / (p - f_w e_w) \tag{2}$$

wherein f_w is a coefficient allowing for *three* separate effects of the admixed air. The first two of these effects are the above-described Raoult and Poynting effects. The third is briefly described as "the effect of intermolecular forces (gas imperfections) on the properties of the moist air itself." Interpolation in a table accompanying the quoted passage gives $f_w = 1.0044$ for the conditions of the present illustrative case. By combining (1) and (2), one obtains in place of (1) the simpler relation

$$e_w' = f_w e_w \tag{3}$$

a relation whose form is ostensibly confirmed by the following statement found on p. 331 of the *Tables*: "The modification in the saturation vapor pressure over water $\cdots$ due to the presence of air has been taken into account by the introduction of the factor $f_w \cdots$."

However, on inserting into (3) the values $e_w = 6.1114$ mb and $f_w = 1.0044$, we obtain $e_w' = 6.1383$ mb in disagreement with the value 6.1161 mb obtained earlier here. Since the latter value is in full agreement with the internationally accepted relations between the ice point and triple point, it appears that something in relation (3) is suspect.

I believe that whereas (2) is correct because the adjusted vapor pressure $f_w e_w$ is used, (1) and hence also (3) are erroneous because (1) is based on the perfect-gas assumption that e_w' is exactly proportional to the actual vapor density. The crux of that point and hence of this note is that intermolecular attractions in the *gas* phase can increase the saturation vapor *density* but cannot *per se* alter the saturation vapor *pressure*. Such an assertion seems internally contradictory until one puts aside notions developed from working with ideal gas relationships. But exactly *because* of the departure from the perfect gas laws, the pressure exerted by any component (here we consider the water vapor molecules, but we could equally well examine the parallel effect on the dry-air partial pressure) on the walls of the containing vessel or, say, on an imaginary "partial-pressure-meter" inserted into the gas mixture is reduced below the pressure value which we should calculate if we erroneously inserted the actual vapor density into the ideal gas equation. This reduction stems from the unbalanced effect of the intermolecular attractions in the neighborhood of a bounding surface or pressure-sensitive surface of any sort, an effect discussed in connection with the van der Waals' law in texts on kinetic theory (e.g., Kennard, 1938, p. 207).

The actual flux of water vapor molecules impinging on the gas-liquid interface in our system, being directly proportional to the water vapor partial pressure, will be proportionally suppressed by intermolecular forces in the same manner as the measureable pressure, so the condensation flux will fall short of that which we would anticipate from consideration of the elevated vapor density. Indeed, by the very nature of the molecular equilibrium implied in the saturation concept, we are assured, *a priori*, that the effective flux of condensing molecules must exactly balance the evaporation molecular flux.[2] Thus the *measurable* saturation vapor pressure here is 6.1161, whereas the larger value 6.1383 computed with the aid of (3) may be viewed as *the partial pressure that would be exhibited by the saturated moist air if the mixture somehow satisfied the perfect gas law and yet was characterized by the actually-prevailing vapor density.* In fact, it does not satisfy that law and the intermolecular forces may be regarded as maintaining an enhanced density of water molecules in the vapor phase by just an amount as to leave the condensation flux equal and opposite to the evaporation flux, which is influenced by Raoult and Poynting effects alone.

In summary of the above, I conclude that (1) and (3) are fallacious, whereas (2) is correct. The reason that (2) is correct is that the mixing ratio is just an indirect measure of the vapor density, so the full effects of all *three* physical factors entering into the carefully formulated and empirically tested Goff-Gratch f_w-coefficient influence r_w. Fortunately, no data actually tabulated in the *Tables* contain the error here discussed, since only e_w and r_w but not also e_w' appear there in table form. I have searched through all of the papers of Goff and associates that might bear on this matter and find no discussion therein of the e_w'-concept, so I presume that (1) is not due to Goff. The relation (1) does, however, appear in the summary (Sheppard, 1949) prepared for the International Meteorological Organization Subcommission whose findings underlie, in part, the cited section of the *Smithsonian Tables*; so it appears that this Subcommission erroneously concluded that (1) holds.

Two quantitative implications are worth noting. First, whereas the combined Raoult and Poynting effects lead to a net excess of e_w' over e_w amounting to 4.74×10^{-3} mb, the above-described misapplication of the Goff-Gratch f_w-coefficient via (3) would predict a corresponding excess of 26.89×10^{-3} mb. Hence, we can give a numerical measure to the intermolecular attraction effects by noting that the shift from a system involving only pure water substance to a system in which dry air constituents raise the total pressure to one atmosphere produces an actual enhancement of the saturation vapor pressure amounting to only 18 *per cent* of the amount by which it would rise if the pressure enhancement due to augmented vapor density could be had without paying the related price of intermolecular-force suppression of vapor pressure.[3] Secondly, Goff

---

[2] We may here take the condensation coefficient as unity since its actual value is logically unrelated to present considerations.

[3] This carries the corollary implication that of the three air effects embraced in the Goff-Gratch f_w-coefficients, molecular attractions are definitely the most important, whereas the discussion in the *Smithsonian Tables* (p. 340) probably leaves most readers with the impression that the Poynting and Raoult effects are larger than intermolecular effects.

(1949) gives estimates of the second virial coefficients (Kennard, 1938) for air-air and water-water attractions and also gives estimates of the unlike-molecule interaction coefficient for air-water attractions from which a useful insight may be drawn. If we take Goff's 0C values and adopt the air-air virial coefficient as our reference value, we find the water-water coefficient to be about 140 times greater (effect of strong dipole-dipole attractions), and the air-water interaction coefficient to be about three times greater than the air-air term (polar nature of water adding only slightly to dispersion forces when interacting with non-polar oxygen and nitrogen molecules). From these we might guess that the dominant intermolecular effect in moist air would be caused by water-water attractions; but because water-vapor mixing ratios are only of order 10^{-2}, use of the virial expansion (Goff and Bates, 1941) reveals that air-water interactions are actually about six times more important than water-water interactions in causing moist air to depart from perfect gas behavior. Most important, by far, for the deviations of the total pressure p from the ideal-gas value, are the air-air interactions, but these are not of direct interest to the point of this note.

REFERENCES

Glasstone, S., 1947: *Thermodynamics for chemists.* New York, D. van Nostrand, 522 pp.

Goff, J. A., 1957: Saturation pressure of water on the new Kelvin temperature scale. *Trans. Amer. Soc. heating and vent. Eng.*, **63**, 347–354.

—— and A. C. Bates, 1941: The interaction constant for moist air. *Trans. Amer. Soc. heating and vent. Eng.*, 47, 373–390.

Kennard, E. H., 1938: *Kinetic theory of gases.* New York, McGraw-Hill, 483 pp.

List, R. J., 1951: *Smithsonian meteorological tables.* Washington, The Smithsonian Inst., 527 pp.

Sears, F. W., 1953: *An introduction to thermodynamics, the kinetic theory of gases, and statistical mechanics.* Cambridge, Mass., Addison-Wesley Publ. Co., 374 pp.

Sheppard, P. A., 1949: The physical properties of air with reference to meteorological practice and the air-conditioning engineer. *Trans. Amer. Soc. mech. Eng.*, **71**, 915–919.