

interaction constant A_{aw} has been available. Preliminary results of a cooperative investigation between the A.S.H.V.E. and the Towne Scientific School, University of Pennsylvania, have indicated that the ratio $2A_{aw}/(A_{aa} + A_{ww})$ has an approximately constant value $\lambda = 0.075$ [10]. However, before attempting to make use of this information it is advisable, in the interest of simplicity, to first ignore the complications arising from intermolecular forces.

Now, in the absence of intermolecular forces, each constituent gas in a mixture such as moist air would behave exactly as if it alone occupied the volume V at the temperature T of the mixture and: (1) the observed pressure P would be the sum of individual partial pressures p ; (2) the total enthalpy H would be the sum of the individual enthalpies. This is the essence of Dalton's Law of Partial Pressures.

Referring to dry air by the subscript a and, to water vapor by the subscript w , Dalton's Law would predict

$$V = \frac{n_a RT}{p_a} = \frac{n_w RT}{p_w} = \frac{(n_a + n_w) RT}{P} \quad (10a)$$

where

$$P = p_a + p_w \quad (10b)$$

From these equations are easily obtained,

$$\frac{n_w}{n_a} = \frac{p_w}{P - p_w} \quad \text{or} \quad \frac{p_w}{P} = \frac{n_w/n_a}{1 + n_w/n_a} \quad (10c)$$

in which,

- p_a = partial pressure of the dry air.
- p_w = partial pressure of the water vapor.
- P = observed pressure of the mixture.
- n_a = weight of dry air (mols).
- n_w = weight of water vapor (mols).

Humidity Ratio

In Equation 10c the ratio by weight of water vapor to dry air, n_w/n_a , is expressed in mols per mol. Most engineers prefer to express it in pounds per pound which can easily be done, since the molecular weights of both water vapor (18.0154 lb per mol) and of dry air (28.967 lb per mol) are known. Thus Equation 10c becomes

$$W = 0.62193 \frac{p_w}{P - p_w} \quad \text{or} \quad \frac{p_w}{P} = \frac{W}{0.62193 + W} \quad (11)$$

There is little doubt but that the weight ratio W is the most convenient parameter in terms of which to express the composition of moist air; but to choose a suitable name and one that would have general acceptance has always been a perplexing problem. In previous issues of the GUIDE, *specific humidity* was adopted even though it was recognized that the adjective *specific* should properly refer to weight of water vapor per pound of mixture, and not per pound of dry air. Various other names have been proposed from time to time including: mixing ratio, proportionate humidity, density ratio, absolute humidity. It is believed that the name *humidity ratio* is most suggestive of the meaning which it is desired to express, that it violates no well established usage as does the name *specific humidity* and that its adoption will avoid much confusion.

To repeat: in the case of moist air, the ratio by weight (pounds) of water vapor to dry air is called *humidity ratio* and denoted by the letter W .

Saturation

It is often stated that moist air is *saturated* when the water vapor in it is itself in the *dry saturated condition* at the given temperature. This statement would imply that the humidity ratio of saturated moist air is, in accordance with Equation 11,

$$W_s = 0.62193 \frac{p_s}{P - p_s} \quad (12)$$

where p_s is the saturation pressure of pure water vapor.

This statement lacks thermodynamic soundness due to actual departures from Dalton's Law, but has real practical merit as an approximation.

Example 3. Calculate the humidity ratio of saturated moist air at 68 F, 30 in. Hg.

Solution. The saturation pressure of pure water at 68 F from Table 6 is 0.68980 in. Hg; hence,

$$W_s = \frac{0.62193 \times 0.68980}{29.3102} = 0.01464 \text{ (pound per pound of dry air).}$$

It is also frequently stated that moist air is saturated when the space (volume) occupied by it contains the *maximum weight of water vapor* at the given temperature. This means that any additional water would have to be in the liquid or solid phase. But under proper circumstances the water vapor can be *supersaturated*, in which case the space occupied by the mixture can contain more than the *maximum possible* water vapor. The statement is therefore meaningless as a definition of saturation.

A precise definition must necessarily refer to the co-existence of at least two distinct phases, say, liquid and vapor. These can only co-exist in stable equilibrium if evaporation of the liquid or condensation of the vapor under conditions of constant total volume and constant total internal energy would have to involve a decrease of total entropy. This would be the situation if, and only if, the pressure, the temperature, and each component chemical potential has the same value in each phase.

In the case of moist air, the general conditions for saturation previously stated can be deduced from Equation 9 together with available data on the solubility of air in the liquid. They can be reduced to the form,

$$W_s = 0.62193 \frac{p'_s}{P - p'_s} \quad (13a)$$

where

$$p'_s = \frac{(PF)(DF)}{(RF)} p_s \quad (13b)$$

The liquid (or solid) phase will contain a small amount of dissolved air and the Raoult factor (RF) expresses the effect of this dissolved air in lowering the vapor pressure in accordance with Raoult's Law. The Poynting factor (PF) accounts for the fact that the very presence of dry air requires the liquid (or solid) to support a higher pressure at saturation than it would if no dry air were present. The Dalton factor (DF) expresses the effect of intermolecular forces in the vapor phase. All three factors depend more or less on pressure as well as on temperature.

The Raoult and Poynting factors are calculable. The order of magnitude of the Dalton factor can now be determined by computing its value at one temperature and pressure using the information previously referred to, namely, $2A_{aw} = 0.075 (A_{aa} + A_{ww})$. At 68 F, 29.921 in. Hg, for example,

$$p'_s = \frac{1.00073 \times 1.0052}{1.00002} p_s$$