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 coexistence of at least two distinct phases, say, liquid and vapor. These can only coexist 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,

$$W_s = 0.62193 \frac{p_s'}{P - p_s'} \tag{13a}$$

where

$$p_s' = \frac{(PF)\ (DF)}{(RF)}\, p_s \tag{13b}$$

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 Dalton factor is the only one of the three factors listed here which cannot at present be calculated with reasonable certainty due to ignorance regarding the interaction constant A_{aw}. Its order of magnitude can be *guessed*, however, by assuming a simple combination rule which has received some confirmation on mixtures similar to moist air, namely,

$$A_{aw} = \frac{A_{aa} + A_{ww}}{2}$$

At 68 F, 30 in. Hg, for example,

$$p_s' = \frac{1.00073 \times 1.05863}{1.00002}\, p_s$$

These figures suggest that Dalton's Law may not be the close approximation it is generally assumed to be. However, until the Dalton factor can be measured, it is better to ignore (call it unity) than guess it. This procedure has been followed in computing the values in Table 6.

Relative Humidity

The ratio of actual humidity ratio W to the saturation humidity ratio W_s corresponding to the actual temperature and the observed pressure is denoted by the symbol μ and may be called alternatively *degree of saturation* or *percent saturation;* thus,

$$W = \mu \cdot W_s \tag{14}$$

Example 4. Air is to be maintained at 70 F, 40 per cent saturation when outside air is at 0 F, 70 per cent. The observed pressure may be taken to be 29.921 in. Hg. Find the weight of water to be added to each pound of dry air using Table 6.

Solution. The desired humidity ratio is $0.40 \times 0.01574 = 0.006296$ while that of outside air is $0.70 \times 0.0007852 = 0.000550$. Hence the weight of water to be added is $0.006296 - 0.000550 = 0.005746$ lb per pound dry air.

Under Dalton's Law the water vapor exerts a partial pressure p_w which may be calculated from the given humidity ratio W and the observed pressure P by means of Equation 11. The ratio of this partial pressure p_w to the saturation pressure of pure water p_s corresponding to the actual temperature is called *relative humidity* and may be denoted by the symbol Φ; thus,

$$\Phi = \frac{p_w}{p_s} \tag{15}$$

The relation between μ and Φ is obtained directly from Equation 11 and 12 and is

$$\mu = \left(\frac{P - p_s}{P - p_w}\right) \Phi \tag{15a}$$

whence it is clear that for ordinary temperatures where p_s and therefore p_w are small compared with P, the two are approximately equal.

As an aid in quickly translating degree of saturation μ into relative humidity Φ or vice versa, the following empirical equation may be substituted for Equation 15a:

$$\Phi - \mu = \alpha \cdot \mu\,(1 - \mu) \tag{15b}$$

where α depends upon temperature *for standard atmospheric pressure*, as shown by the values in Table 7.

TABLE 7. PERCENTAGE DIFFERENCES CORRESPONDING TO TEMPERATURE FOR EQUATION 15b

Temp F t	Per Cent α	Temp F t	Per Cent α	Temp F t	Per Cent α	Temp F t	Per Cent α
5	0.16	30	0.55	55	1.47	80	3.51
10	0.21	35	0.68	60	1.76	85	4.14
15	0.27	40	0.83	65	2.10	90	4.86
20	0.34	45	1.01	70	2.50	95	5.70
25	0.44	50	1.22	75	2.97	100	6.67