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,

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

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 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,

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

This indicates departures from Dalton's Law of the order of 0.5 per cent. The data in Table 6 which are based on an assumed value of unity for the

Dalton factor have not been revised pending final results on the measurement of the interaction constant [10].

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 *per cent saturation;* thus,

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

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 Equations 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, the following empirical equation may be substituted for Equation 15a:

$$\Phi = \mu + C\,\mu\,(1 - \mu) \tag{15b}$$

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

Within the limits of accuracy of (15b) this may also be written

$$\mu = \Phi - C\,\Phi\,(1 - \Phi) \tag{15c}$$

and used to translate relative humidity Φ into degree of saturation μ.

TABLE 7. VALUES OF THE CONSTANT C IN EQUATIONS 15b AND 15c

Temp F t	Per Cent C	Temp F t	Per Cent C	Temp F t	Per Cent C	Temp F t	Per Cent C
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