The Relative Humidity in Radiation Fog

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Abstract

The relative humidity in radiation fog is governed by the rate at which water condenses onto the hygroscopic nuclei and the rate of fall of temperature. An equation describing this is developed and from this equation it is deduced that, with the usual rates of fall of temperature and salt content of the air, the relative humidity is unlikely to exceed 100.1 per cent.

1. Introduction

It is commonly assumed that the relative humidity in radiation fog never exceeds 100 per cent by more than a very small amount, of the order of a fraction of one per cent. This assumption seems very reasonable but it does not appear to have been demonstrated, either theoretically or empirically, that the assumption is valid. Experimental demonstration would probably be a matter of considerable difficulty and accordingly it has seemed worth while examining the question theoretically.

Fog occurs when sufficient water vapour condenses onto hygroscopic nuclei suspended in the atmosphere. The balance of evidence favours the view that these nuclei consist of particles of sea salt. Condensation starts when the relative humidity is about 70 per cent, the raising of the vapour pressure over the droplet by the curvature effect being more than balanced by the lowering of the vapour pressure because the droplet consists of a salt solution. As the relative humidity rises the droplet increases in size but while the relative humidity remains less than a critical value, which exceeds 100 by a very small amount, there will be a drop size at which the resultant vapour pressure over the drop equals the ambient vapour pressure. Having reached this size, the drop ceases to grow unless the relative humidity continues to rise. After the relative humidity exceeds the critical value further growth of the drop leads to a lowering of the vapour pressure over the drop because the effect of curvature in raising the vapour pressure is now very small. Accordingly the drop will now grow indefinitely unless the relative humidity falls. The critical value of the relative humidity and the corresponding critical drop size are governed largely by the mass of the nucleus but are influenced to some small extent by the temperature. If we assume the nucleus consists of sodium chloride it can be shown that at a temperature of 283° *A* the critical relative humidity and drop radius for a nucleus mass of 10^{-12} grams are 100.0036 per cent and 21 μ respectively.

In the early stages of the growth of the drop, while the relative humidity is substantially below 100 per cent, the rate of growth of the drop to its equilibrium size is extremely

rapid (see e. g. BEST, 1951) and the drop can be considered to be in instantaneous equilibrium with the environment. As the relative humidity approaches and finally exceeds 100 per cent the rate of growth slows down enormously.

Radiation fog forms when the air temperature falls sufficiently. If the amount of water —i.e. vapour plus liquid—per unit volume is conservative the relative humidity will rise as the temperature falls unless the rate of condensation of water onto the fog droplets is adequate to prevent it. The rate of condensation will obviously be proportional to the number of fog droplets per unit volume and will increase as the excess of ambient vapour pressure over the vapour pressure at the drop surface increases. It will also depend upon the properties of each droplet, i.e., upon the temperature and the mass of the nucleus. On the other hand the rate at which water must condense to prevent the relative humidity from rising substantially above 100 per cent will depend upon the rate of fall of temperature. It is the balance between these factors which determines the amount of supersaturation which will occur.

We shall formulate a differential equation for the variation of relative humidity in the presence of a number of fog droplets and with a steadily falling ambient temperature. This equation will be based upon the assumption of conservation of total water per unit volume and the rate of growth of a drop of salt solution in air having a specified relative humidity. It is not possible to obtain an explicit solution to this equation but it can be shown that there is an upper bound to the relative humidity. The value of this upper bound depends upon the mass of the nucleus of the drop, the rate of fall of temperature and the temperature and will be evaluated for a number of typical cases.

2. The rate of variation of the relative humidity in radiation fog

The rate of growth of a droplet of salt solution has been discussed elsewhere (BEST, 1951) and from the equations given there it is easily shown that the rate of growth can be described by the equations

$$r \frac{dr}{dt} = A(H - \psi) \tag{1}$$

$$A = \frac{M D k p_\Theta}{R \Theta k + \lambda D \psi (dp_\Theta / d\Theta)} \tag{2}$$

$$\psi = \exp(P/2r) - \frac{m}{6r^3} \tag{3}$$

$$P = 4 TM/R\Theta \tag{4}$$

where

p_Θ = saturation vapour pressure at temperature Θ (dynes cm^{-2})
Θ = temperature of air (°A)
r = drop radius (cm)
T = surface tension (74 dynes cm^{-1} for water)
M = molecular weight of water (18)
R = gas constant per mol ($8.314 \cdot 10^7$ erg deg^{-1} mol^{-1})
m = mass of nucleus in one drop (grams)
λ = latent heat of evaporation (cal mol^{-1})
D = coefficient of diffusion of water vapour in air (cm^2 sec^{-1})
k = thermal conductivity of air (cal cm^{-1} sec^{-1} deg^{-1})
100 H = relative humidity

If now we assume that there are N droplets, all of radius r, per unit volume and that the total amount of water per unit volume (liquid plus vapour) remains constant we have

$$N \frac{4}{3} \pi r^3 + H \varrho_\Theta = \text{constant} \tag{5}$$

where ϱ_Θ is the saturation vapour density at temperature Θ. Differentiating equation 5 with respect to time, substituting for dr/dt from equation 1 and writing α for $-d\Theta/dt$ (the rate of fall of temperature) we get

$$\varrho_\Theta \frac{dH}{dt} = H\alpha \frac{d\varrho_\Theta}{d\Theta} - 4\pi N r A (H - \psi) \tag{6}$$

This is the differential equation describing the variation of H with time. Since p_Θ, r and ψ are also functions of t an explicit solution cannot be obtained. We can, however, determine a condition that dH/dt shall be negative.

3. An upper bound to the relative humidity

We see from equation (6) that dH/dt will be negative, i.e., H will decrease, provided

$$H > \frac{r\psi}{r - K} \tag{7}$$

where

$$K = \frac{\alpha}{4\pi NA}\frac{d\varrho_\Theta}{d\Theta} \tag{8}$$

In order to determine whether or not H will increase the right hand side of the inequality (7) should be evaluated for the value of r appropriate to the existing value of H. Failing a solution to equation (6) we cannot do this but we can show as follows that the right hand side of inequality (7) is bounded and hence that there is a value of H which cannot be exceeded and may not be reached.

Consider first the quantity K. K is a function of A and A is a function of ψ. Now physically ψ represents the ratio of the vapour pressure over the drop of salt solution to the saturation vapour pressure over a plane water surface at the same temperature as the drop (see BEST, 1951). As the drop size increases the variation of ψ follows a well known pattern (see e.g. SIMPSON, 1941) rising to a maximum value and thereafter falling asymptotically to unity. Thus ψ varies with r. The range of ψ in the conditions associated with radiation fog is small and it has been shown (BEST, loc. cit.) that with a nucleus as small as 10^{-14} grams the maximum value of ψ is only about 1.0004. Now at 283° A, for example, A can be written $1.5\times10^{-6}/(0.68+\psi)$ so that we can justifiably replace ψ by unity in this expression for A. Doing this we find that A varies from 6×10^{-7} to 12×10^{-7} as Θ varies from 273° A to 293° A. Over the same temperature range $d\varrho_\Theta/d\Theta$ varies from about 3×10^{-7} to 10×10^{-7}. If now we give α the large value of 8.3×10^{-4}°C/sec (3° C/hour) and N the small value of 10 we get a value of 5×10^{-6} for K. This is much smaller than any value of r likely to be significant in fog.

Now consider the variation of the right hand side of inequality (7) as r increases. Since K is small compared with r the variation of the right hand side of the inequality as r increases will have the same general form as the variation of ψ, that is it will increase to a maximum value and then decrease again. This maximum value will depend upon the value of K and will constitute an upper bound to H. We can determine this upper bound to H by differentiating the right hand side of the inequality with respect to r and equating to zero. In this process A is treated as a constant for the reasons given above.

We may note also that numerical substitution shows that P is of the order 2×10^{-7}. This is much smaller than r and accordingly after differentiating the right hand side of the inequality we may expand the exponential term and neglect second and higher powers of $P/2r$. We then find that we are left with the equation

$$r^3\left(K+\frac{P}{2}\right)+\frac{P^2}{4}r^2-\frac{m}{2}r+\frac{Km}{3}=0 \tag{9}$$

This can be solved graphically, the result substituted in the right hand side of the inequality (7), and thus an upper bound to H determined.

4. Some results for typical cases

Of the coefficients in equation (9) the value of K is influenced by the rate of fall of temperature α, the actual temperature and by N. Substitution of numerical values shows that P can be written $6.4\times10^{-5}/\Theta$. Table 1 gives some values of 100 H_b, where H_b is the upper bound to H determined in the way described, for various values of the parameters involved.

Table 1. Values of the upper bound to the relative humidity

Θ Temp. °A	α Rate of fall of temp. C/hour	N No. of drops per cm³	$m = 10^{-12}$ g Case No.	100 H_b	$m = 10^{-14}$ g Case No.	100 H_b
288	1	10	1	100.221	1 A	102.272
	3	10	2	101.089	2 A	112.795
	3	100	3	100.045	3 A	100.447
	1	1000	4	100.003	4 A	100.030
	3	1000	5	100.0045	5 A	100.045
278	1	10	6	100.169	6 A	101.725
	3	10	7	100.817	7 A	109.166
	1	1000	8	100.003	8 A	100.031
	3	1000	9	100.004	9 A	100.042

We see from table 1 that temperature has only a small effect on H_b and that to a first approximation the order of magnitude of the supersaturation represented by H_b (i.e. H_b—1) varies inversely as $m^{1/2}$. As would be expected H_b increases with α and decreases as N increases. We are primarily concerned, however, with the question whether the relative humidity represented by 100 H_b can exceed 100 to a significant extent. Several entries in table 1 suggest that this may occur but it is necessary to consider the reality of the conditions postulated. According to WRIGHT (1940) the values selected for m are reasonable but we must consider also the implied total salt concentration in the air. Wright quotes observations which vary from 4×10^{-12} to 3×10^{-8} for this quantity. In table 1 the product Nm varies from 10^{-13} to 10^{-9}. In cases 1A, 2A, 3A, 6A and 7A we have $Nm \leq 10^{-12}$. Excluding these five improbable cases we find that in only two cases, viz. numbers 2 and 7, does the supersaturation exceed 0.5 per cent. These two cases occur with a very small salt concentration and a rapid fall of temperature. In two other cases, numbers 1 and 6, the supersaturation exceeds 0.1 per cent and again the salt concentration is very small.

Bearing in mind that H_b is an upper bound to H and that the relative humidity may not reach the corresponding value it is fair to conclude that with the salt concentrations and rates of fall of temperature which are indicated by observation the relative humidity in a radiation fog will seldom exceed 100.1 per cent and will probably be appreciably nearer to 100.0 per cent. If there is any other factor operating which tends to remove water vapour from the air, e.g. upward diffusion, this conclusion will be reinforced.

5. Acknowledgement

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