Aerosol Growth and the Condensation Coefficient for Water: A Review

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The transfer of gas phase species to aerosols depends critically on the condensation (or sticking) coefficient. Reported values for water on water vary from 0.03 to 1. Theoretical arguments indicate that the condensation coefficient should be near unity for polar species on an aqueous surface. As long as heat transfer is properly accounted for, measurements on bulk water support this conclusion. The theory of aerosol growth is reviewed and a somewhat modified form is presented. Experimental measurements of aerosol growth are consistent with a condensation coefficient of unity but indicate that the thermal accommodation coefficient may be somewhat smaller. Aerosols grown on natural condensation nuclei may have smaller condensation coefficients owing to the presence of organic films.

NOMENCLATURE

a drop radius

C_L concentration of the drop

C_S concentration of vapor in equilibrium with the drop

C_∞ concentration of bulk vapor

D diffusion coefficient

D_c corrected diffusion coefficient, Eq. (3)

D_t thermal diffusivity, Eq. (17)

D_r reduced diffusion coefficient, Eq. (20)

K thermal conductivity

L molar heat of vaporization

l_c condensation jump length, Eq. (5)

l_t temperature jump length, Eq. (14)

l mean jump length, Eq. (21)

$\dot{n}$ molar flux to drop, Eq. (4)

α_c condensation coefficient, Eq. (4)

α_t thermal accommodation coefficient, Eq. (11)

λ effective mean free path, Eqs. (1) and (12)

INTRODUCTION

The growth of atmospheric aerosols, or the transfer of reactive chemical species to aerosols, may be thought of as taking place in two steps. First, the vapor phase species must diffuse to the droplet surface, then it must cross the interface. If the droplet growth were controlled only by diffusion, the rate of mass increase would be proportional to the drop radius. In the gas kinetic limit, where transfer across the interface is the slow step, the rate is proportional to the square of the radius and the condensation (or sticking) coefficient (defined as the probability that a vapor molecule enters the liquid phase when it strikes the interface). Thus, the condensation coefficient determines the radius at which the change from the kinetic limit to the diffusion-controlled limit takes place. For a coefficient of unity, this occurs when the radius is comparable to the mean free path of the vapor.

In clouds, the drop radii are about two orders of magnitude larger than the mean free path. Thus the condensation coefficient will affect processes in clouds only if it is substantially less than unity. The importance of the condensation coefficient for nucleation, or for processes in the atmospheric aerosol, will be much more pronounced.

The transfer of free radicals from the gas phase may play an important role in the chemistry of cloud droplets (Chameides and Davis, 1982). Data on the relevant sticking probabilities are sparse but it has been suggested that they might be as low as 10^{-4}. If this is so, then the rates of these processes will be much slower than the diffusion-controlled limit. Part of the rationale for believing that these sticking probabilities might be small is that the value for water on water has been reported to be as small as 0.03.

However, chemical intuition suggests that there is nothing to hinder the sticking of polar species to an aqueous surface. We might therefore expect that sticking coefficients are near unity. In fact, this is the case for most substances (Pound, 1972). In the second section, I review various theoretical approaches for estimating condensation coefficients. These support the view that the values should be near unity.

It has been claimed (Pruppacher and Klett, 1978) that the condensation coefficient for water is small (0.02–0.04) for a quiescent surface and large (0.2–1.0) for a rapidly renewed surface. However, there is no apparent reason why this should be so. One purpose of this paper is to resolve this question.

In the third section I review measurements made on bulk water. Measurements of the rates of growth of aerosol particles are particularly relevant for atmospheric applications. A number of theories of aerosol growth, differing in various details, have been presented; I review these in the fourth section. Experimental measurements of aerosol growth are reviewed in the fifth section. The conclusions of this review are summarized in the last section.

Many of the experimental measurements reviewed here are actually of the evaporation coefficient. This is defined as the ratio of the rate of evaporation into a vacuum to the rate, at equilibrium, of collisions of molecules with the surface. The evaporation and condensation coefficients are generally assumed to be equal; this will be true if either of two conditions holds: (1) the condensing vapor molecules are in thermal equilibrium with the surface, or (2) the coefficients are independent of energy. In many of the experiments discussed below, the departures from thermal equilibrium are small. Also, if the condensation coefficient is near unity, condition (2) will be satisfied since there will be little leeway for this coefficient to vary. In the following discussion, I will assume that the condensation and evaporation coefficients are equal.

THEORETICAL ESTIMATES OF CONDENSATION COEFFICIENTS

As a molecule approaches the surface of its own liquid, it will feel an attractive interaction and the potential energy will decrease. The potential should be purely attractive until the molecule comes in contact with the surface; there should be no energy barrier. In the language of chemical kinetics, such a process is characterized by a "loose" transition state (Benson, 1976). The rates of such processes are very near collision frequency, i.e., the sticking coefficient is near unity.

Wyllie (1949) noted that small values of the sticking coefficient tend to be reported for polar substances and suggested a relationship to the free angle ratio (Kincaid and Eyring, 1938). For nonpolar liquids, this quantity is near unity, while for polar liquids the free angle ratio is much smaller. Wyllie's observation would imply that the rotational motion of a molecule in the transition state would resemble that of a molecule in the

liquid. To explain this, he proposed that, in order to enter the bulk liquid, the molecule must cross a barrier. The energy at the top of the barrier would have to be almost identical to the energy of the gas phase molecule; this seems highly unlikely.

Penner (1948, 1952) derived detailed relationships between the transition state theory rate constant and the condensation coefficient. He showed that, as suggested above, a gaslike transition state implies a condensation coefficient near unity and a liquid-like transition state implies a much smaller value. He gave no explanation for the transition state being liquidlike.

Such an explanation was proposed by Mortensen and Eyring (1960), who argued that, in the condensation process, the molecular rotations should be treated as adiabatic. This leads to a condensation coefficient equal to the free angle ratio. They estimated values for water ranging from 0.022 to 0.17, depending on the method used. However, this analysis considered only the entropy effects associated with the molecular rotations; these are nearly canceled by rotational energy effects (Robinson and Holbrook, 1972).

Heicklen (1976) has addressed the question of condensation coefficients from the viewpoint of collision theory. He concludes that they should be near unity unless the incoming molecule must have a particular orientation. The dipole–dipole interactions between water molecules are strongly dependent on orientation. However, the rapid rotational motion of water molecules and the tendency of dipoles to "lock in" to each other should minimize this effect.

Kochurova (1964) has calculated condensation coefficients for a one-dimensional step potential model. This has little relevance to the problem at hand (Labuntsov, 1965). A theory in which the condensation coefficient depends on surface curvature has been proposed by Okuyama and Zung (1976). They assume that there is an activation energy for absorption due to the Kelvin effect. Since the Kelvin effect is due to the change in surface to volume ratio and not to any change in the energetics of either the surface or bulk molecules, this is clearly incorrect. A theory by Tovbin and Chalenko (1982) appears to treat the condensation process as being endothermic rather than exothermic.

In summary, the theoretical estimation of condensation coefficients is not well developed. However, arguments of the type that are most successful in explaining gas phase reaction rates (i.e., those of Heicklen) indicate that the condensation coefficient should be near unity with perhaps a factor of 2 or 3 reduction if the liquid is highly oriented. These theoretical arguments also imply that the sticking probabilities for any polar species on an aqueous surface should be near unity. The coefficient for condensation of water vapor on ice is near unity at low temperatures (Pruppacher and Klett, 1978). Any orientation effects should be as large for ice as for water.

CONDENSATION COEFFICIENTS ON BULK WATER

Measured condensation and evaporation coefficients for bulk water are summarized in Table 1. In these experiments, the pressure of vapor above the surface is usually quite different from the equilibrium vapor pressure. As a result, the net evaporation or condensation rates are quite large and, as has been pointed out by Mills and Seban and by Bonacci et al., it is difficult to provide or remove the latent heat of vaporization. Since the limiting evaporation or condensation rates depend on temperature, heating or cooling of the surface may cause considerable errors in the measurement of the condensation coefficient.

To gain a feeling for the magnitude of this problem we may consider the worst case of evaporation into a vacuum with a condensation coefficient of unity. For the latent heat to be provided by thermal conduction

TABLE 1. Results of Experimental Measurements of the Condensation Coefficient on Bulk Water

Investigator	Condensation coefficient	Temperature (K)	Remarks
Alty and Mackay (1935)	0.006 to 0.036	285–305	a
Delaney et al. (1964)	0.042 to 0.027	273–316	a
Narusawa and Springer (1975)	0.038, 0.17	290–300	a, b
Fujikawa et al. (1983)	0.04	285	a
Bonacci et al. (1976)	> 0.7	280	
Hickman (1954)	> 0.24	280	c
Maa (1967)	≈ 1	273	d
Jamieson (1964)	> 0.3	?	
Nabavian and Bromley (1963)	> 0.35	283–323	
Mills and Seban (1967)	> 0.45	280	
Tamir and Hasson (1971)	> 0.2	323	e

[a] Probably in error because of inadequate treatment of heat transfer.
[b] Lower value from quiescent surface, larger value from gradually renewed surface.
[c] Reanalysis by Mills and Seban (1967) gives a condensation coefficient of unity.
[d] Reanalysis by Davis et al. (1975) and in this paper gives coefficients of 0.64–1.52.
[e] Authors reported this as 0.20 ± 0.04.

perpendicular to the surface would require a temperature gradient of the order of 10^4 $K\,cm^{-1}$. Under these conditions, it is doubtful that accurate measurements of the surface temperature are possible.

As the vapor pressure, and therefore the evaporation rate, increases, the errors due to inadequate heat transfer will become more severe. This may account for the fact that the condensation coefficient for water on ice is generally reported to be near unity for temperatures below 233 K while smaller values are reported at higher temperatures (Pruppacher and Klett, 1978). Also, it probably accounts for the negative temperature dependence reported by Delaney et al. (1964).

Values of the condensation coefficient less than 0.05 have been reported by a number of investigators.

(1) Alty and Mackay (1935) measured evaporation from a growing, suspended drop. They inferred the surface temperature from the surface tension corresponding to the size of the drop when it fell.

(2) Narusawa and Springer (1975) measured the rate of evaporation from a reservoir. The surface temperature was determined from infrared emission. A larger condensation coefficient was obtained when a slow flow of water was used.

(3) Delaney et al. (1964) studied the evaporation of thin films. A thermistor was used to measure the surface temperature.

(4) Fujikawa et al. (1982) studied condensation on the end wall of a shock tube. The reflection coefficient of the surface was used to determine the density and temperature of the gas near the surface. This was combined with a conductive model of heat transfer to calculate the surface temperature.

These methods of measuring the surface temperature of the liquid phase are probably not applicable in the presence of the large temperature gradients and/or convective heat transfer that should be expected in these experiments.

Bonacci et al. (1976), using a method very similar to that of Delaney et al., attempted to circumvent these heat transfer problems by keeping the vapor near saturation. They found that the condensation coefficient did appear to decrease with increasing initial displacements from equilibrium. They also observed temperature gradients in excess of 100 $K\,cm^{-1}$ and observed convective motions in the water. They conclude that their data are consistent with a condensation coefficient of unity.

Hickman (1954) measured evaporation rates using jet tensimetry. The idea was to minimize surface cooling by exposing a jet of water to a vacuum for a very short time (10^{-3} s). Neglecting surface cooling produced a lower bound of 0.24 for the evaporation coefficient. Mills and Seban (1967) reanalyzed Hickman's results and found that they are consistent with a condensation coefficient of unity.

Maa (1967) also performed jet tensimetry experiments and obtained results very similar to Hickman's. From an analysis of the surface cooling he concluded that the condensation coefficient is near unity. A reanalysis of this data by Davis et al. (1975), using a different set of approximations, arrived at values ranging from 0.64 to 1.52. They attribute values greater than unity to a neglect of the net hydrodynamic flow from the surface. The simplest treatment of this effect is to replace the condensation coefficient, α_c, with $2\alpha_c/(2 - \alpha_c)$ (Nabavian and Bromley, 1963; Schrage, 1950). This correction gives values of α_c in the range 0.64–0.86. Mills and Seban included this correction in their analysis of Hickman's data.

In a similar experiment, Jamieson (1964) measured the condensation of tritium-labeled water onto a jet. Since he was unable to measure the amount of reevaporation, the results only place a lower bound of 0.3 on the coefficient. As the jet is exposed for shorter times, this bound rapidly increases. This implies that the actual value is considerably larger than 0.3.

Another approach has been to measure the rate of heat transfer due to condensation of steam (Mills and Seban, 1967; Nabavian and Bromley, 1963). This method is limited by other thermal resistances present in the apparatus. Although great care was taken to minimize these resistances, if the coefficient is near unity only a lower bound can be obtained.

Finally, Tamir and Hasson (1971) measured the viscous drag on a fan spray sheet passing through steam [see Hasson et al.

(1964) for details]. Assuming that the steam was stationary and the momentum transfer was due to condensation, they obtained a coefficient of 0.20. Since the drag will set the steam in motion, and therefore be reduced, this should be regarded as a lower bound.

In summary, all experiments on bulk water which properly account for heat transfer give results that are consistent with a condensation coefficient of unity. This coefficient is almost certainly greater than 0.5. None of the experiments give an accurate value.

THEORY OF AEROSOL GROWTH

For atmospheric applications the most relevant measurements of condensation coefficients should be those based on the growth, or evaporation, of aerosols. As is shown below, the growth rate of aerosol particles with a radius of a few micrometers is quite close to the diffusion-controlled limit. Consequently, the growth rate is not very sensitive to approximations made in deriving the growth equations. However, the value of the condensation coefficient determined from aerosol growth measurements is quite sensitive to these approximations.

If the aerosol particle radius, a, is very large compared to the gas phase mean free path, λ, then the growth rate is governed by the well-known diffusion theory of Maxwell (Fuchs, 1959). This assumes that the vapor at the surface of the drop is in equilibrium with the drop. Together with the assumption that the vapor at a large distance from the drop has a constant concentration, this provides the boundary conditions for the solution of the diffusion equation.

In the opposite extreme, when $a \ll \lambda$, the growth rate is governed by kinetic theory. Here, the composition of the gas phase is uniform and the rate of condensation is given by the rate of collision of vapor molecules with the drop times the condensation coefficient. Of course, to obtain the net growth

rate we must subtract the rate of evaporation.

There are a number of assumptions that must be made in order to obtain a reasonably tractable theory of aerosol growth. First we may assume steady state conditions with stationary boundaries as long as the time scale of the experiment is long compared to $a^2/\pi D$, where D is the diffusion coefficient (Fuchs, 1959). For drops of 10 μm or smaller, convective mass transport is negligible (Schwartz, 1984). Also, Fuchs (1959) has shown that radiative heat transfer is not important in this size range.

Most theories of aerosol growth for the case $a \simeq \lambda$ are based on that of Fuchs (1959). This theory assumes that kinetic theory may be used in the region very near the drop; far from the drop the flux is calculated from the laws of diffusion. The kinetic and diffusive fluxes are set equal at a distance Δ_c from the surface of the drop.

Simple kinetic theory arguments (Fuchs, 1959) suggest that for a flat surface $\Delta_c = (2/3)\lambda_c$, where λ_c is the effective mean free path for diffusion, and for a point particle $\Delta_c = \lambda_c$, λ_c is defined to satisfy the simple expression for the diffusion coefficient

$$D_c = \lambda_c \bar{v}_v / 3, \tag{1}$$

where $\bar{v}_v$ is the mean speed of the vapor molecules. Equation (1) is based on the same physical arguments that lead to the relations between Δ_c and λ_c.

In the following, subscript ∞ refers to bulk properties of the vapor phase (i.e., far from the drop), Δ refers to properties at a distance Δ_c from the surface of the drop, and 0 refers to equilibrium conditions at the surface of the drop. The equilibrium vapor concentration should take into account the effects of surface curvature and concentration of solute in the drop.

In terms of the molar concentrations, C, the diffusive flux, $\dot{n}$ in moles s^{-1}, up to a sphere of radius $a + \Delta_c$ centered on the drop is

$$\dot{n} = 4\pi(a + \Delta_c)D_c(C_\infty - C_\Delta). \tag{2}$$

D_c is a "corrected" diffusion coefficient. It is related to the actual diffusion coefficient, D, by

$$D_c = D\left(1 - \frac{P_v}{P_t} + \frac{L}{RT}\frac{DP_v}{KT}\right)^{-1}, \tag{3}$$

where P_v is the pressure of the vapor, P_t is the total pressure, L is the latent heat of vaporization, and K is the thermal conductivity. The term P_v/P_t represents a correction for Stephan flow. The last term occurs because we have used concentrations, rather than partial pressure or mole fraction, in Eq. (2) (Wagner, 1982). In the nonisothermal case ($L/K \neq 0$), to be considered below, the partial pressure gradient depends on both the concentration and temperature gradients. Equation (3) may also be derived in a straightforward manner from the general diffusion equations given by Frank-Kamenetskii (1969). Thermal diffusion is neglected here since it should contribute less than 1% to the total flux. Under ambient conditions, D_c is about 10% smaller than D. In Eq. (1) it is appropriate to use D_c rather than D since the simple theory of diffusion is derived in terms of the concentration gradient. The correction due to Stephan flow is only 2%–3%.

At steady state, the diffusive flux, $\dot{n}$, must equal the flux to the droplet surface. According to kinetic theory, this is given by

$$\dot{n} = 4\pi a^2 \alpha_c (C_\Delta - C_0)(\bar{v}_v/4), \tag{4}$$

where α_c is the condensation coefficient. At equilibrium, $C_\Delta = C_0$ and the rates of condensation and evaporation are equal.

Eliminating C_Δ between Eqs. (2) and (4) yields

$$\dot{n} = 4\pi a^2 D_c (C_\infty - C_0)\left[\frac{4D_c}{\alpha_c \bar{v}_v} + \frac{a^2}{(a + \Delta_c)}\right]^{-1}.$$

To simplify this we substitute D_c using Eq. (1) and let

$$l_c \equiv \frac{4\lambda_c}{3\alpha_c} - \frac{\Delta_c}{1 + (\Delta_c/a)}. \tag{5}$$

Also, it is convenient to express the result in

terms of the rate of increase in drop radius

$$\dot{a} = \dot{n}/(4\pi a^2 C_L), \qquad (6)$$

where C_L is the molar concentration of the drop. From these equations we obtain

$$\dot{a} = \frac{D_c(C_\infty - C_0)}{C_L(a + l_c)}. \qquad (7)$$

This is equivalent to the expression derived by Fuchs. The condensation jump distance, l_c, accounts for the reduction in growth rate due to the finite rate of transfer across the interface. Setting $l_c = 0$ reduces Eq. (7) to the diffusion controlled limit. As pointed out by Schwartz (1984), this expression is of the same form as that which occurs with two-step chemical reactions.

If $a \gg \lambda_c$ we may replace Δ_c with $2\lambda_c/3$ and set $\Delta_c/a = 0$. Then Eq. (5) becomes

$$l_c = \frac{4\lambda_c}{3\alpha_c}\left(1 - \frac{\alpha_c}{2}\right). \qquad (8)$$

Monchick and Reiss (1954) solved the Boltzmann equation for droplet growth with $\alpha \gg \lambda_c$. They concluded that one should match fluxes at the droplet surface ($\Delta_c = 0$) and replace α_c with $2\alpha_c/(2 - \alpha_c)$. This is exactly equivalent to Eq. (8). Kennard (1938) arrived at a similar result, via a different argument, for heat transfer problems. Although the equivalence of these approaches has been pointed out by Wright (1960), this does not seem to have been generally recognized.

Fuchs and Sutugin (1970) and Smirnov (1971) have compared Eq. (7) with detailed solutions of the Boltzmann equation for neutron transport problems. They find that, for large a, Δ_c agrees well with the approximation used above. The Fuchs method deviates from the exact results by a maximum of 5% when $\lambda_c \simeq a$ (Smirnov, 1971). Confirmation of these results for the case where $\alpha_c < 1$ has been provided by Sahni (1980). Using the Fuchs and Sutugin expression for Δ_c, Eq. (5) becomes

$$l_c = \frac{4\lambda_c}{3\alpha_c}\left[1 - \frac{0.47\alpha_c}{1 + (\lambda_c/a)}\right]. \qquad (9)$$

Langmuir (1961) derived droplet growth equations by making use of the Cunningham correction for viscous slip. His results correspond to $\Delta_c = 0.7\lambda_c$. Seaver (1984) has proposed a somewhat modified method of flux matching. However, his results do not satisfy microscopic reversibility and do not behave properly in the limits of large and small a/λ_c. A variety of approaches have been used to solve the Boltzmann equation for this problem (e.g., Loyalka, 1982). Other than those mentioned above, these results are not especially useful for the present purposes.

The quantity $(1 - \alpha_c/2)$ in Eq. (8) arises in the Fuch's treatment from the introduction of Δ_c. In the Boltzmann equation solutions it represents the fact that the velocity distribution function of the vapor is perturbed by the absorption process. The principal perturbation is the net velocity towards the surface. By assuming that this is the only perturbation, the same correction factor may easily be obtained for flat surfaces. (Nabavian and Bromley, 1963; Schrage, 1950). In the kinetic limit, where $a \ll \lambda_c$, the Boltzmann distribution is not perturbed and this correction is not appropriate.

Since the experiments considered in the next section all have $a \gg \lambda_c$, I will use Eq. (8) for calculating α_c from the drop growth rates.

As the drop grows, the latent heat must be removed. Otherwise the temperature of the drop will increase until the equilibrium vapor pressure equals the bulk partial pressure of vapor, then growth will cease. Carstens and Kassner (1968) and Fukuta and Walter (1970) have derived growth equations that account for this heat transfer. However, these do not make use of the corrections included in Eq. (3). The integration of these equations has been given by Carstens et al. (1974).

The heat flux from the drop must equal $L\dot{n}$, where L is the latent heat per mole. We can express the heat flux in terms of equations similar to (2) and (4):

$$L\dot{n} = -4\pi(a + \Delta_t)K(T_\infty - T_\Delta) \qquad (10)$$

and

$$L\dot{n} = -4\pi a^2 \alpha_t C_a (\gamma + 1)(c_v/2)$$
$$\times (T_\Delta - T_0)(\bar{v}_a/4). \tag{11}$$

Here, K is the thermal conductivity, $\bar{v}_a$ the mean molecular speed of the air, C_a the molar concentration of air, c_v the heat capacity, and γ the heat capacity ratio of air. α_t is the thermal accommodation coefficient (Kennard, 1938); if the air molecule comes into thermal equilibrium with the drop after one collision then $\alpha_t = 1$. The heat capacity is multiplied by $(\gamma + 1)/2$ to account for the fact that molecules with a larger translational energy are more likely to strike the surface (Kennard, 1938).

In using the above equations we ignore the temperature dependences of K, D_c, $\bar{v}_a$, $\bar{v}_v$, and L. Also, the latent heat flux is strictly equal to $L\dot{n}$ only if $T_\Delta = T_0$. As long as $(T_\infty - T_0)$ is no more than 6 K, the error due to these approximations is less than 1%. With this large a value of $T_\infty - T_0$, the linearization of the vapor pressure curve, introduced below, produces a much larger error.

The effective mean free path for thermal conduction, λ_t, may be defined to satisfy an equation analogous to (1):

$$K = (1/3)\lambda_t \bar{v}_a C_a c_v (\gamma + 1)/2. \tag{12}$$

From (10), (11), and (12) an equation similar to (7) may be obtained:

$$\dot{a} = \frac{K(T_0 - T_\infty)}{C_L L(a + l_t)}, \tag{13}$$

where the temperature jump distance is

$$l_t \equiv \frac{4\lambda_t}{3\alpha_t} - \left[\frac{\Delta_t}{1 + (\Delta_t/a)} \right]. \tag{14}$$

Assuming $a \gg \lambda_t$ and $\Delta_t = 2\lambda_t/3$ we obtain, analogous to Eq. (8):

$$l_t = \frac{4\lambda_t}{3\alpha_t} \left(1 - \frac{\alpha_t}{2} \right). \tag{15}$$

The equilibrium vapor concentration, C_0, in Eq. (7) is a function of the drop temperature, T_0, in Eq. (13). This temperature is unknown, but it may be eliminated between

the two equations. To do this conveniently, we must linearize the Clausius–Clapeyron equation, i.e., we let

$$C_0 = \left[1 + \left(L/RT_\infty^2 \right)(T_0 - T_\infty) \right] C_s, \tag{16}$$

Where C_s is the equilibrium vapor concentration for a drop of radius a at temperature T_∞. C_s may depend on the radius due to both the drop curvature and dilution of any solute in the drop.

It is convenient to replace the thermal conductivity with a quantity having the same dimensions as a diffusion coefficient

$$D_t \equiv KRT_\infty^2/L^2 C_s. \tag{17}$$

Using (16) and (17), Eq. (13) becomes

$$\dot{a} = \frac{D_t(C_0 - C_s)}{C_L(a + l_t)}. \tag{18}$$

Eliminating C_0 between this and (7) yields

$$\left(\frac{a + l_c}{D_c} + \frac{a + l_t}{D_t} \right) \dot{a} = \frac{C_\infty - C_s}{C_L}. \tag{19}$$

Following Carstens et al. (1974), we may introduce a reduced diffusion coefficient

$$\frac{1}{D_r} \equiv \frac{1}{D_c} + \frac{1}{D_t} \tag{20}$$

and a mean jump length, $\bar{l}$, which is a weighted average of l_t and l_c

$$\bar{l} \equiv D_r \left(\frac{l_c}{D_c} + \frac{l_t}{D_t} \right). \tag{21}$$

These transform (19) to a form identical to that of (7) and (18):

$$\dot{a} = \frac{D_r(C_\infty - C_s)}{C_L(a + \bar{l})}. \tag{22}$$

The thermal accommodation and condensation coefficients affect the growth rate through a single parameter, $\bar{l}$. If $\alpha_c = \alpha_t = 1$, then $\bar{l}$ is roughly equal to the mean free path (about 0.1 μm); smaller values of these coefficients produce larger values of $\bar{l}$.

From Eq. (17) we see that D_t decreases rapidly with increasing temperature. In contrast, D_c increases with temperature. From Eq. (21) we should therefore expect the tem-

perature dependence of l to depend on the relative magnitude of l_c and l_t. This may provide a means to determine both α_c and α_t from measurement of aerosol growth rates. Also, since K is independent of pressure while D_c depends inversely on pressure, the pressure dependence of l will depend on the relative values of α_c and α_t.

The linearized Clausius–Clapeyron equation, (16), results from the expansion of an exponential. Letting the second-order term be ε, we have

$$\varepsilon = \frac{1}{2}\left(\frac{L}{RT_\infty^2}\right)^2 (T_0 - T_\infty)^2. \tag{23}$$

If this is treated as a constant, the effect on (18) and (22) is to multiply C_s by $(1 + \varepsilon)$. The percentage change in $\dot{a}$ is therefore

$$g = \varepsilon C_s/(C_\infty - C_s). \tag{24}$$

Eliminating $\dot{a}$ between (13) and (19) gives the temperature difference

$$T_0 - T_\infty = \frac{RT_\infty^2}{L}\left(\frac{C_\infty - C_s}{C_s}\right)$$

$$\times \left[1 + \frac{D_t(a + 1_c)}{D_c(a + 1_t)}\right]^{-1}. \tag{25}$$

Substituting this into (23) and (24) yields

$$g = \frac{1}{2}\left(\frac{C_\infty - C_s}{C_s}\right)\left[1 + \frac{D_t(a + l_c)}{D_c(a + l_t)}\right]^{-2}. \tag{26}$$

Typically, the second quantity in brackets is about 1.4. Thus, if the supersaturation is much more than a few percent, the error due to using Eq. (16) will be significant.

MEASUREMENTS OF AEROSOL GROWTH RATES

Usable results from the measurement of the growth rates of aqueous aerosols are summarized in Table 2. As shown in the previous section, the growth rate depends on a mean jump length, l, which depends on both the condensation coefficient, α_c, and the thermal accommodation coefficient, α_t. Generally, l has not been reported. Instead, a value of α_t has been assumed and then α_c was fit to the growth rate. These values are listed in Table 2.

The values of l recorded in Table 2 were calculated as follows. First, using the reported treatment of Δ_c and values K, D, etc., a value of l was obtained from α_c and α_t. Then, using K and D from Pruppacher and Klett (1978) and L from the *Handbook of Chemistry and Physics* (1972), D_r was calculated from the formulas in the previous section. This was generally about 5% less than that obtained from the parameters reported in the original paper; l was then reduced according to Eq. (22). When the original paper did not report the parameters used, I assumed that D_r should be lowered by 5%. Finally, if the drop size measurements were based on an assumption of Stokes flow, I increased l by 0.04 μm to account for

TABLE 2. Results of Aerosol Growth Rate Measurements[a].

	Drop radius (μm)	Reported		l (μm)	Dev. (%)
		α_c	α_t		
Chodes et al. (1974)	1.5–2.5	0.033	∞	1.3 ± 0.7	40
Golub et al. (1974)	3–7	0.12	1.0	0.3 ± 0.7	6
Sinnarawalla et al. (1975)	0–7	0.026	1.0	1.5 ± 0.7	30
Duguid and Stampfer (1971)	3–9	—	—	< 0.6	< 10
Neizvestnyy and Onishchenko (1979)	1–4	> 0.3	1.0	< 0.25	< 10
Neizvestnyy et al. (1979)	1–4	> 0.3	1.0	< 0.25	< 10
Levine (1973)	0–3	1.0	∞	< 0.20	< 12
Wagner (1982)	1–3	1.0	1.0	0.5 ± 0.5	20
Akoy (1971)	1–3	0.8	1.0	0.15 ± 0.05	8

[a]The mean jump length, l, was recalculated as described in the text. Dev. is the percent deviation from the diffusion control limit.

TABLE 3. Values of α_c and α_t Consistent with Various Possible Values of l

l (μm)	$\alpha_t = 1.0$ α_c	$\alpha_t = \alpha_c$	$\alpha_c = 1.0$ α_t
0.096	1.0	1.0	1.0
0.20	0.30	0.65	0.58
0.50	0.10	0.32	0.27
1.0	0.048	0.18	0.14
1.4	0.034	0.13	0.10

the overestimate of the drop radius (Beard, 1976).

Values of α_c and α_t corresponding to the recalculated values of l in Table 2 may be obtained from Table 3.

There is a possible source of serious error in these calculations: the total pressure at which these experiments were performed is usually not reported. The approximate deviation from the diffusion controlled limit, corresponding to the recalculated values of l and the mean drop size, are listed in Table 2. Since these are so small, l will be very sensitive to small errors in the diffusion coefficient. A total pressure of one atmosphere was assumed for these calculations.

In several of the experiments, the recalculated value of l is less than the minimum value of 0.096 μm, corresponding to $\alpha_c = \alpha_t = 1$. For these, the estimated uncertainty of l was added to l and the results are reported as being less than this value. Uncertainties were determined from the uncertainties in growth rate and supersaturation reported in the original paper.

The most widely quoted measurements of aerosol growth are those on atmospheric condensation nuclei carried out in a diffusion cloud chamber with supersaturations of less than 5% (Chodes et al., 1974; Golub et al., 1974; Sinnarawalla et al., 1975). Taken together, these results indicate that l has a value of about 1 μm. Chodes et al. did not give the values of the parameters used in their analysis.

Duguid and Stampfer (1971) measured the rate of evaporation of drops in a system held a few percent below saturation and obtained results 6%–14% greater than

the diffusion-controlled limit. Their error estimates of $\pm 5\%$ seem overly optimistic considering the scatter in their data and error estimates in other, similar experiments. Uncertainties of 15%–20% seem more reasonable. The drops were grown from atmospheric condensation nuclei. Since experiments in the same apparatus (Hughes and Stampfer, 1971) with deliberately contaminated drops gave substantial evaporation rates under saturated conditions, it is likely that there is a large systematic error in these experiments.

Neizvestnyy and Onishchenko (1979) measured the rate of evaporation of water drops in a system held less than 1% below saturation. Neizvestnyy et al. (1979) measured growth of a droplet formed on a NaCl nucleus in a saturated atmosphere. The results were virtually identical, the best fit lies between the diffusion-controlled limit and a growth rate corresponding to $\alpha_c = \alpha_t = 1$. Distilled water was used in these experiments.

Levine (1973) measured the evaporation, due to the Kelvin effect, of a small drop in a saturated atmosphere. The results are scattered around the diffusion controlled limit.

Experiments in expansion cloud chambers, using supersaturations up to several hundred percent have been carried out by Vietti and Shuster (1973a, b), Wagner (1982), Akoy (1969) and Wakeshima and Takata (1963). As shown in the previous section, the linearization of the Clausius–Clapeyron equation is not valid for such large supersaturations. Also, in these experiments the droplet concentration is large enough that

depletion of the bulk vapor and heating of the bulk gas will be considerable. Ignoring these effects will lead to a low value of the condensation coefficient. Of the above investigators, Wagner (1982) and Akoy (1969) have accounted for these effects, the others do not provide sufficient details to permit reanalysis.

In his analysis, Wagner included the heat flux due to the transport of enthalpy by the diffusing vapor molecules. This is incorrect since this quantity was already included in the latent heat; in Table 2, l was corrected for this. Also, Wagner did not report either the values of the physical parameters used or estimates of the uncertainties. The error bars included in Table 2 for Akoy's results are based on his reported scatter in α_c.

Vietti and Fastook (1975) studied droplet growth using an expansion cloud chamber with a supersaturation of about 5%. They report $\alpha_c = \alpha_t = 1$ (implying $l = 0.1$ μm) but also give $l = 1.6$ μm. I do not understand the source of this discrepancy.

Finally, experiments on the expansion of steam in supersonic jets (Hill, 1966; Moses and Stern, 1978) in the absence of air indicate that α_c and/or α_t (for water on water) equals unity. The sensitivity of these experiments to α_c and α_t is not very great (Hill, 1966).

In summary, we see that of the nine measurements listed in Table 2 only two are not consistent with l taking on the minimum value of 0.096 μm. Whereas experiments done in diffusion cloud chambers give $l = 1.0 \pm 0.6$ μm, the other methods indicate that l is probably less that 0.25 μm.

It is interesting to note that the largest values of l occur for experiments which used atmospheric condensation nuclei. This raises the possibility that these drops were contaminated with surface active organic substances. Films of such substances can apparently increase l by three to four orders of magnitude (Gill et al., 1983).

Gill et al. (1983) have reviewed the literature on organic films on atmospheric aerosols. They find that for sub-micrometer size particles, there is more than enough surface active organic material present to produce a monolayer. As the drop grows, the surface active material spreads out so that by the time the radius is a few micrometers there is only a fraction of a monolayer. Since the growth rate is most sensitive to the condensation coefficient when the droplet is small, this could account for the large values of l measured by Chodes et al. and Sinnarawalla et al. For cloud droplets, with radii of 5–10 μm, an organic monolayer is not likely.

From measurements at a single temperature it is not possible to obtain unique values for both α_c and α_t. It is usually assumed that $\alpha_t = 1.0$. There is no justification for this; α_t has never been measured for air on water. A value of unity for α_t implies that a nitrogen or oxygen molecule comes into thermal equilibrium upon striking the surface. If this is so, then we should expect that a water molecule, which has a much stronger interaction with the surface, would also come into thermal equilibrium. If it does so, it will not have sufficient energy to escape, thus $\alpha_c = 1.0$. We should therefore expect that α_c is at least as large as α_t.

In Table 3 α_t and α_c are given for three cases with each of several values of l. These cases are α_t assumed to be unity, $\alpha_c = \alpha_t$, and α_c assumed to be unity. With $\alpha_t = 1$ and $l = 1.4$ μm we have $\alpha_c = 0.034$, as has often been quoted. This is really an extreme case. The value of α_t does not change much between the cases $\alpha_c = 1$ and $\alpha_c = \alpha_t$. This is because when $\alpha_c > \alpha_t$, the growth rate is dominated by the rate of heat transfer and is therefore insensitive to α_c.

The collision of hard spheres of similar masses results, on average, in the exchange of 50% of the difference in translational energy. About 60% of the internal energy of a diatomic molecule is translational. There should be some exchange of rotational energy, and multiple collisions with the surface might enhance the exchange of translational

TABLE 4. Temperature and Pressure Dependence of the Mean Jump Length, l in μm, for Various Combinations of the Condensation Coefficient, α_c, and the Thermal Accommodation Coefficient, α_t

T (K)	P (atm)	α_c: 1.0 α_t: 1.0	1.0 0.26	0.10 1.0	1.0 0.10	0.034 1.0
273	1.0	0.082	0.32	0.82	0.82	2.41
293	1.0	0.096	0.51	0.51	1.41	1.39
313	1.0	0.017	0.65	0.31	1.83	1.29
293	0.75	0.129	0.72	0.57	2.01	1.51
293	0.50	0.195	1.16	0.67	3.23	1.69

energy. Hence, we can take 0.3 as a conservative estimate of α_t. This is in reasonable agreement with energy transfer efficiencies in unimolecular reactions (Chan et al., 1970). From Table 3 we see that this, together with the assumption $\alpha_c > \alpha_t$, implies that $l < 0.5$ μm, in agreement with most of the experimental results.

On the basis of the above arguments it seems that under ambient conditions we have l less than 0.5 μm with α_c near unity and $\alpha_t > 0.3$. It is possible that l is as large as 1.5 μm with α_t as small as 0.1. Although aerosol growth experiments cannot rule out small values of α_c, this would be inconsistent with measurements on bulk water.

In Table 4, l is given as a function of temperature and pressure for various combinations of α_c and α_t taken from Table 3. For a given value of l at room temperature, choosing $\alpha_c = 1$ rather than $\alpha_t = 1$ produces a very different temperature and pressure dependence. Because of this, we must be careful about extrapolating growth rate data at ambient temperature and pressure to other conditions.

SUMMARY

Simple theoretical arguments, of a type that have been applied quite successfully in chemical kinetics, imply that the condensation coefficient for a vapor on its own liquid should be near unity. For water, these arguments are confirmed by measurements on bulk samples, which show that the condensation coefficient is at least 0.5. As long as the transfer of heat to the surface is properly accounted for, experiments on bulk water give results that are consistent with a coefficient of unity. An accurate value has not been determined.

The rate of growth of aerosol particles depends on the mean jump length, l, which is a function of both the condensation coefficient, α_c, and the thermal accommodation coefficient, α_t. The temperature dependence of l depends strongly on the relative values of these coefficients. This could provide a means of determining both coefficients, however, such experiments have not yet been done. Extrapolation of existing aerosol growth data to conditions much different from the ambient should not be made casually.

For micrometer size drops, the growth rate is not much different from the diffusion controlled limit. As a result, measurements of l are very sensitive to errors in the growth rate, degree of supersaturation, and the diffusion coefficient. In particular, the fact that the diffusion rate is proportional to the partial pressure gradient rather than the concentration gradient should not be neglected. Also, the linearized form of the Clausius–Clapeyron equation may only be applied if the partial pressure of vapor is within a few percent of saturation.

Existing measurements of aqueous aerosol growth rates are highly uncertain. When combined with the results of bulk measurements they indicate that probably $l < 0.5$ μm, $\alpha_c \simeq 1$ and $\alpha_t > 0.3$. However, some experiments indicate that l is as large as 1.5 μm, which would imply that α_t might be as

small as 0.1, or that α_c is as small as 0.03. This latter result could be correct if there is a significant coverage of surface active material on the droplet.

In order to obtain more precise measurements of α_t and α_c it will be necessary to conduct growth experiments on droplets with a radius comparable to l. This would require that the radius be just a few tenths of a micrometer or that the experiments be carried out at reduced pressure. However, reducing the pressure would only be effective if it is α_c, rather than α_t, that is less than one.

For droplet growth calculations in this size range, Eq. (9), and its analogue for l_t, should be used rather than Eqs. (8) and (15). If the simplified equations resulting from the linearization of the Clausius–Clapeyron equation are to be used, the partial pressure of vapor must be kept within a few percent of saturation. It would be desirable to have results on both pure water droplets and on ones grown on atmospheric condensation nuclei in order to assess the possibility that organic films cause a reduction in α_c.

The theoretical arguments presented in the second section imply that the sticking coefficients for all polar species on aqueous surfaces should be near unity. If this is so, then the mass transfer of reactive species, such as OH or HO_2 radicals, to cloud droplets should be diffusion controlled. It does not appear that sticking coefficients, on water, for species other than water have been measured. Rates of disappearance of species at an aqueous surface tend to be limited by either reaction rates (Baldwin and Golden, 1979; Baldwin, 1982; Huntzicker et al., 1980; Jech et al., 1982; Martin et al., 1980) or by liquid phase diffusion (Raimondi and Toor, 1959; Harvey and Smith, 1959). An analysis of the characteristic times of the individual steps has been provided by Schwartz and Freiberg (1981).

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