

## NOTES AND CORRESPONDENCE

## On the Analysis of the Condensational Growth of a Stationary Cloud Droplet in the Vicinity of Activation

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## ABSTRACT

The theory of the growth (or evaporation) of a stationary drop has been cast into a form which reveals explicitly the role of both condensation and thermal accommodation coefficients. The equations for growth are integrated under constant ambient conditions. An application to cloud physics is discussed.

## 1. Introduction

The condensation growth of cloud droplets in the vicinity of activation has received considerable attention in the literature. The purpose of this contribution is two-fold: 1) to cast the conventional theory in an easily assimilable form, readily identifiable with various other forms existing in the literature (Rooth, 1957; Fukuta and Walter, 1970; Fitzgerald, 1970); and 2) to exhibit a certain integration of the growth equation. The integration follows Squires (1952), except here we take into account, and exhibit explicitly, the role of the condensation and thermal accommodation coefficients (hereinafter referred to as "surface effects" or more accurately "surface kinetic effects") in retarding growth. Such a solution provides several of the advantages mentioned by Squires and, in addition, can provide an alternative to the usual numerical procedure.

## 2. Conventional growth equations and their interpretation

The basic physical situation envisaged in describing droplet growth is given by Mason (1971). Very briefly, the theory is based on a quasi-steady-state balance of vapor diffusion and heat conduction; that is, the diffusive mass influx, which causes growth, deposits latent heat of condensation which is compensated by heat conduction outward.

In the elementary treatment of growth (Mason, 1971), surface kinetic effects are neglected, and results are obtained by assuming that equilibrium between vapor and temperature holds at the droplet surface. The growth equation derived from this theory may be

written as

$$a \frac{da}{dt} = \frac{S - S_{\text{sat}} \rho_{\text{eq}}(\infty)}{D + \frac{bL}{K} \rho_l}, \quad (1)$$

where  $D$  is the vapor diffusion coefficient,  $K$  the thermal conductivity of the gas,  $L$  the latent heat of condensation,  $b$  the slope of the vapor-density equilibrium curve (change in vapor/change in temperature) in the presumably small temperature range of interest,  $a$  the drop radius,  $t$  time,  $S$  the bulk (or applied) supersaturation ratio (near unity),  $\rho_l$  the liquid density,  $\rho_{\text{eq}}(\infty)$  the equilibrium vapor density at infinity, and  $S_{\text{sat}}$  the supersaturation ratio describing equilibrium conditions peculiar to the droplet.  $S_{\text{sat}}$ , which is unity over a flat surface of pure liquid, refers to equilibrium conditions appropriate to the droplet and is often identified with the Köhler curve (see, for example, Byers, 1965). The factor  $b$  is often evaluated from the Clausius-Clapeyron equation keeping terms linear in the temperature (the larger  $S$  is, the poorer this linearization). Moreover, in identifying  $b$  with a pure flat surface, we have tacitly assumed  $S_{\text{sat}}$  close to unity.

In the hypothetical case of a non-volatile drop ( $L=0$ ), this equation reduces to one of mass diffusion alone; this suggests that it may be convenient, without being misleading, to introduce an effective vapor diffusion coefficient, or rather "resistivity,"

$$\frac{1}{D_{\text{eff}}} = \frac{1}{D} + \frac{bL}{K}, \quad (2)$$

which accounts for the heat conduction aspect of the problem.

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When surface effects are taken into account, the growth equation for a stationary drop may be written in two forms:

$$\frac{a+s}{D_{\text{eff}}} \frac{d(a+s)}{dt} = \frac{1}{D_{\text{eff}}^*} \frac{da}{dt} = (S - S_{\text{sat}}) \frac{\rho_{\text{eq}}(\infty)}{\rho_l} \quad (3)$$

The introduction of the ‘‘compensated’’ coefficients,

$$\frac{1}{D_{\text{eff}}^*} = \frac{bL}{K^*} + \frac{1}{D^*},$$

(see, for example, Carstens, 1972) or  $s$  (Rooth, 1957), are, under normal atmospheric conditions, equivalent ways of accounting for the extent to which surface effects control the growth (or evaporation) process. Clearly,  $D_{\text{eff}}^* = D[1 + (s/a)]^{-1}$ . The evaluation of  $s$  is usually carried out by matching Fourier and Fick’s law fluxes of heat and vapor with their corresponding molecular fluxes as computed from uniform gas kinetics. Smirnov (1971) has referred to this as the ‘‘diffusion kinetic’’ approach. It has been used, for example, by Carstens and Kassner (1968) and has received perhaps its most detailed elaboration by Fukuta and Walter (1970). The relationship of  $s$  to both condensation and thermal accommodation coefficients is presented in the Appendix.

It is an accepted fact (Rooth, 1957) that  $s$  slows growth compared to what it would be if interfacial equilibrium between liquid and vapor were to be assumed as in (1), or in (3) with  $a \gg s$ ; it is evident from (2) that, at a given radius, the radial growth rate is retarded by a factor  $[1 + (s/a)]^{-1}$ . For example, for a 5- $\mu\text{m}$  drop at 5C with Alty and Mackay’s (1935) values of 0.036 and 1.0 for sticking and thermal accommodation coefficients,  $s$  is about 2  $\mu\text{m}$ , leading to a value  $[1 + (s/a)]^{-1} \approx 0.7$ . On the other hand,  $s$  is about 1  $\mu\text{m}$  at 30C due to the dependence of  $s$  on  $b$ , namely the preferential ‘‘thermal weighting’’ of  $s$  at higher temperatures (see Appendix). Rooth also pointed out the possible role of  $s$  in broadening the cloud droplet spectrum in the early stages of cloud development; and Warner (1969) reported, in his cumulus cloud study, that it would be difficult to account for the continued presence of small droplets in cloud if the sticking coefficient exceeded 0.05. Fitzgerald (1970) found satisfactory agreement with his measured size (continental) distribution and the above growth law [which he extended, by including Fuch’s (1959) jump distance to rather higher Knudsen numbers than are here contemplated] using Alty and Mackay’s (1935) values. Evidently, no one has published an investigation of the possible effects on drop size distributions due to a distribution of values of  $s$  (associated with the chemical heterogeneity of the cloud-producing aerosol); perhaps this is due to a lack of knowledge, even an inability to guess, as to what values of  $s$  might compose such a spectrum.

It should finally be mentioned that, while (1) is a good approximation when  $a \gg s$ , the value  $s = 0$  implies either that the sticking or thermal accommodation coefficients (or both) must take on the absurd values of infinity.

### 3. Integration under constant ambient conditions

The solution of (3) reduces to a single integral if the effective supersaturation,  $S - S_{\text{sat}}$ , is explicitly time independent:

$$t(a) = \frac{\rho_l}{\rho_{\text{eq}}(\infty) D_{\text{eff}}} \int_{a_0}^{a(t)} \frac{(a+s) da}{S - S_{\text{sat}}} = \frac{\rho_l}{\rho_{\text{eq}}(\infty) D_{\text{eff}}} \left[ \int_{a_0}^{a(t)} \frac{ada}{S - S_{\text{sat}}} + s \int_{a_0}^{a(t)} \frac{da}{S - S_{\text{sat}}} \right] \quad (4)$$

If  $S_{\text{sat}}$  can be expressed as a series in  $1/a$ , say

$$S_{\text{sat}} = \sum_{i=1}^k \epsilon_i / a^i,$$

then the integrated solution may be expressed as ( $\rho_l = 1$ )

$$t_0(a) = \frac{1}{D_{\text{eff}} \rho_{\text{eq}}(\infty)} \sum_{i=1}^k \frac{\alpha_i^{k+1}}{G'_k(\alpha_i)} \times \left[ \ln \frac{a - \alpha_i}{a_0 - \alpha_i} + \sum_{j=1}^{k+1} \frac{(a/\alpha_i)^j - (a_0/\alpha_i)^j}{j} \right], \quad (5)$$

$$t_s(a) = \frac{s}{D_{\text{eff}} \rho_{\text{eq}}(\infty)} \sum_{i=1}^k \frac{\alpha_i^k}{G'_k(\alpha_i)} \times \left[ \ln \frac{a - \alpha_i}{a_0 - \alpha_i} + \sum_{j=1}^k \frac{(a/\alpha_i)^j - (a_0/\alpha_i)^j}{j} \right], \quad (6)$$

$$t = t_0(a) + t_s(a), \quad (7)$$

where

$$G_k(a) = a^k (S - S_{\text{sat}}), \quad a_0 = a(0),$$

$$G'_k(\alpha_i) = \partial G_k / \partial a |_{a=\alpha_i},$$

and  $t$  is the total growth time from  $a_0$  to  $a$ , and the  $\alpha_i$  are roots of  $S - S_{\text{sat}} = 0$ .

A commonly used form for  $S_{\text{sat}}$  is the Köhler expression alluded to earlier, i.e.,

$$S_{\text{sat}} = 1 + \frac{\tau^* A}{a a^3}, \quad (8)$$

where  $\tau^*$  is the ‘‘curvature’’ term and  $A$  the solubility term. Limits on the validity of the latter may be analyzed by consulting Low (1969). For this case,  $k = 3$  in (5) and (6). The role of the roots  $\alpha_1$  and  $\alpha_2$  can be

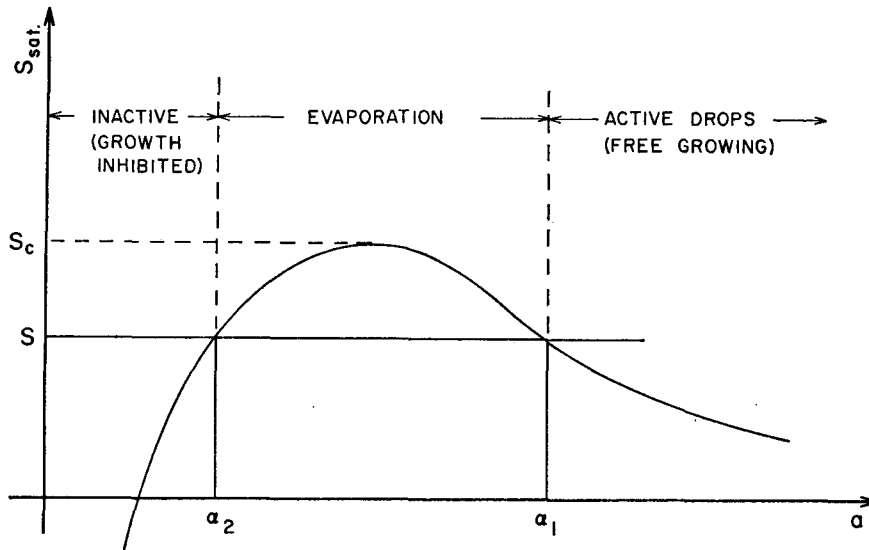


FIG. 1. Schematic plot of the Köhler curve for a certain mass of dissolved salt showing an applied supersaturation  $S < S_c$  and the corresponding equilibrium radii  $\alpha_1$  and  $\alpha_2$ .

understood by referring to Fig. 1;  $\alpha_3$  is negative and is given no direct physical significance.

For  $1 < S < S_c$  ( $S_c$  the critical supersaturation),  $\alpha_1$  and  $\alpha_2$  are real and represent, respectively, the unstable and stable equilibrium radii associated with the applied supersaturation  $S$ , and the Köhler curve. If  $S > S_c$ , these roots are complex conjugates; the solution is, of course, still valid. If  $S = S_c$ , however, the solutions shown break down inasmuch as distinct roots were presupposed in their derivation. A solution for this degenerate case can be derived. The above formalism handles evaporation as well as growth.

The time  $t_s$  represents that part of the time explicitly associated with  $s$ , that is, with surface effects, while  $t_0$  represents that associated with the assumption of vapor equilibrium at the droplet surface. The two terms, of course, differ to the extent  $s$  and  $a$  differ. This difference can be magnified in the case where  $S - S_c$  is small and positive, i.e., is when the droplet is just activated. For example, a salt nucleus having a critical supersaturation of 0.37%, under an applied supersaturation of say 0.4% (300K), results in a time  $t_0$  to reach  $1 \mu\text{m}$  of about 1 sec; with a thermal accommodation coefficient of unity, the corresponding times for sticking coefficient of 0.05 ( $s = 1 \mu\text{m}$ ) is about 5 sec, and for sticking coefficient of 0.02 ( $s = 2.1 \mu\text{m}$ ) about 10 sec.

#### 4. Approximate solutions, inactive droplets

When growth is inhibited, i.e.,  $a < \alpha_2$ ,  $S < S_c$ , Sedunov (1972) has shown that the solution should become a simple exponential in the vicinity of  $\alpha_2$ . Sedunov did this simply by holding all factors in (4) constant except  $(a - \alpha_2)$  and integrating. (He did not, however, restrict himself to Raoult's law.) The same result may be obtained from (5) and (6) by supposing that the

droplet radius is sufficiently close to its stable equilibrium value  $\alpha_2$  to render the term  $\ln[(a - \alpha_2)/(a_0 - \alpha_2)]$  dominant. The exponential solution so obtained is

$$a(t) = a_0 - (a_0 - \alpha_2) \exp(-t/\tau), \quad (9)$$

where

$$\tau = \alpha_2^2 (\alpha_2 + s) \{ D_{\text{eff}} \rho_{\text{ca}}(\infty) [2\tau^* - 3\alpha_2 (S - 1)] \}^{-1}.$$

As expected, even in this approximation, the ratio of the time  $\tau_0(s=0)$  to the total  $\tau$  is  $(1 + s/\alpha_2)^{-1}$ . The actual value of  $\tau$  is given, at least formally, by substitution of  $a_0 + 0.632(\alpha_2 - a_0)$  into (5) and (6).

#### 5. An application

The solution (7) can provide an alternative to the usual numerical procedure (Fitzgerald, 1970; Brown and Arnason, 1973) in the sense that supersaturation, and other bulk quantities, can be stepped without stepping the radius. (Proper attention, of course, must be given to vapor depletion and heat addition.) The inversion  $t(a) \rightarrow a(t)$ , when needed, is attended by no special numerical difficulties. In the region near equilibrium, where a large change in time implies a small change in radius, approximate inversions are helpful. Far from equilibrium, good initial guesses at the final radius may be obtained by letting growth proceed at some reasonably chosen constant effective supersaturation. Thereafter, some numerical procedure must be used. We have thus far achieved satisfactory results using simple stepping techniques. It seems reasonable to suppose fancier techniques, e.g. iterative ones, would be faster.

It should be mentioned that the efficiency of this technique depends in part upon the rapidity with

which the roots of  $S - S_{\text{sat}}$  can be found. Up to  $k=4$ , analytic methods can be used (Burlington, 1933).

6. Conclusion

The equation for droplet growth has been cast into a form which identifies explicitly the role of surface kinetics. It has been integrated under conventional cloud conditions, holding bulk quantities constant. Its possible application in numerical modeling of the diffusive process has been pointed out.

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APPENDIX

Kinetic Parameters

For an evaluation of  $s$  we refer to two "lengths,"  $l_\alpha$  and  $l_\beta$ , corresponding to the thermal accommodation coefficient  $\alpha$  and the condensation, or sticking, coefficient  $\beta$  (Fukuta and Walter, 1970). These lengths are (Kennard, 1938; Fukuta and Walter, 1970)

$$l_\alpha = 8 \left[ \frac{\gamma - 1}{\gamma + 1} \right] \left[ \frac{1 - \alpha/2}{\alpha} \right] \left[ \frac{K}{R} \right] / n_g \bar{v}_g, \tag{A1}$$

$$l_\beta = \frac{1 - \beta/2}{\beta} (4D/\bar{v}), \tag{A2}$$

where  $\gamma$  is the ratio of specific heats,  $\bar{v}_g$  the average molecular speed of the carrier gas,  $\bar{v}$  that of the vapor, and  $n_g$  the molar concentration of the carrier gas. The appearance of  $\beta/(1-\beta/2)$  and  $\alpha/(1-\alpha/2)$  in place of  $\beta$  and  $\alpha$  constitutes a generally minor correction because both  $\alpha$  and  $\beta$  are most important when they are small compared with unity. The correction arises because, in the case of vapor diffusion, the molar flux term  $n\bar{v}/4$  should be "biased" by a factor  $-D\nabla n/2$  so as to account for the diffusion process itself; Kennard (1938) makes this argument with regard to heat conduction. The length  $s$  is simply a weighted average of  $l_\alpha$  and  $l_\beta$ , i.e.,

$$s = \left[ \frac{l_\alpha \beta L}{K} + \frac{l_\beta}{D} \right] / D_{\text{eff}}. \tag{A3}$$

That the surface effects enter the growth law via one parameter, namely  $s$ , and not two ( $\alpha$  and  $\beta$ ) is clear from (A3).

At this point, it can be noted that the dependence of  $s$  on  $\beta$  is not entirely straightforward. Mazin (1968), for example, sets  $s=l_\beta$  on the basis of the fact that  $\beta \ll \alpha$ . Apparently, Warner (1969) follows Rooth (1957)

in putting  $s=l_\beta$ . First, regarding Mazin's inequality, the inequality  $l_\alpha < l_\beta$  implied by it is not as strong. Second, no matter how strong either inequality is, they can *only* be used to justify neglecting the first (thermal) term in the numerator of (A3) and not the thermal contribution to  $D_{\text{eff}}$  in the denominator of (A3). Indeed, especially at higher temperatures, the length  $s$  is heavily weighted toward  $l_\alpha$ . Even with  $\alpha=1$ ,  $s$  can be considerably less than  $l_\beta$ . Of course, the smaller  $s$  is, the less significant is the correction it represents in cloud physics applications. For example, taking  $\alpha=1$  and  $\beta=0.036$ , for air and water vapor, the following values of  $s$ ,  $l_\alpha$  and  $l_\beta$  (in microns) result at the temperatures indicated: 5C,  $l_\alpha=0.2$ ,  $l_\beta=4.3$ ,  $s=2.2$ ; 11C,  $l_\alpha=0.2$ ,  $l_\beta=4.4$ ,  $s=1.9$ ; 17C,  $l_\alpha=0.21$ ,  $l_\beta=4.6$ ,  $s=1.6$ ; 27C,  $l_\alpha=0.22$ ,  $l_\beta=4.8$ ,  $s=1.22$ .

Finally, it should be added that Fuchs' jump distances can be approximately incorporated into the above scheme by replacing  $s$  by  $s - \Delta$  where  $\Delta$  is the weighted average of  $\Delta_D$  and  $\Delta_T$  (see Fitzgerald, 1970). This approximation is valid and represents a small correction so long as the Knudsen number is rather less than unity. Shankar (1970) has suggested setting  $\Delta=0$ .

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