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NASA TECHNICAL MEMORANDUM

NASA TM-82392

AN EXTENDED CLASSICAL SOLUTION OF THE DROPLET GROWTH PROBLEM

(NASA-TM-82392) AN EXTENDED CLASSICAL SOLUTION OF THE DROPLET GROWTH PROBLEM (NASA) 49 p HC A03/MF A01 CSCL 20D

N81-17383

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G3/34 41425

By B. Jeffrey Anderson, John Hallett,
and Maurice Beesley

January 1981

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Marshall Space Flight Center, Alabama

MSFC - Form 3190 (Rev June 1971)

TECHNICAL REPORT STANDARD TITLE PAGE

1. REPORT NO.
NASA TM-82392

2. GOVERNMENT ACCESSION NO.

3. RECIPIENT'S CATALOG NO.

4. TITLE AND SUBTITLE
An Extended Classical Solution of the Droplet Growth Problem

5. REPORT DATE
January 1981

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
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8. PERFORMING ORGANIZATION REPORT #

9. PERFORMING ORGANIZATION NAME AND ADDRESS
George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama 35812

10. WORK UNIT NO.

11. CONTRACT OR GRANT NO.

13. TYPE OF REPORT & PERIOD COVERED
Technical Memorandum

12. SPONSORING AGENCY NAME AND ADDRESS
National Aeronautics and Space Administration
Washington, D.C. 20546

14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES
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Prepared by Space Sciences Laboratory, Science and Engineering Directorate

16. ABSTRACT

Problems of applying the classical kinetic theory to the growth of small droplets from the vapor are examined. A solution for the droplet growth equation is derived which is based on the assumption of a diffusive field extending to the drop surface. The method accounts for partial thermal and mass accommodation at the interface and the kinetic limit to the mass and heat fluxes, and it avoids introducing the artifact of a discontinuity in the thermal and vapor field near the droplet. Consideration of the environmental fields in spherical geometry utilizing directional fluxes yields boundary values in terms of known parameters and a new Laplace transform integral. Different initial assumptions coupled with this method yield various solutions derived by earlier workers. The solution is applicable to drop sizes both larger and smaller than the mean free path.

17. KEY WORDS
Laplace transform integral
Cloud droplet growth
Aerosol droplets

18. DISTRIBUTION STATEMENT
Unclassified—Unlimited

B. Jeffrey Anderson

19. SECURITY CLASSIF. (of this report)	20. SECURITY CLASSIF. (of this page)	21. NO. OF PAGES	22. PRICE
Unclassified	Unclassified	49	NTIS

MSFC - Form 3292 (Rev December 1972)

For sale by National Technical Information Service, Springfield, Virginia 22151

ACKNOWLEDGMENTS

The authors express their gratitude to Gwenevere Jasper and Blair Herren for proofing the text and computations. John Hallett was supported, in part, by grant ATM-7920399 from the National Science Foundation, Division of Atmospheric Sciences.

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LIST OF SYMBOLS

a	drop radius
$A(a/\lambda)$	integral defined by equation (8)
B	defined by equation (28)
$\bar{c}$	mean molecular speed
C	defined by equation (30)
$C(R)$	molar concentration of the moist gas
C_v	specific heat of air
D	diffusivity of water vapor in air
F	heat flux
K	thermal conductivity of air
L	latent heat of vaporization
m	mass of the drop
m_a	mass of air molecule
M_w	molecular weight of water
n	integer
P	environmental pressure
P_{sat}	saturation vapor pressure of water
Q	heat energy
r	radial coordinate from origin on drop surface
R	radial coordinate from origin at drop center
R_a	gas constant for air
R_w	gas constant for water vapor
s	ratio of drop radius to mean free path
S	saturation ratio
t	time, integration dummy
$T(R)$	temperature (variable with position)
T_a	temperature of the air at the drop surface
T_d	temperature of the drop
T_∞	temperature of the environment far from drop
u_i	internal energy of air molecule

LIST OF SYMBOLS (Continued)

v	most probable speed
x	mole fraction of water vapor in the air
x_a	mole fraction of vapor at the drop surface
x_∞	mole fraction of vapor far from the drop
α	accommodation coefficient (fraction of heat energy exchanged)
β	sticking coefficient (fraction of vapor molecules that enter drop)
Δ	"jump length" (denotes position where kinetic free stream region meets diffusion controlled region)
ε	numerical constant of order unity
η	viscosity of air
θ	polar angular coordinate, origin at drop surface
λ	mean free path
π	3.14159
$\rho(R)$	vapor density (variable with position)
ρ_a	vapor density at the drop surface
ρ_g	vapor density of moist air
ρ_L	density of liquid water
ρ_∞	vapor density of environment far from drop
$\rho_{sat}(T)$	saturation vapor density for the temperature implied
ϕ	azimuthal angular coordinate, origin at drop surface
Φ	mass flux of water vapor
$\psi(s,n)$	defined by equation (A-2) in the Appendix

TECHNICAL MEMORANDUM

AN EXTENDED CLASSICAL SOLUTION OF THE DROPLET GROWTH PROBLEM

I. INTRODUCTION

The growth or evaporation of water drops under motionless, steady state conditions in air has been the subject of a number of theoretical studies over the last 100 years. The problem is clearly of importance in cloud physics for the growth of cloud drops up to 10 μm and for the development or dissipation of fog and haze in the atmosphere. Similar applications can be made to aerosol/gas phase reactions and to numerous chemical engineering processes, the dispersion of agricultural sprays, spray drying, combustion, humidification, and spray cooling.

The rate of growth or evaporation is limited by transport processes — of heat by conduction or vapor by diffusion in any inert gas present. The first solution to this problem is attributed to Maxwell [1]. He assumed that the surface of the drop produced a vapor pressure related directly to its temperature through the Clausius Clapeyron equation and that heat and moisture were transported by conduction and diffusion, respectively, in a spherical diffusion field from the drop surface. This first approximation is commonly quoted for growth of particles in cloud physics texts [2-5] because it provides sufficient approximation for particles larger than approximately 10 μm. It was first noted by Langmuir [6] that these assumptions are not accurate, especially for small drop sizes. Three physical factors impact the boundary conditions which were used to represent the drop surface. First, there is not complete "accommodation" at the drop surface — not all vapor molecules which strike the surface stick to the drop, and the energy exchange when an air molecule strikes the surface may be incomplete. Second, there is a kinetic limit to the diffusional heat and mass transfer processes. These fluxes will increase as the gradients increase only to a point, the maximum kinetic free stream limit. Third, the drop disturbs the gas near its surface so that the "equilibrium" and "isotropic" conditions no longer strictly apply — the diffusivity and thermal conductivity are no longer constant and the velocity distributions are no longer Maxwellian. Considerable attention has been given to these difficulties. Many investigators have recognized that an exact solution is, in principle, not to be obtained using kinetic theory based on Maxwellian distributions and have sought a basic solution using Chapman Enskog theory, neutron scattering theory, or similar approaches to the fundamental kinetics. This work has yielded valuable insights into the problem, but it has not yet produced a complete solution to this difficult problem. With the exception of the first-order attempt of Monchick and Reiss [7], this work is beyond the scope of this study.

Other investigators [8-18] have developed solutions using classical kinetic theory methods coupled with various approximations and semiempirical relations to yield solutions with slight differences in empiricism and level of approximation.

The primary problem here is that there is seldom a clear picture of why these differences exist, since the classical physical assumptions which form the basis of these approaches are very similar or even identical from author to author. Thus the question remains as to which solution most accurately reflects the physical situation. Much of the problem results from the use of an artificial computational device, the "jump length," Δ, to reach a solution in analogy with the problem of a hot filament in a rarefied gas. This approach divides the environment around the drop into two regions, a near zone where the vapor flux is controlled by free stream kinetics and a far zone where the flux is controlled by diffusion. The "jump length" is the distance from the drop surface to the boundary between the zones. The jump length must be evaluated to reach a solution of the drop growth problem, but no clear line of physical reasoning has been presented that leads to a definite relationship to the known parameters; the length appears to be only a computational artifice. Thus, various assumptions have been made, and a proliferation of solutions is the result.

This report presents a new solution to the droplet growth problem that extends the solution to drop sizes smaller than the mean free path and that does not rely on the "jump length" artifice. The solution is based on the same classical physics and a boundary value method which closely parallels the original Maxwell method. The impact of the various assumptions can be clearly seen in the final solution. Thus, the method is useful for pedagogical reasons. More importantly, however, it is shown how other initial assumptions yield several of the more popular solutions derived using the "jump length" approach. Thus, the physical basis for some of the discrepancies currently in the literature is made clear.

II. SOLUTION FOR THE GROWTH EQUATION

A. Initial Assumptions

Consider the growth of a drop of pure water (radius = a) at rest in an environment of air and water vapor. The well-known correction for a dissolved impurity in the drop could be easily included, but it has been omitted here for the sake of clarity and brevity. Note that since a classical kinetic theory solution to the problem is sought, the accuracy of this treatment, like any heat or mass transport problem, is limited to a few percent at best because the temperature and density gradients which produce the transport also invalidate the basic assumptions upon which the theory rests. Thus, as a general guideline for this study, approximations and assumptions which could alter the solution by less than

1 percent have been freely made, while larger factors have been treated as rigorously as possible. The resulting composite theory is expected to be accurate to within approximately 3 percent for all drop sizes.

Consider now the three physical factors mentioned previously which affect the Maxwell-type solution. The first two factors, incomplete accommodation and the kinetic limit, represent cutoffs which keep the flux densities from becoming infinite at small drop sizes. Fractional sticking of molecules and exchange of energy proportionally require greater fluxes to obtain the same result. Thus, the accommodation coefficients enter as multipliers in the theory and their consideration is clearly important unless they are known to be near unity. The kinetic limit becomes important for drop sizes approaching the length of the mean free path in the gas, λ, as can be seen readily by evaluating when the kinetic free stream flux equals the diffusion flux. The diffusion flux is approximately proportional to the vapor density gradient

$$\frac{\bar{c}\Delta\rho}{4} \simeq D\,\frac{\Delta\rho}{\Delta R} = \frac{\bar{c}\lambda}{3}\,\frac{\Delta\rho}{\Delta R} \quad .$$

Here we have made use of a classical kinetic theory relationship between the diffusivity, D, and the mean molecular speed, $\bar{c}$ [19]. Thus, $\Delta R \simeq 4\lambda/3$. Since we seek a solution applicable for small drop sizes, this factor must also be included in the analysis.

The third factor to be considered is the change in the gas properties near the drop which result from the composition and temperature gradients in that region. There are first-order effects of these gradients — heat conduction and vapor diffusion — which obviously must be included in the theory. However, these gradients also cause the thermal conductivity and the vapor diffusivity to be functions of distance from the drop, they invalidate the Maxwellian molecular velocity distribution in that region, and they give rise to "thermal diffusion" of the vapor (Soret effect) and a heat flux due to the concentration gradient (Dufour effect). All of these are second-order effects which make a contribution that is small compared to the errors caused by the basic limitations of the classical kinetic theory. For example, examination of an extreme case for a drop in the atmosphere — growth of a pure water drop by the Maxwell equation under a constant 10 percent supersaturation starting from its critical radius, 0.01 μm — shows that the temperature deviates from the environmental value by only a few tenths of a percent and the water vapor concentration, a minor constituent in the gas, deviates by only 3 percent. Because the diffusivity varies as the $\sqrt{T}/\rho_g$, where ρ_g is the gas density, and the conductivity varies approximately as $\sqrt{T}$, assuming that these quantities are constants, will not contribute appreciably to the error already present in the classical approach. This allows us to greatly simplify the problem because it implies that Laplace's equation for the temperature and vapor density is satisfied throughout the region surrounding the drop.

In summary, the following assumptions are made in this analysis:

1) Quasistatic equilibrium; i.e., changes in drop radius and other conditions occur so slowly that equilibrium kinetics can be applied. For justification of this assumption see Reference 2.

2) The air and water vapor behave as inert, ideal gases.

3) Maxwellian kinetic theory applies.

4) The thermal conductivity and vapor diffusivity are assumed to be constants, independent of distance from the drop.

5) Fick's law of diffusion and the heat conduction equation apply throughout the environment of the drop, even near the surface. Thus, the only discontinuity is at the drop-air interface.

6) The drop temperature T_d, the mean temperature near the drop $\bar{T}$, and the environmental temperature T_∞ are sufficiently close that

$$(T_d/\bar{T})^{1/2} \simeq (T_d/T_\infty)^{1/2} \simeq (\bar{T}/T_\infty)^{1/2} \simeq 1$$

where this factor appears as a multiplier.

B. Vapor Density Boundary Condition

Far from the water drop the water vapor density has a constant, known value, ρ_∞. As one approaches the drop along a radial vector, the vapor density must be a smooth, continuous function of radius, R, until the water surface is reached since there are no sources or sinks outside the drop and the environment is assumed uniform (constant diffusivity). Approached in this way, the limiting value of $\rho(R)$ at the drop surface is defined as ρ_a. ρ_a does not equal the equilibrium value of vapor density over the drop surface, ρ_{sat}, as is assumed in the Maxwell-type solution. The difference is the "jump" which is well known from kinetic theory. Note that this is a jump in vapor density at the location of a physical discontinuity in the medium, the drop surface. It is not a jump in position. ρ_a is the boundary condition for the diffusion field. It must be solved for in terms of known parameters and parameters that can be eliminated in the subsequent derivation.

Consider first a drop in equilibrium, $dm/dt = 0$. From elementary kinetic theory one can write the water vapor mass flux (per unit area per unit time) against the drop.

$$\Phi_{in}^{(sat)} = \rho_{sat} \sqrt{R_w T_d/(2\pi)} \quad , \tag{1}$$

because in this case the vapor density is a constant, ρ_{sat}. Equation (1) holds subject only to the static equilibrium assumption, independent of the size of the drop.

An expression for the mass balance at the air-drop interface is also easily obtained for the equilibrium drop:

Flux in = Flux out = Flux reflected + Flux leaving drop

Making the definition, β = the fraction of incident water molecules absorbed into the drop, it follows that

$$\Phi_{in}^{(sat)} = (1 - \beta)\, \Phi_{in}^{(sat)} + \Phi_d \quad .$$

Thus, for the flux leaving the drop

$$\Phi_d = \beta\, \Phi_{in}^{(sat)} \quad . \tag{2}$$

For a drop not in equilibrium, i.e., growing or evaporating, the mass balance condition at the interface is given by a similar equation,

Flux in = Flux reflected + Flux leaving drop
+ Rate of mass change/area;

$$\Phi_{in} = (1 - \beta)\, \Phi_{in} + \Phi_d + \frac{1}{4\pi a^2} \frac{dm}{dt} \quad .$$

Here it can be assumed that the flux leaving the drop, Φ_d, is only a function of drop temperature and not a direct function of the equilibrium condition of the drop. Thus, one may employ equation (2) and arrange terms to yield

$$\Phi_{in} = \Phi_{in}^{(sat)} + \frac{1}{4\pi\beta a^2}\,\frac{dm}{dt} \quad , \tag{3}$$

where $\Phi_{in}^{(sat)}$ is to be computed with equation (1) using the drop temperature.

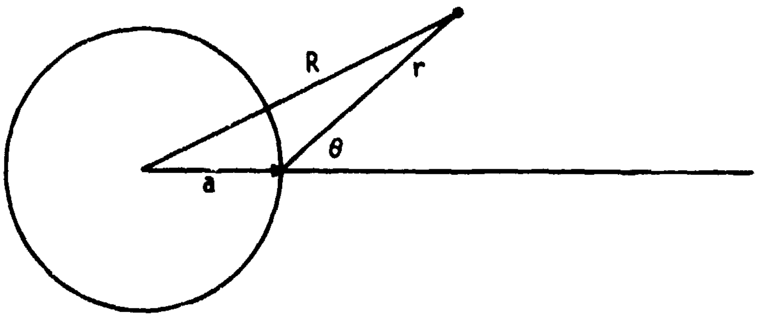
Next an equation is required that is similar in form to equation (1) to relate the flux in to the vapor density field. Equation (1) no longer applies because $\rho(R)$ is not constant near the drop. Thus, it is necessary to return to one of the integral formulations from which equation (1) is normally derived (Loeb [19]) and make the adjustment for a vapor density which is a function of R

$$\Phi_{in} = \frac{1}{\lambda v^3 \pi^{3/2}} \int_{c=0}^{\infty} c^3 e^{-c^2/v^2}\, dc \int_{r=0}^{\infty} \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} \rho(R)\, e^{-r/\lambda} \sin\theta \cos\theta \, d\phi \, d\theta \, dr \tag{4}$$

$$\Phi_{in} = \frac{\bar{c}}{4\pi\lambda} \int_{r=0}^{\infty} \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} \rho(R)\, e^{-r/\lambda} \sin\theta \cos\theta \, d\phi \, d\theta \, dr \quad .$$

The integration is over a half space in a (r, θ, ϕ) coordinate system centered on the surface of the drop. Here λ is the mean free path in the gas, v is the most probable speed, and $\bar{c}$ is the mean molecular speed. From elementary kinetic theory,

$$\bar{c} = \sqrt{8R_w T/\pi} \quad . \tag{5}$$



In Section II-D it is shown that Fick's Law for the diffusion field implies that the vapor density obeys the relation

$$\rho(R) = \rho_\infty + (\rho_a - \rho_\infty)\, a/R + [\rho_a - \rho(R)] \left(\frac{T_a - T_\infty}{T_\infty}\right) a/R \quad .$$

Since $| \rho_a - \rho(R) | < | \rho_a - \rho_\infty |$ for all R and, as noted previously, $(T_a - T_\infty)/T_\infty$ is less than a few tenths of a percent in even extreme cases,* the last term can be ignored; thus

$$\rho(R) = \rho_\infty + (\rho_a - \rho_\infty)\, a/R \quad . \tag{6}$$

Using the law of cosines,

$$R = (a^2 + r^2 + 2ar \cos\theta)^{1/2} \quad .$$

Performing the ϕ integral, breaking the integrand, and performing the elementary c and θ integrals in the first term yields

$$\Phi_{in} = \frac{\rho_\infty \bar{c}}{4} + \frac{(\rho_a - \rho_\infty)\, \bar{c}\, A\,(a/\lambda)}{2} \quad . \tag{7}$$

We have made the definition

$$A(a/\lambda) \equiv a/\lambda \int_0^\infty \int_0^{\pi/2} \frac{e^{-r/\lambda} \sin\theta \cos\theta \, d\theta dr}{(a^2 + r^2 + 2ar \cos\theta)^{1/2}} \tag{8}$$

$$\simeq \left(\frac{1}{2} - \frac{\lambda}{3a}\right) - \left(\frac{-\lambda}{3a} + \frac{1}{6}\right) e^{-a/\lambda} + \left(\frac{a}{2\lambda} + \frac{a^2}{3\lambda^2}\right) E_1\left(\frac{a}{\lambda}\right) - \left(\frac{a}{3\lambda}\right) e^{-a/\lambda} \quad , \tag{9}$$

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* For droplet growth. The error could reach 10 percent for drops evaporating in very dry air.

where $$E_1\left(\frac{a}{\lambda}\right) = \int_1^\infty \frac{e^{-at/\lambda}}{t}\,dt \quad .$$

The expression (9) represents the second-order approximation to the value of the integral. It gives a value for $A(a/\lambda)$ which is 10 percent too low for $a = \lambda$, but the accuracy improves rapidly for larger values of drop radius. Note that an error in the value of $A(a/\lambda)$ causes a much smaller error in the drop growth rate. Evaluation of the integral and expressions for successively better approximate values and upper and lower bounds are discussed in the Appendix.

Substituting equations (7) and (1) into equation (3), one approaches the final solution for the boundary condition.

$$\frac{\rho_\infty \bar{c}}{4} + \frac{(\rho_a - \rho_\infty)\,\bar{c}\,A(a/\lambda)}{2} = \rho_{sat}\sqrt{\frac{R_w T_d}{2\pi}} + \frac{1}{4\pi\beta a^2}\,\frac{dm}{dt} \quad . \tag{10}$$

Using equation (5) and solving for ρ_a, making the approximation

$$(T_d/T_\infty)^{1/2} \simeq 1 \quad ,$$

gives,

$$\rho_a = \frac{\rho_{sat}}{2A\left(\frac{a}{\lambda}\right)} + \rho_\infty\left(1 - \frac{1}{2A\left(\frac{a}{\lambda}\right)}\right) + \frac{1}{8\pi\beta a^2 A\left(\frac{a}{\lambda}\right)}\sqrt{\frac{2\pi}{R_w T_\infty}}\,\frac{dm}{dt} \quad . \tag{11}$$

Equation (11) represents the boundary condition for the vapor diffusion field at the water-air interface. Notice that in the limit of large drop radius $A(a/\lambda) \to 1/2$, so the boundary condition becomes

$$\rho_a = \rho_{sat} + \frac{1}{4\pi\beta a^2}\sqrt{\frac{2\pi}{R_w T_\infty}}\,\frac{dm}{dt} \qquad (a \gg \lambda) \quad . \tag{12}$$

C. Temperature Boundary Condition

The solution for the temperature boundary conditions very closely parallels the vapor density case. If α is defined as the fraction of energy exchange for the air striking the drop surface,

$$\alpha = \frac{\text{Actual energy exchange}}{\text{Maximum possible exchange}} \quad ,$$

consideration of the energy flux balance in equilibrium yields, in analogy to equation (2),

$$F_d = \alpha F_{in}(\text{sat}) \quad , \tag{13}$$

for the flux leaving the drop. Similarly, for a growing or evaporating drop the flux balance condition is

$$F_{in} = (1 - \alpha)\, F_{in} + F_d - \frac{L}{4\pi a^2} \frac{dm}{dt} \quad ,$$

where L is the latent heat of condensation. Assuming the directional energy flux emerging from the drop is independent of the state of equilibrium, one obtains

$$F_{in} = F_{in}(\text{sat}) - \frac{L}{4\pi\alpha a^2} \frac{dm}{dt} \quad . \tag{14}$$

Now expressions must be obtained for the incident energy fluxes for the growing and equilibrium drops. In both cases we begin by noting that the energy flux, F, equals the product of the energy per molecule times the molecular flux. Using equation (4) for the molecular flux with the vapor density replaced by the gas density and writing the energy per molecule as translational energy plus internal energy to separate out the dependence on molecular speed, yields

$$F_{in} = \frac{1}{\lambda v^3 \pi^{3/2}} \int_{r=0}^{\infty} \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} \int_{c=0}^{\infty} \left(\frac{m_a c^2}{2} + \frac{\partial u_i}{\partial T} \; T(R) \right) c^3 e^{-c^2/v^2} \frac{\rho_g(R)}{m_a} \; e^{-r/\lambda} \sin\theta \cos\theta \; dc\,d\theta\,d\phi\,dr \quad .$$

Integrating over c

$$F_{in} = \frac{1}{\lambda v^3 \pi^{3/2}} \iiint \left(\frac{m_a v^6}{2} + \frac{v^4}{2} \frac{\partial u_i}{\partial T} \; T(R) \right) \frac{\rho_g(R)}{m_a} \; e^{-r/\lambda} \sin\theta \cos\theta \; d\phi\,d\theta\,dr \quad .$$

Since $\bar{c} = 2v/\sqrt{\pi}$, $v^2 = 2R_a T$, and $c_v = 3R_a/2 + (m_a)^{-1} \; \partial u_i/\partial T$, where R_a is the gas constant for air,

$$F = \frac{\bar{c}\left(C_v + R_a/2\right)}{4\pi\lambda} \int_0^{\infty} \int_0^{\pi/2} \int_0^{2\pi} T(R) \; \rho_g(R) \; e^{-r/\lambda} \sin\theta \cos\theta \; d\phi\,d\theta\,dr \quad . \tag{15}$$

In equilibrium T(R) and $\rho_g(R)$, the gas density, are not functions of position, so the elementary integration gives

$$F_{in}(\text{sat}) = (C_v + R_a/2) \; T_d \; \rho_g \sqrt{R_a T_d/(2\pi)}$$

$$= (3R_a T_d) \; \rho_g \sqrt{R_a T_d/(2\pi)} \quad , \tag{16}$$

where T_d is the drop temperature (which equals the gas temperature).

For drops not in equilibrium the analysis of the diffusion field given in Section II-D shows that the temperature field is given by

$$T(R) = T_\infty + (T_a - T_\infty)\, a/R \quad , \tag{17}$$

where T_a is the gas temperature at the drop surface and T_∞ is the environment temperature. After inserting equation (17) into equation (15), integration yields the desired solution for the energy flux into the drop, F_{in}. In this case the gas density is constant in the region about the drop (to a close approximation), but the temperature shows the same radial dependence as the water vapor density did in the previous case. The solution is

$$F_{in} = \frac{3R_a \bar{c}\, \rho_g}{4\pi\lambda} \int_0^{2\pi} \int_0^{\pi/2} \int_0^{\infty} \left[T_\infty + (T_a - T_\infty) \frac{a}{R} \right] e^{-r/\lambda} \sin\theta \cos\theta \, dr\, d\theta\, d\phi$$

$$= [3R_a \rho_g] \left[\frac{T_\infty \bar{c}}{4} + \frac{(T_a - T_\infty)\, \bar{c}\, A(a/\lambda)}{2} \right] \quad . \tag{18}$$

$A(a/\lambda)$ is again defined by equation (8). Combining equations (14), (16), and (18) as before, one obtains the final boundary condition:

$$T_a = \frac{T_d}{2A\left(\frac{a}{\lambda}\right)} + T_\infty \left(1 - \frac{1}{2A\left(\frac{a}{\lambda}\right)}\right) - \frac{L\sqrt{2\pi/R_a T_\infty}}{24\pi\alpha R_a\, \rho_g\, a^2 A\left(\frac{a}{\lambda}\right)} \left(\frac{dm}{dt}\right) \quad . \tag{19}$$

Again, since $A(a/\lambda) \to 1/2$ for $a \gg \lambda$, the large drop limit is

$$T_a = T_d - \frac{L\sqrt{2\pi/R_a T_\infty}}{12\pi\alpha a^2 R_a \rho_g} \left(\frac{dm}{dt}\right) \qquad (a \gg \lambda) \quad . \tag{20}$$

D. Solution of the Diffusion Fields

Now that the boundary conditions for the vapor and temperature fields have been established, equations (11) and (19), the solution for the droplet growth rate can be obtained. The problem contains four unknown parameters: the growth rate, the latent heat released at the drop, the drop temperature, and the equilibrium vapor density above the drop. Thus, four equations are required: Fick's law for the diffusion of vapor, Fourier's law for the conduction of heat, the proportionality between latent heat release and change in mass, and the Clausius-Clapeyron relationship between temperature and equilibrium vapor density. These yield a solution in terms of the known environmental parameters. The method parallels the textbook solution of Mason [3] with different boundary conditions and with Fick's law written in terms of the mole fraction, x, rather than the approximate expression in terms of vapor density.

Beginning with Fourier's law of heat conduction and noting that, for a steady state system, the heat flux across any spherical shell concentric with the drop is constant, independent of time and radius, we have

$$\frac{dQ}{dt} = 4\pi R^2 F = -4\pi R^2 K \frac{dT}{dR} = \text{constant}. \qquad (21)$$

An additional term could be included in equation (21) to account for the energy flux carried by the mass flux. However, this term must be less than C_v dm/dt, where C_v is the specific heat. Since the total heat flux must equal L dm/dt, the fraction contributed by the mass flux term must be less than $C_v/L \simeq 0.0005$, which is clearly negligible. Therefore, returning to equation (21),

$$\frac{dQ}{dt}\int\frac{dR}{R^2} = -4\pi K\int dT \quad .$$

Integration and application of the boundary conditions, $T = T_\infty$ at $R \to \infty$, and $T = T_a$ at $R = a$, quickly yields

$$\frac{dQ}{dt} = 4\pi a K\,(T_a - T_\infty) \quad , \qquad (22)$$

and

$$T = T_\infty + (T_a - T_\infty)\frac{a}{R} \quad ,$$

which is equation (17) which was used earlier. If one makes use of the definition of latent heat, L, equation (22) can be related to the growth rate

$$\frac{dm}{dt} = \frac{4\pi a K}{L}(T_a - T_\infty) \quad . \tag{23}$$

Next a similar solution for the diffusion field is obtained using Fick's law [20] and the "steady state" assumption.

$$\frac{dm}{dt} = 4\pi R^2 \Phi \quad = \text{constant}$$

$$= \frac{4\pi R^2\, C(R) M_w D}{(1 - x)} \frac{dx}{dR} \quad , \tag{24}$$

where x is the mole fraction of water vapor, C(R) is the molar concentration of the moist gas (air + water vapor), and M_w is the molecular weight of water. From the gas law,

$$C(R)\, M_w = P/(R_w T(R)) \quad .$$

Inserting equation (13) for T(R) into (24) and integrating from R = a to ∞ gives

$$\frac{R_w}{\rho}\frac{dm}{dt}\int_{R=a}^{\infty}\left(\frac{T_\infty}{R^2} + \frac{(T_a - T_\infty)a}{R^3}\right) dR = 4\pi D \int_{x_a}^{x_\infty} \frac{dx}{1 - x}$$

Or, after integration,

$$\frac{R_w}{\rho}\left(\frac{T_\infty + T_a}{2a}\right)\frac{dm}{dt} = 4\pi D \ \ln\left(\frac{1 - x_a}{1 - x_\infty}\right)$$

$$= 4\pi D\left[\frac{x_\infty - x_a}{1 - x_\infty} - \frac{1}{2}\left(\frac{x_\infty - x_a}{1 - x_\infty}\right)^2 + \ldots\right] \quad .$$

Solving for dm/dt and neglecting the higher order terms leaves

$$\frac{dm}{dt} = \frac{8\pi aPD}{R_w\ (T_\infty + T_a)}\left(\frac{x_\infty - x_a}{1 - x_\infty}\right) \quad . \tag{25}$$

This approximation is quite good. The series expansion is always valid since the absolute value of $(x_\infty - x_a)/(1 - x_\infty)$ is less than one. In the rather extreme case of a drop at 20°C evaporating into dry air; $x_\infty = 0$, $x_a = 0.023$; the error caused by neglecting the second-order term is only 1.2 percent.

The mole fraction is related to the vapor density by the expressions,

$$x_a = \frac{R_w \rho_a T_a}{P} \quad , \ x_\infty = \frac{R_w \rho_\infty T_\infty}{P} \quad .$$

Therefore,

$$\frac{dm}{dt} = \frac{8\pi aD\ (\rho_\infty T_\infty - \rho_a T_a)}{(T_\infty + T_a)\ (1 - R_w \rho_\infty T_\infty / P)}$$

$$= \frac{4\pi aD}{(1 - R_w \rho_\infty T_\infty / P)}\left(\frac{2T_\infty}{T_\infty + T_a}\right)\left[(\rho_\infty - \rho_a) - \frac{\rho_a}{T_\infty}(T_a - T_\infty)\right]$$

$$\simeq \frac{4\pi aD}{(1 - R_w \rho_\infty T_\infty / P)}\left[(\rho_\infty - \rho_a) - \frac{\rho_\infty}{T_\infty}(T_a - T_\infty)\right] \quad . \tag{26}$$

The approximations used to reach the final form of equation (26) introduce negligible error as long as the quasistatic assumption is valid. They can be shown to be equivalent to neglecting the term

$$(\rho_a - \rho_\infty)\,(T_a - T_\infty)/\,2T_\infty$$

plus higher order terms. Considering a drop at 20°C evaporating in 90 percent relative humidity — a significant departure from quasi-static — the error contributed by this approximation would be less than 0.7 percent.

Because of the spherical symmetry and steady state assumptions, the mass flux across any spherical shell concentric with the drop is a constant. Thus, rewriting equation (26) for arbitrary R leads to an expression for the vapor density profile,

$$\frac{dm}{dt} = \text{constant}$$

$$= \frac{4\pi aD}{(1 - R_w \rho_\infty T_\infty / P)} \left[(\rho_\infty - \rho_a) - \frac{\rho_a}{T_\infty} (T_a - T_\infty) \right]$$

$$= \frac{4\pi RD}{(1 - R_w \rho_\infty T_\infty / P)} \left[[\rho_\infty - \rho(R)] - \frac{\rho(R)}{T_\infty} [T(R) - T_\infty] \right] .$$

Solving for $\rho(R)$, using equation (17), gives

$$\rho(R) = \rho_\infty + (\rho_a - \rho_\infty)\,\frac{a}{R} + [\rho_a - \rho(R)] \left(\frac{T_a - T_\infty}{T_\infty} \right) \frac{a}{R}$$

$$\simeq \rho_\infty + (\rho_a - \rho_\infty)\,\frac{a}{R} \quad .$$

This is the vapor density profile, equation (6), which was employed earlier in Section II-B.

Now ρ_a can be eliminated from equation (26) by substituting in the boundary condition, equation (11),

$$\frac{dm}{dt} = \frac{4\pi aD}{\left(1 - \frac{R_w \rho_\infty T_\infty}{p}\right)} \left[\frac{\rho_\infty - \rho_{sat}}{2A\left(\frac{a}{\lambda}\right)} - \frac{\sqrt{2\pi/(R_w T)}}{8\pi\beta a^2 A\left(\frac{a}{\lambda}\right)} \left(\frac{dm}{dt}\right) - \frac{\rho_\infty}{T_\infty} (T_a - T_\infty) \right] .$$

Next, substituting from equation (23), $(T_a - T_\infty)$ is eliminated to give a solution for dm/dt.

$$\frac{dm}{dt} = \frac{4\pi aD\,(\rho_\infty - \rho_{sat})}{2A\left(\frac{a}{\lambda}\right)\left[1 - \frac{R_w \rho_\infty T_\infty}{p} + \frac{D\sqrt{2\pi/R_w T_\infty}}{2\beta a A\left(\frac{a}{\lambda}\right)} + \frac{D\rho_\infty L}{KT_\infty}\right]} ,$$

$$= \frac{4\pi aD}{B} (\rho_\infty - \rho_{sat}) , \qquad (27)$$

where the parameter B is defined to equal the denominator of (27)

$$B = 2A\left(\frac{a}{\lambda}\right)\left[1 - \frac{R_w \rho_\infty T_\infty}{p} + \frac{D\sqrt{2\pi/R_w T_\infty}}{2\beta a A(a/\lambda)} + \frac{DL\rho_\infty}{KT_\infty}\right] . \qquad (28)$$

This expression, equation (27), appears in the original solution by Maxwell [1] with B = 1. It represents a solution for the droplet growth rate which is independent of the thermal conduction field. Thus, one must have independent knowledge of the drop temperature to specify ρ_{sat} in equation (27).

Likewise, an expression for the growth rate can be obtained from the thermal field by substituting the temperature boundary condition, equation (19), into equation (23).

$$\frac{dm}{dt} = \frac{2\pi Ka\,(T_d - T_\infty)}{LA\left(\frac{a}{\lambda}\right)\left[1 + \frac{K\sqrt{2\pi/R_a T_\infty}}{6\alpha a R_a \rho_g A\left(\frac{a}{\lambda}\right)}\right]} \quad . \tag{29}$$

$$= \frac{4\pi Ka}{LC}\,(T_d - T_\infty) \quad ,$$

where, to simplify notation, we have defined

$$C = 2A\left(\frac{a}{\lambda}\right)\left[1 + \frac{K}{6\alpha a R_a \rho_g A(a/\lambda)}\sqrt{\frac{2\pi}{R_a T_\infty}}\,\right] \tag{30}$$

Just as the saturation vapor density over the drop, ρ_{sat}, must be known to use equation (27), the drop's temperature must be known to use equation (29). This difficulty can be eliminated by using an expression which will be derived from the Clausius-Clapeyron equation,

$$\frac{1}{P_{sat}}\,\frac{dP_{sat}}{dT} = \frac{L}{R_w T^2} \quad . \tag{31}$$

Using the gas law to write this in terms of vapor density, rather than pressure, gives

$$\frac{d\rho_{sat}(T)}{\rho_{sat}(T)} = \left(\frac{L}{R_w T^2} - \frac{1}{T}\right) dT \quad .$$

Integrating from T_d to T_∞ yields:

$$\ln\left(\frac{\rho_{sat}(T_d)}{\rho_{sat}(T_\infty)}\right) = \frac{L(T_d - T_\infty)}{R_w T_d T_\infty} - \ln\left(\frac{T_d}{T_\infty}\right) \tag{32}$$

The approximation $T_d \simeq T_\infty$ and the expansion, $\ln(x) \simeq x - 1$, for $x \simeq 1$ applied to equation (32) yields

$$\ln\left(\frac{\rho_{sat}(T_d)}{\rho_{sat}(T_\infty)}\right) \simeq \frac{(L - R_w T_\infty)(T_d - T_\infty)}{R_w T_\infty^2} \quad .$$

Taking the exponential of both sides, expanding, and dropping the higher order terms leaves:

$$\frac{\rho_{sat}(T_d)}{\rho_{sat}(T_\infty)} \simeq 1 + \left(\frac{L - R_w T_\infty}{R_w T_\infty^2}\right)(T_d - T_\infty) \quad .$$

Substituting for $(T_d - T_\infty)$ from equation (29) leaves

$$\frac{\rho_{sat}(T_d) - \rho_{sat}(T_\infty)}{\rho_{sat}(T_\infty)} = \left(\frac{L - R_w T_\infty}{R_w T_\infty^2}\right)\left(\frac{LC}{4\pi aK}\right)\left(\frac{dm}{dt}\right) \quad . \qquad (33)$$

Recalling equation (27) and dividing it by $\rho_{sat}(T_\infty)$, one has

$$\frac{\rho_\infty - \rho_{sat}}{\rho_{sat}(T_\infty)} = \frac{B}{4\pi a D \rho_{sat}(T_\infty)}\left(\frac{dm}{dt}\right) \quad . \qquad (34)$$

Since it is assumed here that the water drops are pure, the equilibrium vapor density over the drop, ρ_{sat}, is related to the equilibrium vapor density over a flat surface of water at T_d, $\rho_{sat}(T_d)$, by the Kelvin equation:

$$\rho_{sat} = \rho_{sat}(T_d) \exp\left(\frac{2\sigma}{\rho_L R_w T_d a}\right)$$

$$\simeq \rho_{sat}(T_d)\left(1 + \frac{2\sigma}{\rho_L R_w T_d a}\right)$$

$$\simeq \rho_{sat}(T_d) + \frac{2\sigma\rho_{sat}(T_\infty)}{\rho_L R_w T_\infty a} \quad . \tag{35}$$

The linear approximation for the exponential is adequate for water drops larger than 0.1 µm. For application to smaller drops the quadratic term should also be included. The term for dissolved impurities could have been included at this point by the textbook method [3,4], but it is omitted here to shorten the solution.

Substituting equation (35) into equation (34) and adding result to equation (33) gives:

$$\frac{\rho_\infty - \rho_{sat}(T_\infty) - \dfrac{2\sigma\rho_{sat}(T_\infty)}{\rho_L R_w T_\infty a}}{\rho_{sat}(T_\infty)} = \left[\left(\frac{L - R_w T_\infty}{R_w T_\infty^2}\right)\left(\frac{LC}{4\pi aK}\right) + \left(\frac{B}{4\pi aD\rho_{sat}(T_\infty)}\right)\right]\left(\frac{dm}{dt}\right) \quad .$$

Using the definition of the saturation ratio, S,

$$S \equiv \frac{\rho_\infty}{\rho_{sat}(T_\infty)} \quad .$$

The final solution can now be written:

$$\frac{dm}{dt} = \frac{4\pi a\left[(S - 1) - \dfrac{2\sigma}{\rho_L R_w T_\infty a}\right]}{\left[\dfrac{LC}{K}\left(\dfrac{L - R_w T_\infty}{R_w T_\infty^2}\right) + \left(\dfrac{B}{D\rho_{sat}(T_\infty)}\right)\right]} \quad , \tag{36}$$

where

$$B \equiv 2A\left(\frac{a}{\lambda}\right)\left[1 - \frac{R_w \rho_\infty T_\infty}{P} + \frac{D\sqrt{2\pi/R_w T_\infty}}{2\beta a\ A(a/\lambda)} + \frac{DL\rho_\infty}{KT_\infty}\right] , \qquad (37)$$

$$C \equiv 2A\left(\frac{a}{\lambda}\right)\left[1 + \frac{K\sqrt{2\pi/R_a T_\infty}}{8\alpha a R_a \rho_g A(a/\lambda)}\right] . \qquad (38)$$

$A(a/\lambda)$ is the integral, equation (8), which is evaluated in the Appendix

$$A(a/\lambda) = a/\lambda \int_0^{\pi/2} \int_0^\infty \frac{e^{-r/\lambda} \sin\theta \cos\theta \, dr \, d\theta}{(a^2 + r^2 + 2ar\cos\theta)^{1/2}} .$$

Since

$$m = \frac{4}{3}\pi a^3 \rho_L ,$$

$$dm/dt = 4\pi a^2 \rho_L \, da/dt ,$$

the radial growth rate can be written

$$a\frac{da}{dt} = \frac{(S - 1) - \dfrac{2\sigma}{\rho_L R_w T_\infty a}}{\left[\dfrac{\rho_L LC}{K}\left(\dfrac{L - R_w T_\infty}{R_w T_\infty^{\,2}}\right) + \dfrac{\rho_L B}{D\rho_{sat}(T_\infty)}\right]} . \qquad (39)$$

As noted previously, a second-order correction to the Kelvin term may be desirable for some applications involving very small droplets.

III. NUMERICAL EVALUATION

The numerical values of $A(a/\lambda)$, B, C, and da/dt are illustrated in Figures 1 through 7 to indicate their magnitudes and dependence upon temperature, pressure, saturation ratio and drop size. Figure 1 illustrates the value of the integral, $A(a/\lambda)$, as a function of drop radius divided by the mean free path. The third-order approximation given in the Appendix, equation (A-6), was used to compute the graph. Note that the value of the integral is well defined for all values of radius. In the limits, $A(a/\lambda) \to 0$ as $a \to 0$ and to 1/2 as $a \to \infty$.

The difference between this formulation of the droplet growth theory and earlier solutions is contained in the terms "B" and "C" which are given by equations (37) and (38). These are plotted against radius in Figures 2 and 3, respectively, for various values of the thermal accommodation coefficient, α, and sticking coefficient, β. If α and β were about equal, then "B" and "C" would be of nearly equal significance; but since it is generally believed that α is near unity and β is small, probably between 0.03 and 0.04, the "B" term must be regarded as having the greatest impact on the growth rate. However, as pointed out by Chodes et al. [21] and others, the measurements upon which this judgement is based are difficult to make with high accuracy, so the values of α and β must still be regarded with some suspicion. In the limits both "B" and "C" become inversely proportional to "a" for small drop sizes; but, since the entire denominator of the growth rate equation is multiplied by the radius, the growth rate would remain bounded as $a \to 0$ except for the Kelvin term in the numerator. As the drops become large, "B" (approximately) and "C" approach unity; thus, equation (39) approaches the classical solution.

The remaining figures (4 through 7) illustrate the magnitude of the radial growth rate, equation (39), as a function of radius with temperature, pressure, saturation ratio and sticking coefficient as parameters. As will be discussed in the following section, the numerical values do not differ appreciably from those presented by other authors. In each of the curves plotted, the growth rate is carried to zero by the Kelvin term. If that were absent, the curves would approach a constant value somewhat greater than the peak values shown. Of course, to accurately reflect the growth of a real drop in the atmosphere one must include, in addition to the Kelvin term, a term to describe the influence of the nucleus and any chemical impurities in the drop.

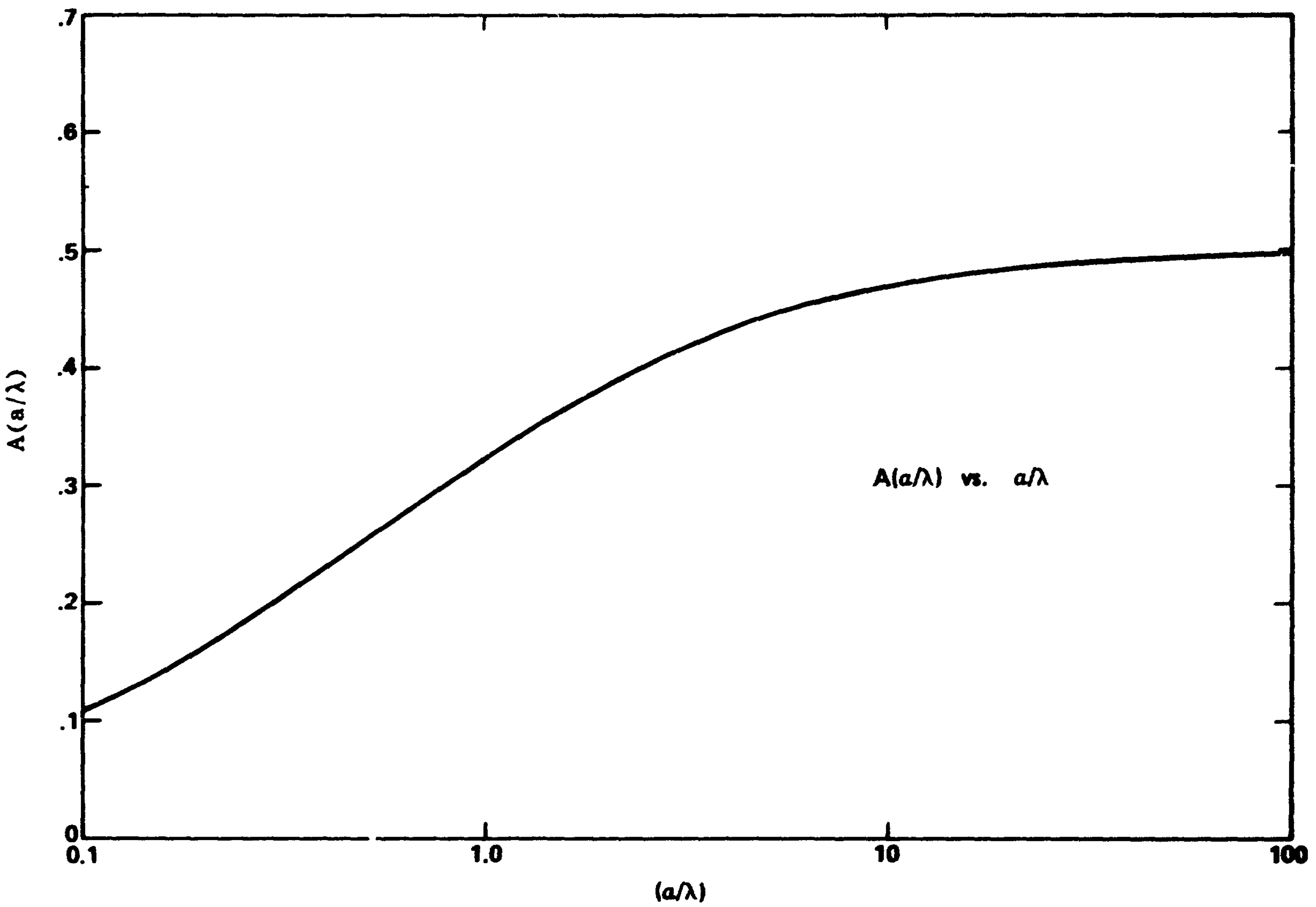

Figure 1. A(a/λ) as a function of (a/λ) computed from the third-order approximation given in the Appendix, equation (A-6).

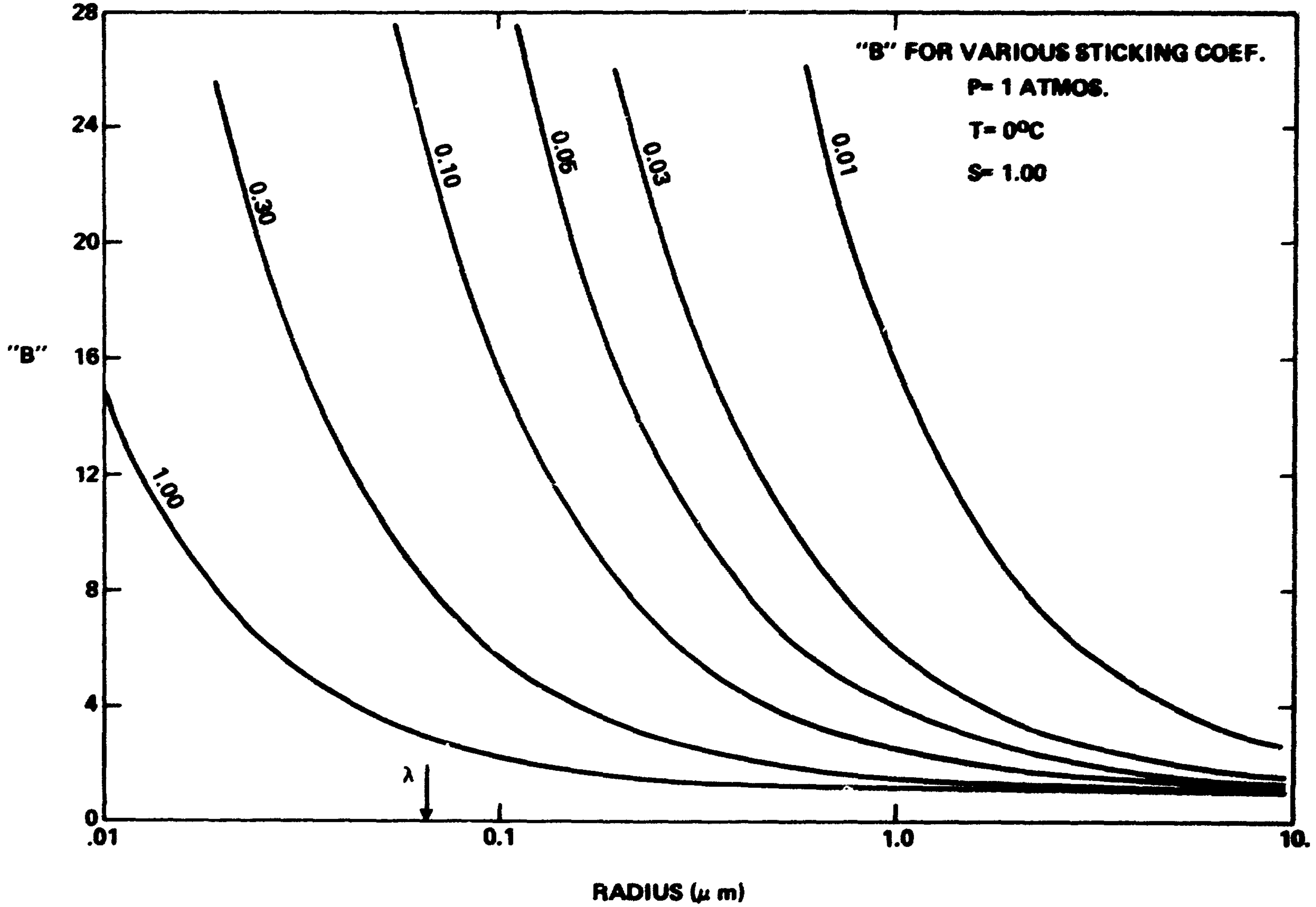

Figure 2. Sample evaluation of B, given by equation (37), as a function of radius for various values of the sticking coefficient, β. λ is the mean free path at the temperature and pressure specified.

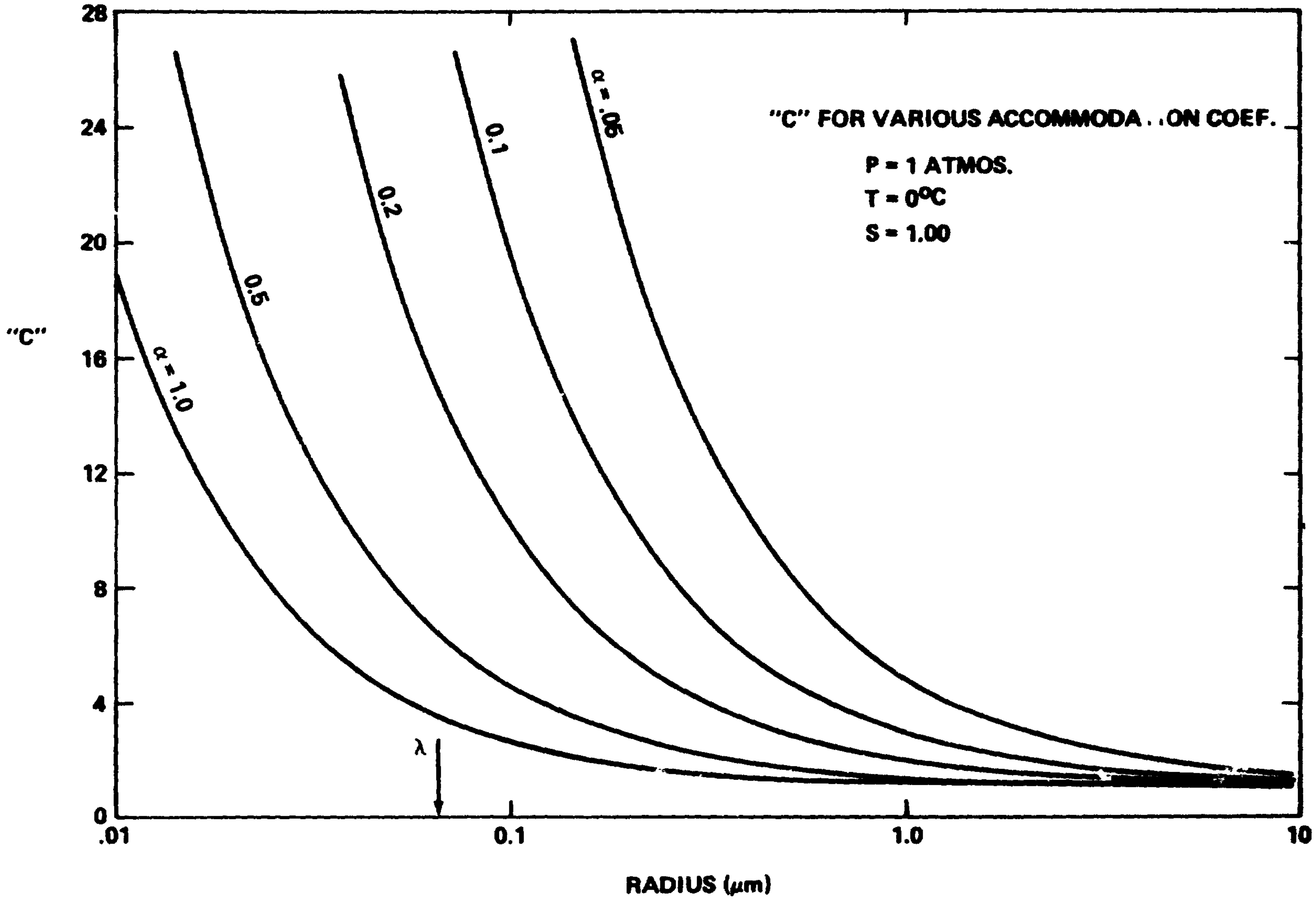

Figure 3. Sample evaluation of C, given by equation (38), as a function of radius for various values of the accommodation coefficient, α.

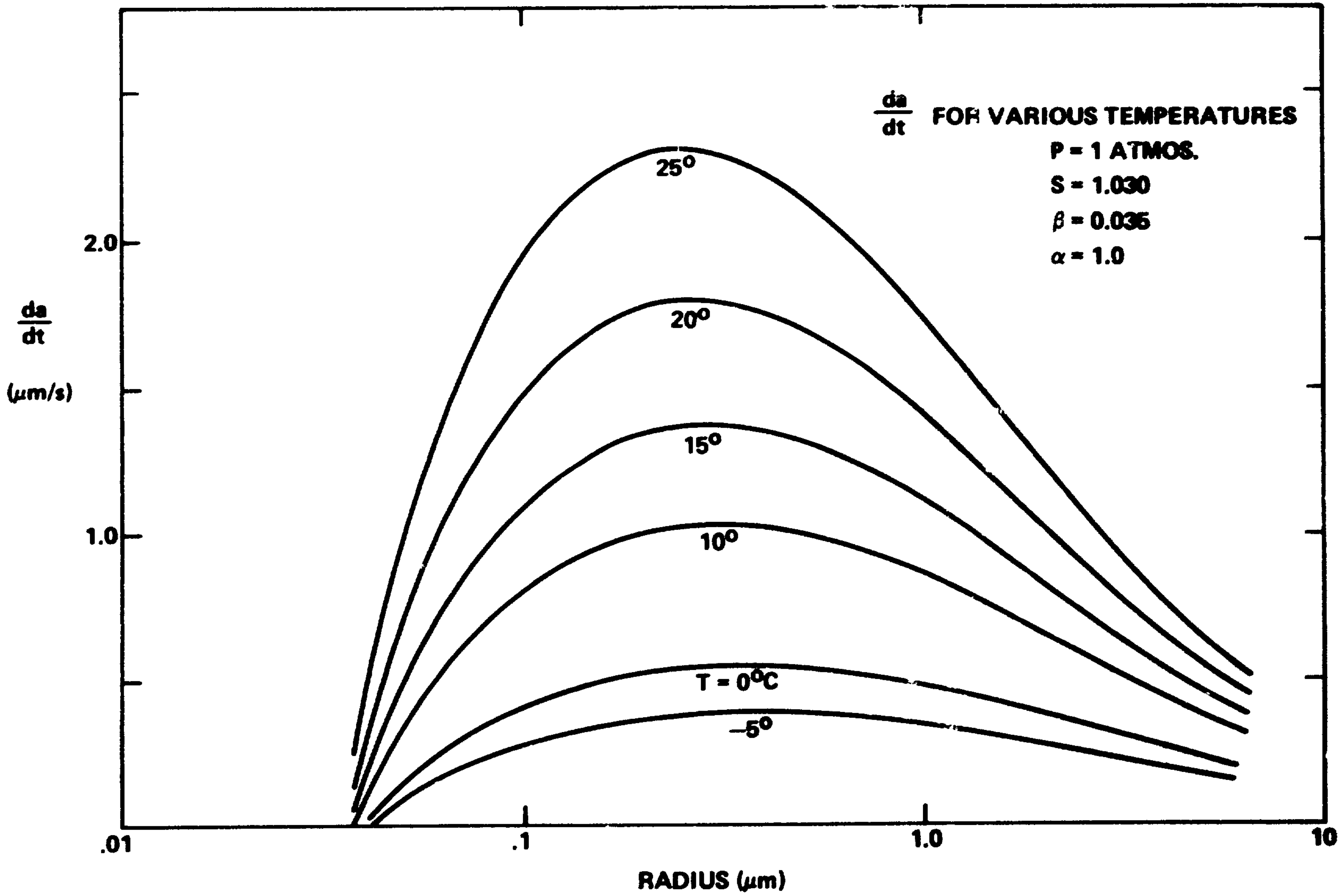

Figure 4. Radial growth rate for a pure water drop as a function of radius, shown for various values of environmental temperature.

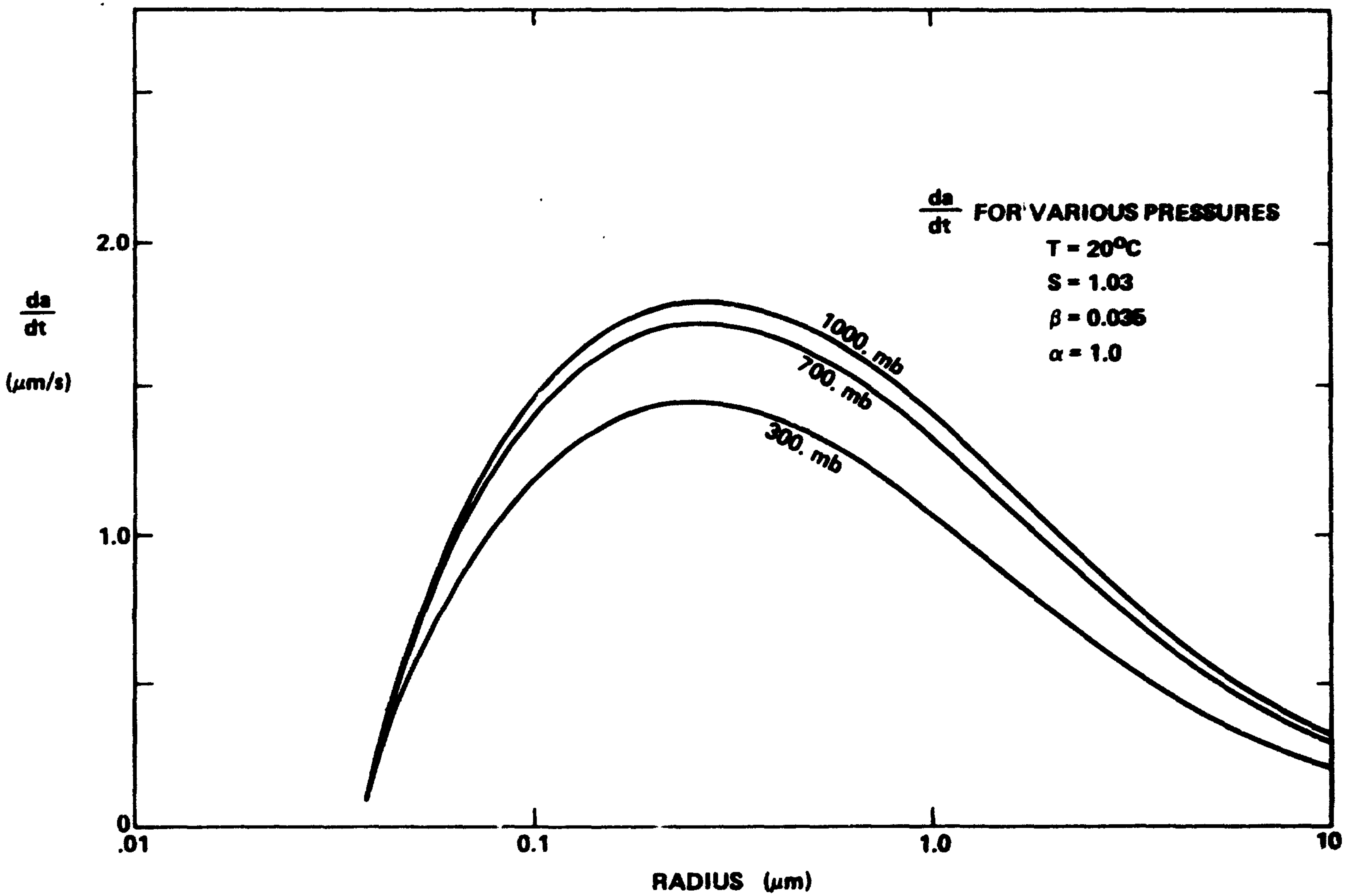

Figure 5. Radial growth rate for a pure water drop as a function of radius, shown for various values of environmental pressure.

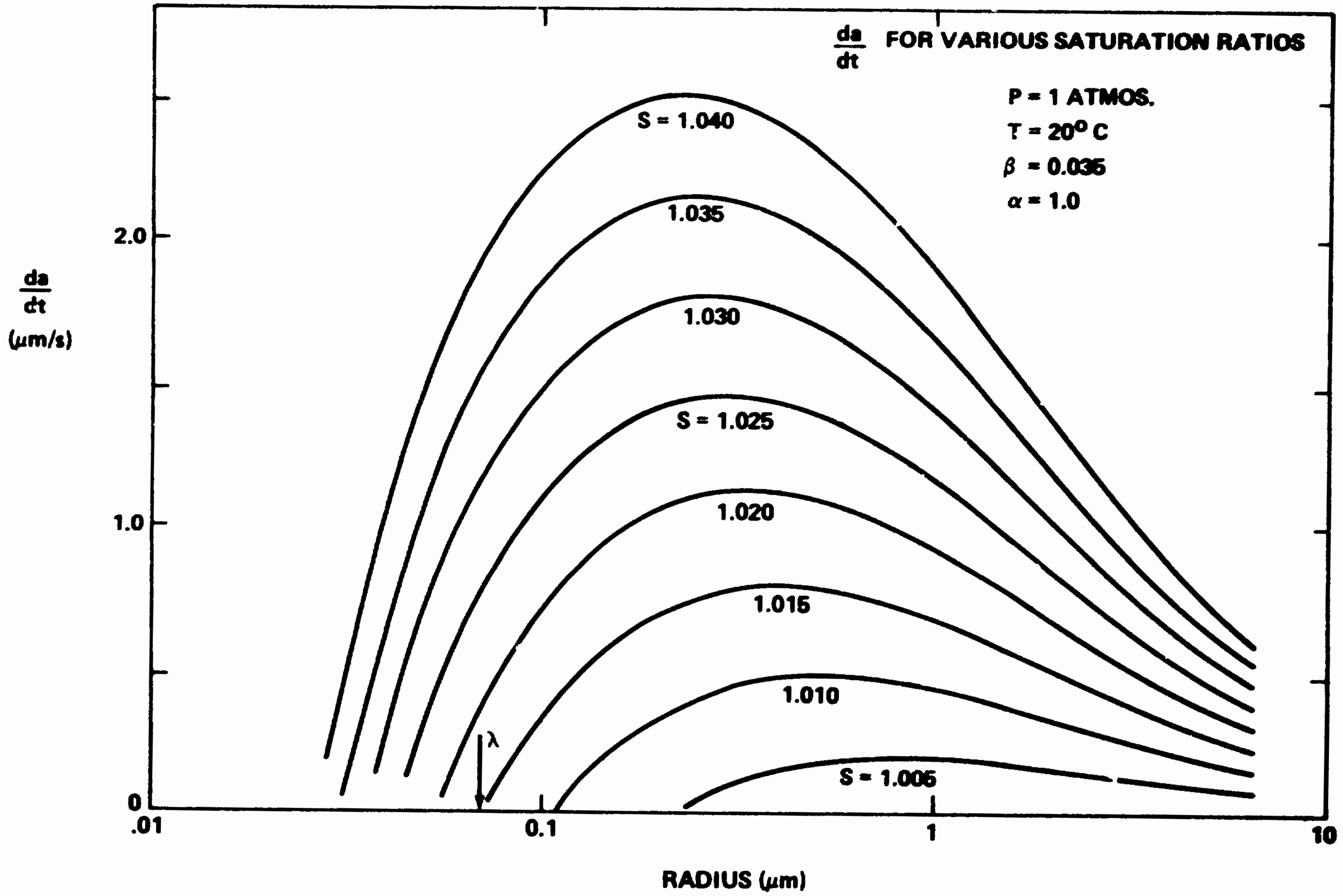

Figure 6. Radial growth rate for a pure water drop as a function of radius, shown for various values of ambient saturation ratio.

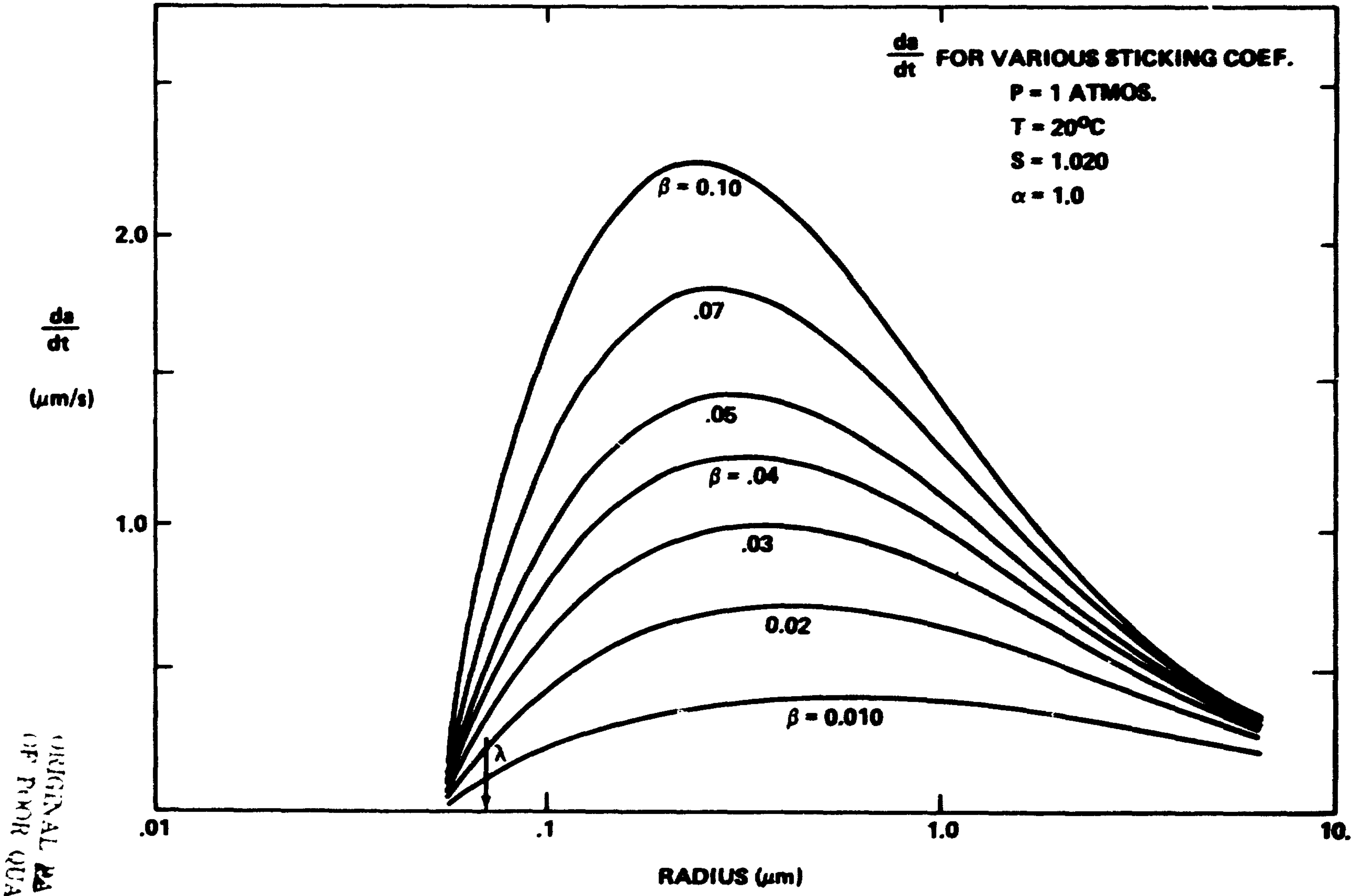

Figure 7. Radial growth rate for a pure water drop as a function of radius, shown for various values of the sticking coefficient, β.

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IV. COMPARISON WITH EARLIER STUDIES

Sorting out the differences in the notation, assumptions, and lines of reasoning which were used in the various prior treatments of this problem is a difficult and generally profitless enterprise because the differences are often quite subtle and not verifiable by experiment. Thus, a comparison of this type will not be attempted in this report. However, it was noticed in the course of this research that several of the more recent and widely used expressions for the droplet growth rate could easily be derived using the line of reasoning presented here – with appropriate changes in the initial assumptions. Thus, it becomes an easy matter to evaluate the differences among these formulations. It is these cases which are discussed in this section.

Consider first the solution presented by Fukuta and Walter in 1970 [14]. It differs from the solution presented here in two aspects: (1) the terms $- R_w \rho_\infty T_\infty / P$ and $DL\rho_\infty / KT_\infty$ in our expression (37) for "B" and (2) $A(a/\lambda) = 1/2$ rather than the integral, equation (8), presented here. The additional two terms in the expression for "B" in the solution presented here derive from the use of equation (24), the basic formulation of Fick's law of diffusion in terms of the mole fraction rather than the approximate formulation in terms of the vapor density gradient. The propriety of using the mole fraction formulation was pointed out by Feard and Pruppacher [22] and Carstens [18]; its influence on the growth rate is illustrated by Figure 8. The second condition, substituting 0.5 for the value of the integral is equivalent to using the large radius limit. As Figure 1 illustrates, $A(a/\lambda)$ approaches to within 10 percent of this value by the time a/λ reaches six. Since the Fukuta and Walter solution is limited to $a >> \lambda$ by their method of derivation, the solution presented here can be viewed as an extension of their work to small drop sizes. However, it is perhaps more revealing to note that making the assumption that the vapor density and temperature are constant near the drop, i.e., $\rho(R) = \rho_a$ in place of equation (6) and $T(R) = T_a$ in place of equation (13), yields $A(a/\lambda) = 1/2$ directly. Thus, the Fukuta and Walter solution fails to account for the vapor density gradient near the drop which, it turns out, is not important unless $a < 6\lambda$. Figure 9 illustrates the absolute value of the total difference between the two solutions.

Another solution which is closely related to the Fukuta and Walter formulation is the one developed by Rooth [12]. Rooth's solution is equivalent to equation (27) if one sets $A(a/\lambda) = 1/2$ and drops the two terms discussed in the preceding paragraph. Rooth considered only mass transport and ignored the heat transport portion of the problem. Thus, his solution and others similar to it can be applied when the drop temperature is known independently, as when the drops are resting on a surface or suspended from a thermocouple. As far as the treatment of the mass transport problem is concerned, the Rooth solution is equivalent to the Fukuta and Walter treatment; therefore, the same comments apply to both.

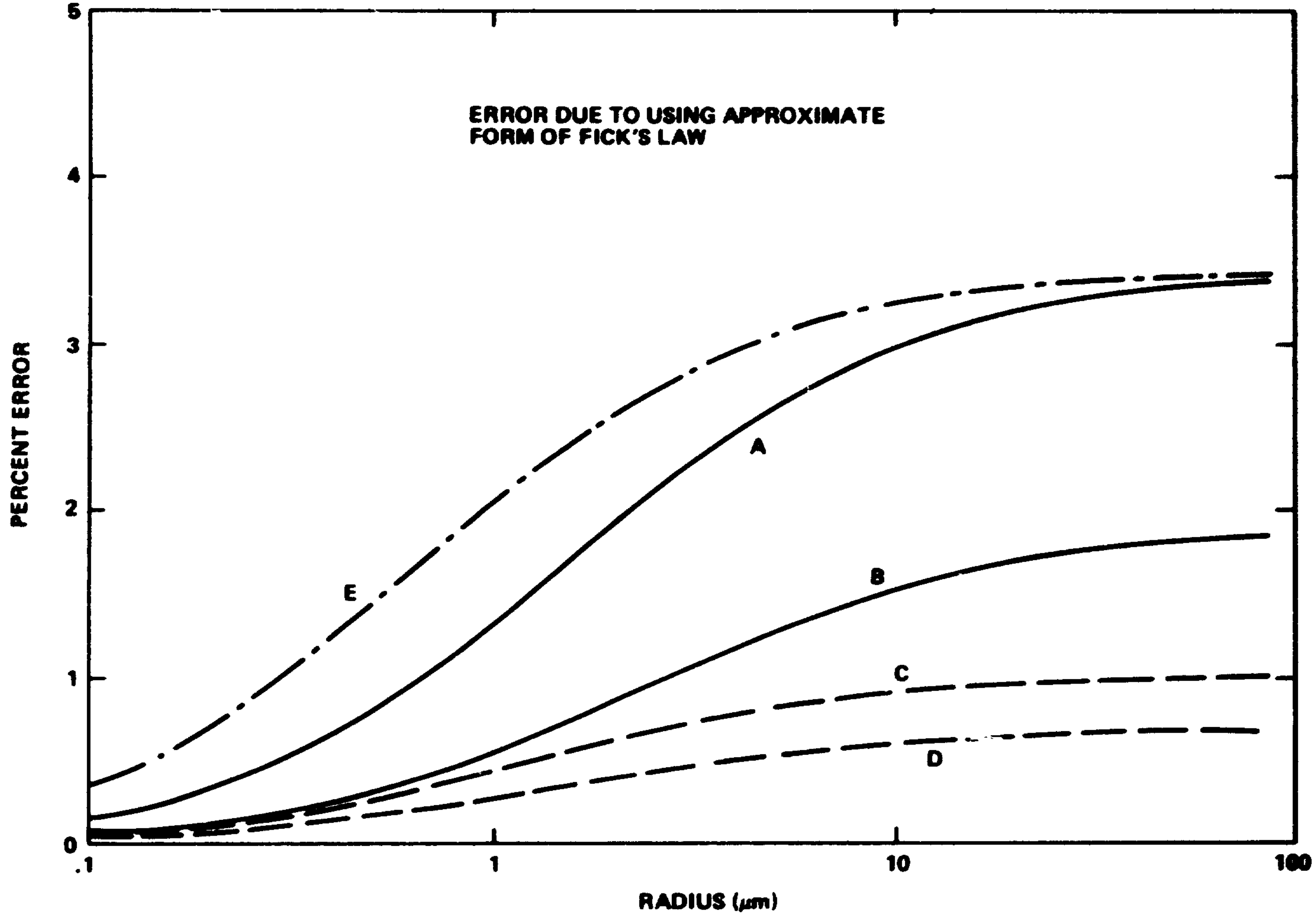

Figure 8. Error in the radial growth rate caused by assuming the mass flux is proportional to the vapor density gradient rather than the mole fraction gradient. Curve A is the baseline, T = 20°C, P = 1000 mb, S = 1.01, $\beta = 0.035$. Curve B shows T = 0°C; C shows P = 500 mb; D shows S = 0.20; and E shows $\beta = 0.10$.

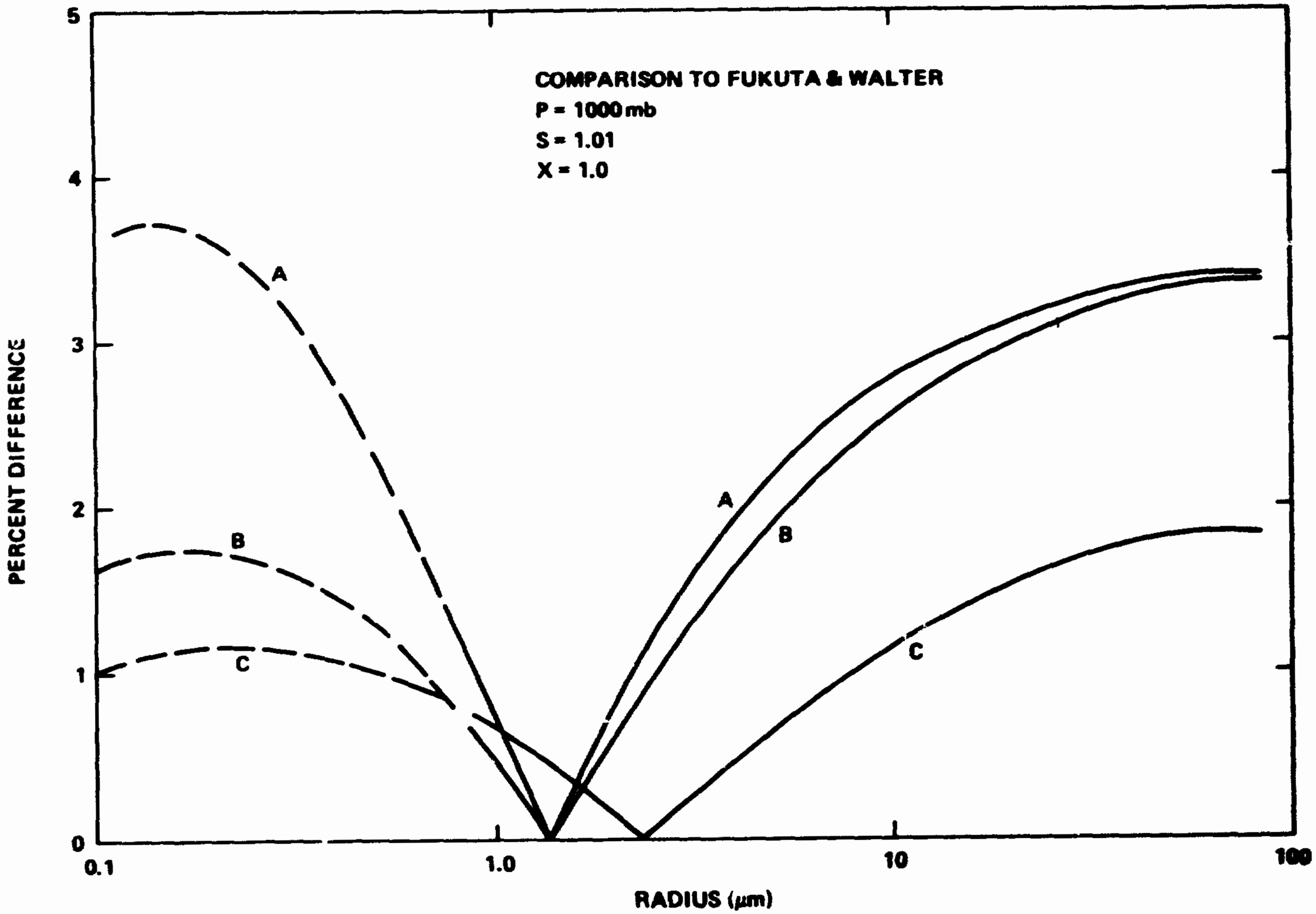

Figure 9. Absolute value of the percentage difference between the Fukuta and Walter solution and the current solution. Curve A, $\beta = 0.1$, T = 20°C; Curve B, $\beta = 0.035$, T = 20°C; Curve C, $\beta = 0.035$, T = 0.0 C. The curves are dashed below 1.0 μm because the Fukuta and Walter solution was not intended to apply in this region.

A third formulation which is widely used and is also closely related to the Fukuta and Walter work was developed by Carstens [17,18]. Carstens employed a classical kinetic theory approach from Kennard [23] to account for the temperature and vapor density gradient near the drop. The method presented here yields the Carstens solution if one replaces equation (6), the solution of Laplace's equation near the drop, with an expression of the form

$$\rho(R) = \rho_a + R \cos\theta \left.\frac{d\rho}{dR}\right|_a \quad , \tag{40}$$

and likewise for the temperature field. This is equivalent to considering a flat water surface and a one-dimensional variation in vapor density when deriving the boundary conditions. Thus, Carstens fails to correctly account for the spherical geometry near the drop. In his second paper [18] he works from the mole fraction formulation of Fick's law, but he makes approximations so the the "mole fraction" terms do not appear in his equivalent of our "B", equation (37). The droplet growth solution developed by Monchick and Reiss [7] bears the same relationship to the Carstens solution as the Rooth solution does to Fukuta and Walter. Thus, the preceding comments apply to it as well.

The difference between Carstens' work and the solution presented here can be evaluated by considering the second-order approximation to the value of $A(a/\lambda)$ presented in the Appendix, equation (A-5). For $a/\lambda > 3$ the three exponential and exponential integral terms provide a negligible contribution and one has

$$A(a/\lambda) \simeq 1/2 - \lambda/3a \quad . \tag{41}$$

Making use of the classical kinetic expressions $D = \bar{c}\lambda/3$ and $K = \frac{5}{2} \epsilon\eta R_a$ where η is the viscosity $(1/3\ \rho_g\bar{c}\lambda)$ and ϵ is a numerical constant between 1 and 2.57, depending upon the mathematical analysis (see Loeb, [19] pp. 245, 441), one quickly obtains

$$\lambda_1 = (3D/4)\sqrt{2\pi/R_w T} \tag{42}$$

and

$$\lambda_2 = \frac{3K}{10\ \epsilon\rho_g R_a} \sqrt{2\pi/R_a T} \quad . \tag{43}$$

Thus, one can write

$$A(a/\lambda) \simeq 1/2 - 4D/a \sqrt{2\pi/R_w T} \qquad (44)$$

and, choosing $\varepsilon = 1.2$,

$$A(a/\lambda) \simeq 1/2 - \frac{K}{12 R_a \rho_g a} \sqrt{\frac{2\pi}{R_a T}} \quad . \qquad (45)$$

Substituted into equations (37) and (38), respectively, these equations yield the Carstens solution. Equation (42) is an expression for the mean free path of the water vapor molecules, while equation (43) refers to the air.

Relations (42) and (43) can also be used to aid intercomparisons of the solution presented here with those developed by Fuchs [9], Bradley et al. [10] and others that leave the final expression written in terms of λ or Δ, the "jump distance" which is not defined analytically in the solution. Consider, for example, the well-known Fuchs solution [9]. Fuchs considers the vapor and heat transport problems separately and does not combine the two, so we compare with our expression (27). Fuchs' expression (5.6) in our notation is

$$\frac{dm}{dt} = \frac{4\pi a D(\rho_{sat} - \rho_\infty)}{\left(\frac{a}{a + \Delta} + \frac{D}{\beta a}\sqrt{\frac{2\pi}{R_w T}}\right)}$$

$$= \frac{4\pi a D(\rho_{sat} - \rho_\infty)}{2A_F\left(1 + \frac{D}{\beta a A_F}\sqrt{\frac{2\pi}{R_w T}}\right)} ,$$

if one defines $A_F = 1/2 - \frac{\Delta}{2(a+\Delta)}$, which compares to our $A(a/\lambda)$. Fuchs argues, based on analogy with heated filament work, that $\Delta = \varepsilon\lambda$ where ε is a number greater than one for small drops. This does not appear correct in light of the present analysis which shows that Laplace's equation for the thermal field is obeyed to within a few percent even for rapidly growing or evaporating drops. The problems associated with the sharp temperature differences near a hot filament do not enter the analysis. Fuchs notes that $\varepsilon \to 2/3$ for large drops, so in this case

$$A_F \simeq 1/2 - \lambda/3a = 1/2 - 4D/a \sqrt{2\pi/R_w T} \quad .$$

This is, again, equation (44). Thus, for large drops the Fuchs solution reduces to the Carstens, Monchick and Reiss solution. As discussed previously, it differs in the presence of the two terms related to the use of the mole fraction gradient form of Fick's Law and in the value of $A(a/\lambda)$.

V. CONCLUSIONS

In this report a solution for the growth of water droplets under quasistatic conditions is presented which is accurate to within the basic limitations of classical kinetic theory, approximately 3 percent. The analysis is based on the concept that the diffusion field and thermal conduction field are continuous right to the drop surface; there are no abrupt changes in the properties of the media in the near vicinity of the drop. The validity of this concept is verified by the analysis for essentially all circumstances of interest in the atmosphere; that is, that "quasistatic" approximation implies that the temperature and vapor density fields near the drop are Laplacian to within an accuracy of just over 1 percent or better. For a drop evaporating in a very dry environment, the vapor field is non-Laplacian to an amount approximately equal to the dew point depression divided by the absolute temperature, i.e., a figure which could reach 10 percent.

The theory presented here is rigorous within the limitations of the classical kinetic theory. Thus, no approximations have been made which would cause a deterioration in the accuracy beyond the few percent level. The solution is applicable to drops small compared to the mean free path as well as to large drops; thus, it represents an improvement over the previous theories which required that the drop radii be large compared to λ.

Numerical evaluation and study of the differences which exist between this and previous theories reveal that the differences are not significant in most cases. Indeed, since it appears that the state of the art limits the precision of growth rate measurements of small drops to something in excess of 10 percent and that α and β are poorly known quantities, separation of the theories does not appear possible based upon experiment. Numerical evaluation shows that the solution presented here lies between the Carstens and the Fukuta and Walter formulations, and even for $a \simeq \lambda$ the solutions do not diverge by more than 7 percent. Thus, it appears that the differences in handling the physical assumptions which gave rise to the many different formulations in the literature are not important to the applied problem.

APPENDIX

EVALUATION OF THE INTEGRAL, A(a/λ)

If we write s for a/λ and t for r/a, then equation (8) in the text becomes

$$A(s) = s \int_0^\infty \int_0^{\pi/2} \frac{e^{-st} \sin\theta \cos\theta}{(1 + 2t \cos\theta + t^2)^{1/2}} \, d\theta \, dt \quad ,$$

and one integration yields

$$A(s) = \frac{s}{3} \int_0^\infty e^{-st} \left(\frac{(1 + t^2)^{3/2} - 1}{t^2} - t \right) dt \quad .$$

According to the Binomial Theorem,

$$\frac{(1 + t^2)^{3/2} - 1}{t^2} = \begin{cases} \displaystyle\sum_{n=0}^{\infty} \frac{3(1) \; . \; . \; . \; (3 - 2n)}{2(4) \; . \; . \; . \; (2 + 2n)} \, t^{2n} & \text{for } 0<t<1 \\[2ex] \displaystyle t - \frac{1}{t^2} + \sum_{n=0}^{\infty} \frac{3(1) \; . \; . \; . \; (3 - 2n)}{2(4) \; . \; . \; . \; (2 + 2n)} \, \frac{1}{t^{2n + 1}} & \text{for } 1<t \end{cases}$$

and, hence,

$$A(s) = \frac{s}{3} \left[\int_0^1 e^{-st} \left(\frac{(1 + t^2)^{3/2} - 1}{t^2} - t \right) dt + \int_1^\infty e^{-st} \left(\frac{(1 + t^2)^{3/2} - 1}{t^2} - t \right) dt \right]$$

$$= \frac{s}{3} \left(\sum_{n=0}^{\infty} \frac{3(1) \; . \; . \; . \; (3 - 2n)}{2(4) \; . \; . \; . \; (2 + 2n)} \int_0^1 e^{-st} \, t^{2n} \, dt - \int_0^1 e^{-st} \, t \, dt \right.$$

$$-\int_1^\infty \frac{e^{-st}}{t^2}\,dt + \sum_{n=0}^\infty \frac{3(1)\ .\ .\ .\ (3-2n)}{2(4)\ .\ .\ .\ (2+2n)} \int_1^\infty \frac{e^{-st}}{t^{2n+1}}\,dt \Bigg) \quad ,$$

or, with some combination of terms,

$$A(s) = -\frac{s}{3}\left(\int_0^1 e^{-st}\,t\,dt + \int_1^\infty \frac{e^{-st}}{t^2}\,dt\right)$$

$$+\frac{s}{3}\sum_{n=0}^\infty \frac{3(1)\ .\ .\ .\ (3-2n)}{2(4)\ .\ .\ .\ (2+2n)}\left(\int_0^1 e^{-st}\,t^{2n}\,dt + \int_1^\infty \frac{e^{-st}}{t^{2n+1}}\,dt\right) \quad . \tag{A-1}$$

Now, if we let

$$\psi(s,n) = \int_0^1 e^{-st}\,t^{2n}\,dt + \int_1^\infty \frac{e^{-st}}{t^{2n+1}}\,dt \quad , \tag{A-2}$$

whenever n is non-negative and s is positive, (A-1) may be written as

$$A(s) = -\frac{s}{3}\,\psi\left(s, \frac{1}{2}\right) + \frac{s}{3}\sum_{n=0}^\infty \frac{3(1)\ .\ .\ .\ (3-2n)}{2(4)\ .\ .\ .\ (2+2n)}\,\psi(s,n) \quad ,$$

or, with the first two terms interchanged,

$$A(s) = \frac{s}{2}\,\psi(s,0) - \frac{s}{3}\,\psi(s,\tfrac{1}{2}) + \frac{s}{2}\sum_{n=1}^\infty \frac{1(-1)\ .\ .\ .\ (3-2n)}{4(6)\ .\ .\ .\ (2+2n)}\,\psi(s,n)$$

$$= \frac{s}{2}\,\psi(s,0) - \frac{s}{3}\,\psi(s,1/2) + \frac{s}{8}\,\psi(s,1) - \frac{s}{48}\,\psi(s,2) + \ .\ .\ .\ \quad . \tag{A-3}$$

In view of (A-2), we see that

$$0 < \psi(s,n) < \begin{cases} \displaystyle\int_0^1 t^{2n} dt + \int_1^\infty \frac{1}{t^{2n+1}} dt = \frac{1}{2n+1} + \frac{1}{2n} < \frac{1}{n} \\ \displaystyle\int_0^1 e^{-st} dt + \int_1^\infty e^{-st} dt = \frac{1}{s} \end{cases}$$

and that

$$\frac{\partial\psi(s,n)}{\partial n} = \int_0^1 e^{-st} t^{2n} (2 \ln t) dt + \int_1^\infty \frac{e^{-st} (-2 \ln t)}{t^{2n+1}} dt < 0 \quad .$$

Thus, $\psi(s,n)$ decreases steadily to zero as n increases and, since the multipliers in (A-3) also decrease in magnitude, it is clear that (A-3) is a convergent alternating series. Moreover, each partial sum is an upper or lower bound for A(s) depending on whether the number of terms included is odd or even. For example:

$$0 < A(s) < \frac{s}{2} \psi(s,0) \quad ,$$

$$\frac{s}{2} \psi(s,0) - \frac{s}{3} \psi\left(s, \frac{1}{2}\right) < A(s) < \frac{s}{2} \psi(s,0) - \frac{s}{3} \psi\left(s, \frac{1}{2}\right) + \frac{s}{8} \psi(s,1) \quad ,$$

and so on.

The following well-known formulas may be verified by successive integration by parts for $s > 0$ and $n \geq 0$:

$$\int_0^1 e^{-st} t^n dt = \frac{n!}{s^{n+1}} \left(1 - e^{-s} \sum_{n=0}^{\infty} \frac{s^k}{k!}\right) \quad ,$$

$$\int_1^\infty e^{-st} t^n dt = \frac{n!}{s^{n+1}} e^{-s} \sum_{n=0}^{\infty} \frac{s^k}{k!} \quad .$$

and

$$\int_1^\infty \frac{e^{-st}}{t^{2n+1}}\,dt = \frac{(-1)^{n-1}\,s^{n-1}}{(n-1)!}\left(E_1\,(s) - e^{-s}\sum_{k=0}^{n-2}\frac{(-1)^k\,k!}{s^{k+1}}\right) ,$$

where

$$E_1(s) = \int_s^\infty \frac{e^{-t}}{t}\,dt = \int_1^\infty \frac{e^{-st}}{t}\,dt \quad .$$

We use these and equation (A-2) to obtain the alternative form

$$\psi(s,n) = \frac{(2n)!}{s^{2n+1}}\left(1 - e^{-s}\sum_{k=0}^{2n}\frac{s^k}{k!}\right) + \frac{(-1)^2 n\,s^{2n}}{(2n)!}\left(E_1(s) - e^{-s}\sum_{k=0}^{2n-1}\frac{(-1)^k\,k!}{s^{k+1}}\right) .$$

In particular, using $A_n(s)$ to denote the sum of the first n terms of equation (A-3), we have

$$A_1(s) = \frac{s}{2}\,\psi(s,0) = \frac{1}{2} - \frac{1}{2}\,e^{-s} + \frac{s}{2}\,E_1\,(s) \quad , \qquad \text{(A-4)}$$

$$A_2(s) = A_1(s) - \frac{s}{3}\,\psi(s,1/2) = \frac{1}{2} - \frac{1}{3s} - \left(-\frac{1}{3s} + \frac{1}{6}\right)e^{-s} + \left(\frac{s}{2} + \frac{s^2}{3}\right)E_1(s) - \frac{s}{3}\,e^{-s} \quad , \qquad \text{(A-5)}$$

$$A_3(s) = A_2(s) + \frac{s}{8}\,\psi(s,1) = \frac{1}{2} - \frac{1}{3s} + \frac{1}{4s^2} - \left(\frac{1}{4s^2} - \frac{1}{12s} + \frac{7}{24}\right)e^{-s} \tag{A-6}$$

$$+ \left(\frac{s}{2} + \frac{s^2}{3} + \frac{s^3}{16}\right) E_1(s) - \left(\frac{13s}{48} + \frac{s^2}{16}\right) e^{-s} \quad .$$

Substitution of a/λ for s shows that equation (9) is the same as $A_2(s)$. By taking higher values for n, we can obtain approximations for A(s) to any desired degree of accuracy. For example, $A_5(1) = 0.31933$. $A_6(1) = 0.31920$, and we see that $A_5(1)$ can be in error by no more than about 1/10 of 1 percent. Also, it can be shown that, if n is positive,

$$\lim_{s \to 0} s^n E_1(s) = \lim_{s \to \infty} s^n E_1(s) = 0 \tag{A-7}$$

and, consequently, the formulas for $A_1(s)$ and $A_2(s)$ are sufficient to imply that

$$\lim_{s \to 0} A(s) = 0 \text{ and } \lim_{s \to \infty} A(s) = \frac{1}{2} \quad . \tag{A-8}$$

The numerical value of $A_3(s)$ is illustrated graphically in Figure 1. This third-order approximation to $A(a/\lambda)$ should be more than adequate for most practical applications of this droplet growth theory.

As a by-product of the preceding derivation, we have obtained a Laplace transform of

$$\frac{(1 + t^2)^{3/2} - 1}{t^2} - t \quad .$$

Generalizations are clearly possible for some exponents other than 3/2.

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APPROVAL

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By B. Jeffrey Anderson, John Hallett
and Maurice Beesley

The information in this report has been reviewed for technical content. Review of any information concerning Department of Defense or nuclear energy activities or programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

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☆U.S GOVERNMENT PRINTING OFFICE: 1981-740-066/280