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A COMPUTATIONAL METHOD FOR DETERMINING THE GROWTH
RATES OF SALINE WATER DROPS

by

ROBERT ALEXANDER FLETCHER, 1948-

A THESIS

Presented to the Faculty of the Graduate School of the

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Approved by

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ABSTRACT

A phenomenological theory is presented which describes the growth or evaporation of cloud droplets containing dissolved NaCl. The main interest is in the early stages of growth. The Maxwell-Fuchs equation is employed with refinements to account for the high salt concentration in small droplets. A computer program is presented that calculates the growth time as a function of radius for cloud droplets nucleated with NaCl.

The growth times obtainable from the Maxwell-Fuchs equation differ significantly from the growth times calculated using the refined Maxwell-Fuchs equation for ambient relative humidities less than or equal to 100%. Growth times for droplets nucleated by NaCl crystals of mass greater than or equal to 10^{-10} grams should be calculated by the refined equation presented here for virtually all ambient vapor densities.

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TABLE OF CONTENTS

ABSTRACT.....	ii
ACKNOWLEDGEMENT.....	iii
LIST OF TABLES.....	v
I. INTRODUCTION.....	1
II. REVIEW OF LITERATURE.....	3
A. The Equilibrium Vapor Pressure of a Drop.....	3
B. Temporal Considerations of Droplet Growth.....	10
III. RESULTS.....	21
A. Early Stages of Growth.....	21
B. Discussion of Data.....	24
IV. CONCLUSION.....	27
BIBLIOGRAPHY.....	29
VITA.....	31
APPENDICES.....	32
A. Computer Program.....	32
B. Alphabetical List of Variables and Constants in Program.....	45
C. Explanation of Computer Program.....	48

LIST OF TABLES

TABLES

- I Comparison of growth times varying surface tension, solution density, and compensated transport coefficient for NaCl crystalline mass of 10^{-4} grams.....51
- II Comparison of growth times varying surface tension, solution density, and compensated transport coefficient for NaCl crystalline mass of 10^{-10} grams.....52
- III Comparison of growth times varying surface tension, solution density, and compensated transport coefficient for NaCl crystalline mass of 10^{-16} grams.....53

I. INTRODUCTION

The present work provides a method for calculating the growth rate of water drops nucleated by sodium chloride crystals. Droplet growth is considered as a steady state diffusion process with heat transfer by means of conduction. Near the drop's surface a diffusion-kinetic* condition is adopted instead of either the thermal equilibrium condition employed in the Maxwell-Fuchs theory or the "annihilation" condition of Smirnov (2). This diffusion-kinetic condition is incorporated into the Maxwell-Fuchs equation for drop growth by "compensating" the transport coefficients.**

This modified Maxwell-Fuchs equation is integrated so that time of growth can be calculated as a function of drop radius explicitly and implicitly through the equilibrium vapor pressure and compensated coefficients.

The initial mathematical treatment of the equilibrium vapor pressure of a water drop nucleated by NaCl was by Kohler and Wright (4). The equation which they developed expresses the ratio of the equilibrium vapor pressure of a saline drop to that of a flat pure water surface in terms of the Kelvin-Thompson equation and Raoult's law. Since the

*terminology adopted by Smirnov (1) to describe a boundary condition near a drop's surface for which a diffusion expression is equated to a uniform kinetic expression

**see Carstens (3)

development of the Kohler equation, a number of workers (Cinkotoi (5), Low (6), and Orr, Hurd, and Corbet (7)) have recognized that, in general, large inaccuracies result from using Raoult's law during the early periods of droplet growth when high concentrations of dissolved salt are present. To account for the high salt concentration, the present writer adopts empirical water activity - salt molality equations to replace Raoult's law. Surface tension and solution density, both found in the Kelvin-Thompson expression, are rendered concentration dependent.

The growth times are calculated by an IBM 360 computer. The computer program may be used in fog and cloud studies where sodium chloride is often a nucleant and the excess vapor density is generally small, barely accommodating growth. The program may also be used for studying droplet growth in cloud chambers and other laboratory experiments.

II. REVIEW OF LITERATURE

A. The Equilibrium Vapor Pressure of a Drop

The drop equilibrium vapor pressure relates to drop growth by providing a reference state from which the growth rate can be determined once the degree of departure from equilibrium made by the ambient vapor pressure is known. Since saline drops are being examined, the equilibrium vapor pressure equation must unite two opposing effects: the solution effect which decreases equilibrium vapor pressure and the curvature effect which increases it. Kohler and Wright (4) were the first to introduce an equation that takes these two opposing effects into account. Kohler's equation and literature containing variations of it will be reviewed since mathematical representation of the equilibrium vapor pressure for a saline drop is relevant to the present work.

The Kohler equation expresses the ratio of the equilibrium vapor pressure of a saline drop to that of a pure, flat water surface by relating Raoult's law (the salt solution effect) and the Kelvin-Thompson equation (the curvature effect). Raoult's law, which specifies the equilibrium vapor pressure reduction occurring when a nonvolatile salt such as NaCl is dissolved in a volatile solvent is

$$(1.1) \quad \frac{P_{x,\infty}}{P_{1,\infty}} = x$$

where x is the mole fraction of solvent, $P_{x,\infty}$ the equilibrium vapor pressure over the solution, and $P_{1,\infty}$ the equilibrium vapor pressure over pure solvent. This expression is valid for a flat surface such as a salt solution and generally becomes increasingly less accurate as the salt concentration increases.

The curvature effect, which increases the equilibrium vapor pressure is represented by the Kelvin-Thompson equation

$$(1.2) \quad P_{x,a}/P_{x,\infty} = \exp(2M_0 \sigma / RT \rho_\ell a) = e^{B/a}$$

where a is the drop radius, $P_{x,a}$ the equilibrium vapor pressure of the solvent over a solution which has a curved surface, $P_{x,\infty}$ the equilibrium vapor pressure of the solvent over a solution which has a flat surface, M_0 the molecular weight of the solvent (water), σ the surface tension of the solution, R the ideal gas constant, T the absolute temperature and ρ_ℓ the solution density.

The combination of (1.1) and (1.2),

$$(1.3) \quad P_{x,a}/P_{1,\infty} = (x) \exp(2M_0 \sigma / RT \rho_\ell a) = (x) e^{B/a}$$

gives the ratio of the equilibrium vapor pressure over a curved salt solution, $P_{x,a}$, to that of a flat, pure water surface. An approximation given by Fletcher (8) and used frequently by meteorologists and cloud physicists alike is

$$(1.4) \quad S(a) = P_{x,a}/P_{1,\infty} = 1 + B/a - A/a^3; \quad A = \frac{16M_0}{4/3 \pi \rho_\ell M}$$

where $S(a)$ is the saturation ratio, B is defined in (1.2), M is the molecular weight of the solute, i is the Van't Hoff factor, and m is the molality. By inspection of (1.4) the solution effect dominates $S(a)$ for small drops, but as the drop grows, curvature becomes the predominate influence.

The Kohler equation can be regarded as the classical equation, but due to inadequacies at high salt concentrations other expressions have been devised. Orr, Hurd, and Corbett (7) concern themselves with the various stages of droplet growth initiated by a number of hygroscopic nuclei, one of which is NaCl. They examine the initial period of growth during which water vapor is adsorbed upon the NaCl crystalline surface and the surface in turn dissolves. It is assumed that there are three phases; aqueous solution, water vapor, and crystalline NaCl, and that these three phases are in equilibrium. They employ an equation that describes the adsorption equation of a gas onto a free surface (one void of cracks and pores) and relate this equation to drop radius assuming a spherical salt crystal. For this adsorption equation, the heat of adsorption less the heat of condensation of gas is assumed to be approximately equal to the surface energy of the solid NaCl. This assumption was made because heat of adsorption values were unavailable. They find very little change in radius during the adsorption period.

The transition period, where the solute particle

completely dissolves, is treated as well as the subsequent free growth. The liquid film surrounding the NaCl particle is assumed to be a homogeneous saturated solution at equilibrium. The vapor pressure of this film is controlled by the dissolved salt concentration and by the curvature effect. The latter is described by the Kelvin-Thompson equation, but unlike the Kohler equation the salt influence is not represented by Raoult's law. Instead

$$(1.5) \quad \ln(a_2/a_1) = \frac{\pi 2M\sigma_s}{RT\rho_s} (1/r_2 - 1/r_1) \quad (9)$$

is used to obtain the activity of the solute, a , in solution in terms of the solid solute radius, r , the surface free energy of solute, σ_s , the molecular weight of solute, M , the density of solute, ρ_s , the ideal gas constant, R , and the absolute temperature, T . A reference state is assumed such that a_1 is the activity of a concentrated solution for which r_1 is extremely large. The solution vapor pressure due to solute particle size was found from a plot of vapor pressure versus solute activity. This value represents the solute vapor pressure lowering effect and was substituted into (1.2) for $P_{x,\infty}$. Then (1.2) could be solved for the equilibrium vapor pressure of a solution drop, $P_{x,a}$. The results clearly indicated that the critical humidity, that which allows transition, decreases for decreasing solid solute particle size. The critical humidity asymptotically approaches 75% as the solid particle size increases. Orr et al. mention that 75% agrees

favorably with Twomey's experimental value of 75.5%.

Since values for the vapor pressure above 6.0 molar solutions were unknown to Orr and workers, they devised an expression from the Gibbs-Duhem relation for extending the curve

$$(1.6) \quad \ln(P_1^*/P_1) = -\int_{a_s}^{a_s^*} \frac{x_s}{a_s(1-x_s)} da_s \quad (10)$$

where P_1^* is the partial pressure of the solvent when the NaCl activity is a_s^* , P_1 the partial pressure of solvent when NaCl activity is a_s , and x_s , the mole fraction of NaCl.

The Kelvin-Thompson equation with attention paid to the solution effect describes the saline drop's growth during the period of free growth, that is, growth after transition stimulated by a supersaturated water vapor condition. This article contains good qualitative discussions on all phases of drop growth. It is also good in that it contains comparisons of experimental and calculated results, both conducted by Orr et al.

Cinkotoi's publication (5) is relevant to the Kohler description of solution drops. This work is concerned with the behavior of NaCl particles in the human respiratory tract. The Kohler equation is adopted to relate the water vapor pressure and salt concentration to drop diameter. Empirical equations, polynomials of percentage NaCl in solution by weight, are used to represent relative humidity, solution density, and surface tension and vapor pressure depression due to the dissolved salt. The last

quantity replaces Raoult's law in (1.3). There seems to be no physical explanations offered for the polynomial representations of the physical parameters.

A conflict exists between Cinkotoi's work and the Orr et al. work with respect to the relative humidity for which an NaCl particle begins to take up water vapor. Cinkotoi does not consider adsorption on free surfaces as do Orr et al. and thus finds that as the NaCl particle size goes to zero, the relative humidity approaches infinity asymptotically. As the NaCl particle size increases, the relative humidity approaches 77-78% asymptotically. Orr et al. considered adsorption and the effect that the NaCl particle size has on the vapor pressure through the nonvolatile salt effect. They found that the relative humidity necessary to dissolve an NaCl particle decreases with decreasing particle size, although appreciable growth may not take place until the ambient vapor pressure increases to comply with that value primarily dictated by the Kelvin-Thompson equation.

Low (6), like Cinkotoi, devises a replacement for Raoult's law in (1.3). However, his equation is rigorously derived from modern solution chemistry. The Gibbs-Duhem equation allows Low to relate the NaCl molality and activity coefficient to the water activity which in turn replaces Raoult's law. Low's work contains a rather extensive table of water activities and calculated Van't Hoff factors for salt molalities ranging from 0.1 to 6.0.

This is done for various electrolytes one of which is NaCl.

Keith and Arrons (11) derive an equation which determines growth time as a function of drop radius. This equation is derived without employing (1.3), although saline drops are being studied. Growth takes place by vapor condensation, the molecules being transferred to the surface by diffusion. Thermal energy is removed by conduction. The ideal gas law and the Clapeyron equation are employed to relate the pressure, vapor density, and change in pressure as a result of thermal fluctuations. The vapor pressure depression due to the dissolved salt is depicted by an empirical equation. Another empirical equation is assumed for saturated salt solutions common to the embryonic stages of growth. Keith and Arrons recognize that equilibrium radii calculated by their equations are, in general, slightly smaller than those predicted by (1.3). They attribute the difference to the fact that (1.3) employs Raoult's law, but overlook the contribution that curvature makes to (1.3). The authors find favorable agreement with their own experimental results discussed fully in the same work.

Orr, Hurd, and Corbett have by far the most detailed description of the physical processes through which the salt particle adsorbs water, develops into a solution drop, and grows to equilibrium size. Their analysis through the transition period contains rather startling results. They find that the NaCl crystal size determines the equilibrium

vapor pressure because of the nonvolatile salt effect. Thus dissolution of small NaCl crystals can occur for much smaller relative humidities than generally suggested by the other works reviewed. After transition, the drop will not grow unless the ambient vapor pressure exceeds the elevated equilibrium vapor pressure resulting from the drop's high degree of curvature expressed by the Kelvin-Thompson equation.

B. Temporal Considerations of Droplet Growth

An equation will be derived which expresses growth time as a function of drop radius. It will be derived from the Maxwell-Fuchs theory of droplet growth. A new boundary condition will be introduced that takes into account surface kinetics; as Carstens (12) points out, the Maxwell-Fuchs equation can be recovered by "compensating" the transport coefficients. Unless specifically stated otherwise, section B follows the Carstens report cited above.

The Maxwell-Fuchs theory assumes that droplet growth takes place by means of a steady state diffusion process and that thermal equilibrium is maintained between vapor and liquid at the drop's surface. We will be studying isolated drops that are stationary and not ventilated.

The steady state vapor field around a pure water drop may be represented by Fick's second law

$$(3.1) \quad \nabla^2 \rho = 0$$

assuming a constant diffusion coefficient. Conduction will be the only mode of heat transport and thus the temperature likewise obeys

$$(3.2) \quad \nabla^2 T = 0.$$

The solutions to (3.1) and (3.2) are:

$$(3.3) \quad \rho(r) = a/r(\rho_a - \rho_\infty) + \rho_\infty, \text{ and}$$

$$(3.4) \quad T(r) = a/r(T_a - T_\infty) + T_\infty,$$

where a is the instantaneous radius (a is less than or equal to r which is less than or equal to infinity) and the subscripts ∞ and a refer to ambient and surface values.

A steady state power balance relates the vapor density-temperature gradients,

$$(3.5) \quad K \nabla T \Big|_{r=a} + LD \nabla \rho \Big|_{r=a} = 0$$

where K and L are the thermal conductivity and latent heat of condensation respectively. Equations (3.3), (3.4), and (3.5) yield the psychrometric equation

$$(3.6) \quad \frac{\rho_a - \rho_\infty}{T_\infty - T_a} = K/LD = \gamma.$$

A linear representation of the temperature can be made for the equilibrium vapor density provided the temperature range is sufficiently narrow. Equation (3.7) represents the empirical curve with b and c constants.

$$(3.7) \quad \rho(a) = (bT + c) \Big|_a$$

By making use of mass conservation, the rate of growth is

$$(3.8) \quad \frac{d}{dt} \left(\frac{4}{3} \pi a^3 \rho_l \right) = -4\pi a^2 D \frac{\partial \rho_l}{\partial r} \Big|_{r=a}$$

where ρ_l is the liquid density and D is the diffusion coefficient of water vapor. Using (3.3), (3.6), and (3.7), equation (3.8) becomes

$$(3.9) \quad (\rho_l/2) \frac{da^2}{dt} = -D(\rho_a - \rho_\infty)$$

$$(3.10) \quad \rho_a = \rho_\infty + \Gamma T - \Gamma(\rho_a - c)/b$$

$$(3.11) \quad \rho_a = \frac{\rho_\infty}{1+\Gamma/b} + \frac{bT_\infty+c}{1+b/\Gamma}$$

$$(3.12) \quad \rho_a - \rho_\infty = (1 - S) \rho_{eq}(\infty) / (1+b/\Gamma).$$

Equation (3.8) can finally be expressed as

$$(3.13) \quad \frac{da^2}{dt} = \frac{2(S-1)\rho_{eq}(\infty)/\rho_l}{1/D + Lb/K} = \frac{2(S-1)\rho_{eq}(\infty)/\rho_l}{1/D_{eff}}$$

where $1/D_{eff} = 1/D + Lb/K$. D_{eff} , the effective diffusion coefficient, is the sum of two resistances to growth,

$$(3.14) \quad 1/D_{eff} = R_{eff} = R_{mass} + R_{heat}.$$

Equation (3.13) is the differential form of the growth equation. It can easily be written to give $t(a)$ or $a(t)$. We wish to propose that although (3.13) includes the fundamental processes that take place in drop growth, the theory is too naive and not entirely correct. Clearly equilibrium cannot exist at the surface since nonequilibrium is necessary for growth or evaporation. A better boundary condition, one

that does not imply equilibrium, is a net rate condition in which the flux would be analyzed at or near the drop's surface.

Smirnov (13) derives a growth rate equation from an analysis of net rates. Smirnov's work is presented because it represents a more rigorous treatment of the growth problem than the conventional theory used by meteorologists and provides a basis for comparison to the latter. The following assumptions apply to Smirnov's model: (1) we are dealing with a grey sphere, that is, one which absorbs and emits particles of the same kind; (2) the movement of particles is mutually independent. From assumption (2) particle concentration, n , and flux intensities, I , are

$$(3.15) \quad n = n_0 + n_r + n_e, \quad I = I_0 + I_r + I_e$$

where n_0 is the concentration of particles that have never collided with the sphere, n_r have collided one or more times, and n_e is the concentration emitted by the sphere. The incident intensities will be denoted by M_i and the reflected by R_i . Here i means the number of ineffective collisions that occurred. For example, M_2 would be the incident flux of particles that collided twice but have not been absorbed. Relations between incident and reflected flux are

$$(3.16) \quad R_{i+1} = -(1-\beta)M_i; \quad M_j = -AR_j; \quad n_j = R_j\phi(\epsilon)$$

where A is the fraction of particles returning to the sphere after at least one collision. $\phi(\xi)$ is a radially dependent function yet to be determined, and both β and A are less than one. Clearly,

$$(3.17) \quad n_r = \sum_{i=1}^{\infty} n_i = \sum_{j=1}^{\infty} R_j \phi(\xi)$$

with $R_{j+1} = A(1 - \beta)R_j$ and $\beta =$ fraction of particles that are condensed. The concentration that has collided one or more times becomes

$$(3.18) \quad n_r = \frac{R_1 \phi(\xi)}{1 - A(1 - \beta)} = \frac{(1 - \beta)M_0 \phi(\xi)}{1 - A(1 - \beta)}$$

by using the sum for a geometric progression. The total flux intensity of a non-emitting sphere is

$$(3.19) \quad I = I_0 + I_r = (M_0 \beta) / (1 - A(1 - \beta))$$

since $I_0 = M_0$, $I_r = \sum_{i=1}^{\infty} M_i + \sum_{i=1}^{\infty} R_i$, and $M_{i+1} = A(1 - \beta)M_i$. By assuming uniform kinetic theory as β goes to zero, for the flux intensity

$$(3.20) \quad \lim_{\beta \rightarrow 0} \frac{M_0 \beta}{1 - A(1 - \beta)} = \pi a^2 v \beta n_{\infty} .$$

A can be determined. $\phi(\xi)$ can be found by noting that as β goes to 0, n goes to n_{∞} , where n_{∞} is the concentration as ξ goes to ∞ , v the velocity, and a the sphere's radius. The total flux intensity for an emitting sphere can be found by assuming at $\xi = \infty$

$$(3.21) \quad I = I_0 + I_r + I_e = 0$$

$$(3.22) \quad n = n_o + n_r + n_e = n_s ,$$

n_s being a constant. The relations (3.19) to (3.22) insure that the final form of the flux will be dependent on M_o , the incident flux.

The incident flux is assumed to be the flux of a black sphere, one that neither reflects nor emits. The treatment for a black sphere by Smirnov is one found in neutron transport theory. The following assumptions are made: (1) the particles move randomly in an infinite medium; (2) scattering off the particles that make up the medium is isotropic; (3) the velocity magnitude (v) is constant and makes an angle $\theta, \theta+d\theta$ with the position vector, ξ . The distribution function $\psi(\xi, \mu)$ satisfies the steady state Boltzman equation

$$(3.23) \quad \mu \frac{\partial \psi}{\partial \xi} + \frac{1-\mu^2}{\xi} \frac{\partial \psi}{\partial \mu} = -\psi / \ell + (1/2\ell) \int_{-1}^1 \psi(\xi, \mu') d\mu'$$

where $\mu = \cos \theta$, $\psi(\xi, \mu) dv \sin \theta d\theta$ is the mean number of particles in volume element $dv = 4\pi \xi^2 d\xi$, and ℓ is the mean free path of particles being absorbed. The boundary conditions for (3.23) are

$$(3.24) \quad \psi(\xi, \mu) = \psi_{\infty} = \text{constant}, \quad \psi(a, \mu) = 0, \quad 0 \leq \mu \leq 1$$

for a as the sphere's radius. The concentration and flux intensity for a unit area are

$$(3.25) \quad n = \int_{-1}^1 \psi(\xi, \mu) d\mu; \quad j = v \int_{-1}^1 \psi(\xi, \mu) \mu d\mu .$$

A "diffusion approximation" is employed for

$$(3.26) \quad \psi_d = \psi_0(\xi) + a(\xi) \mu$$

$$(3.27) \quad \psi_d = \psi_\infty - c/\xi - c\mu/\xi^2, \quad n_d = n_\infty - 2c/\xi$$

by substitution of (3.26) into (3.23). By defining

$$(3.28) \quad \lambda = n_d / \left(\ell \frac{dn_d}{d\xi} \right) \Big|_{\xi=a}$$

as the extrapolation length, the unit concentration and flux become:

$$(3.29) \quad n_d = n_\infty \left(1 - \frac{a}{\xi(1 + \lambda K_N)} \right); \quad j = \frac{-v \ell a n_\infty}{3\xi^2(1 + \lambda K_N)} = -D \frac{dn_d}{d\xi}$$

where K_N is the Knudsen number defined as $K_N = \ell/a$. $D = v\ell/a$ is the diffusion coefficient. Thus the flux intensity on the black sphere is

$$(3.30) \quad I = M_0 = (4\pi D r n_\infty) / (1 + K_N \lambda).$$

Returning to the grey sphere, Smirnov solves for A , ϕ , I_e , and n_e and finds that the net flux intensity on the grey sphere is

$$(3.31) \quad I = 4\pi D r (n_\infty - n_g) / (1 + \lambda(\beta) K_N)$$

where $\lambda(\beta) = \lambda + 4/3\beta - 4/3$ (which results from solving for A). Then by using the ideal gas law

$$(3.32) \quad \frac{dm}{dt} = 4\pi D r \frac{(\rho_{v,\infty}/T_\infty - \rho_g/T_g)}{R/M_v(1 + \lambda(\beta) K_N)}$$

where m is the mass of the sphere, ρ the vapor density, R

the ideal gas constant, M_v the molecular weight of condensing species, and ∞ , a , and s subscripts referring to ambient, **surface**, and equilibrium respectively.

The grey model presented by Smirnov has one fault. It is important to notice that the boundary condition (3.24) is a physical absurdity, that is, $\psi(a, \mu) = 0$ cannot be a correct condition. This is evident since

$$j = v \int_{-1}^1 \psi(a, \mu) \mu d\mu$$

means either the flux at the surface is zero which is impossible or that the velocity is infinite.

Fuchs (Smirnov (14)) was the first to suggest a better condition. It is accepted that diffusion is the appropriate transport process for all molecules sufficiently distant from the surface; the only difficulty lies in analyzing the transport process near the drop surface. Fuchs overcomes this difficulty by assuming that uniform kinetics holds for a small distance away from the immediate drop surface. This assumption, that is the employment of uniform kinetics very near the drop's surface, while not entirely plausible physically, makes the flux analysis much easier to perform. Thus the boundary condition that replaces $\psi(a, \mu)$ very near the drop surface equates the diffusive to the kinetic flux.

The approach taken in the present work follows Carstens which is the same as that of Fuchs except that temperature is included explicitly in the formulation. A sphere of

radius $a+\Delta$ encloses a sphere of radius a . Δ is of the order of a mean free path for the diffusing molecules. Flux is analyzed at $a+\Delta$ by

$$(3.33) \quad D \frac{d\rho}{dr} \Big|_{r=a+\Delta} 4\pi(a+\Delta)^2 = \text{Flux in} - \text{Flux out.}$$

The molecules leaving the drop surface and passing through the shell follow the kinetic theory and thus the flux can be described by

$$(3.34) \quad \text{Flux out} = (1/4) \beta(T_{eq}) v(T_{eq}) \rho_{eq}(T_{eq}) 4\pi a^2$$

where β is the sticking coefficient, the fraction of molecules that condense on the surface. Of course, if uniform kinetics were employed outside of $a+\Delta$, the net flux would be zero which is unsatisfactory. The net flux outside of $a+\Delta$ should be $D \frac{\partial \rho}{\partial r}$. If the flux in this region is taken to have some kinetic qualities and is described by a kinetic term plus $\pm \frac{D}{2} \frac{\partial \rho}{\partial r}$ (sign depending on flux direction), the net flux will be the desired value, $|D \frac{\partial \rho}{\partial r}|$. The molecules moving toward the drop will be described by

$$(3.35) \quad \text{Flux in} = 4\pi(T_a, T_a - T_{eq}) \left((1/4) \rho_a v(T_a) a^2 + \frac{D}{2} \frac{\partial \rho}{\partial r} \right) (a+\Delta)^2$$

when $r = a + \Delta$

The vapor jump (3.36) which is found from (3.33) shows that the vapor density

$$(3.36) \quad \rho_{\infty} - \rho_a = (\rho_{\infty} - \rho_{eq}) / \left(1 + \frac{a+\Delta}{a} \frac{\ell_{\beta}}{a} \right), \quad \ell_{\beta} = \frac{\beta \bar{v}}{4 D (1 - \beta/2)}$$

in the shell is not equal to its equilibrium value at the

drop's surface.

The Maxwell-Fuchs theory may be made to include the above by properly modifying D_{eff} in (3.13). The modification is done by equating the Maxwell-Fuchs flux to the flux described by (3.33).

$$(3.37) \quad D_{M-F}(\rho_{\infty} - \rho_{\text{eq}}(a))4\pi a = D(\rho_{\infty} - \rho_a)4\pi(a+\Delta)$$

and by (3.36),

$$(3.38) \quad D_{M-F} = D^* = D / \left(\frac{\ell_g}{a} - \frac{\Delta}{a+\Delta} + 1 \right)$$

where D^* is the compensated diffusion coefficient. A similar procedure can be carried out for the analysis of the energy flux (see Carstens (15)) and results in a compensated thermal conductivity

$$(3.39) \quad K^* = \frac{K}{1 + \frac{\ell_g - \Delta}{a}} ; \quad \ell_{\alpha} = ((\gamma-1)/(\gamma+1))(\alpha/\alpha-1)^{-1} \left(\frac{K}{IR/2} \right)$$

where $\gamma = C_p/C_v$ (the ratio of specific heats), α the accommodation coefficient -- a measure of how well the gas molecules thermally "acclimate" themselves to the surface, I the uniform kinetic flux, and R the gas constant. The compensated effective diffusion coefficient, D^*_{eff} becomes

$$(3.40) \quad 1/D^*_{\text{eff}} = 1/D^* + Lb/K^* = 1/D_{\text{eff}}(1 + \ell/a);$$

$$\ell = (\ell_g/D + \ell_{\alpha} Lb/K)D_{\text{eff}} .$$

With the incorporation of (3.40), equation (3.13) can be used to describe pure water droplet growth. The non-volatile solute influence can be incorporated into the

"driving" term $S-1$ ($S-1$ represents departure from equilibrium for pure, flat water surface). The saline drop should have the "driving" term of $S-S(a)$ where $S(a)$ is the equilibrium curve appropriate to the salt involved.

By substitution, the integral form of (3.13) becomes

$$(3.41) \quad t(a) = \left(\frac{\rho_L}{\rho_{eq}} \right) D_{eff} \int_{a_0}^a \frac{(a+l) da}{S-S(a)} .$$

It is clear that, in general, the presence of $S(a)$ defeats the inversion $t(a)$ to $a(t)$. This equation is used in the present work in a slightly altered form, one that allows us to describe drops containing large concentrations of dissolved salt.

III. RESULTS

A. Early Stages of Growth

The most important contribution of the present work pertains to the early stages of water droplet growth initiated by NaCl. Previously devised computer programs do not account for the solution effect resulting from high NaCl concentration. The present work includes a computer program that does account for the solution effects by altering $S(a)$ and D^*_{eff} in (3.37).

The corrections made to $S(a)$ will be discussed first. The Kohler equation (1.3) has been represented as a product of a curvature term (Kelvin equation) and a salt concentration term (Raoult's law). The two changes made to the curvature term are the following: (1) $e^{B/a}$ is expanded to include fourth order terms in B/a , and (2) the coefficient $B = \frac{2M_0\sigma}{RT\rho_\ell}$, normally regarded as a constant, becomes radially dependent. This dependence is due to the fact that surface tension σ and density of liquid ρ_ℓ are functions of NaCl concentration. Representing σ and ρ_ℓ as functions of molality, we have

$$(4.1) \quad \sigma = Q(T) - 0.60m$$

$$(4.2) \quad \rho_\ell = 1.0 - m/26.666$$

where $Q(T)$ is constant for constant temperature and m is the molality. The molality is defined by

$$(4.3) \quad m = \frac{\text{mass NaCl/molecular weight of NaCl}}{\frac{4}{3}\pi(a^3 - (\text{salt radius})^3)/1000g.}$$

assuming a spherical NaCl solid particle surrounded by water. Equations (4.1) and (4.2) were found by curve fitting to data found in Low's work (16).

The solution term in (1.3) is Raoult's law, a law most accurate for dilute solutions. A more general way of expressing $\frac{P_{x,\infty}}{P_{1,\infty}}$, which more accurately displays the nonvolatile solute effect over a wider range of salt concentrations, is

$$(4.4) \quad \frac{P_{x,\infty}}{P_{1,\infty}} = a_w$$

where a_w is the activity of water, $P_{x,\infty}$ the equilibrium vapor pressure over a solution having no surface curvature, and $P_{1,\infty}$ the equilibrium vapor pressure over pure water, likewise having no surface curvature.

A number of workers have performed vapor pressure measurements and have tabulated water activities at various molal concentrations of NaCl. The values found in Low (6) are probably those of Robinson and Stokes (17). This data agrees with that of Pepela and Dunlop (18) done in 1972. Both sets of data agree favorably with the International Critical Tables (19). The following empirical expressions represent the experimental a_w versus m curves for values from Low, where c_1 , c_2 , and c_3 are constants.

$$(4.5) \quad a_w = 1 - c_1 m \quad 0 \leq m \leq 1.4$$

$$(4.6) \quad a_w = 1 - c_2 m^{1/3} - c_3 m^{4/3} \quad 1.4 < m < 6.145$$

$$(4.7) \quad a_w = 0.75$$

$$m \geq 6.145$$

these equations, being entirely empirical, allow one to proceed without knowledge of van't Hoff factors and activity coefficients.

The computer program substitutes values for a_w into $S(a)$ depending on the stage of droplet growth. We may regard the molality ranges in (4.5) - (4.7) as three stages of growth. The "boundaries" are then well defined, and for a given salt mass, they correspond to drop radius, r_{boundary} , by (4.3). Thus for a given salt mass, the program compares the droplet radius, a , to r_{boundary} . Through this comparison the correct vapor pressure is assigned to $S(a)$.

The final alteration pertains to D^*_{eff} . The equilibrium vapor density - temperature curve over a flat pure water surface has a slope, let us say, b . The analogue over a pure water droplet is b_d . The two are related by

$$(4.8) \quad b_d = bS(a)$$

where $S(a) = \frac{\rho(a)}{\rho_0(\infty)}$ = (Kelvin equation)(solution term)
and $\rho_0(\infty) = bT_\infty + c$, $\rho_0(\infty)$ being vapor density of a pure flat surface and $\rho(a)$ that of a curved one. Let us omit the subscript, d , and write the b dependent terms of D^*_{eff} as

$$(4.9) \quad 1/D_{\text{eff}} = 1/D + LbS(a)/K$$

$$(4.10) \quad \lambda = (\lambda_\beta/D + \lambda_\alpha LbS(a)/K)D_{\text{eff}}$$

Noting that $S(a)/(S-S(a)) = S/(S-S(a)) - 1$, the final form of (3.41) becomes

$$(4.11) \quad t(a) = (1/(\rho_{eq}(\infty)D_{eff})) \int_{a_0}^a (a+l) da / (S-S(a)) - (1/\rho_{eq}(\infty)) ((\ell_\alpha Lb/KS)(a-a_0) + (bL/2K)(a^2-a_0^2)).$$

Equation (4.11) is the final form used in the computer program to return time of growth as a function of drop radius.

B. Discussion of Data

Tables I-III give comparisons of radially dependent effects of surface tension, solution density, and compensated transport coefficient on the growth time in equation (3.41). Columns 1-4 from left to right are the salt mass in grams, the initial radius, in centimeters, the final radius in centimeters and the saturation ratio. The values in columns 5-12 have been calculated from the following expression

$$(5.1) \quad (w,y,z) = \frac{T(w,y,z) - T(a,a,a)}{T(a,a,a)} \text{ times } 100$$

where $T(a,a,a)$ is time in equation (3.41) for which σ , ρ_ℓ , and H are all radially dependent. $H = 1/(\rho_{eq}(\infty)D_{eff})$. The notation (w,y,z) will always correspond one to one with (σ, ρ_ℓ, H) . If σ is not equal to $\sigma(a)$, $\rho_\ell = \rho_\ell(a)$ and $H=H(a)$, then $(w,y,z) = (k,a,a)$. For column twelve, Kohler means $T(w,y,z) = T_{Kohler}$, that is, the time calculated using Kohler's equation and computed using the computer techniques adopted for (3.41). The last column

represents the magnitude of time necessary for growth from AO to AF (initial to final radius).

Overall it appears that the percentage of time variation increases with decreasing salt mass. However, since the time of growth through the high salt concentration regions is much smaller for decreasing salt masses, the need for application of (4.11) is less for smaller particles. In the opinion of the author, growth times for drops with salt masses less than 10^{-10} grams, depending on the accuracy required, can be obtained from Kohler curve calculations with 50% error or less, but with little time difference as compared to (4.11) due to short growth duration. Above 10^{-10} grams, (4.11) should be used since growth times are very large even for the concentrated region.

The comparison of columns 5-12 in Tables I-III allows one to learn the relative effects of σ , ρ_l and D_{eff} on growth time. Columns 5-7 indicated that H or D_{eff} is about 10^5 times more important in controlling growth than either σ or ρ_l . This implies that thermal accommodation is the major governing factor since only the thermal parts of H and D_{eff} are radially dependent. Columns 8-10 support the theory that H is the most dominant factor of the three. A comparison of columns 11 and 12 suggests that the role of the solution terms in (4.11) becomes less effective as the radius increases, and as expected the two columns approach the same values.

It is hoped that Tables I-III illustrate that (4.11) should be employed for large salt crystals, while existing Kohler calculations suffice for small crystals.

IV. CONCLUSION

An equation that expresses growth time as a function of drop radius has been presented. This equation can be derived from the Maxwell-Fuchs theory provided the net rate diffusion - kinetic boundary condition is employed instead of the thermal equilibrium condition normally assumed and that the transport coefficients are redefined.

The growth rate is dependent upon the degree of departure from the equilibrium saturation ratio made by the ambient saturation ratio. The Kohler equation, an equation normally employed to express the equilibrium saturation ratio condition, has been altered to account for the large concentration of dissolved NaCl by making the surface tension and the solution density radially dependent. Empirical equations of water activity as a function of molality are employed instead of Raoult's law.

A comparison of the new altered equation for growth time (4.11) to an existing expression (3.41) shows that for salt crystals of mass greater than 10^{-10} grams, the new equation should be used. For crystals of salt mass less than 10^{-10} grams in an ambient S greater than or equal to 1.0 condition, it makes little difference which equation is used. However, to obtain the growth time for any NaCl particle in an atmosphere containing S less than 1.0, the result of the present work (4.11) should be employed since such drops never experience free growth or grow

to a size for which the NaCl concentration is negligible.

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VITA

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APPENDICES

A. Computer Program

```
COMPLEX * 16 T,DCMPLX
```

```
IMPLICIT * 16 T, DCMPLX
```

```
COMMON /ZANE/ WTMG,WTMV,ALPHA,BETA,PI,GAS,PR,GAMG,  
1SCALE,COFF1,COFF2,COFF3,COFF4
```

```
TER = 300.
```

```
PI = 3.14159
```

```
S=1.0001
```

```
CMS = 1.D-04
```

```
CC = 3000./(4.*PI*58.45)
```

```
ADRY=(3.*CMS/(2.165*4.*PI))**(1./3.)
```

```
ASAT=(CC*CMS/6.145+ADRY*ADRY*ADRY)**(1./3.)
```

```
ARAØLT=(CC*CMS/1.4+ADRY*ADRY*ADRY)**(1./3.)
```

```
AI=ADRY
```

```
AZ=100.*ARAØLT
```

```
CALL EMBRYØ(AI,AZ,CMS,TER,S,T)
```

```
WRITE(3,1)T
```

```
1 FORMAT(' ',*TIME=',2D14.6)
```

```
STØP
```

```
END
```

```
SUBRØUTINE EMBRYØ(AI,AZ,CMS,TER,S,T)
```

```
C TIME AS A FUNCTION OF RADIUS USING GAUSSIAN QUADRATURE
```

```
C REAL TIME
```

```
IMPLICIT REAL * 8(A-H,Ø-Z)
```

```
DØUBLE PRECISION DSQRT,DEXP
```

```
REAL * 4 X,AIMAG,ABS
```

```

COMPLEX * 16 RS(3),RT(3),T,TI,DCMPLX

EXTERNAL TIME

COMMON /TAME/ CCCMS,ADRY,ASAT,ARAØLT,CØFF1,CØFF2,
1CØFF3,CØFF4,GASTER,H,ST,CL,SURF

COMMON /SAME/ ND

COMMON /ZANE/ WTMG,WTMV,ALPHA,BETA,PI,GAS,PR,GAMG,
1SCALE,CØFF1,CØFF2,CØFF3,CØFF4

400 FØRMAT (5D14.6)

413 FØRMAT (' TRANSPØRT CØEFF: AD=',D13.6,T52,'AK=',
1D13.6//)

409 FØRMAT (' STICKING CØEFF.(BETA) =',D13.6,T52,
1'ACC.CØEFF.(ALPHA)=' ,D13.6/ ' CL=' ,D13.6//)

402 FØRMAT(' ', 'ADRY=' ,D14.6,2X, 'ASAT=' ,D14.6,2X,
1'ARAØLT=' ,D14.6,2X, 'CMS=' ,D14.6)

401 FØRMAT(' ', 'AØ=' ,D14.6,2X, 'AF=' ,D14.6,2X, 'T=' ,
12D14.6,3X, 'S=' ,D14.6)

408 FØRMAT (' TEMP=' ,D13.6,T29, 'S=' ,D14.8, T50, 'PR=' ,
1D13.6/ 'GAMG=' ,D13.6//)

405 FØRMAT(' ', ' FINAL RADIUS MUST BE LESS THAN',
12D25.16)

READ (1,400) WTMG,WTMV,ALPHA,BETA
READ (1,400) PI,GAS,PR,GAMG,SCALE
READ (1,400) CØFF1,CØFF2,CØFF3,CØFF4

PRM=PR

T=DCMPLX(0.D0,0.D0)

ST=S+2.

CC=3000./(4.*PI858.45)

CCCMS=CC*CMS

GASTER=GAS*TER

ADRY=(3.*CMS/(2.165*4.*PI))**(1./3.)

ASAT=(CC*CMS/6.145+ADRY*ADRY*ADRY*ADRY)**(1./3.)

```

```

ARAØLT=(CC*CMS/1.4+ADRY*ADRY*ADRY)**(1./3.)
WRITE(3,402)ADRY,ASAT,ARAØLT,CMS
SURF=-.144*(TER-273.16)+75.6
ADØ=.001* DSQRT (1.DO/18.02+1.DO/29.DO)
ADØ=ADØ/ (20.1**(1./3.)+12.7**(1./3.))**2
U=(GAMG-1.)/(GAMG+1.)
CØNT=SCALE*U*DSQRT(8.*PI*WTMG/GAS)/ALPHA
CØNV= DSQRT( 2.*PI*WTMV/GAS)/BETA
WRITE(3,408) TER,S,PR,GAMG
CALL VPDR (B,C,TER,RHEQ)
CALL CØEPPA(CNLAT,AK,AD,TER,PR,GAMMA,ADØ)
WRITE (3,413) AD,AK
DUM=DSQRT(TER)
CLT=AK*CØNT*DUM/PR*S
CLV=AD*CØNV/DUM
DUM=1./AD + B*CNLAT/AK*S
CL=(CLV/AD+CLT*B*CNLAT/AK)/DUM
H=RHEQ/DUM
WRITE (3,409) BETA,ALPHA,CL
SM1=S-1.
BB=(SURF*36.04)/(GAS*TER)
AA=.147*CMS
CALL DCUBIC (SM1,-BB,0.DO,AA,RT(1),RT(2),RT(3),DISC,
1IND)
CALL RTSØRT (RT,3,RS)
IF(AI-ARAØLT)6,3,3
3 AØ=AI

```

```

AF=AZ
GO TO 20
6 IF(AI-ASAT)14,10,10
10 IF(AZ-ARAOLT) 3,12,12
12 AF=ARAOLT
    AØ=AI
    GO TO 20
14 IF(AI-ADRY)15,15,19
15 AØ=ADRY
16 IF(AZ-ASAT)17,18,18
17 AF=AZ
    GO TO 20
18 AF=ASAT
    GO TO 20
19 AØ=AI
    GO TO 16
20 IF(AF-AØ)100,100,21
21 IF(S-1)22,22,24
22 X=RS(1)
    IF(X .LE. 0) GO TO 27
    IF(AF-X)27,23,23
23 WRITE(3,405)RS(1)
    GO TO 100
24 IF(ND-2)25,27,27
25 X=RS(2)
    IF(AF-X)27,26,26
26 WRITE(3,405)RS(2)

```

```

GØ TØ 100
27 A=AF
CALL DQG32(AØ,A,TIME,TI)
TI=TI-(1/RHEQ)*((CLT*B*CNLAT)/(S*AK)*(A-AØ)+
1(B*CNLAT/(2.*AK))*(A*A-AØ*A))
T=T+TI
WRITE(3,401)AØ,AF,T,S
IF(AZ-AF)100,100,38
38 IF(AZ-ARAØLT)40,45,45
40 AØ=ASAT
AF=AZ
GØ TØ 20
45 IF(AØ-ASAT)55,50,50
50 AØ=ARAØLT
AF=AZ
GØ TØ 20
55 AØ=ASAT
AF=ARAØLT
GØ TØ 20
100 CØNTINUE
RETURN
END

SUBRØUTINE DQG32(XL,XU,FCT,Y)
DØUBLE PRECISIØN XL,XU,A,B,C
CØMPLEX * 16 Y,FCT
A=.5DØ*(XU+XL)
B=XU-XL

```

$$C = .49863193092474078D0 * B$$

$$Y = .35093050047350483D-2 * (FCT(A+C) + FCT(A-C))$$

$$C = .49280575577263417D0 * B$$

$$Y = Y + .8137197365452835D-2 * (FCT(A+C) + FCT(A-C))$$

$$C = .48238112779375322D0 * B$$

$$Y = Y + .12696032654631030D-1 * (FCT(A+C) + FCT(A-C))$$

$$C = .46745303796886984D0 * B$$

$$Y = Y + .17136931456510717D-1 * (FCT(A+C) + FCT(A-C))$$

$$C = .44816057788302606D0 * B$$

$$Y = Y + .21417949011113340D-1 * (FCT(A+C) + FCT(A-C))$$

$$C = .42468380686628499D0 * B$$

$$Y = Y + .25499029631188088D-1 * (FCT(A+C) + FCT(A-C))$$

$$C = .39724189798397120D0 * B$$

$$Y = Y + .29342046739267774D-1 * (FCT(A+C) + FCT(A-C))$$

$$C = .36609105937014484D0 * B$$

$$Y = Y + .32911111388180923D-1 * (FCT(A+C) + FCT(A-C))$$

$$C = .33152213346510760D0 * B$$

$$Y = Y + .36172897054424253D-1 * (FCT(A+C) + FCT(A-C))$$

$$C = .29385787862038116D0 * B$$

$$Y = Y + .39096947893535153D-1 * (FCT(A+C) + FCT(A-C))$$

$$C = .25344995446611470D0 * B$$

$$Y = Y + .41655962113473378D-1 * (FCT(A+C) + FCT(A-C))$$

$$C = .21067563806531767D0 * B$$

$$Y = Y + .43826046502201906D-1 * (FCT(A+C) + FCT(A-C))$$

$$C = .16593430114106382D0 * B$$

$$Y = Y + .45586939347881942D-1 * (FCT(A+C) + FCT(A-C))$$

$$C = .11964368112606854D0 * B$$

Y=Y+.46922199540402283D-1*(FCT(A+C)+FCT(A-C))

C=.7223598079139825D-1*B

Y=Y+.47819360039637430D-1*(FCT(A+C)+FCT(A-C))

C=.24153832843869158D-1*B

Y=B*(Y+.48270044257363900D-1*(FCT(A+C)+FCT(A-C)))

RETURN

END

FUNCTION TIME(X)

IMPLICIT REAL * 8(A-H,Ø-Z)

COMPLEX * 16 TIME, TI

DIMENSION GB(5)

COMMON /TAME/ CCCMS,ADRY,ASAT,ARAØLT,CØFF1,CØFF2,
1CØFF3,CØFF4,GASTER,H,ST,CL,SURF

AA=X

IF(AA-ASAT)30,10,10

10 ØL=CCCMS/(AA*AA*AA-ADRY*ADRY*ADRY)

SØL1=1.-CØFF2*(ØL)**(2./3.)-CØFF3*(ØL)**(4./3.)

SØL2=1.-CØFF4*ØL

IF(AA-ASAT)30,20,15

15 IF(AA-ARAØLT)20,25,25

20 Q=SØL1

GO TO 35

25 Q=SØL2

GO TO 35

30 Q=CØFF1

ØL=6.145

35 TEN=SURF+1.6*ØL

$RH\emptyset = 1. + 0L / 26.6666$

$BB = (36.04 * TEN) / (GASTER * RH\emptyset)$

$GB(1) = ST - 2. - Q$

$GB(2) = -1. * BB * Q$

$GB(3) = -1. * BB * BB * Q / 2.$

$GB(4) = -1. * BB * BB * BB * Q / 6.$

$GB(5) = -1. * BB * BB * BB * BB * Q / 24.$

$G = GB(1) + GB(2) / AA + GB(3) / (AA * AA) + GB(4) / (AA * AA * AA) + GB(5) / (AA * AA * AA * AA)$

$TIME = (AA + CL) / (G * H)$

RETURN

END

SUBROUTINE VPDR(B,C,TE,RH)

C TE IS TEMP. IN DEGREES K; RH IS VAPOR DENSITY IN GMS/CC
C AND B AND C ARE LINEARIZATION CONSTANTS IN "RH=B*TE+C".
C RANGE: -10 TO 29 DEG. C

IMPLICIT REAL*8(A-H,Ø-Z)

DOUBLE PRECISION DEXP

$RH = 4.847D-06 * (273.16 / TE) ** 5.7373104$

$RH = RH * DEXP(6718.235 * (1. / 273.16 - 1. / TE))$

$C = RH - B * TE$

RETURN

END

SUBROUTINE COEFFA (CNLAT,AK,AD,TEK,P,GAMMA,ADØ)

C AIR WATER VAPOR; TEK IN DEGREES K, P IN DYNES PER SQ.
C CENTIMETER

IMPLICIT REAL * 8 (A-H,Ø-Z)

$AK = .1675D-06 * (TEK - 273.16) + .5725D-04$

AD=1013000.*(TEK**(7./4.))*AD/P

CNLAT=737.44-.52*TEK

GAMMA=AK/(AD*CNLAT)

RETURN

END

SUBROUTINE DCUBIC(ϕ ,U,V,W,R1,R2,R3,DISC,IND)

C ϕ ,U,V,W ARE INPUT CUBIC EQUATION COEFFICIENTS IN
C DESCENDING ORDER OF POWERS; R1,R2,R3 ARE OUTPUT ROOTS
C OF EQUATION; DISC AND IND ARE DISCRIMINANT AND INDI-
C CATOR OF TYPE OF ROOTS

IMPLICIT REAL * 8 (A-H, ϕ -Z)

COMPLEX * 16 DCMLX,R1,R2,R3,X1,X2,X3

IF(ϕ .EQ.0.) GO TO 80

P=U/ ϕ

Q=V/ ϕ

R=W/ ϕ

ϕ T=1./3.

A=(3.*Q-P*P)/3.

B=(2.*P*P*P-9.*P*Q+27.*R)/27.

D1=B*B/4.

D2=A*A*A/27.

DISC=D1+D2

S=DSIGN(1.DO,B)

IF(DISC) 10,20,30

10 PHI=DARCS(-1.*S*DSQRT(-D1/D2))

SR=2.*DSQRT(-A/3.)

X1=SR*DCOS(PHI/3.)

X2=SR*DCOS(PHI/3.+2.0944)

X3=SR*DCOS(PHI/3.+2.*2.0944)

IND=1

C IND= 1: THREE REAL UNEQUAL ROOTS

GOTO 50

20 SR=DSQRT(-A/3.)

X1=-2.*S*SR

X2=S*SR

X3=X2

IND=2

C IND=2: THREE REAL ROOTS, TWO EQUAL

GOTO 50

30 C=-B/2.+DSQRT(DISC)

D=-B/2.-DSQRT(DISC)

IF(C) 31,33,33

31 C=-1.*((-C)**DT)

GOTO 35

33 C=C**DT

35 IF(D) 37,39,39

37 D=-1.*((-D)**DT)

GOTO 40

39 D=D**DT

40 X1=C+D

C1=-X1/2.

C2=DSQRT(3.D0)/2.*(C-D)

X2=DCMPLX(C1,C2)

X3=DCMPLX(C1,-C2)

IND=3

```

C      IND=3:  ONE REAL ROOT, TWO CONJUGATE COMPLEX ROOTS
50  R1=X1-P/3.
      R2=X2-P/3.
      R3=X3-P/3.
      RETURN

80  WRITE(3,100)

100  FORMAT(' COEFFICIENT OF CUBED TERM IS ZERO; SOLVE
1  QUADRATIC EQUATION')

      IND=0

C      IND=0:  ONE REAL ROOT = 0, TWO CONJUGATE COMPLEX ROOTS
      R1=0.
      R2=(-V+DSQRT(V*V-4.DO*U*W))/(2.DO*U)
      R3=(-V-DSQRT(V*V-4.DO*U*W))/(2.DO*U)
      RETURN

      END

      SUBROUTINE RTSORT (RT,KM,RS)

C      GENERAL ROOT SORT  KM=# OF ROOTS,RS(1)=LARGEST ROOT
      IMPLICIT REAL * 8 (A-H,O-Z)
      COMPLEX * 16 RS,DCMPLX,RG,RT(3)
      COMPLEX * 8 Y
      REAL * 4 X,AIMAG,ABS
      DIMENSION RS(3),RG(3),R(3)
      COMMON /SAME/ ND

100  FORMAT(' RS ',6D14.6)

101  FORMAT(' ', 'THERE ARE NO REAL ROOTS')

      ND=0

      K=0

```

```
DO 3 I=1,KM
Y=RT(1)
X=AIMAG(Y)
IF((ABS(X))-(1.D-14))1,2,2
1 K=K+1
R(K)=RT(I)
GO TO 3
2 ND=ND+1
M=KM-ND+1
RG(M)=RT(I)
3 CONTINUE
IF(K-1) 4,5,4
4 DO 20 I=1,K
M=I+1
IF(M-K)10,10,25
10 DO 20 J=M,K
IF(R(J)-R(I))20,15,15
15 SAVE=R(I)
R(I)=R(J)
R(J)=SAVE
20 CONTINUE
25 CONTINUE
DO 30 I=1,K
30 RS(I)=DCMPLX(R(I),0.DO)
IF(K-KM)35,50,50
35 K=K+1
DO 40 I=K,KM
```

```
40 RS(I)=RG(I)
   WRITE(3,100)(RS(MM),MM=1,KM)
   GØ TØ 50
45 WRITE(3,101)
50 REUTRN
   END
```

Alternative to DQG32:

```
   SUBROUTINE DQG3(XL,XU,FCT,Y)
   DOUBLE PRECISION XL,XU,A,B
   COMPLEX * 16 Y,FCT
   A=.5*(XU+XL)
   B = XU-XL
   Y=.3872983*B
   Y=.2777778*(FCT(A+Y)+FCT(A_Y))
   Y=B*(Y+.4444444*FCT(A))
   RETURN
   END
```

B. Alphabetical List of Variables and Constants in Program

SUBROUTINE EMBRYO

A = final input radius for Gauss-Quadrature subroutine
AA = salt term in Kohler expression
AD = transport coefficient of water, D
AD ϕ = constant, input to subroutine that calculates AD and AK
ADRY = droplet radius at molality greater than 6.145
AF = dummy final radius
AI = input initial radius into EMBRYO
AK = thermal conductivity of air, K
ALPHA = accommodation coefficient, α
A ϕ = dummy initial radius
ARA ϕ LT = droplet radius, m less than or equal to 1.4
ASAT = droplet radius, 1.4 less than m less than 6.145
AZ = input final radius into EMBRYO
B = slope of equilibrium vapor density - temperature curve
BB = curvature constant in Kohler equation, b
BETA = sticking coefficient, β
CC = constant for calculating radius
CCCMS = (CC)(CMS)
COFF1-4 = constants of salt polynomials SOL1,SOL2
CL = l
CLT = (l_{α})(S)
CLV = l_{β}
CMS = salt mass

CNLAT = latent heat of condensation
 CONT = constant for calculating CLT
 CONV = constant for calculating CLV
 DUM = D_{eff}
 GAMG = ratio of specific heats
 GAS = gas constant in cgs, R
 GASTER = gas constant times temperature, RT
 $H = (D_{\text{eff}})(\rho_{\text{eq}}(\infty))$
 ND = integer number of imaginary roots to Kohler equation
 PI = π
 PR = atmospheric pressure (dynes/cm²)
 RS(I) = array of roots from Kohler equation
 S = supersaturation ratio
 SCALE = conversion constant from ergs to calories
 SM1 = S - 1
 ST = S + 2, to permit common storage of S with subroutine
 TIME(X)
 SURF = temperature dependent surface tension
 T = total time
 TER = absolute temperature
 TI = time interval for growth in respective regions of
 interest, ie. $m = 1.4$ to 6.145
 $U = (\gamma - 1)/(\gamma + 1)$
 WTMG = molecular weight of air
 WTMV = molecular weight of water
 X = single precision real RS(I)
SUBROUTINE VPDR
 C = constant for linear BT+C

RHEQ = equilibrium vapor density over a flat body
(for others, see list for EMBRYO)

SUBROUTINE DQG32,DQG3

A = XU = input final radius

AO = XL = input initial radius

TIME = FCT = function subprogram that evaluates integrand

TI = Y = time interval returned to EMBRYO

FUNCTION SUBPROGRAM TIME(X)

AA = X = radial values from DQG32 or DQG3

BB = radially dependent curvature coefficient

G = S - S(a)

GB(I) = coefficients to the equation S - S(a)

OL = molality, m

Q = dummy variable = SOL1 or SOL2

RHO = ρ (solution density) of the liquid

SOL1 = salt solution term for 1.4 less than m less than 6.145

SOL2 = salt solution term for m less than or equal to 1.4

TEN = $\sigma(a)$

TIME = evaluated integrand

C. Explanation of Computer Program

Subroutine Embryo calculates the time of growth for a salt solution droplet. The input to Embryo is the initial radius, AI, in centimeters, the final radius, A2, in centimeters, saturation ratio S, salt mass CMS, in grams, and the absolute temperature, TER. Embryo returns complex growth time, T, in seconds.

Embryo proceeds by first calculating a number of relevant constants. Then the Kohler curve coefficients (see Fletcher (4)) are fed into subroutine D cubic which returns the exact roots of a cubic equation. The roots (RT) are input into subroutine RTSORT. This subroutine will handle any number of roots by first separating the real roots from the complex ones, arranging reals in descending order, and outputting reals in descending order followed by complex roots. In Embryo, from statement preceeding number 3 to statement 20, region analysis occurs. Here AI and AZ are tested against the radii of drops with molalities 6.145 and 1.4 for purposes of determining which part of the molality-activity curve (equations (4.5) to (4.7)) is entertaining growth. The appropriate "floating" radii (AO,AF) are assigned for each region.

Statements 21-17 determine if the input AZ is too large by comparing each region's AF to the small real root (RS). If the radius AF is larger than the natural terminal radius, RS, then "final radius must be less than RS" is written and

the program terminates for the AI, AZ. However, if AF is less than RS, AO and AF will input into DQG3 or DQG32 (both Gauss-Quadrature subroutines). Either subroutine may be used depending on accuracy or computer time efficiency desired. These subroutines input AO, AF and return TI, the time for growth through that region or interval bounded by AO, AF. Both subroutines call TIME(X) which evaluates the integrand in (4.11).

After returning to Embryo, AO and AF are compared to AZ. If AF is less than AZ, the next region of growth is addressed by reassigning new values for AO and AF. This is done by statements 38-100. The new AO and AF values are returned to follow the same procedure just described. The program for given input values will terminate if one of the following is true: (1) AF is less than or equal to AO, (2) AZ is less than or equal to AF, or (3) AF is greater than or equal to RS. TIME, S, AO, AF, BETA, ALPHA, CL, AD, AK, TER, PR, GAMG, ADRY, ASAT, and ARAOLT will be written.

The growth region for which Embryo is most applicable is the region characterized by large salt molalities (AI = ADRY, AZ = 10. times ARAOLT). It will calculate the growth times for larger drops, but this can better be done by an existing partial fraction-analytic integral technique that can be inserted directly after statement 55 and made to loop back to $T = T + TI$. Termination will naturally occur at the first arithmetic IF statement after $T = T + TI$. The best

way of using Embryo would be to just call Embryo for small drops and call Kohler from the main when size sufficiently increases. This is suggested since some difficulty has been encountered in finding the largest root for applied S values when two real positive roots exist.

TABLE I Comparison of growth times varying surface tension, solution density, and compensated transport coefficient for NaCl crystalline mass of 10^{-4} grams

<u>cms(g)</u>	<u>AI</u>	<u>AF</u>	<u>S</u>	<u>(k,a,a)</u>	<u>(a,k,a)</u>	<u>(a,a,k)</u>	<u>(k,k,a)</u>	<u>(k,a,k)</u>	<u>(a,k,k)</u>	<u>(k,k,k)</u>	<u>KOHLER</u>	<u>T(sec)</u>
10^{-4}	A _D	A _S	S ₁	$-.104 \times 10^{-3}$	$.200 \times 10^{-3}$	36.900	$.711 \times 10^{-4}$	36.900	36.900	36.900	-.415	900
10^{-4}	A _S	A _R	S ₁	$-.509 \times 10^{-4}$	$.910 \times 10^{-4}$	17.430	$.347 \times 10^{-4}$	17.430	17.430	17.430	20.870	4000
10^{-4}	A _R	A ₀	S ₁	$-.367 \times 10^{-8}$	$.623 \times 10^{-8}$	8.370	$.250 \times 10^{-8}$	8.370	8.370	8.370	8.370	10^6
10^{-4}	A _D	A _S	S ₂	$-.128 \times 10^{-3}$	$.245 \times 10^{-3}$	25.030	$.875 \times 10^{-3}$	25.030	25.030	25.030	-12.42	10^3
10^{-4}	A _S	A _R	S ₂	$-.906 \times 10^{-4}$	$.161 \times 10^{-3}$	7.920	$.617 \times 10^{-4}$	7.920	7.920	7.920	11.75	10^4
10^{-4}	A _R	A ₀	S ₂	$-.128 \times 10^{-7}$	$.216 \times 10^{-7}$.779	$.871 \times 10^{-8}$.779	.779	.779	.776	10^9
10^{-4}	A _D	A _S	S ₃	$-.132 \times 10^{-3}$	$.252 \times 10^{-3}$	23.960	$.898 \times 10^{-4}$	23.960	23.960	23.960	-13.63	10^3
10^{-4}	A _S	A _R	S ₃	$-.101 \times 10^{-3}$	$.178 \times 10^{-3}$	7.000	$.686 \times 10^{-4}$	7.000	7.000	7.000	10.755	10^4
10^{-4}	A _R	A ₀	S ₃	$-.296 \times 10^{-7}$	$.497 \times 10^{-7}$.078	$.201 \times 10^{-7}$.078	.078	.078	.061	10^{10}
10^{-4}	A _D	A _S	S ₄	$-.132 \times 10^{-3}$	$.253 \times 10^{-3}$	23.850	$.900 \times 10^{-4}$	23.850	23.850	23.850	-13.75	10^3
10^{-4}	A _S	A _R	S ₄	$-.102 \times 10^{-3}$	$.180 \times 10^{-3}$	6.900	$.694 \times 10^{-4}$	6.900	6.900	6.900	10.65	10^4
10^{-4}	A _R	A ₀	S ₄	$-.644 \times 10^{-7}$	$.108 \times 10^{-6}$	$.783 \times 10^{-2}$	$.439 \times 10^{-7}$	$.783 \times 10^{-2}$	$.783 \times 10^{-2}$	$.783 \times 10^{-2}$	-.064	10^{11}

A_D = .022cm S₁ = 1.100
 A_S = .043cm S₂ = 1.010
 A_R = .067cm S₃ = 1.001
 A₀ = 6.720cm S₄ = 1.0001

TABLE II Comparison of growth times varying surface tension, solution density, and compensated transport coefficient for NaCl crystalline mass of 10^{-10} grams

cms(g)	AI	AF	S	(k,a,a)	(a,k,a)	(a,a,k)	(k,k,a)	(k,a,k)	(a,k,k)	(k,k,k)	KOHLER	T(sec)
10^{-10}	AD	AS	S ₁	$-.96 \times 10^{-2}$.0183	17.46	7.72	2.23	17.45	17.47	-15.49	.13
10^{-10}	AS	AR	S ₁	$-.49 \times 10^{-2}$	$.89 \times 10^{-2}$	5.13	$.34 \times 10^{-2}$	5.12	5.14	5.13	8.33	.6
10^{-10}	AR	A ₀	S ₁	$-.41 \times 10^{-6}$	$.69 \times 10^{-6}$	$.23 \times 10^{-1}$	$.28 \times 10^{-6}$	$.23 \times 10^{-1}$	$.23 \times 10^{-1}$	$.23 \times 10^{-1}$	$.24 \times 10^{-1}$	10^4
10^{-10}	AD	AS	S ₂	$-.12 \times 10^{-1}$	$.23 \times 10^{-1}$	17.46	.228	17.45	17.48	17.47	-19.58	.16
10^{-10}	AS	AR	S ₂	$-.90 \times 10^{-2}$.016	5.82	$.61 \times 10^{-2}$	5.81	5.82	5.82	9.74	1.2
10^{-10}	AR	A ₀	S ₂	$-.14 \times 10^{-5}$	$.23 \times 10^{-5}$	$.21 \times 10^{-2}$	$.94 \times 10^{-6}$	$.21 \times 10^{-2}$	$.21 \times 10^{-2}$.776	$.57 \times 10^{-2}$	10^5
10^{-10}	AD	AS	S ₃	-.013	.024	17.46	$.31 \times 10^{-2}$	17.45	17.48	17.47	-20.03	.22
10^{-10}	AS	AR	S ₃	$-.99 \times 10^{-2}$.018	5.83	$.68 \times 10^{-2}$	5.82	5.85	5.84	9.73	1.3
10^{-10}	AR	A ₀	S ₃	$-.32 \times 10^{-5}$	$.53 \times 10^{-5}$.077	$.22 \times 10^{-5}$.077	.077	.077	.06	10^6
10^{-10}	AD	AS	S ₄	-.013	.024	17.47	$.86 \times 10^{-2}$	17.47	17.49	17.48	-20.07	.24
10^{-10}	AS	AR	S ₄	-.010	.018	5.84	$.69 \times 10^{-2}$	5.83	5.86	5.85	9.73	2.0
10^{-10}	AR	A ₀	S ₄	$-.76 \times 10^{-5}$	$.13 \times 10^{-4}$	$.13 \times 10^{-3}$	$.52 \times 10^{-5}$	$.14 \times 10^{-3}$	$.14 \times 10^{-3}$	$.13 \times 10^{-3}$.082	10^7

AD = $.22 \times 10^{-3}$ cm
AS = $.43 \times 10^{-3}$ cm
AR = $.67 \times 10^{-3}$ cm
A₀ = .067 cm

S₁ = 1.100
S₂ = 1.010
S₃ = 1.001
S₄ = 1.0001

TABLE III Comparison of growth times varying surface tension, solution density, and compensated transport coefficient for NaCl crystalline mass of 10^{-16} grams

<u>cms(g)</u>	<u>AI</u>	<u>AF</u>	<u>S</u>	<u>(k,a,a)</u>	<u>(a,k,a)</u>	<u>(a,a,k)</u>	<u>(k,k,a)</u>	<u>(k,a,k)</u>	<u>(a,k,k)</u>	<u>(k,k,k)</u>	<u>KOHLER</u>	<u>T(sec)</u>
10^{-16}	A _D	A _S	S ₁	-.908	1.79	3.54	7.51	2.64	5.31	4.16	-29.26	.0004
10^{-16}	A _S	A _R	S ₁	-.503	.915	4.77	.346	5.24	3.92	4.45	-.026	.002
10^{-16}	A _R	A _O	S ₁	$-.39 \times 10^{-3}$	$.67 \times 10^{-3}$	1.74	$.27 \times 10^{-3}$	1.74	1.74	1.74	1.74	2.0
10^{-16}	A _D	A _S	S ₂	-1.24	2.47	3.54	1.54	2.30	6.01	4.4	-33.4	.0005
10^{-16}	A _S	A _R	S ₂	-1.05	1.93	.53	.731	.51	2.44	1.25	7.77	.003
10^{-16}	A _R	A _O	S ₂	$-.25 \times 10^{-2}$	$.43 \times 10^{-2}$.194	$.17 \times 10^{-2}$.197	.190	.193	-.235	21.7
10^{-16}	A _D	A _S	S ₃	-1.28	2.57	3.54	.967	2.25	6.11	4.44	-33.8	.0008
10^{-16}	A _S	A _R	S ₃	-1.22	2.24	1.07	.851	.153	3.33	1.92	8.60	.0033

$A_D = .22 \times 10^{-5} \text{cm}$ $S_1 = 1.100$
 $A_S = .43 \times 10^{-5} \text{cm}$ $S_2 = 1.010$
 $A_R = .67 \times 10^{-5} \text{cm}$ $S_3 = 1.001$
 $A_O = .67 \times 10^{-3} \text{cm}$