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DROP GROWTH IN A
SUPERSATURATED VAPOR

BY

ROGER BUECHER, 1941 43P

A

THESIS

submitted to the faculty of the
UNIVERSITY OF MISSOURI AT ROLLA

In partial fulfillment of the requirements for the

Degree of

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ABSTRACT

Using kinetic theory and the thermodynamics of phase transitions, a method is derived for finding the growth rate and temperature increase of a droplet in water vapor which has been supersaturated by the expansion of a cloud chamber. Calculations are performed for a specific numerical example and compared to other work in this field.

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I. INTRODUCTION

Cloud chambers, in addition to their use as devices to observe the tracks of charged particles which pass through them, are currently being used to investigate the spontaneous, homogeneous nucleation of supersaturated water vapor. A knowledge of homogeneous nucleation is important as a stepping stone to an understanding of heterogeneous nucleation, which plays an important role in the formation of clouds and other atmospheric phenomena.

Most of the investigations into homogeneous nucleation involve a determination of the nucleation rate, the rate at which droplets of water are formed in the supersaturated vapor. Theoretical derivations of the nucleation rate include those based on the classical liquid drop theory by Volmer and Weber¹, Farkas², Becker and Doring³, Frenkel⁴, Zeldovich⁵, Sander and Damköler⁶, Mason⁷, Farley⁸, and Courtney⁹ and the one based on statistical mechanics by Reiss¹⁰.

In the development of a nucleation rate theory intended to be applicable to a supersaturated vapor in which droplets are formed over a period of time, a knowledge of the rate of growth of individual drops is desirable. As a drop grows, it removes water molecules from the vapor thus reducing the number available for the formation of new drops. Also the latent heat liberated

by the condensation of the molecules warms the drop and hence the vapor itself. Both of these effects reduce the supersaturation of the vapor and therefore its nucleation rate.

The growth of a drop in a supersaturated vapor will in general be regulated by the diffusion of water molecules to the drop and the diffusion of heat from it. However, when drops are in the region of the critical size, the size above which they will tend to grow and below which they will tend to evaporate; their dimensions are smaller than the mean free path of a water vapor molecule. For instance in an example to be presented later, the mean free path is about 10^{-5} cm while the radius of a critical droplet is only 10^{-7} cm. In a case of this sort, diffusion theory is not applicable, and kinetic theory methods should be employed.

Rate of growth laws are calculated by Bagge, Becker, and Bekow¹¹ using a combination of kinetic theory methods and diffusion theory and by Mason¹² using diffusion theory with corrections for the diffusion constants in the region of small drops.

In the following paper, a rate of growth law will be derived using kinetic theory and the thermodynamics of phase transitions for the rather specialized case of a cloud chamber which contains helium and saturated water

vapor and is expanded instantaneously and adiabatically. However, the general method is easily extendable to other vapors and gases. The method is not applicable to the growth of drops large enough to be treated by diffusion theory, however it will be extended into this region to serve as a rough approximation and an upper limit to the actual growth of the drops. Its main value will probably be to supply the initial conditions for diffusion theory methods.

II. THEORETICAL DERIVATION OF EQUATIONS

A. ADIABATIC EXPANSION.

1. Density before expansion. Before the expansion of the cloud chamber, the helium-water vapor mixture is at room temperature, T_1 , and normal atmospheric pressure, P_1 . In addition the water vapor is saturated.

The initial conditions are then:

| | | |
|----------------------------|---|------------|
| Initial pressure | = | P_1 |
| Initial temperature | = | T_1 |
| Vapor pressure of water | = | P_{H_2O} |
| Partial pressure of helium | = | P_{He} |

The initial density of water molecules and of helium atoms is:

| | | | | |
|----------------------------------|---|--------------|---|-------------------------|
| Density of water vapor molecules | = | $n_{H_2O}^B$ | = | $\frac{P_{H_2O}}{KT_1}$ |
| Density of helium atoms | = | n_{He}^B | = | $\frac{P_{He}}{KT_1}$ |

2. Volume-temperature relation. The chamber then undergoes an expansion which for purposes of simplification will be considered to be adiabatic and instantaneous.

The adiabatic law is:

$$P_1 V_1^\gamma = P_2 V_2^\gamma$$

where P_2 and V_2 are the pressure and volume after expansion.

Assuming that the gases behave approximately as an ideal gas:

$$P = \frac{N K T}{V}$$

$$\frac{N K T_1}{V_1} V_1^\gamma = \frac{N K T_2}{V_2} V_2^\gamma$$

$$\frac{V_2}{V_1} = \left[\frac{T_1}{T_2} \right]^{\frac{1}{\gamma-1}} \quad (1)$$

3. Supersaturation. The supersaturation of a vapor is given by:¹³

$$S = \frac{p_1 V_1 T_2}{p_2 V_2 T_1} \quad (2)$$

where p_1 and p_2 are the equilibrium vapor pressure at temperature T_1 and T_2 respectively.

4. Densities after expansion. Thus the same number of helium atoms and water vapor molecules which occupied a volume V_1 before the expansion now occupy a volume V_2 , so that the density of water vapor molecules and helium atoms is:

$$\text{Density of water vapor molecules} = n_{\text{H}_2\text{O}} = \frac{p_{\text{H}_2\text{O}}}{K T_1} \left[\frac{T_2}{T_1} \right]^{\frac{1}{\gamma-1}} \quad (3)$$

$$\text{Density of helium atoms} = n_{\text{He}} = \frac{p_{\text{He}}}{K T_1} \left[\frac{T_2}{T_1} \right]^{\frac{1}{\gamma-1}} \quad (4)$$

B. INITIAL CONDITIONS.

1. Critical radius formula. After the expansion, the supersaturated water vapor will undergo rapid statistical fluctuations in density which will result in the formation of small droplets of water. Droplets which are smaller than a certain critical radius, r_c , will evaporate immediately. Other droplets, larger than the critical radius, will grow.

The formula for the critical radius is:¹⁴

$$r_c = \frac{2\sigma T_0 v_B}{\lambda(T_0 - T)} \quad (5)$$

where σ is the ordinary surface tension, T_0 is the temperature at which the vapor would be in equilibrium, v_B is the molecular volume of the liquid phase, λ is the latent heat of evaporation of one molecule, and T is the actual temperature of the supersaturated vapor.

A drop of this size contains N_c molecules.

$$N_c = \left(\frac{4}{3} \pi r_c^3 \right) \left(\frac{1}{v_B} \right) \quad (6)$$

2. Initial vapor depletion. In the following derivation of the formulas involved in the growth of a drop, it is assumed that the formation of the initial droplet

does not appreciably deplete the vapor immediately surrounding it. This assumption will be valid if the number of water vapor molecules in a volume of one mean free path radius around the droplet is much larger than the number of molecules needed to form the droplet itself.

When the density of helium atoms is considerably greater than the density of water vapor molecules, it is reasonable to assume that the mean free path of the water molecules is determined solely by collisions with helium atoms. The mean free path of molecules of type 1 colliding with those of type 2 but having no collisions with particles of its own type is given by the formula:¹⁵

$$L_1 = \frac{1}{\sqrt{2} n_2 \pi r_{12}^2} \quad \text{where: } r_{12} = r_1 + r_2$$

So that:

$$L_{\text{H}_2\text{O}} = \frac{1}{\sqrt{2} n_{\text{He}} \pi (r_{\text{H}_2\text{O}} + r_{\text{He}})^2} \quad (7)$$

where $r_{\text{H}_2\text{O}}$ and r_{He} are the molecular radii of water and helium.

The number of water vapor molecules within a sphere of radius one mean free path is:

$$N_{\text{H}_2\text{O}} = n_{\text{H}_2\text{O}} \left(\frac{4}{3} \pi L_{\text{H}_2\text{O}}^3 \right) \quad (8)$$

If this number is considerably larger than the number of molecules in the initial droplet, the assumption

of no initial vapor depletion is justified.

G. DYNAMIC CONDITIONS.

1. General power balance. Several dynamic processes are involved in the growth of the drop. Water vapor molecules strike the drop, condense, and supply energy to the drop in the form of their heat of condensation. Some of this energy is used in raising the temperature of the drop and in creating surface area. Energy is removed from the drop by evaporating water molecules and by helium molecules, which upon striking the drop will be raised to its higher temperature and then, upon evaporating, carry away this excess energy.

Thus a power balance exists among the dynamic processes.

$$\begin{array}{l} \text{Rate that energy} \\ \text{is supplied by} \\ \text{condensing water} \end{array} = H R_I$$

where R_I is the rate at which water molecules strike the drop, and H is the heat of condensation of each molecule.

$$\begin{array}{l} \text{Rate at which} \\ \text{energy is used} \\ \text{to heat the drop} \end{array} = C_d \frac{dT}{dt}$$

where C_d is the heat capacity of the drop, and $\frac{dT}{dt}$ is the rate of change of the temperature of the drop with time.

$$\begin{array}{l} \text{Rate at which} \\ \text{energy is used} \\ \text{to create surface} \end{array} = \Delta S (R_I - R_E)$$

where ΔS is the change in surface energy caused by the addition of one molecule.

$$\begin{array}{l} \text{Rate at which} \\ \text{energy is taken} \\ \text{from the drop by} \\ \text{helium atoms} \end{array} = P_{\text{He}}$$

$$\begin{array}{l} \text{Rate at which} \\ \text{energy is taken} \\ \text{from the drop by} \\ \text{evaporating water} \end{array} = H R_E$$

where R_E is the rate at which water molecules evaporate from the drop.

So that the power balance is:

$$H R_I = C_d \frac{dT}{dt} + \Delta S (R_I - R_E) + H R_E + P_{\text{He}}$$

The rate of change of the temperature of the drop is:

$$\frac{dT}{dt} = \frac{(H - \Delta S)(R_I - R_E) - P_{\text{He}}}{C_d} \quad (9)$$

2. Water vapor condensation. The rate that energy is supplied by condensing water molecules can be found by using a kinetic theory formula for the rate at which particles having a Maxwellian distribution of velocity

will cross unit area.¹⁶

$$n_r = \frac{1}{2\sqrt{\pi}} n C_o \quad (10)$$

where n is the particle density, and C_o is the mean speed given by:

$$C_o = \left[\frac{2 K T}{m} \right]^{\frac{1}{2}} \quad (11)$$

where m is the mass of the particle.

The number of water molecules striking the drop per second is:

$$R_I = n_{H_2O}^r \text{ (Area of Drop)}$$

$$R_I = \left[\frac{K T_2}{2 \pi m_{H_2O}} \right]^{\frac{1}{2}} n_{H_2O} (4 \pi r^2) \quad (12)$$

where r is the radius of the drop.

In the derivation of this formula, it was assumed that the water molecule density, n_{H_2O} , remained constant throughout the entire growth of the drop. This assumption will be valid when the drop is small, but as the drop grows, it starts to deplete vapor from the volume surrounding it, and the water molecule density will actually change. The solution of the growth of large drops belongs

in the realm of diffusion theory. However, this method is used here as a first approximation, and sets an upper limit on drop size.

3. Heat capacity of droplet. The heat capacity of the drop, C_d , is:

$$C_d = (1 \frac{\text{cal}}{\text{C gm}}) (1 \frac{\text{gm}}{\text{cm}^3}) (4.18 \times 10^7 \frac{\text{erg}}{\text{cal}}) (\frac{4}{3} \pi r^3)$$

$$C_d = (4.18 \times 10^7) (\frac{4}{3} \pi r^3) \quad (13)$$

4. Surface effects. From Frenkel¹⁷, the change in surface energy caused by the addition of one molecule, ΔS , is:

$$\Delta S = \frac{2W}{r} v_B \quad (14)$$

where v_B is the volume of one molecule, and W is the surface energy.

5. Water evaporation. The rate of evaporation from the drop will depend on the temperature and radius of the drop. The rate at which molecules leave the drop is equal to the rate at which they would strike it from a vapor the density and temperature of which are such that the radius of the drop is the critical radius.

The formula for the critical radius is:

$$r_c = \frac{2 \sigma T_0 v_B}{\lambda (T_0 - T)}$$

So that:

$$T_E = \frac{r \lambda T}{r \lambda - 2 \sigma v_B} \quad (15)$$

Where T_E is the equilibrium temperature for a certain vapor which has an actual temperature of T and the critical radius of which is r .

Eventually the rate at which water vapor molecules would strike the drop from this fictitious vapor must be found. In order to do this we must have the vapor pressure expressed as a function of the equilibrium temperature of the vapor. In the numerical example below, an expansion is chosen which has room temperature or 293°K as its initial temperature and 0°C or 273°K as its final temperature. The graph of Figure 1 shows vapor pressure as a function of temperature.

This curve can be closely approximated by using Newton's forward difference interpolation formula of the second degree¹⁸.

$$y(x) = y_0 + \frac{x-x_0}{h} \Delta y_0 + \frac{(x-x_0)(x-x_0-h)}{2! h^2} \Delta^2 y_0 \quad (16)$$

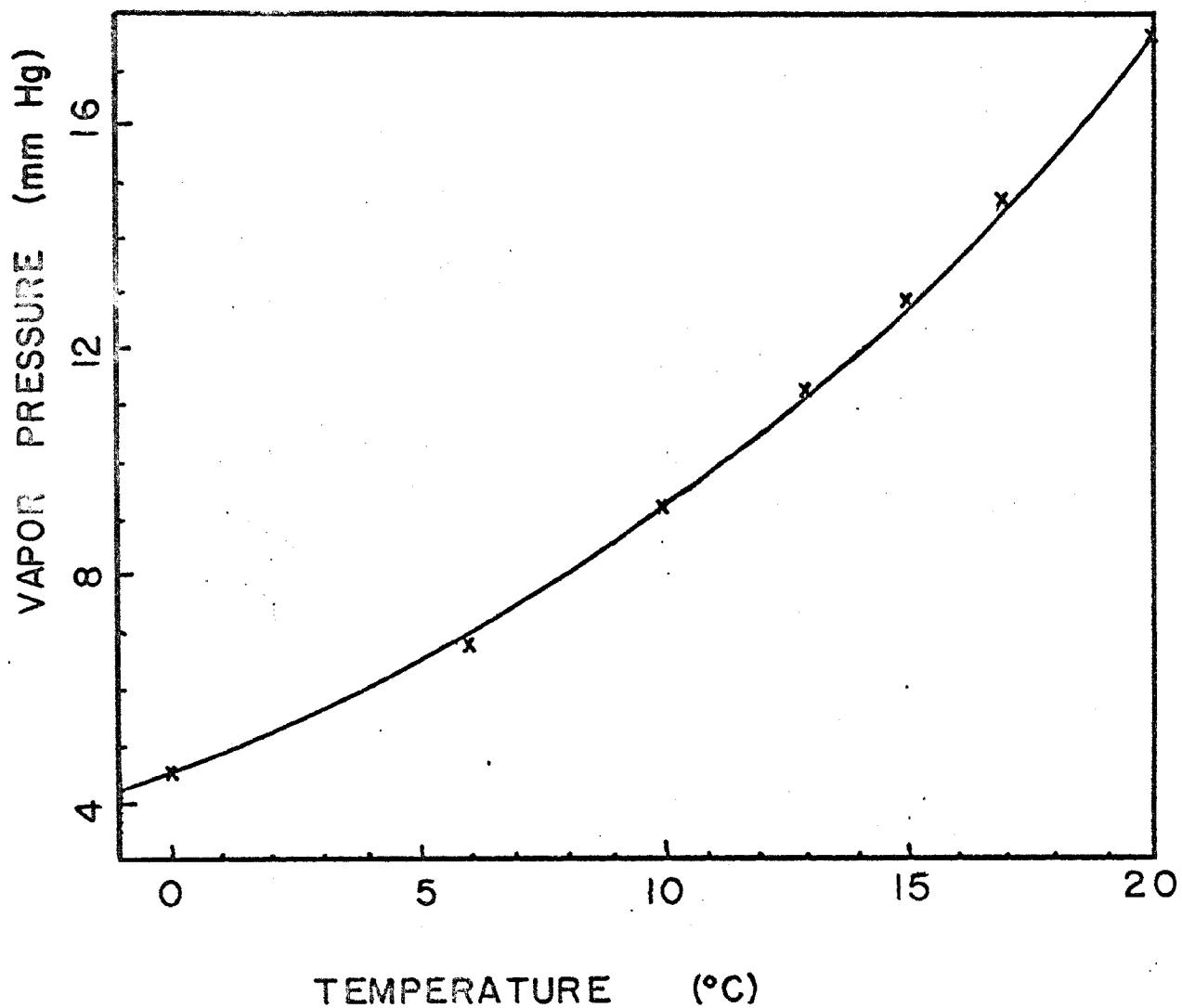


Figure 1. Vapor pressure over water as a function of temperature. Values taken from the Handbook of Chemistry and Physics, p. 2326.

The following values are used:¹⁹

| T (°K) | P _{H₂O} (mm Hg) | Δy | Δ ² y |
|--------|-------------------------------------|-------|------------------|
| 273 | 4.579 | | |
| 283 | 9.209 | 4.630 | 3.696 |
| 293 | 17.535 | 8.326 | |

h = 10°K

So that an approximate formula for water vapor pressure as a function of temperature is:

$$P_{H_2O}^{\circ} = 4.579 + \frac{T_E - 273}{10}(4.630) + \frac{(T_E - 273)(T_E - 283)}{2(100)}(3.696) \quad (17)$$

Several values were calculated using the above formula and are indicated on the graph of Figure 1 by the starred points. It can be seen that the formula is a very good approximation to the actual values.

In order for a vapor whose equilibrium temperature is T_0 to exist at temperature T , in other words to be supersaturated, it must have undergone an expansion. The density of water vapor molecules of this fictitious vapor is then:

$$n_{H_2O}^{\circ} = \frac{P_{H_2O}^{\circ}(1333)}{K T_E} \left[\frac{T}{T_E} \right]^{\frac{1}{\gamma - 1}}$$

where (1333) is a factor introduced to change the units

of the vapor pressure from mm Hg to dynes/cm².

The rate at which these molecules would strike a unit area is:

$$o_{n_r}^{\text{H}_2\text{O}} = \left[\frac{K T}{2 \pi m_{\text{H}_2\text{O}}} \right]^{\frac{1}{2}} n_{\text{H}_2\text{O}}^o$$

The rate at which these molecules would strike the drop, or in other words, the rate at which molecules will evaporate from the drop is:

$$\begin{aligned} R_E &= o_{n_r}^{\text{H}_2\text{O}} (\text{Area of Drop}) \\ &= o_{n_r}^{\text{H}_2\text{O}} (4 \pi r^2) \end{aligned}$$

Substituting from the above equations and simplifying:

$$\begin{aligned} R_E &= (1333) \left[\frac{8 \pi}{K m_{\text{H}_2\text{O}}} \right]^{\frac{1}{2}} r^2 \frac{T^3}{T_E^{3.5}} \left[4.579 \right. \\ &\quad \left. + (T_E - 273)(.4630) + (T_E - 273)(T_E - 283)(.01848) \right] \end{aligned}$$

where: $T_E = \frac{r \lambda T}{r \lambda - 2 \sigma v_B}$ (18)

6. Helium cooling. Using formula (10), the rate at which helium atoms will cross a unit area is:

$$n_r^{\text{He}} = \left[\frac{K T_2}{2 \pi m_{\text{He}}} \right]^{\frac{1}{2}} n_{\text{He}}$$

The rate at which helium atoms will strike the drop is:

$$R_{\text{He}} = n_{\text{r}}^{\text{He}} (\text{Area of Drop})$$

$$R_{\text{He}} = \left[\frac{K T_2}{2\pi m_{\text{He}}} \right]^{\frac{1}{2}} (4\pi r^2)$$

The heat capacity of each helium atom is:

$$C_{\text{He}} = \frac{3}{2} K = 2.07 \times 10^{-16}$$

Assuming that the helium atoms strike the drop, are raised to its temperature, and then leave it, the rate at which energy is taken from the drop by helium is:

$$P_{\text{He}} = C_{\text{He}} R_{\text{He}} (T - T_2) \quad (19)$$

D. OUTLINE OF SOLUTION.

An inspection of the formulas for the dynamic processes involved in the growth of a droplet will show that they are all functions of the radius of the drop and its temperature only. An iterative method for finding the growth of a droplet is outlined below.

This process can be altered to show the evaporation of a drop by inserting an initial drop radius which is smaller than the critical radius.

1. Assume an initial radius for the drop which is slightly larger than the critical radius and an initial temperature equal to the post expansion equilibrium temperature, T_2 .

$${}^{\circ}r = r_c + \text{Small amount}$$

$${}^{\circ}T = T_2$$

2. Calculate the following values:

$$(R_I - R_E) = f_1({}^{\circ}r, {}^{\circ}T)$$

$$\frac{dT}{dt} = f_2({}^{\circ}r, {}^{\circ}T)$$

3. Calculate new values for r and T which result from a short period of growth Δt .

$$l_r = \left[\frac{\frac{4}{3}\pi ({}^{\circ}r)^3 + (R_I - R_E) v_B \Delta t}{\frac{4}{3}\pi} \right]^{\frac{1}{3}}$$

$$l_T = {}^{\circ}T + \frac{dT}{dt} \Delta t$$

4. Iterate the process.

III. NUMERICAL EXAMPLE.

A. INITIAL CONDITIONS.

1. Expansion ratio. The sequence of steps followed in solving the numerical example will closely parallel the steps of the derivation. A cloud chamber will be imagined in which the helium-saturated water vapor mixture is initially at room temperature and normal atmospheric pressure. The chamber then expands adiabatically and instantaneously with an expansion ratio such that the temperature after the expansion is 0°C.

Assuming that γ is equal approximately to 1.4, the necessary expansion ratio is:

$$\begin{aligned} \frac{V_2}{V_1} &= \left[\frac{T_1}{T_2} \right]^{\frac{1}{\gamma-1}} = \left[\frac{293}{273} \right]^{2.5} & (1a) \\ &= 1.2 \end{aligned}$$

2. Initial conditions. The initial conditions are:

$$\begin{aligned} P_1 &= 760 \text{ mm Hg} \\ T_1 &= 293^\circ\text{K} \\ P_{\text{H}_2\text{O}} &= 17.5 \text{ mm Hg} \\ P_{\text{He}} &= 742.5 \text{ mm Hg} \end{aligned}$$

3. Supersaturation. The supersaturation is:

$$\begin{aligned} S &= \frac{P_1 V_1 T_2}{P_2 V_2 T_1} & (2a) \\ &= 2.97 \end{aligned}$$

4. Densities. The density of water vapor molecules and of helium atoms after the expansion are:

$$n_{\text{H}_2\text{O}} = \frac{p_{\text{H}_2\text{O}}}{k T_1} \left[\frac{T_2}{T_1} \right]^{\frac{1}{\gamma-1}} \quad (3a)$$

$$\frac{n_{\text{He}}}{n_{\text{H}_2\text{O}}} = \frac{2.04 \times 10^{19}}{4.8 \times 10^{17}}$$

$$= 42.5$$

So that the assumption that the mean free path of the water vapor molecules is determined solely by the helium atoms is a good approximation.

$$L_{\text{H}_2\text{O}} = \frac{1}{\sqrt{2} n_{\text{He}} \pi (r_{\text{H}_2\text{O}} + r_{\text{He}})^2} \quad (7a)$$

$$= 9.6 \times 10^{-6}$$

The number of water molecules within a sphere of radius one mean free path is:

$$N_{L_{\text{H}_2\text{O}}} = n_{\text{H}_2\text{O}} \left(\frac{4}{3} \pi L_{\text{H}_2\text{O}}^3 \right) \quad (8a)$$

$$= 1.79 \times 10^3$$

Since only 95 molecules are needed to make a drop of critical size, and 1,790 molecules are readily available within a sphere of one mean free path radius, it appears that the assumption made in the derivation, that initial vapor depletion effects can be ignored, is justified.

7. Water vapor condensation. The rate at which water vapor molecules will strike a drop of radius r is:

$$\begin{aligned}
 R_I &= \left[\frac{K T_2}{2\pi m_{H_2O}} \right]^{\frac{1}{2}} n_{H_2O} (4\pi r^2) & (12a) \\
 &= 8.53 \times 10^{22} r^2
 \end{aligned}$$

The energy brought to the drop by each condensing water molecule or taken away from it by each evaporating molecule is:

$$\begin{aligned}
 H &= (5.955 \times 10^2 \frac{\text{cal}}{\text{gm}}) (3 \times 10^{-23} \frac{\text{gm}}{\text{molecule}}) (4.18 \times 10^7 \frac{\text{erg}}{\text{cal}}) \\
 &= 7.49 \times 10^{-13} \frac{\text{erg}}{\text{molecule}}
 \end{aligned}$$

8. Heat capacity of droplet. The heat capacity of the drop is:

$$\begin{aligned}
 C_d &= (4.18 \times 10^7) (\frac{4}{3} \pi r^3) & (13a) \\
 &= 1.75 \times 10^8 r^3 \frac{\text{erg}}{\text{molecule}}
 \end{aligned}$$

9. Surface effects. The change in surface energy per molecule is:

$$\begin{aligned}
 \Delta S &= \frac{2 W v_B}{r} & (14a) \\
 &= 8.58 \times 10^{-21} \frac{1}{r} \frac{\text{erg}}{\text{molecule}}
 \end{aligned}$$

10. Water evaporation. The rate at which water molecules will evaporate from the droplet is:

$$R_E = (1.04 \times 10^{23}) r^2 \frac{T^3}{T_E^{3.5}} \left[4.579 + (T_E - 273)(.4630) \right. \\ \left. + (T_E - 273)(T_E - 283)(.01848) \right]$$

where:

$$T_E = \frac{(7 \times 10^{-13}) r T}{(7 \times 10^{-13}) r - 4.2 \times 10^{-21}} \quad (18a)$$

11. Helium cooling. The rate at which energy is taken from the drop by helium atoms is:

$$P_{He} = C_{He} R_{He} (T - T_2) \quad (19a) \\ = 1.59 \times 10^9 r^2 (T - 273)$$

B. THE ITERATIVE PROCESS.

The iterative process in detail at the n'th iteration is:

$$T_E = \frac{(7 \times 10^{-13})(n_r)(n_T)}{(7 \times 10^{-13})(n_r) - 4.2 \times 10^{-21}}$$

$$R_I = 8.53 \times 10^{22} (n_r)^2$$

$$R_E = (1.04 \times 10^{23})(n_r)^2 \frac{(n_T)^3}{(T_E)^{3.5}} \left[4.579 \right.$$

$$\left. + (T_E - 273)(.4630) + (T_E - 273)(T_E - 283)(.01848) \right]$$

$$\frac{dT}{dt} = \frac{\left[7.49 \times 10^{-13} - \frac{8.58 \times 10^{-21}}{r} \right] (R_I - R_E)}{1.75 \times 10^8 r^3}$$

$$\frac{-1.59 \times 10^9 (n_r)^2 (n_T - 273)}{1.75 \times 10^8 r^3}$$

$$n+1_T = n_T + \frac{dT}{dt} \Delta t$$

$$n+1_r = \left[(n_r)^3 + 7.15 \times 10^{-24} (R_I - R_E) \Delta t \right]^{\frac{1}{3}}$$

C. COMPUTER PROGRAM.

A computer program was developed and run which was based directly on the iterative process described. However, it was found that in order to avoid unstable oscillations in the results for droplets near the critical radius, it was necessary to use a very small interval of growth, Δt . To reduce the running time, a procedure was used in which twenty iterations were followed by an extrapolation for the equivalent of eighty time intervals, thus reducing the running time to one fifth of what it would have required.

The notation used in the program is:

| | | |
|----------------------------|----------------------|--------------------------------|
| $R_I \rightarrow RI$ | $r \rightarrow R$ | $\frac{dT}{dt} \rightarrow DT$ |
| $R_E \rightarrow RE$ | $T \rightarrow T$ | $t \rightarrow CT$ |
| $R_I - R_E \rightarrow RN$ | $T_E \rightarrow TE$ | $t \rightarrow TM$ |

| | | |
|-----------------|--------------------------------|--------------------------------|
| $A(1) = 4.579$ | $A(6) = 1.04 \times 10^{23}$ | $A(11) = 1.59 \times 10^9$ |
| $A(2) = .4630$ | $A(7) = 7 \times 10^{-13}$ | $A(12) = 7.15 \times 10^{-24}$ |
| $A(3) = .01848$ | $A(8) = 4.2 \times 10^{-21}$ | $A(13) = 1.75 \times 10^8$ |
| $A(4) = 273$ | $A(9) = 7.49 \times 10^{-13}$ | |
| $A(5) = 283$ | $A(10) = 8.58 \times 10^{-21}$ | |

The computer program is:

```

1 DIMENSION A(14)
  READ 100, (A(J),J=1,13)
  READ 100,DT,RN,TM,T,R,CT
  PRINT 300,TM,R,RN,DT
  A(14)=A(1)+(293.-A(4))*(A(2)+(293.-A(5))*A(3))
  A(14)=(A(14)*A(6)*(A(4)**3))/(293.**3.5)
  CTA=CT*100.
9 DO 19 N=1,45
  RA=R
  TMA=TM
137 DO 138 J=1,20
  RI=A(14)*(R**2)
  TE=(A(7)*R*T)/(A(7)*R-A(3))
  RE=A(1)+(TE-A(4))*(A(2)+(TE-A(5))*A(3))
  RE=(RE*A(6)*(T**3)*(R**2))/(TE**3.5)
14 RN=RI-RE
  DT=((A(9)-A(10)/R)*RN*A(11)*(R**2)*(T-A(4)))/(A(13)*(R**3))
  R=(R**3+RN*CT*A(12))**(1./3.)
  TM=TM+CT
138 CONTINUE
  R=(RA**3+RN*CTA*A(12))**(1./3.)
  TM=TMA+CTA
19 PRINT 300,TM,R,T,RN,TE
  STOP
100 FORMAT (7E10.4)
300 FORMAT (5E14.4)
  END

```

D. NUMERICAL RESULTS.

1. Growth of drop. The initial radius of the drop was chosen as 10^{-7} cm, and it was necessary to use a Δt of 10^{-9} sec. As the drop grew, the program became less sensitive to the size of the time interval, Δt , so that it was possible to increase the size of the interval, usually by a power of ten for each power of ten that the radius of the drop increased. The results are shown in Figure 2.

2. Evaporation of drop. The program was also run with an initial radius of 7×10^{-8} cm, which is smaller than the critical radius. The results are shown in Figure 2.

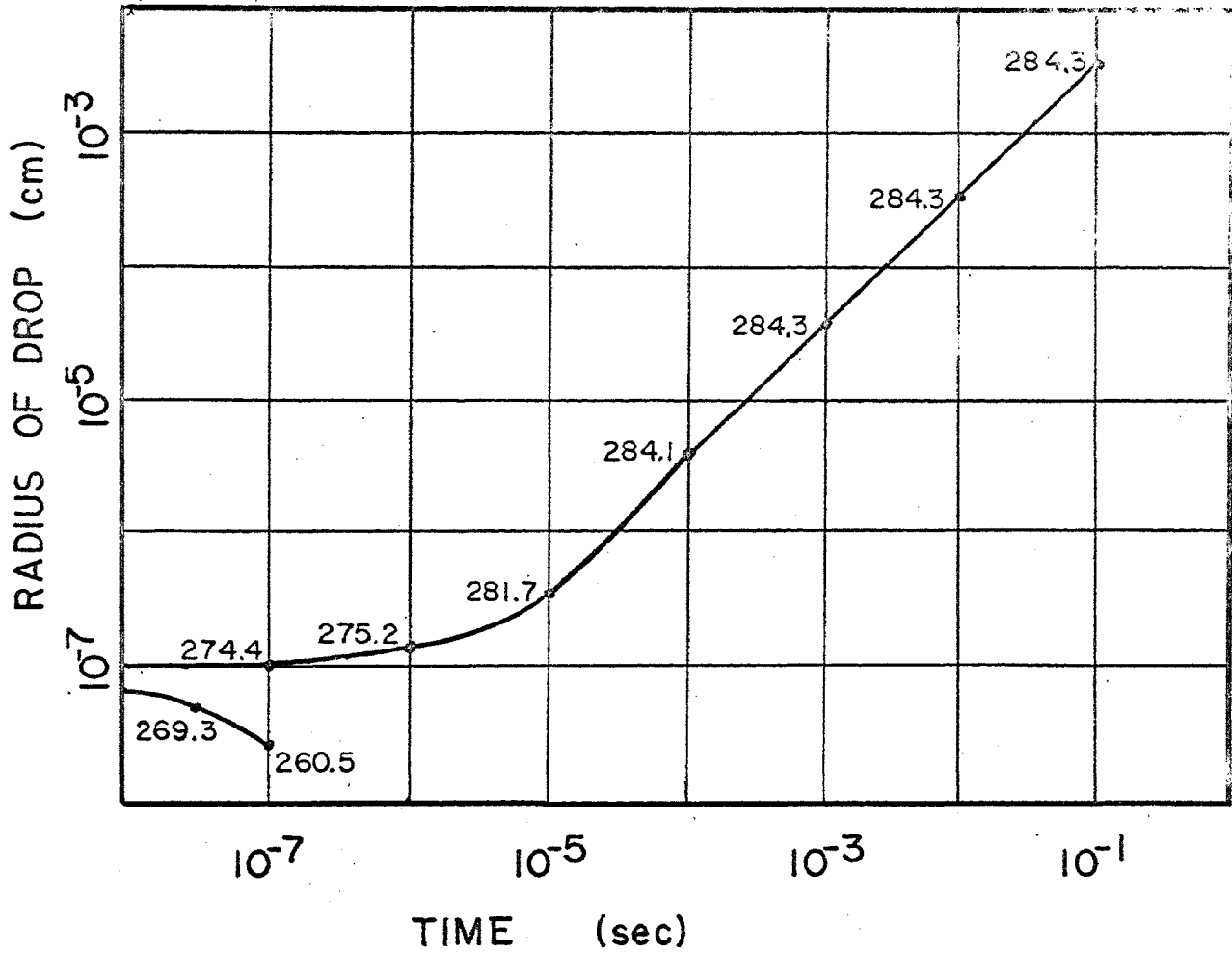


Figure 2. Radius of a drop as a function of the growth time. Numbers located near points indicate the temperature at that point.

IV. DISCUSSION OF RESULTS

A. LINEARITY AFTER 10^{-5} SEC.

1. Condensation function of r^2 . An examination of the graph of Figure 2 shows that after the drop has been growing for about 10^{-5} sec, further changes in its radius are approximately linear. This is due to the nature of the functions for R_I and R_E .

The rate at which water molecules strike the drop, R_I , is a function of r^2 .

$$R_I = 8.58 \times 10^{22} r^2$$

2. Evaporation function of r^2 . As the radius of the drop gets large, the temperature T_E , which controls the evaporation rate approaches the actual temperature of the drop, T . This means that the evaporation rate approaches the normal, equilibrium, plane surface rate.

The function for the evaporation rate is:

$$R_E = 6.21 \times 10^{22} r^2$$

Thus the net rate at which molecules are added to the drop is:

$$(R_I - R_E) = 2.32 \times 10^{22} r^2$$

The rate of change of the volume of the drop is:

$$\frac{d \left(\frac{4}{3} \pi r^3 \right)}{dt} = (R_I - R_E) v_B$$

$$\frac{4}{3} \pi (3r^2) \frac{dr}{dt} = 2.32 \times 10^{22} r^2 \cdot 3 \times 10^{-23}$$

$$\frac{dr}{dt} = 5.52 \times 10^{-2} \frac{\text{cm}}{\text{sec}}$$

So that the rate of change of the radius of the drop is linear in this region.

B. ENERGY DISSIPATION ANALYSIS.

It is interesting to analyze the relative effect of the various mechanisms which dissipate the energy brought to the drop by the net influx of water molecules. The formula for the rate of temperature change of the drop is:

$$\frac{dT}{dt} = \frac{(H - \Delta S)(R_I - R_E) - P_{\text{He}}}{C_d}$$

where: $H(R_I - R_E)$ is the net rate that energy is supplied to the drop by water molecules.

$\Delta S(R_I - R_E)$ is the net rate at which energy is used to create new surface of the drop.

P_{He} is the rate at which energy is dissipated by the helium.

C_d is the heat capacity of the drop.

When the time of growth is 10^{-7} sec.

$$\frac{dT}{dt} = \frac{(7.49 \times 10^{-13} - 8.58 \times 10^{-14})(3.72 \times 10^7) - (2.27 \times 10^{-5})}{1.8 \times 10^{-13}}$$

The energy supplied by
condensing water $\quad\quad = P_w = 2.78 \times 10^{-5}$

The energy used to
create surface $\quad\quad = P_s = 3.16 \times 10^{-6}$

The energy dissipated
by helium atoms $\quad\quad = P_{He} = 2.27 \times 10^{-5}$

The energy used to
heat the drop $\quad\quad = P_d = 1.94 \times 10^{-6}$

The fraction of the
energy brought to the
drop which is used in
the creation of surface $\quad = \frac{P_s}{P_w} = .114$

The fraction of the
energy brought to the
drop which is dissipated
by helium atoms $\quad = \frac{P_{He}}{P_w} = .814$

The fraction of the
energy brought to the
drop which is used to
heat the drop $\quad = \frac{P_d}{P_w} = .072$

Similar calculations were made for other growth times, and the results are shown in the table below.

| Time | Radius | $\frac{P_{He}}{P_w}$ | $\frac{P_s}{P_w}$ | $\frac{P_d}{P_w}$ |
|-----------|-----------------------|----------------------|-------------------|-------------------|
| 10^{-7} | 1.01×10^{-7} | .814 | .114 | .072 |
| 10^{-6} | 1.10×10^{-7} | .830 | .104 | .066 |
| 10^{-5} | 4.17×10^{-7} | .907 | .027 | .066 |
| 10^{-4} | 5.05×10^{-6} | .997 | .002 | .001 |
| 10^{-3} | 5.35×10^{-5} | 1.00 | .000 | .000 |
| 10^{-2} | 5.40×10^{-4} | 1.00 | .000 | .000 |
| 10^{-1} | 5.40×10^{-3} | 1.00 | .000 | .000 |

C. COMPARISON WITH BAGGE, BECKER, AND BEKOW.

1. Droplet growth. The graph of Figure 3 shows the droplet radius as a function of the growth time as calculated by the method of this paper and as calculated for air and water vapor at a supersaturation of 3.18 by Bagge, Becker, and Bekow²⁰.

The curve as calculated by this paper has a more rapid growth rate in the region of large radii, because diffusion effects were not considered.

2. Temperature increase. The graph of Figure 4 shows the temperature of the drop as calculated by the two methods. Bagge, Becker, and Bekow used an expansion for which the initial temperature was 315°K and the final temperature was 290°K. The supersaturation is 3.18.

The shape of the two curves is similar, and both methods predict approximately the same temperature increase for the drop. Bagge, Becker, and Bekow predict a slightly higher increase of 14°, while the method of this paper predicts only 11.3°. However, the ratios of the changes in temperature of the drop to the changes in temperature of the expansions are approximately the same.

For the method of this paper:

$$\frac{\Delta T_d}{T_1 - T_2} = \frac{11.3}{20} = .565$$

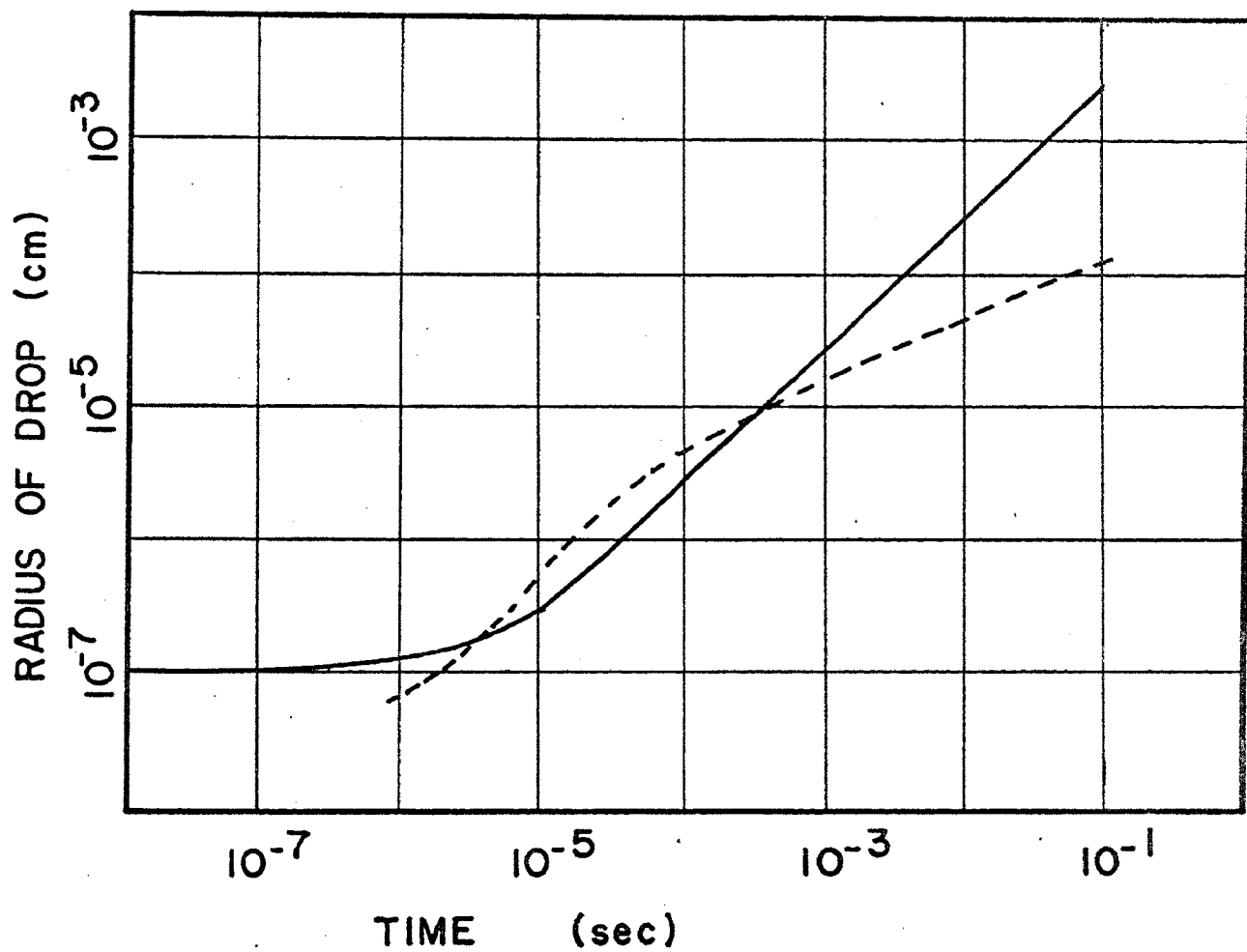


Figure 3. Radius of a drop as a function of the growth time. Solid curve is by the method of this paper. Dashed curve is from Bagge, Becker, and Bekow.

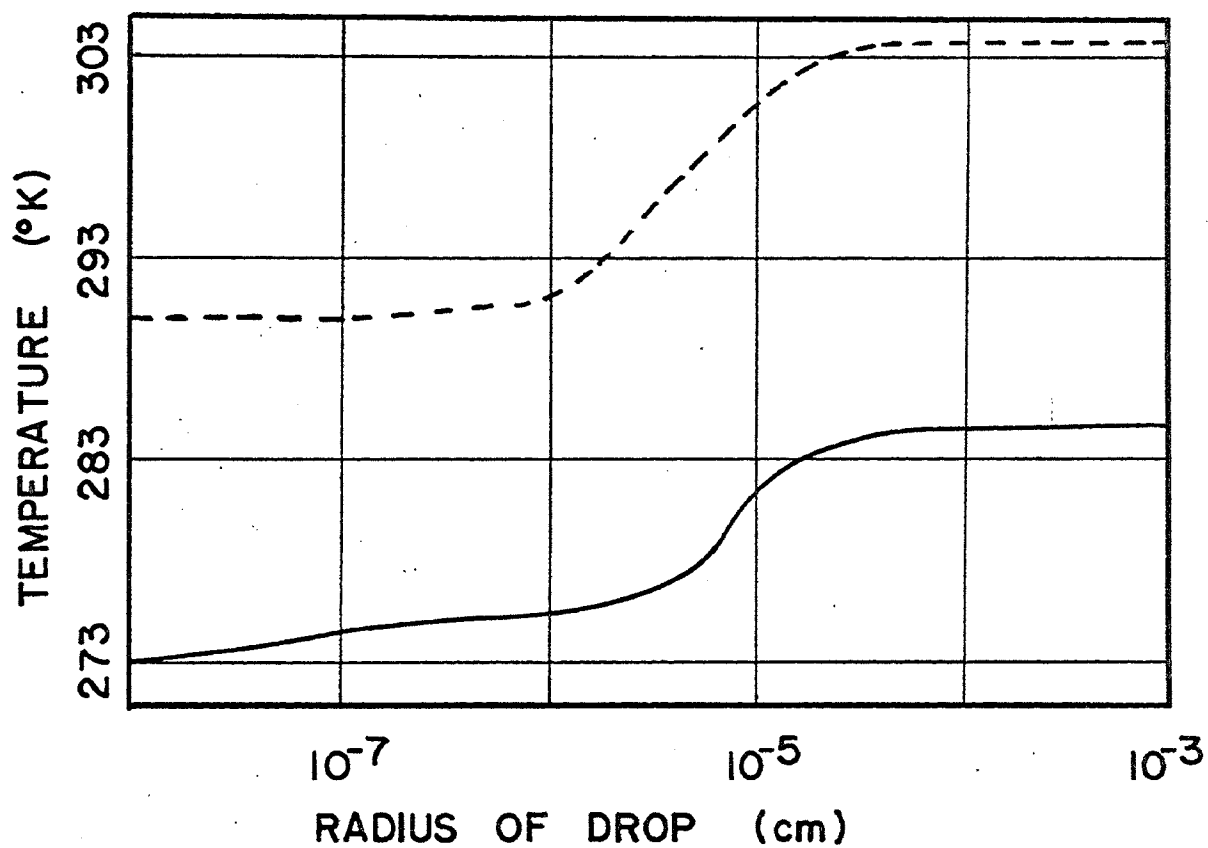


Figure 4. Temperature of the drop as a function of the radius of the drop. Solid curve is by the method of this paper. Dashed curve is from Bagge, Becker and Bekow.

while for Bagge, Becker, and Bekow:

$$\frac{\Delta T_d}{T_1 - T_2} = \frac{14}{25} = .560$$

D. COMPARISON WITH MASON.

Mason derives an expression for the time rate of increase of the square of the radius of a drop using classical vapor and heat diffusion²¹. For growth in the region where the dimensions of the drop are on the order of the mean free path of the vapor, he uses diffusion constants with Langmuir²² corrections.

For ethyl alcohol in nitrogen and a 15% expansion from an initial temperature of 290°K, he calculates that $\frac{d r^2}{dt}$ equals 5×10^{-6} by one method and 4.5×10^{-6} by another.

He compares these to an experimental value of 4.5×10^{-6} found by Hazen²³.

Using the method of this paper, the time rate of increase of the radius of the drop is:

$$\frac{dr}{dt} = \frac{v_B}{4 \pi r^2} (R_I - R_E)$$

Also:

$$\frac{d r^2}{dt} = 2r \frac{dr}{dt}$$

So that:

$$\frac{d r^2}{dt} = \frac{v_B}{2 \pi r} (R_I - R_E)$$

Using this equation, the values of the time rate of increase of the square of the radius of the drop at various growth times were calculated and are shown in the table below.

| Time | $\frac{d r^2}{dt}$ |
|-----------|-----------------------|
| 10^{-5} | 4.06×10^{-8} |
| 10^{-3} | 6.04×10^{-6} |
| 10^{-2} | 6.17×10^{-5} |

V. CONCLUSIONS

The calculations performed for the growth rate of a droplet and for its temperature increase seem to agree reasonably well with other work done in this field. The advantages of this method are that the method and the equations are very simple, and numerical results can be easily obtained. The results of this method can be used as a rough approximation to the growth of large drops and, if applied only to the growth of small drops, can supply the initial conditions for a treatment involving diffusion theory.

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