

The Evaporation Rates of Small, Freely Falling Water Drops

H. A. DUGUID^{1,2} AND J. F. STAMPFER, JR.³

Graduate Center for Cloud Physics Research, University of Missouri-Rolla

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ABSTRACT

The evaporation rates of small (radius 3–9 μ), freely falling water droplets were determined. The droplets, produced in a diffusion cloud chamber, were allowed to fall through air of known relative humidity (95–99%) and at three ambient temperatures (25, 30 and 35C) in a vertical drift tube. The rates of evaporation were ascertained by recording the drop positions on film at fixed time intervals. The results are compared with several existing theories, and are found to lie between the formulation of Kinzer and Gunn and the quasi-stationary theory based on Maxwell's equation.

1. Background

Many models of varying complexity have been proposed for the theory of droplet growth and evaporation. These can generally be classified into two major types depending on whether they were derived from simple diffusion theory or a combination of diffusion and kinetic theory. The kinetic theory ordinarily used is most applicable when considering the volume of space very close to the drop surface, i.e., within a distance of about a mean free path of the gas molecules. For a drop with diameter much larger than this, kinetic considerations, in general, become the less important of the two. Kinetic theory may also be applicable to problems dealing with ventilation and turbulence. Where the above factors are not involved, diffusion theory has proven to be successful in describing the evaporation of droplets. Since the present problem does not involve those aspects for which kinetic theory would be more applicable, the background material to be presented will be primarily concerned with diffusion theory.

a. Non-ventilated drops

Diffusion theory, as a description of drop evaporation, was proposed by Maxwell in 1877 (Fuchs, 1959). Maxwell's model assumed that the rate of evaporation was solely dependent on the rate at which evaporating molecules diffused through the surrounding gaseous medium and that this rate was described by Fick's second law of diffusion. Also, he assumed that the drop was spherical and at rest with respect to the surrounding medium, the vapor concentration at the surface of the drop was equal to the saturation concentration corre-

sponding to the temperature of the drop surface, and the evaporation was a steady-state equilibrium process. Maxwell's equation for the evaporation of a drop is⁴

$$dm/dt = 4\pi aD(\rho_\infty - \rho_a). \quad (1)$$

In terms of radius, the rate may be written as

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

Houghton (1933) experimentally determined the rates of evaporation of water drops, 25–2600 μ in diameter, that were suspended from fine wires or glass filaments. His results, with approximate corrections made for the cooling of the drop, showed a linear relationship between the concentration difference, $\rho_\infty - \rho_a$, and the rate of evaporation, and were in "general agreement with the theoretical evaporation equation."

Whereas Maxwell was only concerned with mass diffusion, in reality the evaporation process involves not only mass transfer but also heat flow. Therefore, when solving the drop evaporation problem, both the mass diffusion and heat flow problems have to be solved simultaneously. This was done by Fuchs (1934). In his model, he assumed that heat transfer was solely due to conduction, and radiation and convection were neglected. Also, he assumed that the coefficient of thermal conductivity, K , was constant throughout the surrounding gas. Then, for stationary state conditions, it follows that the temperature should follow laws analogous to those for mass diffusion, i.e.,

$$\frac{d^2T}{dr^2} \Big|_{r>a} + \frac{2}{r} \frac{dT}{dr} \Big|_{r>a} = 0,$$

¹ Department of Physics.

² Present affiliation: Hopkinsville Community College, Hopkinsville, Ky.

³ Department of Chemistry.

⁴ See the Appendix for definitions of the symbols used here and elsewhere in this report.

for which the solution is

$$T = -\frac{a}{r}(T_a - T_\infty) + T_\infty \quad (3)$$

Also, steady-state conditions require that the heat used in evaporation be equal to the heat flux to the drop from the surrounding gas, or

$$DL \frac{d\rho}{dr} \Big|_{r=a} = -K \frac{dT}{dr} \Big|_{r=a} \quad (4)$$

Obtaining the partial derivative of (3) and for the corresponding equation for the vapor concentration, (4) becomes

$$T_\infty - T_a = (\Gamma/\rho_a)(\rho_a - \rho_\infty), \quad (5)$$

where $\Gamma = K/(DL)$. To relate the vapor density at the drop surface to the temperature of the drop, Fuchs (1959) used the Clausius-Clapeyron equation. However, for very small temperature ranges a linear relationship ($\rho_{\text{equil}} = bT + c$) between equilibrium vapor density and temperature is a good approximation. Since the maximum dew point depression in this investigation was 0.6C, this approximation was substituted in (5); then solving for T_a and then ρ_a , (2) becomes

$$\frac{da^2}{dt} = \frac{2D}{\rho_l} \left(\frac{\Gamma}{\Gamma + b} \right) [\rho_\infty - (bT_\infty + c)],$$

where ρ_∞ and T_∞ are measurable quantities. Similarly, as the humidity was characterized by the dew point depression, it was convenient to express ρ_∞ in terms of the dew point temperature, i.e., $\rho_\infty = bT_{dp} + c$, where b and c are numerically the same as above. The rate of evaporation is then given by

$$-\frac{da^2}{dt} = \frac{2D}{\rho_l} \left(\frac{\Gamma b}{\Gamma + b} \right) (T_\infty - T_{dp}) = \beta \Delta T, \quad (6)$$

where $(T_\infty - T_{dp})$ is the dew point depression. One often mentioned factor in the evaporation of droplets, the increased vapor pressure over a curved surface as compared to a flat surface, has been ignored. Although at the smallest dew point depressions used in this work, 0.1C, the error in ignoring this factor for the smallest drops is about 6%, in the great majority of the data the error is less than 1½%. The possible effects of dissolved impurities have also been neglected for reasons covered in Section 5.

Whereas the development of the evaporating droplet model presented so far has been for stationary evaporation, the evaporation of a droplet, in reality, is a nonstationary process with a continually decreasing droplet surface area. The mathematics can become quite complicated in trying to solve completely the nonstationary evaporation problem. Because of this, Fuchs and others

assumed a quasi-stationary model. This assumes that at any given instant, the rate of evaporation is the same as in the stationary state with boundary conditions that correspond to those of the stationary state at the instant of time in question. It also assumes that the time required for the nonstationary process to become stationary is quite small compared to the time required for the radius of the drop to change appreciably.

Although Fuchs investigated the problem of nonstationary evaporation and concluded that the quasi-stationary assumption was a good approximation for the evaporation of water droplets, others have questioned this. Kirkaldy (1958) studied the problem of time-dependent diffusion theory and arrived at a rate law identical to that given by the quasi-stationary model. He stated, however, that this agreement should not be used as a justification for the quasi-stationary calculation as the mathematical procedure used for the quasi-stationary model was questionable. It is Kirkaldy's opinion that the evaporation phenomenon will not have an acceptable theoretical description until the theory is derived without any reference to stationary states. Philip (1965) also studied the nonstationary problem but in a more general form. The solution for the case of droplet evaporation can be found in Carslaw and Jaeger (1959) as well as for the nonstationary evaporation problem in which the radius is held constant. Philip, using a perturbation method, arrived at an approximate expression for the case in which the radius changes. He states that, even with the shortcomings in the mathematical procedure, the quasi-stationary model is sufficient for most meteorological purposes.

A more important refinement to the Maxwell rate of evaporation concerns the change in the vapor concentration at the surface of an evaporating drop. It was known to early investigators that the temperature of a gas rises abruptly in the vicinity of a surface at a temperature higher than that of the surrounding media beginning at a distance from the surface comparable to the mean free path, λ , of the air molecules. Since the laws governing mass diffusion and temperature conductivity are analogous, this gave reason to believe that there was a change in the gradient of the vapor concentration at the surface of an evaporating drop. The idea of the concentration jump distance was first proposed by Fuchs (1934). He assumed Fick's law was only applicable to a distance Δ from the drop, and that between the drop surface and the distance Δ the rate of evaporation was for that in a vacuum. The distance Δ was assumed to be the same order of magnitude as λ . The resultant rate of evaporation as given by Fuchs is

$$I_F = I_M / \left(\frac{D}{aa\bar{v}} + \frac{a}{a+\Delta} \right). \quad (7)$$

Bradley *et al.* (1946) report experimental results on the

evaporation of dibutyl phthalate and butyl stearate drops at various ambient pressures which support Fuchs' equation for the rate of evaporation.

Some of the other investigators who have derived similar rate laws or who have investigated discontinuities at the drop surface are Tsuji (1950), Monchik and Reiss (1954), Wright (1960, 1961-62), Brock (1964), Okuyama and Zung (1967), and Carstens and Kassner (1968). The paper by Okuyama and Zung, which is primarily concerned with the calculation of the evaporation-condensation coefficient, includes a comparison of the rate equations given by Maxwell, Fuchs, and Monchik and Reiss.

Experiments to determine the rates of evaporation of nonventilated drops can be classified in two categories: those that involve evaporating drops that were supported, and those that involve free drops. Both methods have their limitations. The smallness of a supported drop is dependent on the size of support available. The interpretation of the data is complicated by the corrections that have to be made for heat flow along the support, and distortion of the drop's shape by the support. Fuchs (1959) has given the results of a number of these investigations. For free drops, a Millikan oil drop type experiment has usually been performed. The electric fields necessary to support water droplets has limited the largest sizes to about 5μ . Although convection currents and Brownian movement with these smaller drops made accurate measurements hard to obtain, the results have tended to confirm the Fuchs type formulation. Snead and Zung (1968) have a fairly complete bibliography of the data available.

b. Ventilated drops

The problem of an evaporating drop moving with respect to a medium is quite complicated, as not only is diffusion involved, but also fluid mechanics. Fuchs (1934) looked at possibly the simplest case, laminar flow, for which Stokes' law holds and for which a stationary state exists. His method was to let

$$\rho = \rho_a(a/r) + V_F \phi$$

where V_F is the flow velocity at a large distance from the drop, and the term $V_F \phi$ the perturbing effect of the flow on the concentration distribution. With this model, Fuchs found that any increase in evaporation from the front face of the drop tended to be balanced by a decrease in the rate from the rear face. Fuchs concluded, for Stokes flow, that the motion would have a vanishingly small influence on the evaporation rate.

Frossling (1938), Ranz and Marshall (1952), and Hsu *et al.* (1954), among others, also studied the problem of ventilated drops. All arrived at a rate of evaporation of the form

$$I = I_M(1 + \delta \text{Re}^{\frac{1}{2}} \text{Sc}^{\frac{1}{3}}) = I_M f, \quad (8)$$

where δ is a constant that varied between 0.272 and 0.300 depending on the investigator. For a 5μ drop, because of the very low Reynolds number, the error in the rate due to ignoring f is of the order of 2%. An expression derived by Squires (1952) for the rate of growth of a ventilated drop, which should also apply to evaporation, again indicates a negligible effect due to ventilation.

A notable exception to the rate law given by Eq. (8) was proposed in a theoretical and experimental study by Kinzer and Gunn (1951). Theoretically, the model assumed quasi-transient heat transfer to successive packets of air making thermal contact with a ventilated sphere. They derived a rate equation given by

$$I_{K\&G} = (2D/\rho_l)(\rho_\infty - \rho_a)[1 + F \text{Re}^{\frac{1}{2}}/(4\pi\rho_a D/\eta)^{\frac{1}{2}}], \quad (9)$$

where the term in brackets is the ventilation factor. At STP, the ventilation factor is approximately equal to

$$f = 1 + 0.22F \text{Re}^{\frac{1}{2}}.$$

To determine the factor F , the authors state that an exact knowledge of the air flow around the sphere must be known (see Abraham, 1968). Experimentally they found that F is a function of Re ; their formulation thus differs from that given in (8). However, for drops with $\text{Re} < 1$, F is approximately zero. For these smaller drops, then, Kinzer and Gunn's formula also reduces to the rate given by Maxwell [Eq. (2)]. These investigators found that the temperatures of their ventilated drops were within $\pm 0.3\text{C}$ of the ventilated wet bulb temperature and appear to have used this value to calculate ρ_a . Fuchs (1959) states that the temperature reduction for a small, freely falling drop is approximately the same as for a stationary drop, regardless of its velocity with respect to the medium. This would indicate that the drop temperature is different from the wet bulb temperature. The use of the wet bulb temperature is also questioned by Aroesty and Koenig (1969).

It is evident from the literature that theory has outdistanced experimental work on drop evaporation. This is notably so for ventilated drops with radii from $5-20\mu$. Of the literature reviewed, only Kinzer and Gunn (1951) have reported any data for this size range and that for only one drop. Thus, the present work, besides laying a foundation for future investigations, is an attempt to determine experimentally the behavior of small, freely falling water droplets.

2. Apparatus

As already mentioned, the work that has been reported for the evaporation of ventilated water drops has been mostly for drops that are supported by fine filaments, or thermocouples. This method is limited by the size of the support and the complications due to heat flow. The work presented here is part of a larger problem that may be of interest to the atmospheric

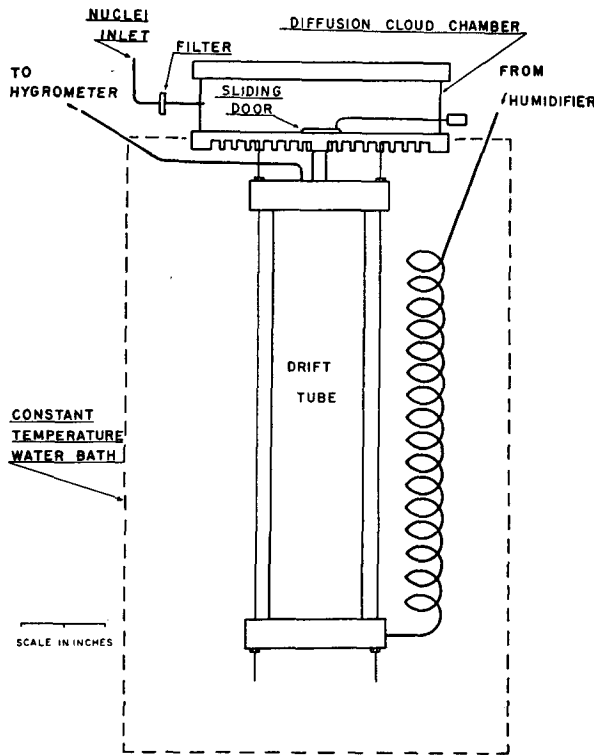


FIG. 1. Drop generator and drift tube.

sciences, namely, the effects of surface active materials on cloud droplet evaporation. Therefore, it was desirable to design the apparatus so that the experimental conditions would correspond as closely as possible to actual atmospheric conditions. With this in mind, a thermal diffusion cloud chamber was used which provided an ample supply of drops of the size range of interest, $3\text{--}9\ \mu$ in radii. Rather than supporting the drops, they were allowed to fall freely through air of various humidities in a drift tube. It was possible to determine, photographically, the terminal velocities and thus the evaporation rates under conditions less artificial than in the methods mentioned above.

The thermal diffusion cloud chamber in which the drops formed is shown in Fig. 1. It was approximately 13 cm in diameter and 2.5 cm high. The upper, electrically heated plate had a water reservoir on its underside which was covered with a porous ($5\ \mu$ diameter pore size), sintered, stainless steel plate. The bottom plate of the chamber had a threaded hole through which the drops passed and which allowed attachment of the drift tube. Provision was made to close this hole with a sliding door.

Condensation nuclei were obtained by injecting room air into the cloud chamber through an $8.0\ \mu$ pore size, Millipore SCWPO2500 filter. The purpose of the filter was to keep contamination of the droplets by these nuclei to a minimum. Filters of smaller pore size were

tried, but nucleation either did not occur or did not produce a sufficient number of droplets.

The drift tube, $25\times 5\times 5$ cm, was constructed from four pieces of polished, double-thick plate glass, sealed with Dow Corning Silastic 732 RTV, and plastic end pieces. It was attached to the bottom plate of the cloud chamber by a 0.6-cm i.d. copper tube which was screwed into the threaded hole in this plate.

Two water baths, thermostatically controlled to $\pm 0.005\text{C}$ by mercury thermoregulators, were used. The entire drift tube and the bottom plate of the cloud chamber were placed in bath A. This bath served three purposes. First, it acted as a heat sink for the bottom plate of the cloud chamber. Second, a thermostated, constant temperature water bath proved to be the best way to eliminate temperature gradients and the accompanying convection currents in the drift tube. Finally, the temperature of the bath, which determined the temperature of the air inside the drift tube, was used as the reference temperature for the experiment. This temperature was measured to the nearest 0.05C by a mercury-glass thermometer.

The other water bath B was used to regulate the humidity in the drift tube. A 30 cm square, 5 cm deep, lucite box was filled with water to a depth of 4 cm. Lucite baffles attached to the top of the box extended down into the water and formed a path approximately 1 cm wide and 7.5 m long over the water surface. This humidifier was maintained at a constant temperature, the desired dew point temperature, by submerging it completely in bath B. To produce the desired vapor density (dew point) in the drift tube, air was pumped at a rate of $1\ \text{liter min}^{-1}$ through a preconditioner, the humidifier, and finally the drift tube (Fig. 2). The preconditioner was simply a flask of water maintained at a temperature at least 5C higher than the drift tube. To prevent unwanted condensation, all of the $\frac{1}{4}$ -inch copper tubing which connected the various parts of the humidifying system and which was exposed to room temperature was heated to a temperature higher than that of the humidifier. Also, before entering the humidifier or drift tube, the air passed through at least 2 m of copper tubing immersed in the appropriate bath.

In the discussion which follows this section, the water vapor density is reported as dew point depression ΔT . [As shown in Eq. (6), Maxwell's equation can be written in terms of dew point depression with negligible error.] In each run, ΔT was determined by measuring the difference output of a pair of copper-constantan thermocouples, one in the drift tube bath and one in the humidifier. Another pair of thermocouples measured the difference in temperature between the humidifier itself and the bath it was in. Both these difference potentials were measured with a Leeds and Northrup K-5 potentiometer which had a sensitivity of $0.02\ \mu\text{V}$ and a limit of error of $0.1\ \mu\text{V}$ (0.0025C).

As they fell in the drift tube, the drops were photographed with an Automax, 35-mm, G-1 movie camera

produced by Traid Corporation. A 55-mm, $f/3.5$ Auto Micro-Nikkor lens was used. The framing rate, externally controlled, was 2 ± 0.02 frames per second. The light source was a 30 cm long, GE 1000-T-3/CL quartz, incandescent bulb. The light from the bulb was collimated by a cylindrical lens, and the width of the beam further reduced by masking the front of the lamp housing so that the emitted beam was 1 cm wide. The lamp was positioned so that it illuminated the cloud chamber and the upper two-thirds of the drift tube. The center of the beam coincided with the center of the drift tube and the hole in the bottom plate of the cloud chamber, and the camera looked at about a 30° angle to this incident light. Eastman Kodak Linograph Shellburst film was used and developed in a 1:1 dilution of Acufine film developer for 18 min. This gave an effective ASA rating of about 800 with high contrast and fine grain size.

The positions of the drops in the drift tube were determined by projecting the film onto a previously calibrated screen. The screen was calibrated by photographing a grid hung in the center of the drift tube and then projecting this film on the screen. The grid, 6 cm long by $2\frac{1}{4}$ cm wide, was a metal frame with $40\ \mu$ diameter wires stretched horizontally at 2-mm intervals. The actual spacing was measured to $10\ \mu$.

3. Experimental procedure

After the temperature of the bath surrounding the drift tube was established, the temperature of the bath surrounding the humidifier was adjusted to the desired dew point. The difference in temperature between the two baths, ΔT , was monitored for a period of at least an hour before a run was initiated. When the temperature differences between the baths and between bath B and the humidifier had stabilized, air was pumped through the system (Fig. 2) at a rate of $1\ \text{liter}\ \text{min}^{-1}$ for at least a half-hour. The relatively long period of time between the start of the humidifying process and the initiation of data taking was to insure that even if water vapor were adsorbed by the system, equilibrium had been reached and the dew point of the air going through the drift tube was the same as the temperature of bath B.

At this time room air was injected into the cloud chamber, the humidifier pump turned off, and the drift tube closed off from the humidifier. The room air was introduced into the cloud chamber while the humidifier pump was still on to prevent forcing air under the door and into the drift tube. The droplet concentration in the cloud chamber was observed until it was at the desired level. This concentration was arrived at by trial and error and was dependent on the rate that drops fell into the drift tube. With an overabundance, a cloud rather than a few drops entered the tube. Not only did this cause difficulty in keeping track of individual drops from one frame to the next, but it raised the possibilities

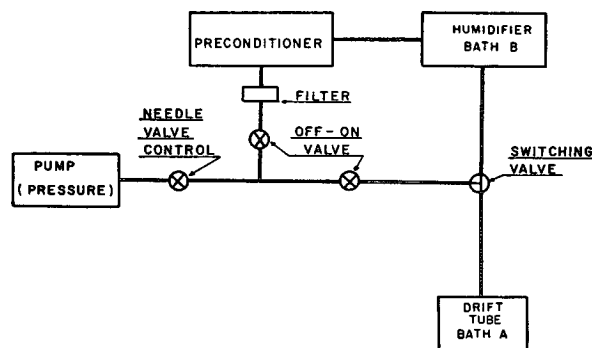


FIG. 2. Humidification system.

of drop interaction and humidity change. The optimum condition was a single drop. However, for about half the runs, up to six drops were present in the field of view at any one time. If the population in the cloud chamber did not decrease to a usable value within 1 min, the humidifier was again connected, and the drift tube rehumidified for about a minute. This was also done when there was a paucity of drops in the chamber.

When the drops fell into the field of view, the camera was started. At the end of 20–30 sec, or when drops ceased to fall into the drift tube, the camera was stopped. The maximum data acquisition time of 30 sec was due to the length of film that could be conveniently handled during the developing procedure and the concern that a longer time might allow a change in the humidity in the drift tube.

Following the end of the run, the drift tube was reconnected to the humidifier, the air pump started, and the door separating the drift tube from the cloud chamber closed. At this time the difference in temperature between the baths and between bath B and the humidifier were noted. The humidification process was continued for about a minute to insure that the drift tube had been thoroughly flushed and then the data acquisition process repeated. This was continued until four runs had been obtained for each dew point temperature at each ambient temperature.

4. Results

The raw data consisted of the measured position of the drop in the drift tube, as a function of time, as well as the ambient temperature and dew point depression. From the position of the drop in two successive film frames, an average drop size was calculated using Stokes law:

$$a^2 = \frac{9\eta V}{2(\rho_l - \rho_A)g} \quad (10)$$

The numerical values of the constants used in this and the other equations discussed in this report are listed in Table 1.

TABLE 1. Physical constants used in the analysis and the temperature variation.

Property	Symbol	Temperature			Units	Source
		25C	30C	35C		
Viscosity of air	η	183.2	185.6	188.0	μ poise	<i>International Critical Tables</i> (1926)
Density of air	ρ_A	1.124	1.101	1.077	gm liter ⁻¹	Hodgman (1963)
Thermal conductivity of air	K	6.067×10^{-5}	6.14×10^{-5}	6.229×10^{-5}	cal[sec cm (°K)] ⁻¹	Taylor and Johnston (1946)
Density of water	ρ_l	0.997	0.996	0.994	gm cm ⁻³	Hodgman (1963)
Diffusion coefficient	D	0.261	0.270	0.278	cm ² sec ⁻¹	Reid and Sherwood (1958); Fuller <i>et al.</i> (1966)
Coefficient of T from $\rho_{equil} = bT + c$	b	1.26×10^{-6}	1.60×10^{-6}	2.03×10^{-6}	gm [cm ³ (°K)] ⁻¹	Hodgman (1963)
Heat of vaporization of water	L	582.8	579.5	576.8	cal gm ⁻¹	<i>International Critical Tables</i> (1926)

Data were taken at three different ambient temperatures, 25, 30 and 35C, and dew point depressions ranging from 0.1-0.6C. For the moment let it be assumed that the evaporation is adequately described by Maxwell's theory. If this is the case then the size of the drop is related to time by

$$\left. \begin{aligned} a^2 &= -\gamma t + a_0^2 \\ -da^2/dt &= \gamma \end{aligned} \right\} \quad (11)$$

where γ is a function of the ambient temperature and dew point depression. The data for each individual drop were fitted with a straight line, by the method of least squares. Fig. 3 shows the data for three drops at 30C. The slopes of these lines, γ , are plotted in Figs. 4-6 as a function of dew point depression for the three ambient temperatures. Again, straight lines were fit to these

data [see (8)] to give

$$-da^2/dt = \beta \Delta T + R_0. \quad (12)$$

The slopes β and the Y intercept R_0 of these computed curves are listed in Table 2. The error limits are at the 95% confidence level. Finally, the data from these three figures are combined in Fig. 7 which is a plot of the rate of evaporation vs the ambient temperature for three relative humidities.

Subsequent to obtaining the data reported above, the nuclei inlet system was changed so that nuclei which contained surface active materials could be introduced into the cloud chamber (Hughes, 1970). This modification included pumping room air through a trough which could be heated and could contain the surface active material, a glass cylinder, and, finally, an "absolute" filter. To show that this change in the

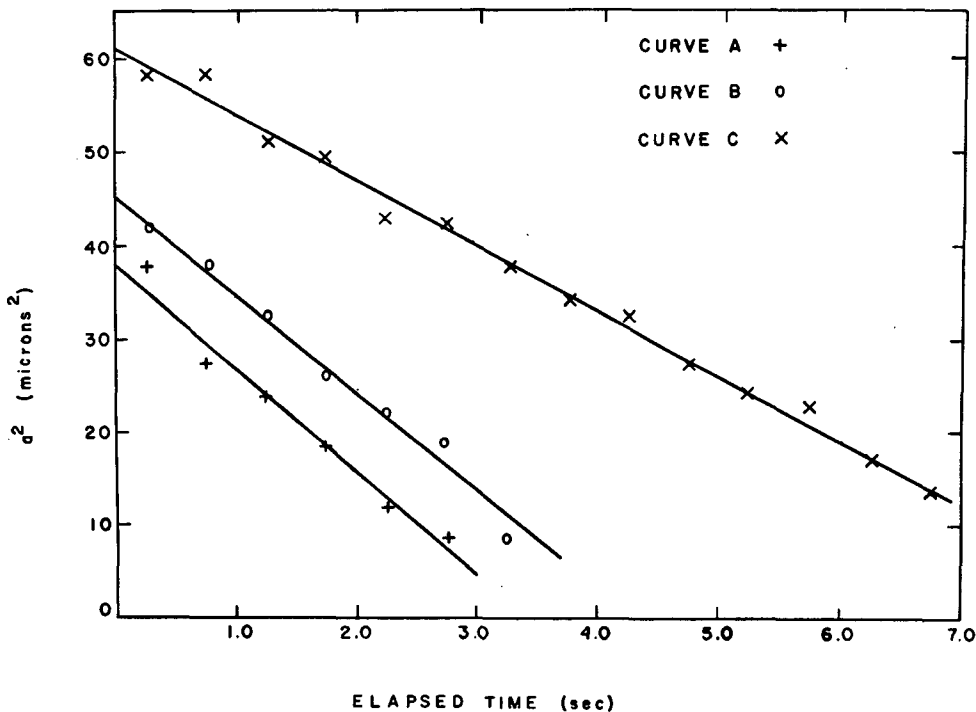


FIG. 3. Examples of evaporation of individual drops.

introduction system did not change the behavior of "pure" drops, additional data were taken at 29.9C. (It can be seen from Fig. 7 that there is no appreciable difference in rates between 29.9 and 30.0C.) As there were no apparent differences in these two sets of data, they were combined and are shown as "all data" in Table 2.

5. Discussion

Our main purpose in what follows is to compare the experimentally determined evaporation rates to those which would be predicted from simple concentration diffusion without ventilation, simple diffusion with ventilation, and combination diffusion-kinetic theories. To do this, we will compare the experimental results with the theories of Maxwell, Kinzer and Gunn, and Fuchs, respectively.

The comparison which will be made initially (shown in Table 2) is between the calculated and experimental slopes and intercepts of the $-da^2/dt$ vs ΔT curves. As already noted, the calculated slope for the Maxwell equation is simply $(2D/\rho_l)[\Gamma b/(\Gamma+b)]$, where $\Gamma=K/(DL)$. In the case of Kinzer and Gunn, (9) reduces to

$$-d(a^2)/dt = (2D/\rho_l)(\rho_{wb} - \rho_\infty) \tag{13}$$

for small Re, where ρ_{wb} is the saturation vapor density at the temperature of the ventilated wet bulb. Using the same approximation for the relationship between vapor density and temperature as before, the rate may also be written as

$$-d(a^2)/dt = (2Db/\rho_l)(T_{wb} - T_{dp}). \tag{14}$$

In order to compare this with the experimental results, it was necessary to calculate the dew point correspond-

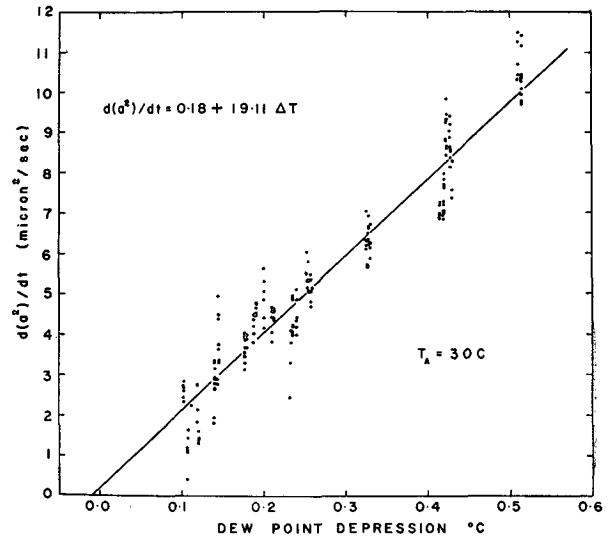


FIG. 5. Rates of evaporation at 30C.

ing to a given wet bulb temperature. This was done by determining the relative humidity at the given wet bulb temperature using the psychrometric equation for a ventilated wet bulb given by the U. S. Weather Bureau (1953). Once the relative humidity was known, the corresponding vapor density was determined from which the dew point, and dew point depressions were calculated.

The slope from Fuchs' theory [Eq. (7)], for a given drop size, is simply the Maxwell rate divided by $[D/(a\bar{v}) + a/(a+\Delta)]$, where $a/(a+\Delta)$ is assumed to be 1. That is,

$$I_F = -\beta\Delta T/[D/(a\bar{v}\alpha) + 1]. \tag{15}$$

It must be pointed out that (15) only gives an upper

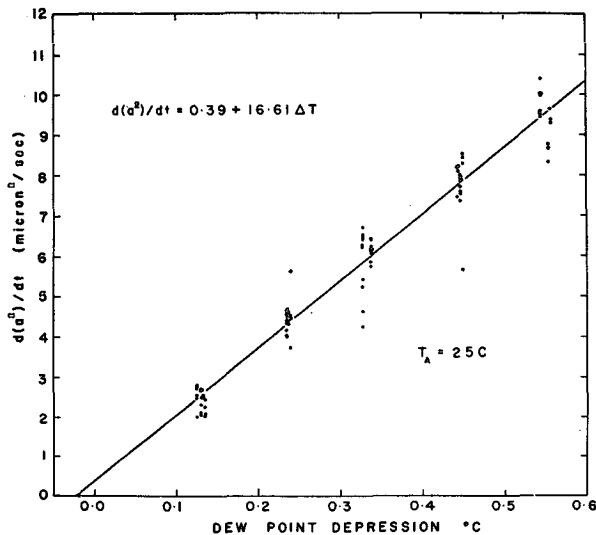


FIG. 4. Rates of evaporation at 25C.

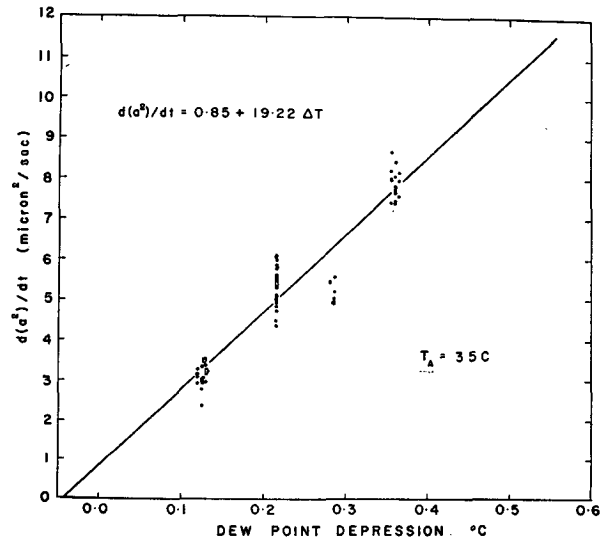


FIG. 6. Rates of evaporation at 35C.

TABLE 2. Comparison of theoretical and experimental evaporation rates.

Temperature (°C)	No. of drops	Experimental results*			Theoretical values of β				
		β	R_0	x intercept	Maxwell Col. 1**	Maxwell Col. 2***	Kinzer and Gunn	Fuchs 3μ	Fuchs 7μ
25	96	16.6±0.7	0.4±0.3	0.02	15.9	16.5	20.7	6.2	9.6
30 (partial data)	182	19.1±0.8	0.2±0.2	0.01	17.1	17.8	23.8	6.7	10.4
30 (all data)	286	19.3±0.7	0.1±0.2	0.01	17.1	17.8	23.8	6.7	10.4
35	75	19.2±1.5	0.9±0.4	0.04	18.2	19.0	26.65	7.1	11.1

* Errors are at the 95% confidence level.

** Based on values for K given by Taylor and Johnston (1946).

*** Based on values of K 5% greater than those used in column (1).

limit for the evaporation according to Fuchs. Although the effect of the discontinuity in the vapor density close to the drop surface is included, no account is taken of the corresponding temperature discontinuity. In the same way as the flow of water molecules away from the drop is hindered, so the transport of heat from the gas to the drop is also decreased. Thus, for a given amount of evaporation, the drop would actually be cooler with the discontinuity present than if it were absent. This, in turn, would decrease the rate of evaporation even more so that the actual rate should be less than that shown by (15).

In Table 2, two sets of rates are given for the simple diffusion theory. In the first of these, the values for the thermal conductivity K of air given by Taylor and Johnston (1946) were used. However, there is a question whether these are correct. The latest measured values (Saksena and Saxena, 1966) are numerically larger than those of Taylor and Johnston, the differences becoming greater at lower temperatures. At the lower limit of the temperature range over which K was measured, 40C,

the value was 5–6% greater than that of Taylor and Johnston. Because of this discrepancy, the evaporation rates were also calculated using values of K 5% greater than used previously. The results using these latter values are listed in the second column under Maxwell.

As is readily apparent, the experimental rates are most closely predicted by Maxwell's theory. However, it is also true that all the experimental rates are higher than the theoretical values and that all the Y intercepts indicate finite evaporation rates under saturated conditions. The rates predicted by Kinzer and Gunn, who assumed that a drop is ventilated to such an extent that it takes on the ventilated wet bulb temperatures, are much too high. This is in accord with Fuchs (1959) and Aroesty and Koenig (1969) who state that ventilation is not a factor with drops of this size. We cannot, however, rule out the possibility that some ventilation is responsible for the slightly higher rates than are predicted by Maxwell. Finally, in the last two columns are shown the rates which would be predicted by Fuchs for drops of two different sizes. The larger radius, 7μ , is typical of a drop at the beginning of evaporation, while 3μ is a typical final size. These rates are considerably lower than the experimental rates. Another indication of the possible incorrectness of the Fuchs formulation may be obtained by examining the evaporation history of each of the individual drops. It is evident from (7) that a plot of a^2 vs time should exhibit a curve which is concave upward. To determine whether this curvature was exhibited by the data, second-degree polynomials were fit to the data for each drop. As many of these polynomials exhibited downward curvature as upward. Further, this curvature was often due to data obtained at either the very beginning or end of the data run. Fig. 3 shows the data for three individual drops. Curve A is for a drop with a large calculated upward curvature, curve B for large downward curvature, and curve C for negligible curvature.

Although there is disagreement about the true value for α [see Mills and Seban (1967) for a recent compilation], the most commonly accepted value, at least in the literature pertaining to the atmospheric sciences, is 0.036 (Alty and Mackay, 1935). This is the value

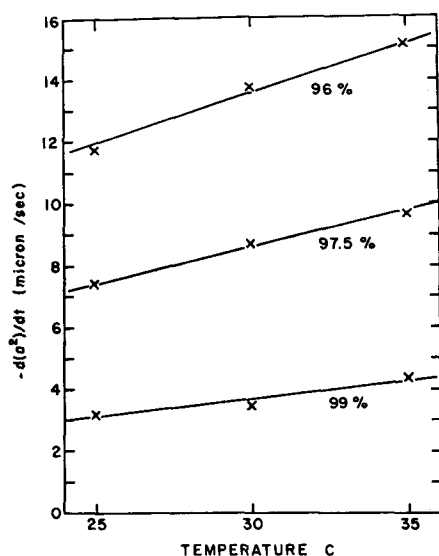


FIG. 7. Rates of evaporation as a function of relative humidity.

which has been assumed in the discussion above. If the true value is less than this, the above arguments still hold. However, as the assumed value increases, the differences between theory and experiment decreases. For example, for values of α equal to 0.036, 0.1, 0.5 and 1.0, the rates calculated by (15) for an "average" $5\ \mu$ drop would be 8.9, 13.1, 16.6 and 17.1, respectively. Further, the plots of a^2 vs time should exhibit less curvature the greater the value of α which is assumed. It is obvious that any final argument about the validity of a Fuchs type formulation must await a final determination of α . However, unless this value is about 0.5 or greater, we feel these data cast serious doubt on the correctness of this theory.

The discussion above implies that the evaporation of pure water droplets is probably best described by simple diffusion theory with, possibly, a small ventilation effect. However, to put this in proper perspective, a discussion of the experimental errors is mandatory.

The primary measurements in the experiment were the position of the image of the drop on the film, the time between successive film frames, and the difference in temperature between the two water baths. The error in measuring the position of the drop image was ± 0.05 mm which resulted in a most probable error in the displacement of ± 0.07 mm. For the smaller displacements between successive frames, this could amount to a 10% error. The time interval between film frames was determined by measuring the time for 30 frames to an accuracy better than 0.1 sec. This error, as already noted, was $\pm 1\%$. The temperature difference between the two water baths was measured with a pair of thermocouples. Because of the method of temperature control, the temperature of each bath fluctuated slightly, $\pm 0.005^\circ\text{C}$, over a period of a few minutes. Since there was also a lag between the change of temperature in the humidifier and the surrounding water bath, it was possible that the error in the dew point depression was as much as $\pm 0.01^\circ\text{C}$.

Looking at Figs. 4–6, there is a noticeable amount of scatter in the evaporation rates. For a given dew point depression, the difference between the maximum and minimum values of $-d(a^2)/dt$ is of the order $1.5\ \mu^2\ \text{sec}^{-1}$. The most probable error in $-d(a^2)/dt$, $\pm 0.27\ \mu^2\ \text{sec}^{-1}$, due to the errors in drop position, time and ΔT , is not sufficient to explain this scatter. This indicates that the variation in the experimental results is due to factors other than those inherent in the measurements.

One non-random error we know to exist is a result of using Stokes' law. Davies (1945) has shown that the true terminal velocity is found by multiplying the Stokes' velocity by a slip factor. However, this factor is only 1.02 for a $5\ \mu$ drop and 1.04 for a $2\ \mu$ drop. We believe that neglecting this factor has introduced a negligible error.

Two other possibilities were investigated. A change in the humidity of the air in the drift tube during the course of a data run could have produced a difference

in the rates of evaporation for drops at the beginning and end of the run. However, an examination of the data did not reveal time-dependent trends. Another possibility was the existence of convection currents within the drift tube. The data would seem to indicate that this was not a problem. If the convection currents were steady, all the drops in one run should have exhibited very nearly the same evaporation behavior. However, there appeared to be as much spread in the rates for drops in any one run as between runs. If, on the other hand, there were small turbulent eddies present, a greater scatter in the a^2, t data for individual drops should have been evident. In addition, while there should have been noticeable horizontal motion, no such motion was observed.

A further possibility involves the drops themselves. It has been assumed that these were pure water. Since they were formed in a diffusion cloud chamber on condensation nuclei, they were, in fact, contaminated to varying degrees. Soluble impurities would tend to lower the water vapor density over the drops and thus decrease the evaporation rates. Although this could produce scatter in the results, it would mean that the rates for truly pure drops would be even greater than the values reported here. Insoluble surface active materials (SAM) present in large enough quantities have also been shown to lower evaporation rates (Eisner *et al.*, 1960; Derjaguin *et al.*, 1966; Snead and Zung, 1968). This effect would produce results similar to soluble impurities. In experiments subsequent to the ones reported here (Hughes, 1970) and alluded to in a previous section, it has been found that small quantities of SAM, affording less than full surface coverage, can increase the rate of evaporation over that for untreated drops. Some of the rates reported herein might, then, be associated with drops having a very small quantity of impurity, allowing them to evaporate more rapidly than pure drops. Preliminary, unpublished analyses of the amounts of SAM in precipitation, measured with a Langmuir film balance, have shown values as high as $10\ \text{cm}^2$ per milliliter of collected precipitation. It is logical to assume that at least some of this SAM existed originally on the atmospheric aerosol and might be incorporated on the drops formed in the cloud chamber. Previous to the work with SAM, we had found it difficult to explain the scatter in these data. Now, although we can offer no proof, we feel that the scatter in the rates as well as observed magnitudes—greater than might be predicted theoretically—can be explained.

6. Conclusions

The original purpose in conducting these experiments was to establish the rates of evaporation for freely falling, pure water droplets with which the rates for drops contaminated with SAM could be compared. At the time these data were taken, the authors were at a loss to explain the results, particularly the large scatter

in the data. More recent data (Hughes, 1970) allow a possible explanation.

From the work reported in this article we would draw the following conclusions:

1) Although the drops, the rates of evaporation for which are reported herein, were undoubtedly not pure, the results are best described by Maxwell's simple theory of diffusion-controlled evaporation without ventilation.

2) While the effects of contamination of the drops might well be to increase the rates, it is unlikely that this effect is great enough to overshadow the relatively small rates predicted by a Fuchs type, diffusion-kinetic theory for pure drops, unless it can be shown that the true value of the condensation coefficient is greater than 0.5.

3) The evaporation rates which were determined are undoubtedly closer to the evaporation rates of true atmospheric cloud droplets than one could calculate from the best of theories applied to pure water or water solution droplets.

4) Small concentrations of unknown substances, probably always present in atmospheric processes, may have a measurable effect on these processes.

5) In heterogeneous processes, of which evaporation and growth are examples, surface rather than bulk properties may be all important.

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APPENDIX

List of Symbols

a	radius of drop
a_0	radius of drop at time zero
b, c	coefficients in equation, $\rho_{\text{equil}} = bT + c$
f	ventilation factor
g	gravitational acceleration
m	mass
r	distance from center of drop
t	time
\bar{v}	$(kT/2\pi m)^{-1/2}$
D	diffusion coefficient of water vapor in surrounding gaseous medium
I	rate of evaporation, $-da^2/dt$
K	coefficient of thermal conductivity
L	latent heat of evaporation
R_0	Y intercept in equation, $-da^2/dt = \beta\Delta T + R_0$
Re	Reynolds number
Sc	Schmidt number

T	temperature
ΔT	dewpoint depression, $T_\infty - T_{dp}$
V	terminal velocity of falling drop
α	evaporation-condensation coefficient
β	slope of line given by $-da^2/dt = \beta\Delta T + R_0$
γ	slope of line given by $a^2 = -\gamma t + a_0^2$
ρ	density
Γ	$K/(DL)$
η	viscosity of air

Subscripts

a	surface of drop
dp	dew point
l	liquid
wb	wet bulb
A	surrounding air
F	Fuchs
K & G	Kinzer & Gunn
M	Maxwell
∞	conditions prevailing infinitely far from the drop and assumed to be the bulk value in the surrounding gas

REFERENCES

- Abraham, F. F., 1968: A physical interpretation of the structure of the ventilation coefficients for freely falling water drops. *J. Atmos. Sci.*, **25**, 76-81.
- Alty, T., and C. A. Mackay, 1935: The accommodation coefficient and the evaporation coefficient of water. *Proc. Roy. Soc. London*, **A149**, 104-116.
- Aroesty, J., and L. R. Koenig, 1969: Note on the temperature and evaporation of small droplets. *J. Atmos. Sci.*, **26**, 780-782.
- Bradley, R. S., M. G. Evans and R. W. Whytlaw-Gray, 1946: The rate of evaporation of droplets. *Proc. Roy. Soc. London*, **A185-186**, 368-390.
- Brock, J. R., 1964: Evaporation and condensation of spherical bodies in noncontinuum regimes. *J. Phys. Chem.*, **68**, 123-128.
- Carlsaw, H. S., and J. C. Jaeger, 1959: *Conduction of Heat in Solids*. Oxford University Press, 230-237.
- Carstens, J. C., and J. L. Kassner, Jr., 1968: Some aspects of droplet growth theory applicable to nuclei measurements. *J. Rech. Atmos.*, **3**, 33-40.
- Davies, C. N., 1945: Definitive equations for the fluid resistance of spheres. *Proc. Phys. Soc. London*, **57**, 259-270.
- Derjaguin, B. V., V. A. Fedoseyev and L. A. Rosenzweig, 1966: Investigation of the adsorption of cetyl alcohol vapor and the effect of this phenomenon on the evaporation of water drops. *J. Colloid. Sci.*, **22**, 45-50.
- Eisner, J., B. Quince and C. Slack, 1960: The stabilization of water mists by insoluble monolayers. *Disc. Faraday Soc.*, **30**, 86-95.
- Frossling, N., 1938: On the evaporation of falling drops. *Beitr. Geophys.*, **52**, 170.
- Fuchs, N. A., 1934: Concerning the velocity of evaporation of small droplets. *Phys. Z. Sowj.*, **6**, 224-243; also, NACA Tech Memo. 1160, August 1947.
- , 1959: *Evaporation and Droplet Growth in Gaseous Media*. New York, Pergamon Press, 72 pp.
- Fuller, E., P. D. Schettler and C. J. Giddings, 1966: A new method for prediction of binary gas-phase diffusion coefficients. *Ind. Eng. Chem.*, **58**, 19-27.
- Hodgman, C. D., 1963: *Handbook of Chemistry and Physics*, 44th ed. Cleveland, The Chemical Rubber Publishing Co.
- Houghton, H. G., 1933: A study of the evaporation of small water drops. *Physics*, **4**, 419-424.

- Hsu, N. T., K. Sato and B. H. Sage, 1954: Material transfer in turbulent gas streams: Influence of shape on evaporation of drops of *n*-heptane. *Ind. Eng. Chem.*, **46**, 870-876.
- Hughes, R. B., 1970: Enhanced evaporation of water droplets due to surface contamination. M.S. thesis, The University of Missouri, Rolla.
- , and J. F. Stampfer, Jr., 1971: Enhanced evaporation of small, freely falling water drops due to surface contamination. *J. Atmos. Sci.*, **28**, 1244-1251.
- International Critical Tables of Numerical Data, Physics, Chemistry and Technology*, Vol. 5, 1926; New York, McGraw-Hill.
- Kinzer, G. D., and R. Gunn, 1951: The evaporation, temperature, and thermal relaxation time of freely falling water drops. *J. Meteor.*, **8**, 71-83.
- Kirkaldy, J. S., 1958: The time-dependent diffusion theory for condensation on spherical and plane surfaces. *Can. J. Phys.*, **36**, 446-455.
- Mills, A. F., and R. A. Seban, 1967: The condensation coefficient of water. *Intern. J. Heat Mass Transfer*, **10**, 1815-1827.
- Monchick, L., and H. Reiss, 1954: Studies of evaporation of small drops. *J. Chem. Phys.*, **22**, 831-836.
- Okuyama, M., and J. T. Zung, 1967: Evaporation-condensation coefficient for small droplets. *J. Chem. Phys.*, **46**, 1580-1585.
- Philip, J. R., 1965: Kinetics of growth and evaporation of droplets and ice crystals. *J. Atmos. Sci.*, **22**, 196-206.
- Ranz, W. E., and W. R. Marshall, Jr., 1952: Evaporation from drops. *Chem. Eng. Prog.*, **48**, 141-146, 173-180.
- Reid, R. C., and T. K. Sherwood, 1958: *The Properties of Gases and Liquids*. New York, McGraw-Hill, 281-282.
- Saksena, M. P., and S. C. Saxena, 1966: Measurement of thermal conductivity of gases using thermal diffusion columns. *Phys. Fluids*, **9**, 1595-1599.
- Snead, C. C., and J. T. Zung, 1968: The effects of insoluble films upon the evaporation kinetics of liquid droplets. *J. Colloid Interface Sci.*, **27**, 25-31.
- Squires, P., 1952: The growth of cloud drops by condensation, I. General characteristics. *Australian J. Sci. Res.*, **A5**, 59-86.
- Taylor, W. J., and H. L. Johnston, 1946: Thermal conductivity measurement. *J. Chem. Phys.*, **14**, 219-233.
- Tsuji, M., 1950: On the rate of evaporation and condensation of falling drops. *Geophys. Mag. (Tokyo)*, **22**, 11-14.
- U. S. Weather Bureau, 1953: Relative humidity-psychrometric tables, revised edition.
- Wright, P. G., 1960: On the discontinuity involved in diffusion across an interface (The Δ of Fuchs). *Disc. Faraday Soc.*, **30**, 100-112.
- , 1961-62: The effect of the transport of heat on the rate of evaporation of small droplets, I. Evaporation into a large excess of a gas. *Proc. Roy. Soc. Edinburgh*, **A66**, Part 2, 65-80.