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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL MEMORANDUM

No. 1160

15 DEC 1947

CONCERNING THE VELOCITY OF EVAPORATION OF SMALL DROPLETS
IN A GAS ATMOSPHERE

By N. Fuchs

Physikalische Zeitschrift der Sowjetunion
Vol. 6, 1934



Washington
August 1947

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CONCERNING THE VELOCITY* OF EVAPORATION OF SMALL DROPLETS

IN A GAS ATMOSPHERE¹

By N. Fuchs

SUMMARY

The evaporation velocity of liquid droplets under various conditions is theoretically calculated and a number of factors are investigated which are neglected in carrying out the fundamental equation of Maxwell. It is shown that the effect of these factors at the small drop sizes and the small weight concentrations ordinarily occurring in fog can be calculated by simple corrections. The evaporation process can be regarded as quasi-stationary in most cases.

The question at hand, and also the equivalent question of the velocity of growth of droplets in a supersaturated atmosphere, is highly significant in meteorology and for certain industrial purposes. Since the literature concerning this is very insufficient and many important aspects either are not considered at all or are reported incorrectly, it seems that a short discussion is not superfluous. Especial consideration will be given to the various assumptions and neglections that are necessary in deriving the fundamental equation of Maxwell. The experimental work available, which is very insufficient and in part poorly dependable, can be used as an accurate check on the theory only in very few cases.

I. THE FUNDAMENTAL EQUATION

The theory of the evaporation process in a gas atmosphere owes its beginnings to Maxwell (reference 1) and Stefan (reference 2). The theory rests on the assumption that the vapor in the immediate neighborhood of the liquid surface is completely saturated, and that consequently the velocity of evaporation depends simply on the velocity of diffusion of the vapor into the surrounding space. This viewpoint was experimentally

*The term "Velocity" as used in this report corresponds to "rate" as currently used in American reports.

¹From *Physikalische Zeitschrift der Sowjetunion*, vol. 6, 1934, pp. 224-243.

substantiated by Stefan himself, and also by Winkelmann (reference 3) and except for a limitation later discussed further, is regarded as an established fact.

Since diffusion and heat conduction are physically related concepts and are also completely equivalent processes from a mathematical viewpoint, use can be made of the heat transfer theory, which has been worked out in great detail, in the theoretical calculation of the velocity of evaporation.

Now, turn to the derivation of the fundamental equation for the velocity of evaporation of small droplets in a gas atmosphere. To do so, a series of simplifying assumptions must be made. Later, these assumptions will be examined one by one and corresponding corrections will be introduced in the fundamental equation. The assumptions are:

1. The drop is spherical.
2. There is no motion of the drop relative to the gas atmosphere.
3. The atmosphere extends unbounded in all directions.
4. The atmosphere is all at the same temperature and pressure. The lowering of temperature of the drop is neglected because of the evaporation.
5. The evaporation process is stationary.
6. The vapor is saturated on the surface of the drop.
7. The vapor pressure of the drop is vanishingly small in comparison with the total pressure.

Since the process takes place sphero-symmetrically, Fick's law,

$$\frac{\partial c}{\partial t} = D \Delta c \quad (1)$$

expressed in spherical coordinates, becomes

$$\frac{\partial (cr)}{\partial t} = D \frac{\partial^2 (cr)}{\partial r^2} \quad (2)$$

In the stationary instance this reduces to

$$\frac{\partial^2 (cr)}{\partial r^2} = 0 \quad (3)$$

or, integrated

$$c = A + \frac{B}{r} \quad (4)$$

If c_0 is the concentration of the saturated vapor, and c_1 the concentration at infinite distance from the drop, then there is obtained:

$$c - c_1 = (c_0 - c_1) \frac{a}{r} \quad (5)$$

where a is drop radius.

The amount of substance (expressed in moles) diffusing away per unit time is (reference 1),

$$I_0 = -4\pi D r^2 \frac{dc}{dr} = 4\pi a D (c_0 - c_1) \quad (6)$$

Therefore the velocity of evaporation of the drop in a gas atmosphere, as opposed to evaporation in a vacuum, is proportional to the diameter and not the surface. (Results are substantiated by Sresnewski (reference 4) and Morse (reference 5.) Topley and Whytlaw-Gray (reference 6) checked experimentally formula (6). Since

$$I_0 = -\frac{\gamma}{M} \frac{dv}{dt} = -\frac{2\pi a \gamma}{M} \frac{d(a^2)}{dt} \quad (7)$$

where

γ liquid density

v drop volume

M molecular weight of liquid

Then, from equations (6) and (7)

$$\frac{d(a^2)}{dt} = -\frac{2(c_0 - c_1)MD}{\gamma} = k, \quad \text{a constant,} \quad (8)$$

that is, the drop surface changes linearly with time. Here, equation (6) is assumed to hold even for constantly changing drop size. This is true, down to a certain drop size, for the most widely different experimental conditions.

A correction must be applied to equation (6) if the previous assumptions are not fulfilled. Also, without loss of generality, c_0 can be written for c_1 . Then equation (5) becomes

$$c = c_0 a/r \quad (5')$$

and equation (6)

$$I_0 = 4\pi a D c_0 \quad (6')$$

II. FINITE VAPOR PRESSURE

First, let fall the assumption that the vapor pressure of the liquid is vanishingly small compared to the gas pressure. Since the total pressure is everywhere the same, so must there be a concentration lowering of the gas equal and opposite to that of the vapor. Since, however, in the stationary state no flow of the gas can take place, so must the diffusion of the vapor be compensated by a convection current of the gas mixture directed toward the outside. The velocity of this current will be determined by the following equation:

$$c'u = D' \frac{dc'}{dr}$$

where the concentration of the gas has been designated as c' , and the diffusion coefficient of this in the vapor as D' . But $D' = D$ and

$\frac{dc'}{dr} = -\frac{dc}{dr}$. Therefore

$$u = -\frac{D}{c'} \frac{dc}{dr} \quad (7')$$

The total vapor flow then becomes

$$I = -4\pi r^2 \left(D \frac{dc}{dr} - cu \right) = -4\pi r^2 D \frac{dc}{dr} \left(1 + \frac{c}{c'} \right) \quad (8')$$

If C is designated as $c + c'$, the constant total molar concentration, then

$$I = -\frac{4\pi r^2 D C}{C - c} \frac{dc}{dr}$$

from which (reference 2)

$$I = -4\pi aDC \ln\left(1 - \frac{c_0}{C}\right) \quad (9)$$

(Concentration of saturated vapor is c_0 .) (For $r = \infty$, $c_1 = 0$.)

Expansion of the logarithm leads to

$$I \approx 4\pi aDc_0 \left(1 + \frac{c_0}{2C}\right) = I_0 \left(1 + \frac{c_0}{2C}\right) \quad (10)$$

As a first approximation, the percent errors involved in using (6') instead of (10) is $c_0/2C$. For water vapor at 20° C and atmospheric pressure, this amounts to only 1.2 percent.

III. LIMITED SPACE OF EVAPORATION

Here will be considered only the case of absorbing walls, on which there obtains a constant vapor pressure. With nonabsorbing walls the process is obviously not stationary and will be dealt with in another section.

If, for the sake of simplicity, it is assumed that the vessel is spherical and that the drop is located in the center, then there is obtained, instead of (5) and (6),

$$c = c_R + \frac{(c_0 - c_R)a}{r} \frac{R - r}{R - a} \quad (11)$$

$$I = \frac{4\pi(c_0 - c_R)aD}{1 - \frac{a}{R}} = \frac{I_0}{1 - \frac{a}{R}} \quad (12)$$

where R is the vessel-radius, and the constant vapor concentration at the wall is designated by c_R . A vessel large with respect to the drop size has practically no influence on the velocity of evaporation.

IV. THE LOWERING OF TEMPERATURE OF THE DROP
BECAUSE OF ITS EVAPORATION

This correction is the most important for volatile liquids. For the derivation of this, first of all, the radiation of heat and convection currents will be neglected, and only the flow of heat to the drop by conduction will be considered. If it is also postulated that the coefficient of heat conduction is constant at all points of the gas atmosphere - that is, independent of the temperature or composition of the gas-vapor mixture within certain limits - then, in the stationary case the distribution of the temperature and the magnitude of the heat flow are expressed, respectively, in the same formulas as the distribution of concentration and the velocity of evaporation, and can be expressed as:

$$T_1 - T = \frac{a}{r} (T_1 - T_0) \quad (13)$$

$$Q = 4\pi Ka (T_1 - T_0) \quad (14)$$

where T and T_1 are the temperatures at r and at infinite distance, and T_0 is the drop temperature with K the coefficient of heat conductivity and Q the heat flow per unit time. The heat used in evaporation, however, is:

$$Q' = I_0 l = 4\pi a l D c_0 \quad (15)$$

(l = molar heat of evaporation) where D is assumed independent of temperature.

(Translator's Note: By virtue of its evaporative potential, a drop initially at the same temperature as its surroundings, if quite volatile, will evaporatively self-cool to a temperature below that of its surroundings such that the heat flow from the outside will supply the latent heat of vaporization.)

In the stationary state Q must equal Q' or (reference 1),

$$T_1 - T_0 = \frac{l D c_0}{K} = \frac{l D c_0}{K R T_0} \quad (16)$$

since Maxwell states $c_0 = \frac{p_0}{R T_0}$. But T_0 and p_0 are also related by the vapor pressure equation

$$p_0 = f(T_0) \quad (17)$$

By (16) and (17) T_0 and p_0 are clearly determined and are independent of the size of the drop. The above-mentioned linear relationship (equation (8) between the surface of the drop and the time remains undisturbed by the lowering of the temperature.

In order to compare these formulas with experimental results, or to determine the value of the diffusion coefficient, (16) and (17) are not solved, but there is obtained directly from (14), (15), and (7)

$$T_1 - T_0 = \frac{I_0 l}{4\pi K a} = \frac{\gamma l}{2MK} \frac{d(a^2)}{dt} \quad (18)$$

From the measured values of $\frac{d(a^2)}{dt}$ there can be calculated $T_1 - T_0$, T_0 and p_0 (from (17)), and, finally, D (from (8)).

For small $T_1 - T_0$ equations (16) and (17) can be solved by means of the Clausius-Clapeyron equation, and the following explicit expression for the temperature lowering can be obtained:

$$I = I_0 \left(1 - \frac{l^2 D c_1}{K R T_1^2} \right) \quad (19)$$

This correction was used by Topley and Whytlaw-Gray (reference 6) in their investigation of the rate of evaporation of small spheres of iodine by means of a spiral-spring balance. The values of D obtained in the manner described at various temperatures (14° to 30° C) differ only about 1 to 3 percent from values determined directly. The temperature lowering of the small spheres in this investigation was, however, comparatively small (0.3° to 0.5° C).

Similar measurements were recently made by Houghton (reference 7) on water droplets ($a = 50\mu - 300\mu$), which were hung on very fine glass fibers. The decrease in volume of the drop was measured microscopically. The conventional psychrometric formula which Houghton used for calculating the temperature lowering led, of course, to markedly varying values of D . Since, in this case, the temperature lowering has a significant value (about 15° at 25° C and in dry air), a study must be made of the dependence of D on temperature. As a first approximation, the assumption can be made that the coefficient of heat conductivity is constant, as is the distribution of temperature (13), and then the average value of $1/2(K_1 + K_0)$ can be taken for K in (16). The integration of equation (6) yields - for a variable D :

$$I = \frac{4\pi c_0}{\int_a^{\infty} \frac{dr}{Dr^2}} \quad (20)$$

By differentiating (13), there is obtained:

$$\frac{dr}{r^2} = \frac{dT}{a(T_1 - T_0)}$$

For D it can be said, approximately,

$$D = D_0 \left(\frac{T}{T_0} \right)^2 \quad (21)$$

(Translator's Note: Other investigators give

$$\frac{D}{D_0} \sim \left(\frac{T}{T_0} \right)^{3/2}$$

See, for example, Sherwood, "Absorption and Extraction," McGraw-Hill Book Co., Inc., 1937.)

By substitution of this expression in (20) there is obtained:

$$I = \frac{4\pi c_0 a (T_1 - T_0)}{\int_{T_0}^{T_1} \frac{dT}{D}} = 4\pi c_0 D_0 \frac{T_1}{T_0} = 4\pi c_0 a \sqrt{D_1 D_0} \quad (22)$$

(where D_1 corresponds to temperature T_1).

Therefore D must be replaced in equation (6) by the geometric mean $\sqrt{D_1 D_0}$; but for small temperature lowering the ordinary arithmetic mean can be used.

Use of that curve will now be made in Houghton's results, which shows the evaporation of a water droplet at 21.7°C in perfectly dry air, and corresponds to a $\frac{d(a^2)}{dt} = 3.38 \times 10^{-5}$ square centimeters per second.

If there is set, in equation (18), $\gamma = 1$, $l = 10600$ calories, $2M = 36$, $K^{130} = 6.0 \times 10^{-5}$ cal/cm sec⁰. (reference 8) then,

$T_1 - T_0 = 16.56^\circ$; $T_0 = 5.14^\circ$ C; $c_0 = 3.79 \times 10^{-7}$ moles per cubic centimeter

from which, according to (8), where $c_1 = 0$,

$$D = \sqrt{D_0 D_1} = 0.248$$

Finally, there can be calculated for D at 0° C, according to (21), the value $D = 0.224$, which is a good approximation of the tabulated value 0.220 (reference 9). On the other hand, the curves given by Houghton for evaporation in partially saturated air show strongly varying values of D ; there could be considerable measurement error in the determination of the vapor concentration.

In order to evaluate the magnitude of the heat transfer by radiation, which has been neglected, it will be assumed that the drop and also the walls of the vessel are perfect black bodies. Then the heat influx to the drop by radiation can be expressed by the Stefan-Boltzmann equation:

$$Q_1 = 4\pi a^2 \sigma (T_1^4 - T_0^4)$$

If this equation is divided by (14), then:

$$\frac{Q_1}{Q} \approx \frac{4a\sigma T_1^3}{K}$$

(Translator's Note: This approximation assumes that $T_0 < \frac{T_1}{4}$.)

By substituting the values $\sigma = 5.7 \times 10^{-5}$ and $K = 2540$ absolute units, (air at $T_1 = 290^\circ$ K), there is obtained:

$$\frac{Q_1}{Q} = 2.19a$$

Therefore, the neglecting of radiated heat in the calculation of the temperature lowering can introduce an error of only 2 percent at most for $a = 100 \mu$. According to an investigation of Langmuir (reference 10) the effect of thermal convection can also be neglected.

V. CONCENTRATION JUMP AT THE DROP SURFACE

The unanswered question of Stefan and Winkelmann concerning the exact value of the concentration of vapor at the surface of an evaporating body can be solved in the usual manner of gas kinetics. Quite analogous to the changes of velocity and temperature, respectively, present at a solid wall, there is a jump in concentration upon the start of evaporation - which was first reported by Langmuir (reference 11). This jump at atmospheric pressure generally has a vanishing value on a flat surface, but it is quite otherwise in the case of small drops, when the diameters become comparable with the mean free path λ of the vapor molecules.

One of the molecules escaping from the surface will be, after traveling the distance λ , at an average distance Δ from the surface. The ratio $\beta = \Delta/\lambda$ certainly depends on the value of λ/a and lies within the limits $2/3$ (for $a \gg \lambda$) and 1 (for $a \ll \lambda$). Per unit time $4\pi a^2 v c_0$ molecules escape from the drop surface, if $v c_0$ is the number of molecules impinging on a square-centimeter-per-unit time at a gas concentration c_0 . Here the usual presumption is made that the coefficient of accommodation of the vapor molecules on the liquid surface is exactly 1. At the same time $4\pi a^2 v c_1$ vapor molecules condense on the same surface, where c_1 is the vapor concentration at a distance Δ from the surface. Therefore, the resultant amount evaporating is equal to $I_1 = 4\pi a^2 v m (c_0 - c_1)$. This must equal the amount carried through by diffusion, $I_2 = 4\pi (a + \Delta) D c_1$. If there is substituted for D the expression of Meyer $4/3 \lambda v m$, then there is obtained:

$$c_1 = \frac{c_0}{1 + \frac{4/3 \lambda (a + \beta \lambda)}{a^2}} \quad (23)$$

$$I = \frac{I_0}{1 + \frac{4}{3} \frac{\lambda}{a} - \frac{\beta \lambda}{a + \beta \lambda}} \quad (24)$$

For the larger small drops ($a \gg \lambda$, $\beta \approx \frac{2}{3}$), therefore:

$$I \approx \frac{I_0}{1 + \frac{2}{3} \frac{\lambda}{a}} \quad (25)$$

However, for the very small drops ($a \ll \lambda$, $\beta \approx 1$)

$$I \approx \frac{4\pi a D c_0}{1 + \frac{4}{3} \frac{\lambda}{a} - \frac{\lambda}{a + \lambda}} = \frac{4\pi a^2 c_0 v m}{1 + \frac{3}{4} \frac{a}{\lambda} - \frac{3}{4} \frac{a}{a + \lambda}} \approx \frac{4\pi a^2 c_0 v m}{1 + \frac{3}{4} \frac{a^2}{\lambda^2}} \quad (26)$$

Therefore, very small drops evaporate in a gas atmosphere with the same velocity as in a vacuum. Moreover, in solving equation (24) it is possible also to start from the velocity of evaporation in a vacuum, in that this is multiplied by the probability that an evaporated molecule does not again encounter the drop in its subsequent motion.

Equation (25) shows that the usual linear change of drop surface holding for small drops is no longer valid. Since λ at atmospheric pressure is of the order of 10^{-5} centimeter, the correction calculated by (25) is already 7 percent for $a = 1\mu$, and 40 percent for $a = 0.1\mu$. A decrease in the rate of change of the drop surface, which began to be noticeable at $a \approx 1\mu$, was actually observed by Speakman and Sever (reference 12) on a series of organic compounds. The explanation by these authors that this phenomenon was due to a lowering of the vapor pressure of the drop by dissolved nonvolatile impurities, can perhaps also be true. Unfortunately, the curves presented in the above-mentioned book do not permit a quantitative comparison with equation (25).

In a recent work by Woodland and Mack (reference 13) an opposite observation was made - an increase in $d(a^2)/dt$ upon diminishing the size of the drop. The cause of this discrepancy must lie in something else; in the proposed explanation of their findings, however, these authors come to very erroneous conclusions, such as the presence of a layer of vapor, 0.5μ thick, surrounding the droplet, and so on.

It is easy to see that the correction of the change of vapor pressure as a consequence of the curvature of the surface and the charge of the drop can be neglected in comparison with the correction just discussed.

VI. NONSTATIONARY PROCESS

The exact calculation of the velocity of evaporation in the nonstationary case meets, in general, the greatest mathematical difficulties. Fortunately, in practice most of the conditions of the process can be regarded as quasi-stationary (that is, the process has at every instant the same velocity as in the stationary state which corresponds to the boundary conditions at that instant) as follows:

Into the infinitely extended gas atmosphere, in which the vapor concentration is everywhere zero, a drop of radius a is introduced at time $t = 0$. Apart from the jump in concentration at the surface, and so forth, the primary problem is the solution of the differential equation (2) with the following boundary and initial conditions, respectively:

$$c = 0 \text{ at } t = 0 \text{ and } r > a,$$

$$c = c_0 \text{ at } t > 0 \text{ and } r = a.$$

The solution is given by the following expression:

$$c = \frac{2c_0a}{r\sqrt{\pi}} \int_{\frac{r-a}{2\sqrt{Dt}}}^{\infty} e^{-x^2} dx$$

From this there is obtained,

$$I = -4\pi a^2 D \frac{dc}{dr} \Big|_{(r=a)} = 4\pi a D c_0 \left(1 + \frac{a}{\sqrt{\pi D t}} \right) = I_0 \left(1 + \frac{a}{\sqrt{\pi D t}} \right) \quad (28)$$

Since $\sqrt{\pi D}$ at atmospheric pressure is of the order of magnitude 1, there can be substituted $I \approx I_0 \left(1 + \frac{a}{\sqrt{t}} \right)$. The correction amounts to only 1 percent after 1 second, even in a heavy fog ($a = 100\mu$). In order to decide to what extent the evaporation of a drop can be regarded as stationary, the time interval t_1 is compared, after which the correction term $a/\sqrt{\pi D t}$ reaches a definite small value Δ , with the time t_2 necessary for complete evaporation of the drop.

Thus

$$t_1 = \frac{a^2}{\Delta^2 \pi D}$$

and from (8)

$$t_2 = \frac{a^2 \gamma}{2M D c_0}$$

therefore

$$\frac{t_1}{t_2} = \frac{2c_0M}{\Delta^2 \pi D^2} \tag{29}$$

If there are substituted the values $\Delta = 0.01$, $M = 18$, and $c_0 = 3.79 \times 10^{-7}$ moles per cubic centimeter, which correspond to the evaporation of water drops in dry air at 21.7°C (see above), then

$$\frac{t_1}{t_2} = 0.043, \text{ or in other words, even after the course of the twentieth}$$

part of the time of total evaporation the velocity of evaporation exceeds the velocity corresponding to the stationary state by only 1 percent. In damp air or with less volatile liquids the approximation to the stationary state is realized still more quickly. The effect of the gradual reduction of drop size which was left unconsidered in the discussion will be described further.

For the calculation of the velocity of evaporation of droplets of solutions, the nature of the variation of vapor pressure at the surface with time becomes important. If it is assumed that the concentration of the saturated vapor is a time function $c(t)$, then, instead of (27), there is obtained

$$c = \frac{2a}{\sqrt{\pi r}} \int_0^{\frac{r-a}{2\sqrt{Dt}}} c \left[t - \frac{(r-a)^2}{4Dx^2} \right] e^{-x^2} dx \text{ (reference 15)} \tag{30}$$

which can be easily verified. From this is obtained (omitting the repetition of the somewhat detailed calculations):

$$I = -4\pi a^2 D \frac{\partial c}{\partial r} \Big|_{(r=a)} = 4\pi a D c(t) \left[1 + \frac{a}{\sqrt{Dt\pi}} \frac{c(0) + 2t \int_0^1 c'[t(1-x^2)] dx}{c(t)} \right] \tag{31}$$

where c' means dc/dt .

Whether or not an approximation to the stationary state is possible here depends on the special form of $c(t)$. In general, the following can be said; wherein it is necessary to take into account the most important practical cases of the decrease in $c(t)$ with time. In order to reach a good approximation of the stationary state, it is sufficient that $a/\sqrt{Dt\pi}$ increase by a definite amount Δ after a time interval t , which is small relative to the interval t_3 , meanwhile the factor times $a/\sqrt{Dt\pi}$ remains of the order of magnitude of 1. If $|c'(t)|$ is designated by $f(t)$ and it is noted that:

$$c(t) = c(0) + \int_0^t c'(t)dt = c(0) - t \int_0^1 f(tx)dx$$

then this factor takes the following form:

$$F = \frac{c(0) - 2t \int_0^1 f[t(1-x^2)]dx}{c(0) - t \int_0^1 f(tx)dx}$$

With decreasing $f(t)$

$$\int_0^1 f(tx)dx = \int_0^1 f[t(1-x)]dx > \int_0^1 f[t(1-x^2)]dx$$

and for t_3 the interval will be taken after which $c(t)$ is half of its original value, that is, the root of the equation

$$\frac{c(0)}{2} = t \int_0^1 f(tx)dx$$

In this interval $F < 2$.

With increasing $f(t)$, that value of t can be chosen for t_3 such that F vanishes; $c(t)$ will then not reach $1/2c(0)$. In this interval $F < 1$. It is sometimes more convenient to use $t_3' < t_3$ instead of t_3 ; so that the equation $c(0) = 2tf(t)$ is satisfied.

Now, consider the continuous diminishment of the evaporating droplet due to disturbance of stationariness. The strict treatment of this problem is extremely complicated; as an approximate estimate use can be made of

the following consideration. If there is originally a stationary state corresponding to drop radius a and vapor concentration c_0 , then the states arising from a decrease in a of Δa at constant c_0 , and a decrease in c_0 of Δc_0 at constant a , respectively, are given by the following expression:

$$c = \frac{1}{r} \left\{ c_0 a - c_0 \Delta a \left[1 - \psi \left(\frac{r - a + \Delta a}{2\sqrt{Dt}} \right) \right] \right\}$$

and, respectively,

$$c = \frac{1}{r} \left\{ c_0 a - a \Delta c_0 \left[1 - \psi \left(\frac{r - a}{2\sqrt{Dt}} \right) \right] \right\}$$

(ψ = Gauss' probability function.)

If, now, $a\Delta c_0 = c_0\Delta a$, then these expressions can differ from each other only by an infinitely small amount in the second order. If, therefore, the time function $c_0(t) = c_0(0)\varphi(t)$ is a good approximation of the stationary state, then the equation $a(t) = a(0)\varphi(t)$ should apply for decrease in drop size with time. For the evaporation of the drop there can be substituted, as a first approximation, from (8)

$a(t) = \sqrt{a(0)^2 - kt}$. Here then:

$$f(t) = -\frac{da}{dt} = \frac{k}{2\sqrt{a(0)^2 - kt}}$$

and for t_3' there is obtained

$$a(0) = \frac{t_3' k}{\sqrt{a(0)^2 - kt_3'}}$$

from which

$$t_3' \approx 0.6 \frac{a(0)^2}{k} = 0.6 t_2$$

(t_2 is time of total evaporation.)

Then, return to a numerical factor 0.6 for equation (29); it follows from this, that there can be assumed a quasi-stationary course of evaporation of water droplets as a good approximation. This conclusion obviously agrees with the experimental results of Houghton:

Thus far, the evaporation of a single drop in an infinitely extended medium has been considered. In practice it is necessary to do, however, with a large number of droplets. In this case the evaporation of a drop takes place as though it were in a vessel with nonabsorbing walls, the volume of which vessel being equal to the average volume enclosing each drop. The rigorous solution of this problem is very difficult. Practically, for the small weight concentrations occurring in fog, that is, a large mean distance between the drops relative to their diameter, a simple approximation will serve. Then, assume that the droplet is in the midpoint of a spherical vessel of radius R with nonabsorbing walls. The distribution of concentration for different times is shown in figure 1 with dashed curves; the solid curves correspond to the stationary state (for absorbing walls with various vapor pressure, see sec. III). (Translator's Note: The solid curve represents the stationary state for the same boundary conditions that exist at a particular instant in the nonstationary state.) It is easy to see that a curve of the first type must, in fact, lie under the curve of the second type with the same end-points. These results, therefore, for the velocity of evaporation in a known time $t + \Delta t$, a lower limit. (See equation (12).)

$$I_1 = \frac{4\pi a D (c_0 - c_{t+\Delta t})}{1 - \frac{a}{R}}$$

An upper limit can be obtained as follows. If the drop is placed at time t in an unbounded space with vapor concentration c_t , then its evaporation will take place more quickly than in the vessel. In time $t + \Delta t$ it will reach the following value:

$$I_2 = 4\pi a D (c_0 - c_t) \left(1 + \frac{a}{\sqrt{\pi D \Delta t}} \right)$$

(see equation (28)).

If the time interval Δt is chosen such that

$$1 + \frac{a}{\sqrt{\pi D \Delta t}} = \frac{1}{1 - \frac{a}{R}}$$

then the pictured curves are actually obtained, which do not intersect each other more than once. The equivalence of the two expressions for the amount of material evaporated in time interval Δt and stored in the gas atmosphere, respectively, yields:

$$\frac{1}{1 - \frac{a}{R}} 4\pi a D (c_0 - c_t) \Delta t \approx 4\pi \int_a^R [(c_{t+\Delta t}(r) - c_t(r))] r^2 dr$$

where $c_t(r)$ is the value c_t corresponding to the stationary distribution. By substituting the expression for $c(r)$ (equation (11)), there is obtained

$$\Delta c = c_{t+\Delta t} - c_t \approx \frac{3Da(c_0 - c_t)\Delta t}{R^3} \tag{32}$$

or, since

$$\Delta t \approx \frac{R^2}{\pi D}$$

$$\Delta c \approx (c_0 - c_t) \frac{a}{R} \tag{33}$$

At small values of a/R the stationary curves give a good approximation. With the same approximation (32) can be regarded as a differential equation. By integration, obtain

$$I = 4\pi a D c_0 e^{-3Dat/R^3} = I_0 e^{-3Dat/R^3}$$

This equation is obviously only applicable when the decrease in volume of the drop can be neglected (at very small vapor pressures or pressure differences). Otherwise, the system of differential equations (8) and (32) must be solved, which usually presents no difficulties.

VII. MOTION OF THE DROPLETS

The exact calculation of the velocity of evaporation of a droplet moving with respect to the gas medium is scarcely possible. In a coordinate system relative to the drop (that is, drop at $r = 0$, $Z = 0$, $\alpha = 0$), this problem leads to the differential equation:

$$\frac{\partial c}{\partial t} = D\Delta c - \bar{v} \text{ grad } c \tag{35}$$

where with \bar{v} is meant the velocity vector of the gas stream, the value of this vector being determined in space by the nature of the flow.

Even in the simplest case of laminar flow, for which Stokes' law holds, and a stationary state, equation (35) is practically insolvable. It can be solved only for an infinitely small flow velocity: if this velocity is called V at a great distance from the drop, then let

$$c = \frac{c_0 a}{r} + V\phi$$

where the term $V\phi$ represents the disturbance of the concentration distribution caused by the flow. From (35) there is obtained (with $\partial c/\partial t = 0$):

$$DV\Delta\phi + \bar{v} \left(\frac{c_0 a \bar{v}}{r^3} + V \text{grad } \phi \right) = 0$$

and, since the last term can be neglected;

$$\Delta\phi = \frac{c_0 a}{Dr^3} \bar{v} r$$

If the Stokes expression for \bar{v} is substituted in this equation, the following result is obtained: At two points which are symmetrical with respect to the plane passing through the drop middle perpendicular to the flow direction, $\Delta\phi$ possesses the same absolute value, but reversed sign. Since further, ϕ vanishes on the surface of the drop and at infinite distance from it, then the application of the potential theory leads to the conclusion that at two diametrically opposite points on the surface $\text{grad } \phi$ has the same length and direction, that is, that the acceleration of the evaporation produced by the stream on one side of the drop is exactly compensated by the slowing down of the process on the other side.

This conclusion could approximately hold for a flow velocity, wherein the transfer of material by convection can be neglected in comparison with the transfer by diffusion - at least at distances not too far from the drop, that is, when $c|\bar{v}| \ll D|\text{grad } c|$. If by substitution here $c = c_0 a/r$, there is obtained,

$$\frac{c_0 a V}{r} \ll \frac{D c_0 a}{r^2}, \quad \text{or} \quad \frac{aV}{D} \ll 1$$

$$(a \approx r)$$

Since it is known that $D \approx \frac{\eta}{\rho}$ (η is coefficient viscosity of the medium, ρ its density), then aV/D becomes the familiar Reynolds expression $\rho V/\eta$. For small Reynolds numbers (for example, for free fall of fog droplets) a vanishingly small influence of the motion on the evaporation velocity would be expected. The validity of this conclusion obviously can only be decided by an experimental procedure.

In conclusion, it should be said again that all the considerations and conclusions carried out here are also directly applicable to the reverse process - the growth of drops in a supersaturated vapor.

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