

ON VAPORIZATION OF MIST BY RADIATION

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Abstract—A variety of different evaporation regimes are identified for the steady vaporization of a radiantly heated spherical particle. Formulae for the vaporization rate are obtained in many of these regimes. As an application of the results, the evaporation time for a water droplet in a mist is estimated for various radiant energy fluxes.

NOMENCLATURE

A ,	a constant defined in equation (35) [dimensionless];	T ,	temperature in the gas [$^{\circ}\text{K}$];
B ,	rate factor for gasification [$\text{g}/\text{cm}^2\text{s}$];	T_b ,	boiling (or sublimation) temperature at the local ambient pressure [$^{\circ}\text{K}$];
c_p ,	specific heat at constant pressure for the gas [$\text{cal}/\text{g degK}$];	T_0 ,	temperature of the condensed material [$^{\circ}\text{K}$];
c_v ,	average velocity in the direction normal to the surface for vapor molecules in the gas [cm/s];	T_r ,	a reference temperature [$^{\circ}\text{K}$];
D ,	diffusivity of the vapor in the gas [$\text{g}/\text{cm s}$];	T_{∞} ,	ambient temperature at $r = \infty$ [$^{\circ}\text{K}$];
E ,	activation energy for gasification [cal/mole];	T_b^0 ,	normal boiling point [$^{\circ}\text{K}$];
F ,	incident radiant flux [$\text{cal}/\text{cm}^2\text{s}$];	t ,	time [s];
k ,	absorption coefficient of the condensed material [cm^{-1}];	W ,	molecular weight of the vapor [g/mole];
L ,	heat of vaporization at temperature T_0 [cal/g];	\bar{W} ,	average molecular weight of the gas [g/mole];
m ,	net mass flux [$\text{g}/\text{cm}^2\text{s}$];	Y ,	mass fraction of the vapor in the gas [dimensionless];
\dot{m} ,	mass flow rate [g/s];	$Y_{\infty s}$,	saturation mass fraction of vapor at $r = \infty$ [dimensionless];
p_a ,	ambient pressure [atm];	α ,	evaporation coefficient [dimensionless];
p_e ,	equilibrium vapor pressure [atm];	λ ,	thermal conductivity of the gas [$\text{cal}/\text{cm s degK}$];
p_r ,	constant reference equilibrium vapor pressure, evaluated at temperature T_r [atm];	ν ,	mass rate at which molecules leave the condensed material [$\text{g}/\text{cm}^2\text{s}$];
p_v ,	vapor pressure [atm];	ρ ,	density of the condensed material [g/cm^3];
R ,	radius of the sphere [cm];	ρ_a ,	ambient density [g/cm^3];
R^0 ,	universal gas constant [various units];	ρ_v ,	density of vapor molecules in the gas [g/cm^3];
R_t ,	initial radius of the sphere [cm];	σ ,	surface energy of the condensed material [cal/cm^2].
r ,	radial distance from the center of the sphere [cm];		

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Subscripts

0, conditions in the gas at the surface of the sphere;

∞ , conditions at $r = \infty$;
c. s. T. as subscripts on R , identify radii defined in equations (27), (22) and (40), respectively, at which transitions in the gasification mechanism occur.

1. INTRODUCTION

WE SHALL consider a solid or liquid sphere (in an infinite and uniform gaseous atmosphere) that is subjected to a time independent, spacially uniform radiant energy flux. The sphere will be assumed to be nearly transparent to the incident radiation, and the absorption coefficient will be assumed to be constant, whence energy is absorbed at a constant and uniform rate per unit volume.* The absorption of energy will cause the sphere to vaporize or sublime, and the principal objective of our study is to determine the steady-state vaporization or sublimation rate. By "steady-state", we mean that time-dependent terms in the governing conservation equations are neglected. This approximation has been justified for burning and vaporizing droplets subjected only to molecular transport processes [1], and should also be applicable to the present system provided the rate of absorption of radiant energy is not extremely large. We shall obtain the steady-state gasification rate of the sphere under a number of different sets of conditions.

First we shall discuss the general interface molecular conservation formula (the Knudsen equation), from which we shall infer the gasification rate when heat conduction is negligible. Next we shall consider unopposed surface rate processes, including the effect of heat conduction in the gas. Finally we shall treat systems that maintain surface equilibrium, considering first heat conduction (in the gas) alone, next both heat conduction and molecular diffusion (in the gas), and finally the effect of surface tension. The results are applied to the calculation of the evaporation time of an irradiated water droplet.†

* We neglect any effects arising from differences between the index of refraction of the sphere and that of its surrounding medium.

† In what follows, the terms gasification, sublimation and vaporization will be used interchangeably.

2. THE KNUDSEN EQUATION

Knudsen [2] was the first to recognize that the net rate of efflux of molecules from the surfaces of a condensed material is the difference between the rate at which surface molecules enter the gas and the rate at which gas molecules return to the surface. Expressed in terms of the mass flow rate, Knudsen's equation is

$$m = \nu - \alpha \rho_v c_v, \quad (1)$$

where the vacuum vaporization rate ν and the evaporation coefficient α (the "sticking" fraction of molecules that strike the surface) may both reasonably be assumed to depend only upon the temperature of the surface. Basically, equation (1) *always* determines the vaporization rate of the condensed material; the rest of this paper is concerned merely with the evaluation of the terms appearing on the right-hand side of equation (1).

It is useful to distinguish two distinct classes of condensed materials. For some materials (identified as class A) the probability of an incident molecule attaching itself to the surface is so small that one cannot conceive of an experiment for measuring the last term in equation (1). For materials of class A, the relationship $\alpha = 0$ either is precisely correct or represents an excellent approximation for all environmental conditions, and, empirically,

$$\nu = B \exp[-E/R^0T_0], \quad (2)$$

where the activation energy E is constant by definition and the rate factor B (which sometimes depends weakly upon the surface temperature T_0) may also be assumed to be approximately constant. Condensed materials with complex structures (such as Plexiglas and Teflon) belong to class A.

For other materials (identified as class B), α is measurable, and ν may be related to α by applying equation (1) to a hypothetical experiment in which the vapor pressure is adjusted so that surface equilibrium prevails. Since $m = 0$ in equilibrium, if we assume that the vapor behaves as an ideal gas then equation (1) yields

$$\nu = \alpha p_e/[2\pi(R^0/W)T_0]^{1/2}, \quad (3)$$

where the formulae

$$\rho_v = \rho_v/(R^0/W)T_0,$$

$$c_v = [(R^0/W)T_0/2\pi]^{1/2},$$

and

$$p_v = p_e$$

have been employed. Over a sufficiently limited temperature range, one may employ the equation

$$p_e = \{p_r \exp [LW/R^0T_r]\} \exp [-LW/R^0T_0] \quad (4a)$$

for the equilibrium vapor pressure and, when more accurate data are not available, one may use Trouton's rule (which states that the molar entropy of vaporization is 21 cal/mole degK at the normal boiling point) to obtain

$$p_e = \exp [10.5] \exp [-10.5 (T_b^0/T_0)] \text{ atm.} \quad (4b)$$

Equations (3) and (4) show that equations (2) and (3) assume the same functional form provided we set

$$E = LW \quad (5)$$

and

$$B = \alpha p_r \exp [LW/R^0T_r]/[2\pi(R^0/W)T_0]^{1/2}. \quad (6)$$

The only essential difference between materials of the two classes is therefore that the last term in equation (1) is absent for materials of class A. Materials falling within class B include water, many organic liquids, and metals; for metals with monatomic vapors usually $\alpha = 1$, [3].

3. THE VAPORIZATION RATE WHEN THERE IS NO HEAT CONDUCTION IN THE GAS

The preceding formulae imply that, in order to determine m from equation (1), we need only specify T_0 and ρ_v . In order to relate ρ_v simply to T_0 , we shall assume (only in this section) that ρ_v is a known constant (viz. the initial partial pressure of the vapor in the ambient atmosphere); the value assigned to ρ_v cannot exceed ρ_a .* The remaining parameter T_0 is determined by an energy balance for the sphere.

Neglecting molecular transport processes in the gas, in a steady state we may equate the rate

* Throughout this paper we assume that the ambient pressure p_a is a known constant.

of absorption of energy in the sphere to the energy flux leaving the sphere, thus obtaining†

$$4/3 \pi R^3 F k = 4\pi R^2 m [L + m^2/2\rho_a - m^2/2\rho^2], \quad (7)$$

in which the last two terms represent the change in the (ordered) kinetic energy of the material leaving the sphere. Since generally $\rho \gg \rho_a$, the last term in equation (7) is generally negligible compared with the term preceding it, and use may be made of the ideal gas equation of state in order to cast equation (7) into the dimensionless form

$$R F k/3L m = 1 + m^2(R^0/\bar{W})^2 T_0^2/2\rho_a^2 L. \quad (7a)$$

Unless the vaporization rate is very large, the ordered kinetic energy of the gas adjacent to the surface will be small compared with the change in thermal energy in the gasification process (viz. the enthalpy of vaporization), whence the last term in equation (7a) will be small compared with unity. In this case, T_0 disappears from equation (7a), and m is determined from equation (7a) directly, regardless of the form taken by equation (1).‡ Thus, we obtain

$$m = R F k/3L. \quad (8)$$

Equation (1) now merely serves to determine the temperature T_0 . Since the equation of mass conservation for the sphere implies that

$$dR/dt = -m/\rho, \quad (9)$$

equation (8) enables us to determine the radius of the sphere as a function of time through a simple integration;

$$R = R_i \exp [-(Fk/3\rho L)t]. \quad (10)$$

The characteristic evaporation time appearing in equation (10) is

$$t_1 = 3\rho L/Fk.$$

From equations (7a) and (8) we infer that the

† Throughout this paper we assume that the temperature inside the sphere is uniform. The thermal conductivity of the condensed material is usually high enough to make this a good approximation.

‡ We assume here (and often in what follows) that the variation of L with T_0 is negligible. Generally T_0 remains within sufficiently narrow bounds for this to be a good approximation.

last term in equation (7a) becomes of order unity when

$$[R F k (R^0/\bar{W}) T_0 / 3 L p_a]^2 / 2 L \approx 1. \quad (11)$$

For large values of $R F k$ (spheres subjected to extremely high radiation fluxes) and for small values of L and p_a , the parameter in equation (11), and consequently the last term in equation (7a), may greatly exceed unity. When this condition is satisfied, equation (7a) yields

$$m = [2 R F k p_a^2 / 3 (R^0/\bar{W})^2 T_0^3]^{1/3}, \quad (12)$$

which is now coupled with equation (1) because T_0 appears in equation (12). Neglecting the (usually relatively small) effect of the variation of T_0 , we see from equation (12) that m increases slowly with $(R F k)$ [$m \sim (R F k)^{1/3}$ from equation (12), while $m \sim (R F k)$ from equation (8)] and that R^2 decreases linearly with time [see equation (9)]. A system that obeys equation (12) over part of its vaporization history will, of course, pass into the regime in which equation (8) is obeyed after R decreases to a value at which equation (11) is satisfied. The kinetic energy term in the surface energy conservation equation will be neglected throughout the subsequent analysis (i.e. it will be assumed that the parameter in equation (11) is small compared with unity).

4. THE VAPORIZATION RATE WITH AN UNOPPOSED SURFACE RATE PROCESS

The vaporization rate formulae obtained in the preceding section may be reasonably accurate provided the thermal conductivity of the gas surrounding the sphere is sufficiently low. In order to obtain an assessment of the effect of gas conductivity, molecular transport processes will be studied in the rest of this paper. When molecular transport effects are included, the general form of equation (1) is too complex to admit a simple analytical treatment. Therefore we shall study separately two limiting cases of equation (1). In the present section we shall neglect the last term in equation (1). In view of equation (2), equation (1) then becomes

$$m = B \exp[-E/R^0 T_0]. \quad (13)$$

The analysis in the present section will always be

valid for materials of class A, and it will also be valid for materials of class B when the system under study is far removed from the condition of surface equilibrium. Studies employing equation (13) have been given previously [4]. In the next section we shall consider systems in which the left-hand side of equation (1) is small compared with each term on the right-hand side.

When the conductive energy transport from the surface of the sphere is taken into account, the energy balance for the sphere [equation (7)] becomes

$$(4/3) \pi R^3 F k = \dot{m} L - 4 \pi R^2 \lambda (dT/dr)_0. \quad (14)$$

where the total (mass) vaporization rate is

$$\dot{m} \equiv 4 \pi R^2 m.$$

The energy conservation equation for the gas around the sphere is*

$$\dot{m} c_p dT/dr = d(4 \pi r^2 \lambda dT/dr)/dr, \quad (15)$$

in which, according to the law of mass conservation, \dot{m} is independent of r . The general solution to equation (15) is

$$T = a + b \exp\left[-\frac{\dot{m} c_p}{4 \pi \lambda r}\right], \quad (16)$$

where a and b are arbitrary constants. Since $T = T_0$ at $r = R$ and $T = T_\infty$ at $r = \infty$, we find from equation (16) that

$$T = \left\{ T_0 - T_\infty \exp\left[-\frac{\dot{m} c_p}{4 \pi \lambda R}\right] - (T_0 - T_\infty) \exp\left[-\frac{\dot{m} c_p}{4 \pi \lambda r}\right] \right\} / \left\{ 1 - \exp\left[-\frac{\dot{m} c_p}{4 \pi \lambda R}\right] \right\}. \quad (17)$$

Hence,

$$(dT/dr)_0 = -\frac{\dot{m} c_p}{4 \pi \lambda R^2} (T_0 - T_\infty) \left\{ \exp\left[\frac{\dot{m} c_p}{4 \pi \lambda R}\right] - 1 \right\}^{-1}. \quad (18)$$

* For simplicity, we assume throughout this paper that c_p and λ are constant.

Equations (14) and (18) yield the formula

$$R F k / 3 L m = 1 + [c_p (T_0 - T_\infty) / L] \{\exp [R m c_p / \lambda] - 1\}^{-1} \quad (14a)$$

for the energy conservation equation with heat conduction included.

Equations (13) and (14a) comprise two independent equations in the two unknowns m and T_0 . When $R m c_p / \lambda \gg 1$, the last term in equation (14a) is small compared with unity, and heat conduction in the gas is negligible. Equation (14a) then reduces to equation (8), and the associated results (described previously) follow. Evidently [see equation (8)] the condition

$$R^2 F k c_p / 3 \lambda L \approx 1 \quad (19)$$

roughly defines the boundary of the regime in which heat conduction effects are important; when the parameter on the left-hand side of equation (19) becomes less than unity, conduction must be considered. Thus, heat conduction is important at low radiant fluxes ($F k$) and must always be considered when R becomes sufficiently small.

In the regime where heat conduction can be of paramount importance, $R m c_p / \lambda \ll 1$, and a reasonable approximation to equation (14a) is found (by expanding the exponential in powers of its argument) to be

$$R F k / 3 L m = 1 + \lambda (T_0 - T_\infty) / L R m. \quad (20)$$

In view of equation (13), equation (20) may be treated as a quadratic equation for R as a function of T_0 . Solving the quadratic, we obtain

$$R F k / 3 L m = 1/2 \{1 \pm [1 + 4 F k \lambda (T_0 - T_\infty) / 3 L^2 m^2]^{1/2}\}. \quad (21)$$

The resulting R dependence of m is quite complex; it is determined by the solution to the transcendental equation obtained by employing equation (13) to express the T_0 appearing in equation (21) in terms of m .

As R approaches zero, one can see from equation (20) that T_0 approaches T_∞ . By expanding equation (20) about $R = 0$, we find that $(T_0 - T_\infty) \approx -L R m / \lambda$; i.e. T_0 becomes less than T_∞ . Thus, radiant heating becomes negligible in the terminal stage of vaporization, and heat conducted into the sphere from the ambient

gas supplies the energy required to vaporize the last bit of material. The lower (negative) sign in equation (21) applies in this region. This sign continues to hold until $T_\infty - T_0$ attains its maximum value, determined by

$$T_0 - T_\infty = -3 L^2 m^2 / 4 F k \lambda,$$

at which point we must begin to use the upper sign in equation (21); (i.e. the negative sign holds for $R < 3 L m / 2 F k$ and the positive sign holds for $R > 3 L m / 2 F k$). Heat is conducted from the gas into the sphere so long as $R < R_s$, where

$$R_s \equiv 3 L m / F k, \quad (22)$$

in which m is evaluated from equation (13) by setting $T_0 = T_\infty$. At $R = R_s$, $T_0 = T_\infty$. For $R > R_s$, $T_0 > T_\infty$ and the radiant input supplies all of the energy required for vaporization as well as some heat conduction losses. When T_∞ is less than or equal to room temperature, representative gasification rates are very low (evaporation times are of the order of years) for $R < R_s$; the present analysis will be applicable only to materials of class A in this regime because all materials of class B will be in surface equilibrium. Thus, so long as R_s exceeds molecular dimensions,* radiant energy input is totally ineffective as a method for causing evaporation of small spheres composed of materials of class A.

For $R > R_s$, it is of interest to attempt to determine from equations (13) and (21) whether or not the conductive energy loss exceeds the convective energy flow [i.e. whether or not the last term in equation (20) exceeds unity]. Boundaries of regimes in which conduction may be large are determined by the formula

$$\lambda (T_0 - T_\infty) / L R m = 1. \quad (23)$$

If equation (21) is used to eliminate R from equation (23),† then [in view of equation (13)] a transcendental equation is obtained for T_0 . With a little algebra, we find this transcendental equation to be

$$T_0 - T_\infty = 6 L^2 m^2 / F k \lambda. \quad (23a)$$

* Often m is so small at $T_0 = T_\infty$ that R_s is less than the size of a molecule and the regime identified in this paragraph is nonexistent.

† The upper (positive) sign in equation (21) holds throughout the regime $R > R_s$.

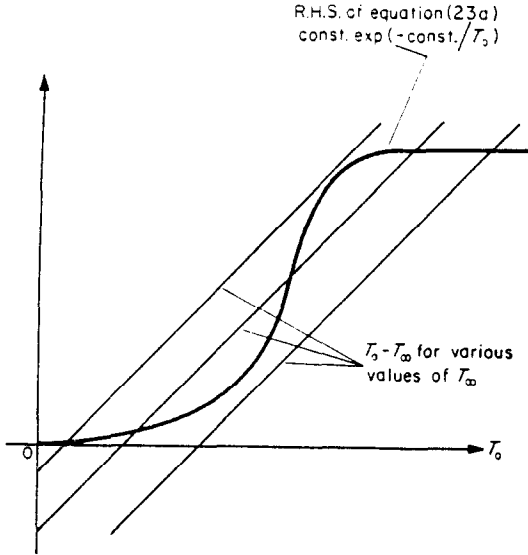


FIG. 1. Schematic diagram of solution to equation (23a).

The two sides of this equation are illustrated schematically in Fig. 1, from which it can be seen that either one or three solutions to the equation exist. A detailed analysis shows that three distinct solutions exist if and only if both

$$2R^0 T_\infty/E < 1$$

and

$$\frac{\exp\{-2/[1 - (1 - 2R^0 T_\infty/E)^{1/2}]\}}{1/2 [1 - (1 - 2R^0 T_\infty/E)^{1/2}] - R^0 T_\infty/2E} < \frac{E \lambda F k}{3R^0 L^2 B^2} < \frac{\exp\{-2/[1 + (1 - 2R^0 T_\infty/E)^{1/2}]\}}{1/2 [1 + (1 - 2R^0 T_\infty/E)^{1/2}] - R^0 T_\infty/2E}$$

Representative estimates indicate that, unless T_∞ is unreasonably large, both of these conditions are usually satisfied. Therefore the middle $T_0 - T_\infty$ curve in Fig. 1 is representative. Further calculation shows that the two upper intersections in Fig. 1 usually occur at unreasonably large values of T_0 (which correspond to unreasonably large values of R and of Fk) and that the lower intersection usually occurs very near $T_0 = T_\infty$. Therefore heat conduction losses appear to be dominant throughout most of the range of values of $R > R_s$ for which the parameter in equation (19) is less than unity.

Having inferred that heat conduction is dominant in the regime currently under study, we may obtain a rough estimate of the vaporization rate by neglecting unity in comparison to the last term in equation (20). Equation (20) then yields

$$T_0 = T_\infty + R^2 F k / 3\lambda,$$

which, when substituted into equation (13), gives

$$m = B \exp\{-E/[R^0 T_\infty + R^2 F k R^0 / 3\lambda]\}. \quad (24)$$

The quadrature that must be performed to obtain $R(t)$ after substituting equation (24) into equation (9) cannot be expressed in terms of elementary functions, but a representative evaporation time in this regime is roughly

$$t_2 = (B/\rho R) \exp\{-E/[R^0 T_\infty + R^2 F k R^0 / 3\lambda]\}.$$

5. THE VAPORIZATION RATE AT SURFACE EQUILIBRIUM

The results of the preceding sections imply that m decreases as R decreases. For materials of class B we may therefore infer that, at some stage in the evaporation history of the sphere, surface equilibrium conditions are very nearly attained [see equation (1)]. As a very rough approximation, one may assume that surface equilibrium is established suddenly as soon as T_0 reaches T_b , the boiling (or sublimation) point (corresponding to the ambient pressure) of the condensed material.* When $T_0 \leq T_b$, equation (13) will then be invalid for materials of class B. Instead, the appropriate approximation to equation (1) will be

$$p_{v0} = [p_r \exp(LW/R^0 T_r)] \exp[-LW/R^0 T_0], \quad (25)$$

in which use has been made of equations (1) (with $m = 0$), (3) and (4a). Systems for which equation (25) replaces equation (13) are considered in this section.

For steadily vaporizing or burning liquid fuel droplets in the absence of radiant energy transfer, the approximation that $T_0 = T_b$ has

* When $T_0 > T_b$, surface equilibrium is impossible because then the last term in equation (1) cannot be as large as ν .

been well justified [1]. Therefore, initially, we shall attempt to employ this same approximation in the present problem. The statement $T_0 = T_b$ is equivalent to an approximate solution to equation (25), whence equation (14a) alone (with T_0 now a known constant) determines the vaporization rate m . Equation (14a) is difficult to solve for m . But, when heat conduction is of any importance, we expect equation (20) to be a reasonable approximation to equation (14a), and therefore we find, approximately,

$$m = R F k / 3L - \lambda(T_b - T_\infty) / L R. \quad (26)$$

The corresponding characteristic vaporization time is

$$t_3 = [F k / 3\rho L - \lambda(T_b - T_\infty) / \rho L R^2]^{-1}.$$

Equations (14a) (with $T_0 = T_b$) and (26) both exhibit one interesting effect. As R decreases, the conduction loss becomes more and more important, and m begins to decrease very rapidly. The value of m , in fact, approaches zero before $R \rightarrow 0$ (if $T_\infty < T_b$)! From equation (14a) or equation (26) we find that $m \rightarrow 0$ when $R \rightarrow R_c$, where

$$R_c \equiv [3\lambda(T_b - T_\infty) / F k]^{1/2}. \quad (27)$$

The time required for complete vaporization is therefore infinite because when R reaches R_c the entire radiant energy input is conducted away and no further decrease in R occurs.

This result constitutes a paradox since, whenever $T_0 > T_\infty$, the equilibrium vapor pressure at the surface exceeds that at infinity, and vaporization must occur at a non-zero rate. The reason for the paradox is, of course, that T_0 is a function of time ($T_0 \neq T_b$). In order to compute the actual vaporization rate for $R \lesssim R_c$, we must consider the equation for the molecular diffusion of the vapor, employing equation (25) (instead of the formula $T_0 = T_b$) as a boundary condition at the surface of the sphere. Unless T_∞ is very close to T_b , the value of R_c given by equation (27) is within a factor of 10 of the limiting value of R for conduction to be of importance [as determined by equation (19)]. Therefore equation (26) and the approximation $T_0 = T_b$ are of very restricted utility, and the rate equation derived below [equation (37)] is

applicable throughout most of the (surface equilibrium) regime in which conduction must be considered.

The diffusion equation for the vapor in the gas is

$$\dot{m} dY/dr = d(4\pi r^2 D dY/dr)/dr, \quad (28)$$

the solution to which is of the same form as the solution to equation (15).*

Hence,

$$Y = \{ Y_0 - Y_\infty \exp[-(\dot{m}/4\pi DR)] - (Y_0 - Y_\infty) \exp[-(\dot{m}/4\pi Dr)] \} / \{ 1 - \exp[-(\dot{m}/4\pi DR)] \} \quad (29)$$

and

$$(dY/dr)_0 = - \frac{\dot{m}}{4\pi DR^2} (Y_0 - Y_\infty) [\exp(\dot{m}/4\pi DR) - 1]^{-1}. \quad (30)$$

Conservation of mass of the vaporizing material at the surface implies

$$\dot{m} = \dot{m} Y_0 - 4\pi R^2 D (dY/dr)_0, \quad (31)$$

whence

$$1 - Y_0 = (Y_0 - Y_\infty) [\exp(\dot{m}/4\pi DR) - 1]^{-1}. \quad (32)$$

Since, by definition,

$$Y = W p_v / \bar{W} p_a, \quad (33)$$

equation (25) implies that

$$Y_0 = A \exp[-LW/R^0 T_0], \quad (34)$$

where

$$A \equiv (W p_r / \bar{W} p_a) \exp[LW/R^0 T_r]. \quad (35)$$

Equations (34) and (32) yield

$$\exp[Rm/D] = (1 - Y_\infty) \{ 1 - A \exp[-LW/R^0 T_0] \}^{-1}, \quad (36)$$

(since $\dot{m} = 4\pi R^2 m$). With A and Y_∞ as known constants,† equation (36) represents the independent relationship that is needed in addition

* We assume that the diffusivity D is constant.

† We assume that the variation in \bar{W} is negligible.

to equation (14a) in order to determine T_0 and m .

Unfortunately eliminating T_0 between equations (14a) and (36) yields a fairly complicated transcendental equation for m as a function of R even after the approximations (valid in the regime under study) $Rm c_p/\lambda \ll 1$ and $Rm/D \ll 1$ are introduced. If we make the additional approximation that $(T_0 - T_\infty)/T_\infty \ll 1$ (which is often reasonable in the regime under study), then this transcendental equation reduces to

$$m = \frac{RFk}{3L} - \frac{\lambda R^0 T_\infty^2}{R L^2 W} \ln \left[\left(\frac{Y_\infty}{Y_{\infty_s}} \right) \left(\frac{1 + Rm/D Y_\infty}{1 + Rm/D} \right) \right], \quad (37)$$

where

$$Y_{\infty_s} \equiv A \exp [(-LW/R^0 T_\infty)] \quad (38)$$

is the mass fraction of vapor at infinity at saturated conditions. The further approximation that $Rm/D Y_\infty \ll 1$ (which can be shown to be equivalent to $(T_0 - T_\infty)/T_\infty \ll R^0 T_\infty/LW$ when $Y_\infty = Y_{\infty_s}$ and which usually is not very accurate until $R \ll R_c$) enables us to solve equation (37) explicitly for m . The result is

$$m = \left[\frac{RFk}{3L} + \frac{\lambda R^0 T_\infty^2}{R L^2 W} \ln \left(\frac{Y_{\infty_s}}{Y_\infty} \right) \right] / \left[1 + \frac{\lambda R^0 T_\infty^2 (1 - Y_\infty)}{D L^2 W Y_\infty} \right]. \quad (39)$$

In most problems, initially the ambient atmosphere will be saturated with vapor (i.e. $Y_\infty = Y_{\infty_s}$), and equations (9) and (39) will therefore yield an exponential time decay of R [analogous to the result given in equation (10)], with a characteristic evaporation time of

$$t_4 = [1 + \lambda R^0 T_\infty^2 (1 - Y_\infty)/D L^2 W Y_\infty] (3\rho L/Fk).$$

Equations (37) and (39) show that, provided $Y_\infty \leq Y_{\infty_s}$, the vaporization rate m is positive for all values of $R > 0$. Thus the paradox is removed. However, with $Y_\infty = Y_{\infty_s}$, the vaporization rate does become smaller after R drops to R_c . This result can be inferred from equation (39) or from the formula for t_4 ; the rate is decreased from that given in equation (8) by the factor

$$[1 + \lambda R^0 T_\infty^2 (1 - Y_{\infty_s})/D L^2 W Y_{\infty_s}]^{-1},$$

which is very small compared with unity when Y_{∞_s} is very small. Thus, radiantly heated sphere with $R \lesssim R_c$ will usually vaporize slowly.

For large values of Fk , the value of R_c defined in equation (27) can be so small that the effects of surface tension would be expected to be of importance for $R \lesssim R_c$. The surface tension of liquid droplets will always enter the picture at sufficiently small values of R ; the criterion for it producing a measureable effect is roughly $R \lesssim R_T$, where

$$R_T \equiv 50\sigma/\rho L. \quad (40)$$

When $R \lesssim R_T$, equation (25) must be replaced by [5]

$$p_{v0} = [p_r \exp [(LW/R^0 T_r)] \exp [(-LW/R^0 T_0)] \exp [(2\sigma W/R \rho R^0 T_0)]. \quad (25a)$$

Consequently, the final factor in equation (25a) appears as an additional factor in equation (34), and equation (36) is modified accordingly. In equation (37), Y_{∞_s} is replaced by

$$Y_{\infty_s} \exp [(2\sigma W/R \rho R^0 T_\infty)]$$

and the additional factor $(1 - 2\sigma/R\rho L)^{-1}$ appears in front of the logarithm.* Equation (39) becomes

$$m = \left\{ \frac{RFk}{3L} + \frac{\lambda R^0 T_\infty^2}{R L^2 W} \left(1 - \frac{2\sigma}{R\rho L} \right)^{-1} \left[\frac{2\sigma W}{R\rho R^0 T_\infty} + \ln \left(\frac{Y_{\infty_s}}{Y_\infty} \right) \right] \right\} \cdot \left[1 + \frac{\lambda R^0 T_\infty^2 (1 - Y_\infty)}{D L^2 W Y_\infty} \right] \cdot \left(1 - \frac{2\sigma}{R\rho L} \right)^{-1} \quad (41)$$

which now makes equation (9) difficult to integrate even when $Y_\infty = Y_{\infty_s}$. When

$$2\sigma/R\rho L \rightarrow 1,$$

the quantity $(1 - 2\sigma/R\rho L)^{-1}$ approaches infinity and the terms involving σ are dominant in equation (41). Although this limit is not reached

* We neglect the dependence of the surface energy σ upon T_0 . The surface energy is related to the surface tension s by $\sigma = s - T_0 ds/dT_0$.

until the sphere contains but a few molecules, we may obtain a rough estimate of m when $R < R_T$ by neglecting the terms that do not involve σ . When $Y_\infty = Y_{\infty_s}$, by substituting this simplified estimate into equation (9) and performing the integration, we find that the cube of the radius of the sphere decreases linearly with time; viz.

$$R^3 = R_i^3 - [6\sigma WD Y_{\infty_s} / \rho^2 R^0 T_\infty (1 - Y_{\infty_s})] t, \quad (42)$$

from which the representative evaporation time is seen to be

$$t_3 = R^3 \rho^2 R^0 T_\infty (1 - Y_{\infty_s}) / 6\sigma WD Y_{\infty_s}.$$

Numerical evaluations show that surface tension effects greatly accelerate the evaporation rates of small droplets.

Since the radius R_T is often small compared with a molecular mean free path, one may ask whether molecular gas kinetic effects will mask the behavior deduced in the preceding paragraph (from continuum flow theory). Rough kinetic estimates indicate that any "temperature jump" [6] at the surface of the sphere will be negligible. The preceding formulae should therefore be approximately correct so long as the predicted vaporization rates do not approach the maximum rate given in equation (13).

6. THE EVAPORATION TIME FOR A RADIANTLY HEATED WATER DROPLET

As an application of the notions developed above, we shall consider the radiant vaporiza-

Table 1. The physical constants employed in analysing the vaporization of a water droplet in saturated air

p_a	1 atm
T_∞	293°K
T_b	373°K
c_p	0.25 cal/g degK
λ	5×10^{-3} cal/cm s degK
D	3×10^{-4} g/cm s
\bar{W}	30 g/mole
W	18 g/mole
L	540 cal/g
$(E/R^0 = LW/R^0 = 4850^\circ\text{K})$	
Y_{∞_s}	1.38×10^{-2}
ρ	1 g/cm ³
σ	142 ergs/cm ²
α	0.03 and 1

tion of a water droplet in saturated atmospheric air at 20°C. The physical constants adopted for the calculation are given in Table 1. There is some disagreement in the value of the evaporation coefficient for liquid H₂O; numbers cited in the literature range from [4] 0.03 to [3] 1. The more recent work appears to favor values near unity [7]. Since we do not wish to enter the argument, we carried out computations for both extreme values.

The boundaries of the various vaporization regimes, defined by equations (11), (19), (22) and (40), are shown in Figs. 2 and 3.* The boundary

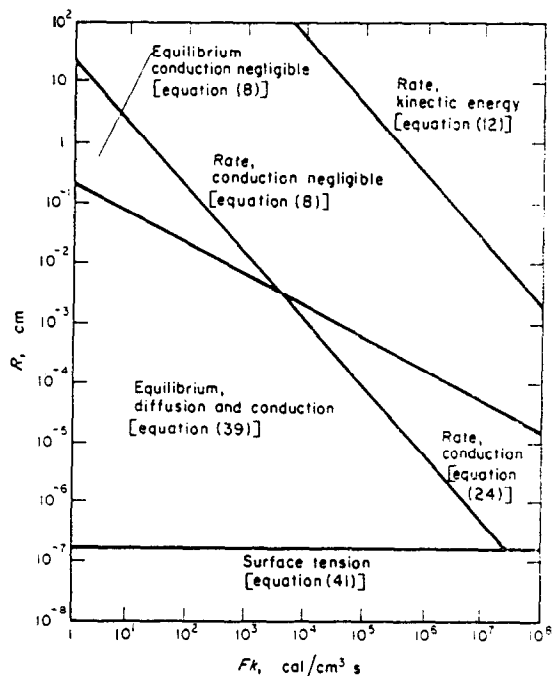


FIG. 2. Diagram of vaporization regimes of the water droplet if $\alpha = 0.03$.

dividing regimes of surface rate processes and surface equilibrium processes is not given by any of our previous formulae. It was determined by computing the rates for surface equilibrium and for surface rate processes and then noticing where these two rates became equal.† In this

* The surface rate regime in which $R < R_s$ [equation (22)] does not appear for water under the conditions chosen.

† Where the rates are unequal, the lower rate is the correct one.

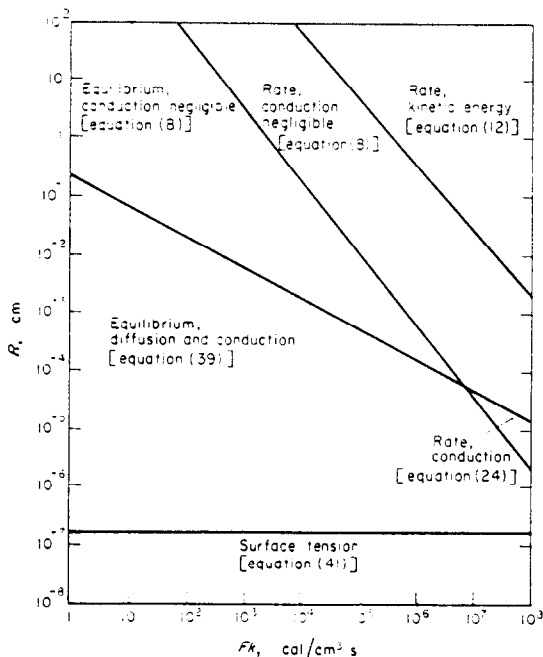


FIG. 3. Diagram of vaporization regimes of the water droplet if $\alpha = 1$.

manner, it was found that, under our present conditions, the boundary can roughly be defined by equating the value of m given by equation (39) to the value of m given by equation (13) with $T_0 = T_\infty$. Of course, transition from one regime to another is not always sharp; the locations of the lines in the figures are accurate to only about a factor of 10 in R . If $\alpha = 0.03$, $R_i = 1$ cm and $Fk = 10^6$ cal/cm²s, for example, it can be seen from Fig. 2 that vaporization begins in a regime in which heat conduction is negligible and the change in kinetic energy upon gasification is important, enters a regime in which conduction is negligible and the enthalpy of vaporization limits the rate, passes through a regime in which heat conduction is important while the surface process is still a rate process, enters a regime in which surface equilibrium prevails and heat conduction and diffusion in the gas govern the rate, and finally emerges into the regime in which surface tension causes the droplet to disappear rapidly.

At $T_\infty = 20^\circ\text{C}$, Y_{∞_s} is high enough so that the rate given by equation (39) (at $Y_\infty = Y_{\infty_s}$) is not very much less than the rate given by

equation (8). Consequently equation (39) is valid throughout most of the diffusion-conduction regime. If T_∞ were dropped to -15°C , then the consequent large decrease in Y_{∞_s} would cause the rate given by equation (39) to drop markedly (by almost a factor of 100), and a sizeable transition region, in which equation (37) would have to be used instead of equation (39), would develop in the diffusion-conduction zone. Also, the surface rate process-surface equilibrium boundary would be moved to somewhat lower values of R by the decrease in T_∞ . The other boundaries would be unaffected.

The evaporation rate m [as determined by equations (8), (12), (24), (39), or (41)] is listed as a function of Fk and R in Tables 2 and 3. The horizontal bars appearing in these tables mark the values of R at which transitions from one regime to another occur. The total time required for evaporation of a droplet of initial radius R_i is listed as a function of Fk and R_i in Tables 4 and 5.

From Table 2 it can be seen that for $Fk \gtrsim 10^7$ cal/cm²s there is a rapid large decrease in m when heat conduction sets in at $R \lesssim 10^{-4}$ cm. This results in longer evaporation times at high values of Fk than would be indicated by extrapolation of the results for lower Fk (see Table 4). The value of m is so large in the region where surface tension is important that, for practical purposes, droplets disappear instantaneously as soon as they reach a size of roughly 3×10^{-7} cm. The entry in Table 4 under $Fk = 1$ cal/cm²s, $R_i = 10^{-5}$ cm implies that bright sunlight ($F \sim 1$ kW/m²) will vaporize a representative droplet of mist with $k \sim 30$ cm⁻¹ in about 1 h under our chosen conditions. Focused rays of the sun, or other energetic radiation sources, ($Fk \rightarrow 10^6$ to 10^8 cal/cm²s) can vaporize the mist droplet in a few milliseconds, or perhaps in less than 1 ms, if $\alpha = 1$ (see Tables 4 and 5).

7. CONCLUDING REMARKS

One is tempted to use our results to speculate on a number of natural processes. For instance, should we not be able to calculate the time required for the morning sun to vaporize the mist that sometimes gathers above streams? Unfortunately (or, perhaps fortunately) natural processes such as this one are too complex to

conform to our simple picture; the gas properties are coupled with the behavior of the droplets, and additional phenomena (non-radial diffusion, natural convection, etc.) may set in. Our analysis contributes only one small piece to the puzzle.

In conclusion, it is worth re-emphasizing the principal criticism of our study. Steady-state evaporation has been postulated. Since the time required to heat the droplet to its steady-state temperature is roughly independent of R (with volume heating), one might expect our analysis to be valid, after a heat-up period, for droplets of sufficiently large initial radii. However, unsteady effects might also come into play in the transition from one vaporization regime to another,

and, for regimes spanning only one or two orders of magnitude in R , may completely obscure our computed vaporization rates.

REFERENCES

1. F. A. WILLIAMS, *J. Chem. Phys.* **33**, 133 (1960).
2. M. KNUDSEN, *Ann. Phys.* **29**, 179 (1909).
3. S. M. SCALA and G. L. VIDALE, *Int. J. Heat Mass Transfer* **1**, 4 (1960).
4. R. E. WILFONG, S. S. PENNER and F. DANIELS, *J. Phys. Chem.* **54**, 863 (1950); S. S. PENNER, *J. Phys. Chem.* **56**, 475 (1952).
5. J. FRENKEL, *Kinetic Theory of Liquids*, p. 369. Dover, New York (1955).
6. E. H. KENNARD, *Kinetic Theory of Gases*, p. 311. McGraw-Hill, New York (1938).
7. R. LITTLEWOOD and E. RIDEAL, *Trans. Faraday Soc.* **52**, 1598 (1956).

Résumé—Différents régimes d'évaporation sont identifiés pour la vaporisation permanente d'une particule sphérique chauffée par rayonnement. Des formules pour la vitesse de vaporisation sont obtenues dans la plupart de ces régimes. En application des résultats, le temps d'évaporation pour une gouttelette d'eau dans un brouillard est estimé pour divers flux d'énergie de rayonnement.

Zusammenfassung—Für die stationäre Verdampfung eines durch Strahlung beheizten kugelförmigen Teilchens wird eine Anzahl verschiedener Verdampfungsarten festgestellt. Bei vielen dieser Vorgänge erhält man Formeln für die Verdampfungsgeschwindigkeit. Als Anwendung der Ergebnisse wird die Verdampfungszeit eines Wassertröpfchens in Nebel bei verschiedenen Strahlungsintensitäten abgeschätzt.

Аннотация—В статье рассмотрен ряд различных режимов стационарного процесса испарения радиально нагретой сферической частицы. Для многих из этих режимов получены формулы для определения скорости испарения. В качестве примера применимости полученных результатов проведена оценка времени испарения капельки воды в тумане для различных потоков лучистой энергии.