Fog Formation in Boundary Value Problems

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For a Lewis number one gas, the equations of energy and diffusion state that if local equilibrium exists in a fog region, fog may form in a continuous manner, but it may be vaporized only discontinuously at the boundary between fog and nonfog regions. The local rate of formation of fog is proportional to the square of the local gradient of temperature or concentration. A class of solutions to the transport equations has been obtained for problems in which no vaporization occurs at the fog boundary. Under these conditions, the temperature and concentration at the boundary of the fog region are both shown to be constant at values that depend only upon the initial and/or boundary values of temperature and concentration and upon the equilibrium curve.

When a fog is formed by the adiabatic expansion of a mixture of a vapor and a noncondensable gas, temperature and concentration changes take place over distances that are the order of the scale of the fog droplets formed. When a fog is formed by mixing two different masses of gas at different temperatures and vapor concentrations or by cooling the gas mixture at a boundary, then the temperature and concentration changes take place over distances much larger than the scale of the fog droplets. The large scale fields which result are superimposed on the fine scale thermal and concentration fields.

We will consider this large scale problem and we will treat the limiting case in which the large scale processes are slow enough so that the processes on the fine scale are close to equilibrium. How slow the large scale processes must be depends, in part, upon the number of condensation nuclei present in the gas at the beginning of the process. This situation not only defines a limit to the large scale problem but also is approached in certain situations of practical importance. The goal is to predict the temperature and the concentrations of vapor and fog.

The turbulent analogue of this problem has been solved by Matvejev (*8*). On a time average basis, fog droplets diffuse in the turbulent case and do not diffuse in the nonturbulent case, a situation that leads to different solutions. The present work is restricted to nonturbulent systems.

Rhode (*10*), who also considered the turbulent problem, has reviewed the early meteorological literature. Recent work concerned with technological applications has been done by Johnstone, Kelley, and McKinley (*6*) who studied fog formation in condensers, by Levine and Friedlander (*7*), by Hidy and Friedlander (*4*) who studied turbulent jets, and by Rosner and Epstein (*12*) who considered boundary layers. Amelin (*1*) gives further references.

The field equations (convective transport equations) were used to obtain a detailed view of the processes by Milburn (*9*), Levine and Friedlander (*7*), Rhode (*10*), and Matvejev (*8*). Milburn treated a nonturbulent problem of fog vaporization, and Levine and Friedlander obtained rigorous conditions for fog formation. Hills and Szekely (*5*) and Rosner (*11*) calculated the effect of fog formation on heat and mass transfer across a boundary.

TRANSPORT EQUATIONS

Under the usual conditions of fog formation the condensation of the vapor results in a large number of very small fog droplets. Since the scale of the droplets is small compared to the scale of the large scale processes, we may treat fog formation or removal as a continuous sink or source in the gas phase.

We consider the fog to be a third component in the gas phase so that the gas mixture is made up of component 1, condensable vapor; component 2, noncondensable gas; and component 3, the condensed vapor or fog. Hence we can write the usual conservation equations for a mixture (*2*) as

$$\frac{\partial \rho_1}{\partial \theta} = - \nabla \cdot \mathbf{n}_1 - r_3 \qquad (1a)$$

$$\frac{\partial \rho_2}{\partial \theta} = - \nabla \cdot \mathbf{n}_2 \qquad (1b)$$

$$\frac{\partial \rho_3}{\partial \theta} = - \nabla \cdot \mathbf{n}_3 + r_3 \qquad (1c)$$

where the small volume occupied by the liquid has been neglected. Assuming that only ordinary diffusion is important, that the fog is dilute enough so that its effect on the diffusion of species 1 and 2 is negligible, and that the fog droplets move at the local mass average velocity of the fluid, Equation (1) becomes

$$\rho \frac{Dw_1}{D\theta} = \nabla \cdot D\rho \nabla w_1 - (1 - w_1)\, r_3 \qquad (2a)$$

$$\rho \frac{Dw_3}{D\theta} = (1 + w_3)\, r_3 \qquad (2b)$$

where

$$\frac{D}{D\theta} = \frac{\partial}{\partial \theta} + \mathbf{V} \cdot \nabla \qquad (2c)$$

$$\rho = \rho_1 + \rho_2 \qquad (2d)$$

$$w_j = \rho_j / \rho, \qquad j = 1, 2, 3 \qquad (2e)$$

and the redundant equation for w_2 has been deleted.

Equation (2*b*) neglects Brownian motion of the fog droplets. This assumption is satisfactory insofar as large scale motion of the fog is concerned because the diffusivity of the droplets is small compared to the diffusivities of heat and vapor. The assumption does exclude the possibility of coagulation of droplets, but in this analysis we are concerned primarily with large scale phenomena rather than fine scale ones such as coagulation.

At the limit $w_1, w_3 << 1$, Equations (2*a*) and (2*b*) become

$$\rho \frac{Dw_1}{D\theta} = \nabla \cdot D\rho \nabla w_1 - r_3 \tag{3a}$$

$$\rho \frac{Dw_3}{D\theta} = r_3 \tag{3b}$$

At this limit ρ may also be considered to be the total mixture density and w_j the mass fraction based on the total mixture. The dilute equations, (3*a*) and (3*b*), will be taken as the starting point in most subsequent developments.

Energy Equation

As the mixture is analogous to a reacting three-component mixture, we can write the usual energy equation for the fluid mixture (2). Assuming that the mixture of vapor and gas is ideal, that heat generation due to friction and body forces is negligible, that pressure is constant and that only ordinary conduction takes place, one eventually obtains

$$\rho\, C_P \frac{DT}{D\theta} = \nabla \cdot k\nabla T + r_3\lambda + D\rho\,(C_{P1} - C_{P2})\,\nabla w_1 \cdot \nabla T \tag{4}$$

where

$$C_P = \sum_{1}^{3} C_{Pj}\, w_j \tag{4a}$$

Rate of Fog Formation with Local Equilibrium

We assume that supersaturation is negligible so whenever fog is present, local equilibrium exists. Hence the concentration and temperature in the fog region are related by the equilibrium equation for the vapor

$$w = w(T) \tag{5}$$

where subscript 1 on w has been dropped. From Equation (5)

$$\frac{Dw}{D\theta} = w' \frac{DT}{D\theta} \tag{5a}$$

$$\nabla w = w'\ \nabla T \tag{5b}$$

Substitution of these expressions into Equation (2), followed by combination with Equation (4), leads to the expression below for the local rate of fog production

$$r_3 = \frac{D\rho w'}{1 + \dfrac{w'\lambda}{C_P}} \left[(1 - N_{Le})\ \nabla^2 T + \left\{ \frac{w''}{w'} + \frac{(D\rho)'}{D\rho} - N_{Le}\frac{k'}{k} - w'\,\frac{(C_{P1} - C_{P2})}{C_P} \right\} \nabla T \cdot \nabla T \right] \tag{6}$$

where prime signifies differentiation with respect to temperature. The minor effect of w_3 on $D\rho$ is neglected here and, at the dilute limit we wish to consider, w in the denominator may be neglected.

The terms representing the variation of properties with temperature and the term accounting for the difference in heat capacities are small compared to w''/w' (that is, in the air-water system) so to a good approximation

$$r_3 = \frac{D\rho w'}{1 - w + \dfrac{w'\lambda}{C_P}} \left[(1 - N_{Le})\ \nabla^2 T + \frac{w''}{w'} (\nabla T \cdot \nabla T) \right] \tag{6a}$$

and for a Lewis number one gas*

$$r_3 = \frac{D\rho w''}{1 + \dfrac{w'\lambda}{C_P}} \nabla T \cdot \nabla T \tag{7}$$

Although N_{Le} is generally near one, the rate of fog formation can be sensitive to N_{Le} even though the temperature and concentration fields are not. In the air-water system at 300°K. and 1 atm. for example, the numbers are

$$r_3 = \frac{D\rho w'}{1 + \dfrac{w'\lambda}{C_P}} [0.15\ \nabla^2 T + 0.054\ \nabla T \cdot \nabla T] \tag{8}$$

so under certain conditions the first term may be important even though $N_{Le} = 0.85$ in this system. However, because of the great simplification in the field equations, we wish to treat here the Lewis number one case for the insight it can give to systems in which $N_{Le} \neq 1$. We will return to Equation (8) later.

Lewis Number = 1

Equation (7) gives the rate of fog formation in a Lewis number one gas whenever fog is present and local equilibrium exists. As w' and w'' are positive, r_3 is always positive. Hence there can be a continuous source of fog, but there cannot be a continuous sink. We conclude that under these conditions, fog can be removed only discontinuously, that is, by vaporization at a fog boundary.

Equation (5*b*) can be used to write Equation (7) in terms of concentration and, if we define

$$dH = C_P dT + \lambda dw \tag{9}$$

in terms of enthalpy

$$r_3 = \frac{D\rho w''\ \nabla H \cdot \nabla H}{C_P^2 \left(1 + \dfrac{w'\lambda}{C_P}\right)^3} \tag{10}$$

Equation (7) combined with Equation (4) gives for $N_{Le} = 1$

$$\frac{DT}{D\theta} = D\nabla^2 T + \frac{\lambda D w''}{C_P \left(1 + \dfrac{w'\lambda}{C_P}\right)} \nabla T \cdot \nabla T \tag{11}$$

where second order terms have been dropped. A similar equation is obtained from Equations (3), (5*b*), and (7)

$$\frac{Dw}{D\theta} = D\nabla^2 w - \frac{Dw''}{(w')^2 \left(1 + \dfrac{w'\lambda}{C_P}\right)} \nabla w \cdot \nabla w \tag{12}$$

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* Equations (6), (6a), and (7) do not depend upon the assumption that the fog does not diffuse. They are valid *instantaneously* in turbulent as well as nonturbulent flow if local equilibrium exists and the other conditions appropriate to each equation hold.

Equations (11) and (12), with appropriate initial and boundary conditions, describe the large scale fields when local equilibrium is obtained for a Lewis number one gas; it is recognized that the last terms are to be taken as zero when w is less than the local equilibrium value.

Solutions to these nonlinear equations will now be constructed in an indirect manner. The vapor and fog concentrations will be taken to be small enough so that the temperature and/or concentration dependent quantities D, λ, ρ, and C_P can be assumed to be constant at their average values.

Enthalpy Equation

The usual equation for the conservation of enthalpy is obtained from Equations (3) and (4) with the earlier assumptions

$$\frac{DH}{D\theta} = D\nabla^2 H \tag{13}$$

We note that this equation is valid whether or not fog is present.

SOLUTION OF EQUATIONS

In order to fix ideas we consider a specific situation. Assume that at time zero a fogfree gas at a uniform vapor concentration w_∞ and a uniform temperature T_∞ is brought into contact with a horizontal liquid surface at a temperature T_I where $T_I < T_\infty$. The liquid extends to infinity in both directions. The gas-vapor mixture extends to infinity in the vertical direction as well. The velocity of the medium is assumed to be zero,* and the gas at the liquid interface is assumed to be in equilibrium with the liquid.

Suppose w_∞ is low enough so that no fog forms. Then Equations (11) and (12) give

$$\frac{\partial T}{\partial \theta} = D\frac{\partial^2 T}{\partial x^2} \tag{14}$$

$$\frac{\partial w}{\partial \theta} = D\frac{\partial^2 w}{\partial x^2} \tag{15}$$

Because the initial and boundary conditions on T and w are of the same form, the solution to Equations (14) and (15) can be shown (7) to be related by the equation

$$\frac{T - T_I}{T_\infty - T_I} = \frac{w - w_I}{w_\infty - w_I} \tag{16}$$

On a concentration-temperature diagram (Figure 1), Equation (16) is the straight line connecting (w_I, T_I) and (w_∞, T_∞). For any value of w_∞ less than w_B, w is less than the local saturation value everywhere except at the liquid surface and no fog forms (line A, Figure 1). Line B is tangent to the equilibrium line at T_I and, if w_∞ is greater than w_B, Equation (16) intersects the equilibrium line (line C, Figure 1). Hence fog must form because supersaturation is ruled out. Equation (16) therefore cannot be valid as it is obtained assuming $r_3 = 0$.

Consider this situation further. Fog must form, but we would expect that at any time we could go far enough from the plate to find a fogfree region where Equations (14) and (15) are still valid. The fog should form close to the liquid where Equations (11) and (12) must be used. Hence we look for a solution in which a fog region extends from the liquid surface to some vertical distance which we expect to increase with time.

Call the inner solution the solution in the fog region and the outer solution the solution in the fogfree region. These two regions are separated by the fog boundary where boundary conditions connecting the two regions may be written.

A reasonable hypothesis is that the temperature and concentrations are continuous at this boundary, so that at the boundary

$$T_i = T_o \tag{17}$$

$$w_i = w_o \tag{18}$$

As ρ is continuous and there is no velocity change across the boundary due to the assumption of dilute fog and vapor, the convection of vapor into the boundary equals the convection away from the boundary. Thus, for the vapor flux at the fog boundary

$$-D\rho\frac{\partial w_i}{\partial x} = -D\rho\frac{\partial w_o}{\partial x} + \frac{dx_s}{d\theta}\rho w_{3i} \tag{19}$$

because the convective terms cancel. The last term represents the removal or formation of vapor by condensation or vaporization at the boundary. Along with the assumption that w is continuous we assume that $\partial w/\partial x$ is continuous. Equation (19) then implies that the fog concentration is also continuous at the boundary, for the assumption is equivalent to the assumption that w_3, the mass fraction of fog, approaches zero as the fog boundary is approached from the *inner side—the fog side of the boundary.** Hence at the boundary

$$\frac{\partial w_i}{\partial x} = \frac{\partial w_o}{\partial x} \tag{20}$$

It follows that the temperature gradient is also continuous at the boundary

$$\frac{\partial T_i}{\partial x} = \frac{\partial T_o}{\partial x} \tag{21}$$

Combination of the above equations also gives at the boundary

$$H_i = H_o \tag{22}$$

$$\frac{\partial H_i}{\partial x} = \frac{\partial H_o}{\partial x} \tag{23}$$

These last two equations are, of course, necessary since Equation (13) holds throughout the field.

The assumptions that w and T and their gradients are continuous at the fog boundary are plausible. They will be justified by showing that a solution to the overall equations does indeed exist which satisfies these conditions.

Inner and Outer Equations

From the preceding discussion the equations that must be solved are the inner equations, $x \leq x_s$

$$\frac{\partial w_i}{\partial \theta} = D\frac{\partial^2 w_i}{\partial x^2} - \frac{r_3}{\rho} \tag{24}$$

$$\frac{\partial T_i}{\partial \theta} = D\frac{\partial^2 T_i}{\partial x^2} + \frac{r_3 \lambda}{\rho\, C_P} \tag{25}$$

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* Natural and forced convection may be suppressed in real cases, but a positive or negative vertical mass average velocity due to the change of density with T and w must exist. We assume this velocity may be neglected.

* This assumption effectively restricts the analysis to problems of fog formation because it was shown earlier that, in a Lewis number one gas, fog can be removed only by vaporization at a fog boundary. Terms like the last in Equation (19) will have to be retained in any analysis which hopes to describe fog vaporization. Solutions developed using Equations (20) and (21) are invalid if they lead to the presence of fog in a region in which the vapor is unsaturated.

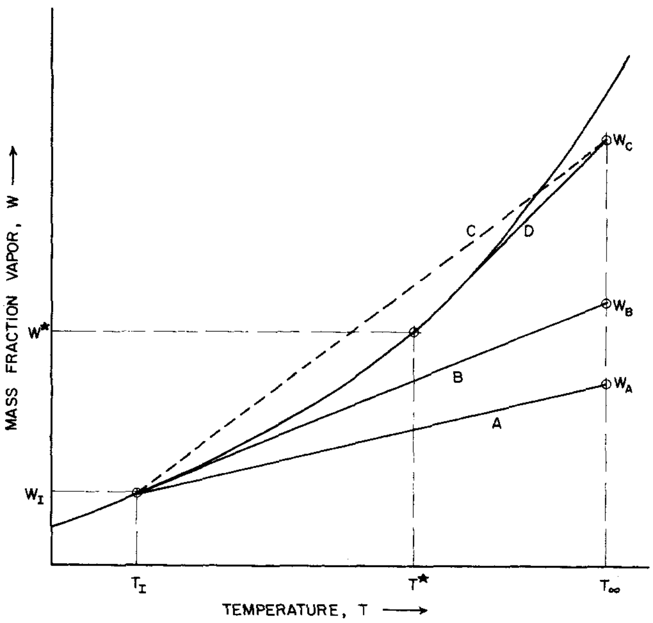

Fig. 1. Concentration-temperature relations $T_I < T_\infty$.

and

$$w_i = w_i(T) \tag{26}$$

and the outer equations, $x \geqq x_s$

$$\frac{\partial w_o}{\partial \theta} = D\,\frac{\partial^2 w_o}{\partial x^2} \tag{27}$$

$$\frac{\partial T_o}{\partial \theta} = D\,\frac{\partial^2 T_o}{\partial x^2} \tag{28}$$

with boundary conditions

$$\theta = 0\,,\quad w_o = w_\infty\quad,\quad T_o = T_\infty \tag{29a}$$

$$x = 0\,,\quad w_i = w_I\quad,\quad T_i = T_I \tag{29b}$$

$$x = \infty,\quad w_o = w_\infty\quad,\quad T_o = T_\infty \tag{29c}$$

$$x = x_s,\quad w_i = w_o\quad,\quad T_i = T_o \tag{29d}$$

$$\frac{\partial w_i}{\partial x} = \frac{\partial w_o}{\partial x}\quad,\quad \frac{\partial T_i}{\partial x} = \frac{\partial T_o}{\partial x} \tag{29e}$$

r_3 is given by Equation (7) although this equation is not necessary since it is not independent.

Equations (24) to (29) completely define the problem, but we can also write the enthalpy equation for both regions from Equation (13),

$$\frac{\partial H}{\partial \theta} = D\,\frac{\partial^2 H}{\partial x^2} \tag{30}$$

$$\theta = 0,\quad H = H_\infty \tag{30a}$$

$$x = 0,\quad H = H_I \tag{30b}$$

$$x = \infty,\quad H = H_\infty \tag{30c}$$

The solution to Equation (30) is well known (3):

$$\frac{H - H_I}{H_\infty - H_I} = \operatorname{erf}\eta \tag{31}$$

$$\eta = x/\sqrt{4D\theta} \tag{31a}$$

Equation (31) yields a linear relationship between T and w. In the inner region T and w are related by Equation (26) so that Equations (31), (9), and (26) give for the inner solution $x \leqq x_s$

$$\frac{T - T_I}{T_\infty - T_I} + \frac{\lambda(w(T) - w_I)}{C_P(T_\infty - T_I)} = \left[1 + \frac{\lambda(w_\infty - w_I)}{C_P(T_\infty - T_I)}\right]\operatorname{erf}\eta \tag{32}$$

(The subscript i has been dropped.)

To complete the solution, the outer solution must be developed and the position of the fog boundary determined. To do this, we make the tentative hypothesis that at the fog boundary where $x = x_s$, T and w are independent of time and equal to the constant values T^* and w^*, respectively. The resulting solution will be shown to satisfiy Equations (24) through (29).

If T^* and w^* are constant, it follows from Equations (27) to (29) that, in the outer region even though the boundary is moving,

$$\frac{T - T^*}{T_\infty - T^*} = \frac{w - w^*}{w_\infty - w^*} \tag{33}$$

(The subscript o has been dropped.)

Combining Equation (33) with (31), which is also valid here, gives for the outer solution $x \geqq x_s$

$$\frac{T_\infty - T}{T_\infty - T_I} = \frac{1 + \dfrac{\lambda}{C_P}\,\dfrac{(w_\infty - w_I)}{(T_\infty - T_I)}}{1 + \dfrac{\lambda}{C_P}\,\dfrac{(w_\infty - w^*)}{(T_\infty - T^*)}}\,(1 - \operatorname{erf}\eta) \tag{34}$$

and Equations (33) and (34) give w in this region.

T^* and w^* are then obtained from Equations (29*d*), (29*e*), (32), and (34). These equations require that at $x = x_s$

$$\frac{w_\infty - w^*}{T_\infty - T^*} = w'(T^*) \tag{35}$$

Equations (33) and (35) fix T^* and w^*. They are the coordinates of the point at which a straight line from (T_∞, w_∞) is tangent to the equilibrium curve. This is line D (Figure 1) which also gives the T-w relationship in the fogfree region. Note it is below line C, the line which would describe the T-w relationship if no fog were to form.

Letting $T = T^*$ in Equation (35) or (32) fixes x_s

$$\operatorname{erf}(\eta_s) = \left(\frac{T^* - T_I}{T_\infty - T_I}\right)\frac{\left[1 + \dfrac{\lambda(w^* - w_I)}{C_P(T^* - T_I)}\right]}{\left[1 + \dfrac{\lambda(w_\infty - w_I)}{C_P(T_\infty - T_I)}\right]} \tag{36}$$

where

$$x_s = \eta_s\sqrt{4D\theta} \tag{37}$$

If w_∞ is reduced holding T_∞ constant (Figure 1), T^* and w^* decrease and η_s decreases—the fog region gets thinner. When w_∞ reaches w_B, T^* reaches T_I, w^* goes to w_I and the fog vanishes. (Line B, Figure 1.)

Equations (32) to (37) may be shown by direct substitution to satisfy the differential equations and boundary conditions of the problem, Equations (24) to (29). These are subsidiary conditions, however, and if we specialize Equations (11) and (12) for this problem, we find that Equations (32) to (37) do indeed satisfy the differential equations as well as the appropriate initial and boundary conditions. Hence, our assumptions about the fog boundary lead to a solution to the problem.

We conclude that the concentration of liquid water indeed falls to zero at the fog boundary, that the vapor concentration and temperature and their spacial derivatives are continuous at the boundary, that the temperature and vapor concentration are constant at the boundary, and that the tangent line to the equilibrium curve does describe the vapor concentration-temperature path. These conditions* hold because fog vaporization does not occur in a problem of this type. It should be emphasized that in this problem the fog region is well defined, for the fog concentration is not asymptotic to zero; it falls to zero at the fog boundary. Thus, the fog "phase" is that region in which liquid water droplets exist.

The outer solution, Equation (34), is essentially Von-Neumans solution for heat transfer into a semi-infinite slab with a constant temperature boundary moving at a rate proportional to $\theta^{-1/2}$, a problem which arises in freezing (3).

Equations (7) and (32) give the rate of fog production in the region $x \leqq x_s$

$$r_3 = \frac{\rho w'' (\Delta T)^2}{\pi\theta} \; \frac{\left[1 + \dfrac{\lambda}{C_P}\,\dfrac{\Delta w}{\Delta T}\right]^2}{\left[1 + \dfrac{\lambda}{C_P}\,w'\right]^3}\; e^{-x^2/2D\theta} \tag{38}$$

From Equation (3*b*)

$$\frac{\partial w_3}{\partial \theta} = \frac{r_3}{\rho} \tag{39}$$

and the local fog concentration can be obtained from Equations (38) and (39) with w'' and w' from the equilibrium relation and Equation (32).

Fluxes

The sensible heat and mass fluxes are given by Fourier's and Fick's Laws so that using Equation (32), we obtain in the fog region

$$\frac{n_1}{\hat{n}_1} = \frac{w'}{\Delta w/\nabla T} \; \frac{\left(1 + \dfrac{\lambda \Delta w}{C_P \Delta T}\right)}{\left(1 + \dfrac{\lambda w'}{C_P}\right)} \tag{40}$$

$$\frac{q}{\hat{q}} = \frac{1 + \dfrac{\lambda}{C_P}\,\dfrac{\Delta w}{\Delta T}}{1 + \dfrac{\lambda}{C_P}\,w'_I} \tag{41}$$

where $\hat{n}$ and $\hat{q}$ are the fluxes which would be obtained if no fog formed. As $w'_I < \Delta w/\Delta T$ (see Figure 1), the mass flux is decreased in magnitude at the interface by the fog formation and the sensible heat flux is increased. However, the total heat supplied to the gas at the liquid interface

$$q_T = [n_1 \lambda + q]_{x=0}$$

is not affected by the fog formation. The determination of the fluxes at the interface does not require a complete solution to the problem; it is merely necessary to assume that fog exists adjacent to the interface. This was taken advantage of by Hills and Szekely (5) who determined the fluxes at the interface for transfer to a boundary layer.

Other Cases

The solutions (32) through (41) also hold when the liquid is warmer than the gas, as is shown in Figure 2. When $w_\infty = w_A$ no fog forms and line *A* [Equation (16)] relates w and T. Line *B* is tangent to the equilibrium curve at T_I so that for any higher value of w_∞ fog forms. Line *D* gives the w-T relationship for a case of fog formation. As in the previous example, the fog zone grows out from the liquid surface.

Now suppose that the liquid surface is replaced by a solid surface. If $T_I > T_{\infty e}$ no fog forms, but if $T_I < T_{\infty e}$ liquid will condense on the surface, and the problem becomes identical to the first case treated.

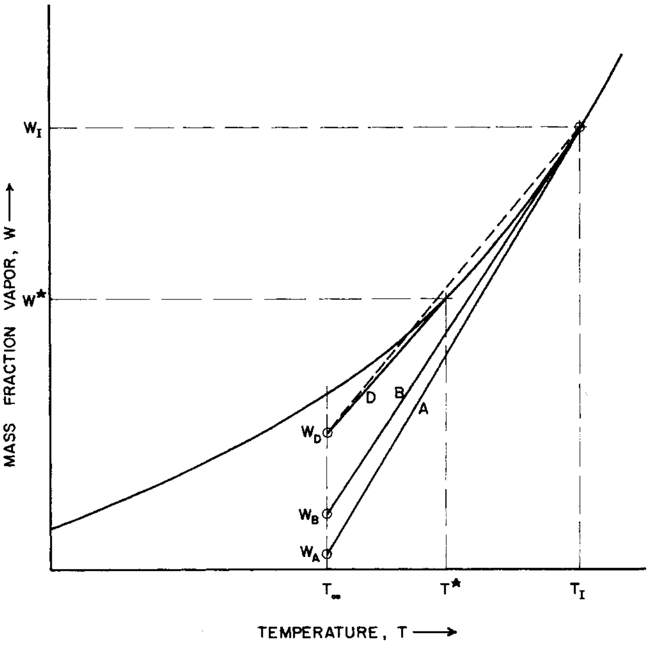

Fig. 2. Concentration-temperature relations $T_I > T_\infty$.

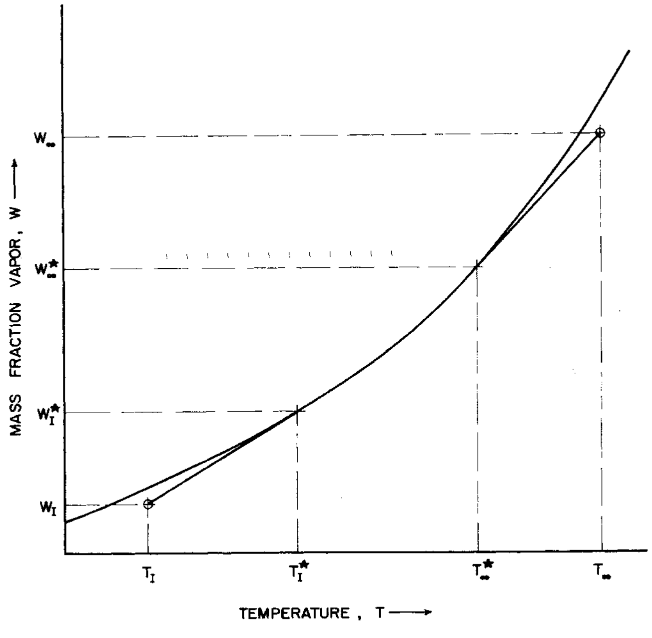

Fig. 3. Two fog boundaries.

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* In a later paper we show that if conditions are changed so that fog is forced to vaporize, discontinuities can appear at the fog boundary. In particular, the concentration of liquid water at the fog boundary may not be zero on the fog side of the boundary.

An Incorrect Solution

In the examples given the fog, once formed, remains stationary and is retained within the growing fog region. Hence, the condition that fog cannot exist in a region in which the vapor is unsaturated is satisfied.

Consider an experiment, however, in which the lower surface is not saturated, as in Figure 3. By drawing two tangent lines, we can show that this problem apparently has a solution in which there is a lower fog boundary at T^*_I and an upper fog boundary at T^*_∞. But this solution cannot be valid, for the lower fog boundary (defined by T^*_I) starts at the lower surface and moves upward with time, leaving fog in the unsaturated region below. In order to solve a problem of this type therefore, vaporization at the lower fog boundary must be taken into account. Correct solutions to problems with two fog boundaries, however, can be obtained in certain cases where there is no vaporization of the fog at either boundary, as shown later.

As w_∞ approaches $w_{\infty e}$, a situation occurs like that shown in Figure 2. At this limit the present method of solution is still incorrect even though there is only one fog boundary, for the fog region is on the upward side of the moving boundary. Hence, the fog boundary must move into the fog region, and fog vaporization must occur just as in the example having two fog boundaries.

NUMERICAL EXAMPLE

The solutions which have been developed represent an idealized limit, and their limitations can be better understood by considering a numerical example. Figure 4 presents the case of water at 20°C. brought into contact with air above it at 50°C. and 1 atm. total pressure in which the initial mass fraction is 88.5% of the saturated value at 50°C. The insert shows the equilibrium curve and the w-T relationship in the gas. The tangent line gives $T^* = 38°\text{C}$. and $w^* = 0.0416$. C_P has been taken constant at 0.25 and λ at 577 g.-cal. Both quantities vary only slightly throughout the field. (The conditions used here are quite extreme compared to, say, atmospheric problems.)

Curve I is a plot of Equation (31) and is also the reduced temperature and concentration profile which would exist if no fog formed. Curve II is the reduced temperature profile from Equation (32) and the equilibrium curve for $\eta \leq \eta_s$ and, from Equation (34), for $\eta \geq \eta_s$. Curve II is above Curve I throughout the field. The maximum difference between the temperatures at any η, with and without fog formation, is about 4°C.

Curve III is the reduced concentration profile from the equilibrium data and Curve I for $\eta \leq \eta_s$ and from Curve I and Equation (33) for $\eta \geq \eta_s$. Curves I and III are close together —the formation of fog does not greatly change the vapor concentration.

The local fog concentration w_3 obtained by numerical integration of Equations (38) and (39), is also shown in the figure. The fog concentration is logarithmically infinite at $\eta = 0$ which means, of course, that the model is invalid very close to the interface. (At $\eta = 10^{-6}$, $w_3 = 0.33$.)

The failure occurs for at least three reasons. Firstly, when the distance scale is the order of the scale of the nuclei or fog particles, the continuum model fails. For a one-second time scale, this failure occurs at values of η the order of 10^{-4}. Secondly, the local equilibrium assumption fails when the fluxes are very high, and thirdly, the assumption of motionless fog particles fails when the distances are very small and fog concentrations high. These last two points will be considered later. Because the computed fog concentration falls off very rapidly with distance from the surface (it is down to 0.056 at $\eta = 0.02$), the computed fog concentrations are consistent with the assumption of a dilute fog over the major part of the fog region.

Integration of w_3 from $\eta = 0$ to $\eta = \eta_s$ gives $\overline{w}_3$, the mean fog concentration over the fog region, as 0.0126. (This figure is also obtained by a material balance on the gas phase.) By comparison, if the original gas mixture were cooled to the interfacial temperature without removing any liquid at the boundary, the resulting fog concentration would be $w_\infty - w_I$ or 0.0556.

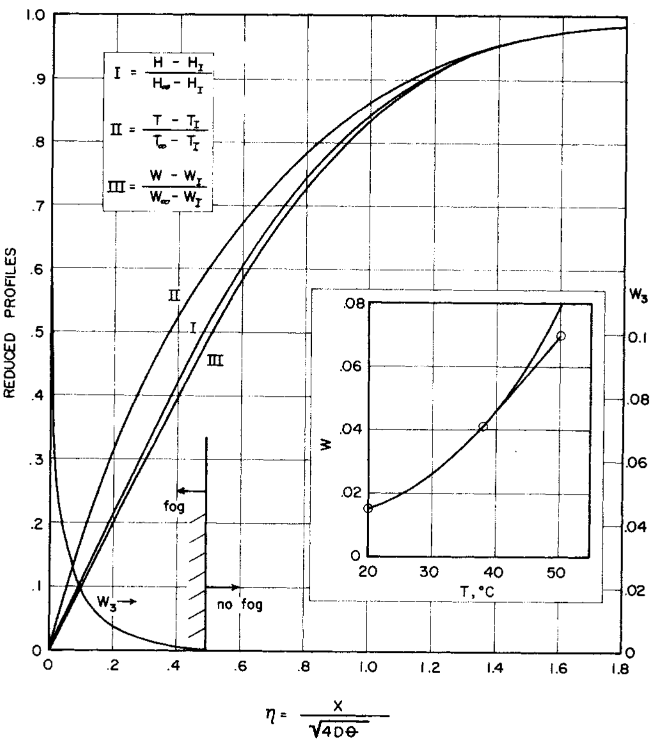

Fig. 4. Concentration and temperature profiles with fog formation, semi-infinite air-water system.

ASSUMPTIONS BASED ON EXAMPLE

Effect of Lewis Number

An estimate of this effect is obtained by using the temperature field from Equation (32) for $N_{Le} = 1$ in Equation (6*a*)

$$\frac{r_3(N_{Le})}{r_3(1)} = 1 + (N_{Le} - 1)$$

$$\left[\frac{w'}{w''} \frac{\left(1 + w' \dfrac{\lambda}{C_P}\right) \sqrt{\pi}\, \eta\, e^{\eta^2}}{\left(1 + \dfrac{\lambda}{C_P} \dfrac{\Delta w}{\Delta T}\right) \quad \Delta T} + \frac{\dfrac{\lambda}{C_P} w'}{1 + \dfrac{\lambda}{C_P} w'} \right] \tag{42}$$

and for the example in Figure 4 where $N_{Le} = 0.85$; at $\eta = 0$, $r_3\,(N_{Le})/r_3(1) = 0.88$ and at $\eta = \eta_s$, $r_3\,(N_{Le})/r_3(1) = 0.76$. $r_3(N_{Le})/r_3(0)$ increases as w_∞ approaches saturation and approaches 0.88 as w_∞ decreases. These calculations suggest that the $N_{Le} = 1$ solution will overestimate the rate of fog formation in the air-water system (and probably the thickness of the fog region), but the error does not appear to be serious unless the gas starts out near saturation.

Time Scale

The assumption of local equilibrium requires that the fine scale condensation process be rapid compared to the large scale transport of heat and vapor. Following Hidy and Friedlander (4), we estimate roughly the rate of condensation by using the relationship for the steady diffusion to a spherical sink from an infinite stagnant medium

$$j = 4\pi a D\rho \, (w - w_e) \tag{43}$$

where w_e is the local equilibrium concentration. When there are n nuclei per unit volume, $r = nj$ so we can write

$$\delta = \frac{w - w_e}{w^* - w_I} = \frac{r}{4\pi n D a \, (w^* - w_I)} \tag{44}$$

and if δ is small compared to one, the local equilibrium assumption is satisfactory. Hence using Equation (38) to estimate r,

$$\delta = \frac{w'' \, (\Delta T)^2}{4\pi^2 \, naD\theta \, (w^* - w_I)} \, \frac{\left(1 + \dfrac{\lambda}{C_P} \dfrac{\Delta w}{\Delta T}\right)^2}{\left(1 + \dfrac{\lambda}{C_P} w'\right)^3} e^{-x^2/2D\theta} \tag{45}$$

For the semi-infinite example this gives

$$x = 0, \quad \delta = \frac{0.15}{na\theta}$$

where θ is seconds and na is cm.$^{-2}$, and

$$x = x_s, \quad \delta = \frac{0.017}{na\theta}$$

If we assume an average number density of 10^5 particles/cc. and a mean radius of 10^{-5} cm., conditions for a rather dirty city, $na = 1$ cm.$^{-2}$ and we see that

$$x = 0 \quad , \ \delta = 0.15/\theta$$

$$x = x_s \ , \ \delta = 0.017/\theta$$

Hence, near the interface we would expect significant supersaturation only for times of the order of 10 sec. or less, and lesser amounts away from the interface. For experiments carried out for times of the order of 10^3 sec., the initial supersaturation near the interface should have little effect, and the local equilibrium assumption appears reasonable over most of the field.

Thus, the large values of w_3 which were predicted for very small values of η will not occur; rather local supersaturation will occur until the growth of the temperature and concentration boundary layers slows down the large scale process enough for the fine scale diffusion to bring the system to local equilibrium. Increasing na by the introduction of additional nuclei, of course, will reduce the time required for the attainment of local equilibrium.

Droplet Size

If we neglect the small mass of the condensation nuclei, the mean droplet radius when the fog concentration is w_3 is given by

$$a = \left[\frac{3}{4\pi} \frac{\rho}{\rho_L} \frac{w_3}{n} \right]^{1/3} \tag{46}$$

The continuum model requires that the interparticle distance be large compared to the droplet diameter which in turn requires that

$$w_3 \leq \frac{\pi}{6} \frac{\rho_L}{\rho} \frac{1}{b^3} \tag{47}$$

where b is the ratio of distance between droplets to droplet diameter. If b is taken as ten, this gives

$$w_3 \leq 0.7$$

which is considerably larger than the upper value one would accept with this constant density model as well as much larger than values computed everywhere except very close to the interface. Thus the assumption of sparse particles will cause no difficulty.

Droplet Settling

Combining Equation (46)with Stokes Law for the terminal settling velocity in a gravitational field yields,

$$u = \frac{g\rho_L}{18\mu} \left[\frac{6}{\pi} \frac{\rho}{\rho_L} \frac{w_3}{n} \right]^{2/3} \tag{48}$$

When $n = 10^5$ and $w_3 = 0.01$, this equation gives $u =$ 0.1 cm./sec. But in 100 seconds $x_s = 4.9$ cm. from Equation (37). From Figure 4, if the fog did not settle, w_3 would equal 0.01 at $x = 1.6$ cm. Consequently, significant settling of the fog must take place under these conditions; the calculated values of w_3 will not be correct in a gravitional field. The larger particles nearest the surface will settle most rapidly. As the fog droplets are moving downwards and the fog boundary is moving upwards, however, the primary effect of the downward motion of the droplets is to remove condensation surface from the gas. At the same time surface is being formed by the condensation, and more nuclei are being added to the fog region by the upward motion of the fog boundary. Although not treated here, this rather complicated problem could lead to the conclusion that, after a period of operation at local equilibrium, a second period of supersaturation could occur.

GENERALIZATION

We now consider a more general class of problems. An arbitrary nonturbulent velocity field and arbitrary geometry are allowed. Equations (3) and (4) hold, and with the earlier assumptions they become

$$\frac{Dw}{D\theta} = D\nabla^2 w - \frac{r_3}{\rho} \tag{49a}$$

$$\frac{DT}{D\theta} = D\nabla^2 T + \frac{r_3 \lambda}{\rho C_P} \tag{49b}$$

$$\frac{Dw_3}{D\theta} = \frac{r_3}{\rho} \tag{49c}$$

Equation (7) remains valid so that only fog formation can take place continuously. With the local equilibrium assumption, Equations (11) and (12) are equivalent to Equations (49a) and (49b).

Boundary conditions of the following form are considered: At one boundary (the first)

$$T = T_I \ , \quad w = w_I \text{ so } H = H_I \tag{49d}$$

At the other boundary or at time zero (the second)

$$T = T_\infty \ , \quad w = w_\infty \text{ so } H = H_\infty \tag{49e}$$

These boundary conditions include the problems considered earlier as well as problems of steady flow external to surfaces, nonturbulent mixing, etc. For the present we assume that w_I is the equilibrium value at T_I and that a boundary exists which separates the fog and nonfog regions. At this boundary w and T and their derivatives normal to the boundary are assumed to be continuous. w and T are also assumed to be constant at w^* and T^* at the fog boundary. This can be shown to imply, as before, that the fog concentration approaches zero as the fog boundary is approached from the fog side and that there is no vaporization or formation of fog at this boundary.

Equation (49) gives

$$\frac{H - H_I}{H_\infty - H_I} = f\,(\theta, x) \tag{50}$$

where f solves the equation

$$\frac{Df}{D\theta}(\theta, \mathbf{x}) = D\nabla^2 f(\theta, \mathbf{x}) \tag{51a}$$

at the first boundary

$$f = 0 \tag{51b}$$

and at the second boundary

$$f = 1 \tag{51c}$$

For steady state processes, f depends only upon $\mathbf{x}$.

Equation (50) holds everywhere in the fluid. In the inner region where fog exists $w = w(T)$, so that we obtain from (50) an equation similar to Equation (32):

$$\frac{T - T_I}{T_\infty - T_I} + \frac{\lambda\,(w(T) - w_I)}{C_P\,(T_\infty - T_I)} = \left[1 + \frac{\lambda\,(w_\infty - w_I)}{C_P\,(T_\infty - T_I)}\right] f\,(\theta, \mathbf{x}) \tag{52}$$

which holds for the inner region. The equilibrium equation and Equation (52) give w in this region.

In the outer region where $r_3 = 0$

$$\frac{Dw}{D\theta} = D\nabla^2 w \tag{53}$$

$$\frac{DT}{D\theta} = D\nabla^2 T \tag{54}$$

As T and w are assumed constant at the fog boundary, it follows from Equations (53) and (54) that Equation (33) is valid in the outer region. Thus Equations (33) and (50) give for the outer region

$$\frac{T_\infty - T}{T_\infty - T_I} = \frac{1 + \dfrac{\lambda}{C_P}\left(\dfrac{w_\infty - w_I}{T_\infty - T_I}\right)}{1 + \dfrac{\lambda}{C_P}\left(\dfrac{w_\infty - w^*}{T_\infty - T^*}\right)}\,[1 - f\,(\theta, \mathbf{x})] \tag{55}$$

and Equation (33) gives w in this region.

T^* and w^* are obtained by requiring the continuity of the gradients of w and T at the fog boundary. Thus, equating the gradients of T at $\mathbf{x}_s$ obtained from Equations (52) and (55) gives Equation (35). Hence, as before, the values of T and w at the fog boundary are defined by the straight line from T_∞, w_∞ which is tangent to the equilibrium line. This means that T^* and w^* depend only upon the initial and/or boundary values of T and w and upon the equilibrium curve; they are independent of the solution function f.

The fog boundary is then obtained from Equation (52) or (55),

$$f\,(\theta, \mathbf{x}_s) = \left(\frac{T^* - T_I}{T_\infty - T_I}\right) \frac{1 + \dfrac{\lambda\,(w^* - w_I)}{C_P\,(T^* - T_I)}}{1 + \dfrac{\lambda\,(w_\infty - w_I)}{C_P\,(T_\infty - T_I)}} \tag{56}$$

Equations (26), (35), (52), (55), and (56) represent a generalization of the semi-infinite problem considered earlier. As in that problem, they can be shown to represent a solution to the original differential equations—in this case, Equation (49). Also, they describe only fog formation and are not valid if they lead to the presence of fog in the outer region. Furthermore, they are limited to situations in which the initial and/or boundary values of T and w are constant. The simplicity and generality of the solutions may well be lost when other kinds of boundary conditions are imposed, as may occur in certain meteorological problems (*10*)

Laminar Boundary Layer

The previous results can be applied to various cases of a laminar boundary layer. If the surface is initially dry and if its temperature is greater than $T_{\infty e}$, no fog forms; if the surface temperature is less than $T_{\infty e}$, however, the plate will be wet. If the surface temperature is less than T^*, fog forms. The geometrical construction gives T^* and w^*, and Equation (56) fixes the fog boundary. Equations (52) and (55) then give w and T on either side of the boundary. For the simplest case of Schmidt and Prandtl numbers equal to one, with a flat plate at zero incidence (*13*):

$$f = \frac{u(\epsilon)}{u_\infty} \tag{57}$$

where

$$\epsilon = y\sqrt{\frac{U_\infty}{\gamma x}} \tag{58}$$

The fog boundary is defined by a fixed value of ϵ so that the fog region has a boundary layer shape.

Since vertical velocity components exist, the fog particles move in a direction inclined to the plate (assuming that they follow the stream lines). In order to determine whether any fog particles cross the fog boundary (which would invalidate the solution), the particle trajectories are examined. The tangent of the angle between the trajectory and the plate is given by v/u and from the Blasius solution

$$\frac{v}{u} = h(\epsilon)\ \ (N_{Re})^{-1/2} \tag{59}$$

where $h(\epsilon)$ is given by Schlichting (*13*).

The tangent to the fog boundary is given by

$$\frac{dy_s}{dx} = \frac{\epsilon_s}{2}\ (N_{Re})^{-1/2} \tag{60}$$

If no fog particle is to cross the fog boundary, we require that

$$\frac{dy_s/dx}{v/u} \geqq 1.0 \tag{61}$$

or

$$\frac{\epsilon_s\,h\,(\epsilon_s)}{2} > 1.0 \tag{62}$$

which, from the Blasius solution for $h(\epsilon)$, can be shown to be satisfied everywhere in the boundary layer (*13*). After being formed, the fog particles remain inside the saturated fog region, thus satisfying our assumption at the fog boundary.

We will not attempt an estimate of the "goodness" of the model in this case. It is clear that this solution is only a limiting case.

Steady Unidirectional Transfer

In this case Equations (49*a*) and (49*b*) become

$$D\,\frac{d^2T}{dx^2} + \frac{r_3\lambda}{\rho\,C_P\,N_{Le}} = 0 \tag{63a}$$

$$D\,\frac{d^2w}{dx^2} - \frac{r_3}{\rho} = 0 \tag{63b}$$

Here the previous relations hold even if N_{Le} is not equal to one. Decreasing or increasing N_{Le} is the same as increasing or decreasing λ. (This is true also for the multidimensional version of this problem.) If the boundaries $x = 0$ and $x = x_\infty$ (x_∞ is finite here) are held at T_I, w_I, and T_∞, w_∞, respectively, the solution function is linear,

$$f = \frac{x}{x_\infty} \tag{64}$$

In this simple case the rate of fog formation is given by Equation (7) even if $N_{Le} \neq 1$ if λ is replaced by λ/N_{Le}. (This is again true for the multidimensional version of the problem.)

Steady Unidirectional Flow Normal to a Wet Surface

A porous wet plate is held at T_I, and a gas whose temperature and concentration far from the plate are T_∞ and w_∞ flows toward the plate with a velocity u. The function f is then given by

$$f = 1 - e^{-\frac{u}{D}x} \tag{65}$$

where x is the distance from the plate. For the conditions of the water-air example treated earlier $x_s = 1.7$ cm. when $u = 0.1$ cm./sec.

Two Fog Boundaries

When the gas is unsaturated at the first and second boundaries, there will be either no fog or two fog boundaries. As with one fog boundary, it can be shown that a solution apparently exists for the double boundary case with the temperatures and concentrations defined by the two tangent lines (Figure 3). The inner solution is still given by Equation (52), but now there are two outer solutions.

Equation (55) gives the solution for $T^*_\infty \leq T \leq T_\infty$ if T^* and w^* in that equation are replaced by T^*_∞ and w^*_∞, respectively. The solution for $T_I \leq T \leq T^*_I$ is given by

$$\frac{T - T_I}{T_\infty - T_I} = \frac{\left[1 + \frac{\lambda}{C_P}\left(\frac{w_\infty - w_I}{T_\infty - T_I}\right)\right]}{\left[1 + \frac{\lambda}{C_P}\left(\frac{w^*_I - w_I}{T^*_I - T_I}\right)\right]} f(\theta, x) \tag{66}$$

The solution requires that there be no vaporization at either fog boundary. An example has already been given which violates this condition, thus negating the solution. We now give two more examples, one in which the above solution is valid throughout the field, and the other in which the solution holds in one part of the field but not in the other:

1. Infinite one-dimensional gas—initial step change

$x < 0$

$$T(0, x) = T_I \tag{67}$$

$$w(0, x) = w_I \tag{68}$$

$x > 0$

$$T(0, x) = T_\infty \tag{69}$$

$$w(0, x) = w_\infty \tag{70}$$

For the situation pictured in Figure 3, two fog boundaries form, one growing to the right and one to the left. The double tangent solution is valid for all time.

2. Infinite one-dimensional gas—initial pulse of width $2a$

$-a < x < a$,

$$T(0, x) = T_I \tag{71}$$

$$w(0, x) = w_I \tag{72}$$

$a < x < -a$,

$$T(0, x) = T_\infty \tag{73}$$

$$w(0, x) = w_\infty \tag{74}$$

Assume as before that the initial values are such that Figure 3 holds. Although fog must form initially, it is clear that it must eventually dissipate. The double tangent solution holds up until the first occurrence of fog vaporization. After this time another type of solution which allows for vaporization at the fog boundary must be obtained.

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NOTATION

a = radius
b = ratio of lengths
C_P = heat capacity
D = diffusivity
f = solution function
h = function
H = enthalpy
j = fine scale rate of diffusion
k = thermal conductivity
n = number of nuclei
n_1 = flux of vapor
$\hat{n}_1$ = n_1 if no fog formation
$\mathbf{n}_j$ = vector flux of species j
N_{Le} = Lewis number = $k/\rho\, C_P\, D$
N_{Re} = Reynolds number
q = heat flux
$\hat{q}$ = q if no fog formation
r = mass rate of generation per unit volume
T = temperature
u = velocity
v = velocity
$\mathbf{V}$ = velocity vector, mass average
w = mass fraction
x = distance
$\mathbf{x}$ = distance vector
y = distance normal to plate

Greek Letters

γ = kinematic viscosity
δ = local equilibrium measure, see Equation (44)
Δ = value at ∞ minus value at I
ϵ = $y\sqrt{\frac{U_\infty}{\gamma x}}$
η = $x/\sqrt{4D\theta}$
θ = time
λ = latent heat
μ = viscosity
ρ = density of gas
ρ_L = density of liquid

Subscripts

1, 2, 3 = vapor, inert, liquid, respectively
e = equilibrium value
i = inside fog region
I = boundary I
j = 1, 2 or 3
o = outside fog region
s = fog boundary

∞ = boundary ∞

Superscripts

* = constant value at fog boundary
′ = d/dT
″ = d^2/dT^2

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Behavior of Countercurrent Liquid-Liquid Columns with a Liquid Metal

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Packed columns are being considered for contacting liquid metals with molten salts to extract fission products from spent nuclear fuel. Extraction rates between a liquid cadmium alloy and a liquid chloride salt were measured at 530°C. in a prototype column. With a system of water and a low melting metal alloy, measurements of the pressure drop, limiting flow rates, and hold-up were made and compared with the predictions of existing correlations. These data indicate that packed columns might be effective contacting devices for pyrochemical processes.

Countercurrent extraction columns are being studied as a means of contacting liquid metals and liquid salts in pyrochemical processes (*1*) to recover spent nuclear fuel from fast breeder reactors. Metals and salts in the range of 500 to 800°C. are used as the solvents for uranium and plutonium. The metals used are alloys of magnesium with zinc, copper, or cadmium, and the usual salts are mixtures of the chlorides of magnesium, calcium, and alkali metals. The rare earth fission product elements can be separated from uranium and plutonium by oxidation-reduction reactions with magnesium between the salt and metal phases, as the rare earths distribute more strongly to the salt phase than uranium and plutonium (*2*).

TABLE 1. SELECTED LIQUID METAL AND SALT PROPERTIES

(at 600°C.)

Liquid metals	Density, g./cc.	Viscosity, cp.	Surface tension, dynes/cm.
Bi	9.66	1.5	350
Cd	7.72	1.5	590
Mg (660°C.)	1.57	1.2	570
Zn	6.80	2.2	770
Cd-6 wt. % Mg-2 Zn	6.3*	1.5*	590*
Cu-33 wt. % Mg	4.0 (*6*)	3 (*6*)	800*
Wood's metal (100°C.) (Bi-25 wt. % Pb-13 Cd-12 Sn)	9.66 (*6*)	3.4 (*6*)	500*
Liquid salt			
$MgCl_2$– 20 wt. % NaCl-20 KCl	1.76	1.7	87

* Estimated

Future fuel recovery processes for fast breeder reactors will be required to recover at least 99% of the plutonium and more than 90% of the uranium with an overall decontamination factor from 100 to 10,000 for fission products. Larger fission product decontamination factors will not significantly reduce the radioactivity of the recovered fuel because of the buildup of short-lived uranium and plutonium isotopes in recycled fuel.

A conceptual pyrochemical reprocessing plant serving several power reactors with a total thermal power of the order of 20,000 MW would receive about 200 kg./day of core fuel having an average burnup of 100,000 MW-days/tonne and containing 20 wt. % plutonium and about 500 kg./day of blanket fuel (*3*). The plutonium-rare earth partition column would have four to eight theoretical stages and would be roughly 2 to 5 in. in diameter.

PREVIOUS STUDIES

The technology (*4, 5*) of liquid-liquid extractions columns is based primarily on investigations with aqueous-organic