A Model for Evaporation of a Multicomponent Droplet

The object of this study was to derive a model which would accurately describe the evaporation of a multicomponent droplet, especially near its boiling point. The model is derived and is shown to have the following properties: the transport of one component can be augmented by the bulk (Stefan) flow of the other components, and the droplet can never exceed its boiling point, a property not realized by previous models. The ordinary differential equations which constitute the model were integrated numerically, and results are given for both two- and three-component droplets.

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SCOPE

The object of this study was to derive a mathematical model which would give an improved description of the evaporation of a multicomponent droplet in a stagnant gas, especially near the droplet boiling point. A large number of processes, such as spray drying, spray humidification, and combustion of liquid fuels in furnaces and in various types of engines, involve the evaporation of droplets. In addition, many of these processes operate at high temperatures where the droplet approaches a wet-bulb temperature very near its boiling point. Attempts to model such processes usually rely on a fairly simple model for the evaporation of a single-component droplet. Models exist which give an adequate description of evaporation under these conditions. However, in the multicomponent case it was found that the only model available was an adaptation of the single-component expression. Furthermore, this model gives erroneous results near the boiling point of the droplet and even permits the droplet to exceed its boiling point by a substantial amount. Hence, an improved droplet model is required if high-temperature, multicomponent spray processes are to be described with any accuracy.

CONCLUSIONS AND SIGNIFICANCE

A model was derived which gives an improved description of the evaporation of a multicomponent droplet. It was discovered that the augmentation of diffusive mass transfer by Stefan (bulk) flow from the droplet plays an essential part in the improved model. The importance of Stefan flow in single-component evaporation has been known for some time. However, it was found to play an even greater role in the multicomponent case, where the transport of one component can be augmented by the transport of another. The inclusion in the model of this coupling of the transfer rates leads to the correct description of evaporation near the boiling point, and, in particular, keeps the droplet temperature from exceeding the boiling point. The remaining features of the droplet model were readily deduced from an analysis of the ordinary differential equations in the temperature-concentration phase plane. The behavior of evaporating droplets was further illustrated with the results of numerical calculations carried out for two- and three-component droplets. The model presented here represents a definite improvement over models previously available, notwithstanding its failure to include the effects of intraparticle diffusion. Moreover, it agrees with results observed by others for similar problems.

The multicomponent droplet model will be derived following a review of the pertinent literature. Next, the ordinary differential equations which constitute the model are analyzed to determine their general features. Finally the method of integrating the equations is described, and results are presented for both two- and three-component droplets.

PREVIOUS WORK

Much work has been done on the problem of evaporation from drops and porous spheres into flowing as well as stagnant gases and several comprehensive reviews are available (Galloway and Sage, 1967; Pritchard and Biswas, 1967; Keey and Glen, 1965; Rowe et al., 1965). Therefore, we limit the following review to literature which pertains directly to our topic, that is, to evaporation of single-component and multicomponent drops in stagnant gases.

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One of the earliest investigations of evaporation in stagnant gases was made in 1877 by Maxwell (Niven, 1965) who considered constant-temperature evaporation from a wetted sphere in an attempt to describe the phenomenon of the wet-bulb temperature. Assuming equilibrium of liquid and vapor at the interface and negligible convective effects, Maxwell solved the steady state conservation equations of mass and energy (Laplace's equation) in the gas phase and obtained the following expressions for the fluxes of heat and mass from the sphere:

$$q = -\frac{k}{r}(T - t_{WB}) \qquad (1)$$

and

$$J = -\frac{DC_T}{P_T}\frac{1}{r}[P_v - P_v^*(t_{WB})] \qquad (2)$$

Now, from film theory,

$$q = -h_G(T - t_{WB}) \qquad (3)$$

$$= -N_{Nu}\frac{k}{2r}(T - t_{WB}) \qquad (4)$$

and

$$J = -k_G[P_v - P_v^*(t_{WB})] \qquad (5)$$

$$= -N_{Sh}\frac{DC_T}{2P_T}\frac{1}{r}[P_v - P_v^*(t_{WB})] \qquad (6)$$

so that Maxwell's results are equivalent to using values of two for the Nusselt and Sherwood numbers, that is,

$$N_{Nu} = N_{Sh} = 2 \qquad (7)$$

Equation (2) was derived also by Langmuir (1918) to explain the data of Morse (1910), who had observed that a sphere of iodine subliming in air showed a linear change in surface area with time. Indeed, comparison of the flux given by Equation (2) with the change in moles $-\frac{d}{d\theta}\left(\frac{1}{mv_s}\frac{d^3}{6}\right)$ of a subliming sphere yields

$$\frac{d}{d\theta}(d^2) = -\frac{8DC_T mv_s}{TP_T}[P_v^*(t_{WB}) - P_v] \qquad (8)$$

which confirms Morse's data when the sphere maintains a constant (wet-bulb) temperature. In integrated form, Equation (8) becomes

$$(d^0)^2 - d^2(\theta) = \epsilon\theta \qquad (9)$$

where ϵ, the evaporation constant, equals

$$\epsilon = \frac{8DC_T mv_s}{P_T}[P_v^*(t_{WB}) - P_v] \qquad (10)$$

Here the wet-bulb temperature t_{WB} is determined by noting that, for constant-temperature sublimation,

$$J = -\frac{q}{\lambda}$$

so that ϵ is also given by

$$\epsilon = \frac{d}{d\theta}(d^2) = \frac{8kmv_s}{\lambda}[T - t_{WB}] \qquad (11)$$

Then equating (10) and (11) gives an implicit expression for t_{WB}. In addition to describing sublimation, Equation (9), known as the *D*-squared law, has been verified for evaporation from a sphere into a stagnant gas by a number of experimentors, including Hall and Diederichsen (1952), Kobayasi (1955), and Hoffman and Gauvin (1960).

At this point several comments are in order on the analyses of Maxwell and Langmuir. First, it should be pointed out that use of the steady state heat and mass conservation equations constitutes an assumption (the pseudo steady state assumption) for the case of a drop or sphere which diminishes in size as it evaporates or sublimes. However, the steady state equations apply rigorously for the case of evaporation from a porous sphere, and for cases where the size of the drop is held constant, for example, by feeding liquid to the drop through a capillary. Next, note that the assumption of equilibrium between the liquid and its vapor at the drop interface implies that the diffusive resistance of the gas to evaporation is large compared to the interfacial resistance. This is considered to be a good assumption under all conditions, except at very low gas pressures or for droplets whose size is on the order of the mean free path of the gas molecules (about 0.1 micron). Thus, equilibrium has been assumed in most analyses dealing with evaporation of drops.[*] Finally, observe that Equations (1) and (2) were derived neglecting the radial convective transport due to bulk flow of gases away from the drop or sphere. Unlike natural and forced convection which can be neglected as a special case, radial convection is always present, although its effects will be small at low evaporation rates.

Stefan (1881) was the first to note the importance of radial convection (Stefan flow), and his observation led to a revised mass flux expression of the form (Fuks, 1959)

$$J = -DC_T\frac{1}{r}\ln\left[\frac{P_T - P_v}{P_T - P_v^*}\right] \qquad (12)$$

Sometime later, Godsave (1952) arrived at the corresponding equation for the heat flux with radial convection:

$$q = -\frac{k}{r}\frac{a}{e^a - 1}[T - t] \qquad (13)$$

Stefan flow has the effect on the Nusselt and Sherwood numbers of applying correction factors to the values of two obtained by ignoring radial convection. Thus, with radial convection included

$$N_{Nu} = 2\frac{a}{e^a - 1} \qquad (14)$$

and

$$N_{Sh} = 2\frac{a'}{1 - e^{-a'}}\frac{1}{1 - P_v/P_T} \qquad (15)$$

where

$$a = \frac{JrC_{pv}}{k} \qquad (16)$$

and

$$a' = \frac{Jr}{C_T D} \qquad (17)$$

It is easily shown that N_{Nu} approaches two as J approaches zero. The Sherwood number, however, approaches $2/(1 - P_v/P_T)$, as noted by Fuks (1959).

More recently, the transient equations describing evaporation in a stagnant gas and including Stefan flow were solved numerically by Kotake and Okazaki (1969). They compared the resulting histories of drop size and drop temperature with those obtained from the pseudo steady state solution neglecting Stefan flow, that is, with those

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[*] For exceptions see Fuks (1959), Williams (1965), and Lambert and Quince (1969).

obtained using $N_{Nu} = N_{Sh} = 2.0$. The agreement was poor, indicating the magnitude of the combined errors due to the pseudo steady state approximation and the assumption of negligible radial convection.

The problem of evaporation of a drop containing a mixture of distinct volatile materials has received little attention. The evaporation of a single component into a multicomponent gas has been considered by Hsu and Bird (1960). Also, a related problem of multicomponent mass transfer from a reacting solid sphere has been solved (Fuks, 1959), but only for the case where the fluxes remain in stoichiometric proportions. On the experimental side, a study of the evaporation of two-component drops showed that the *D*-squared law was not satisfied exactly and that the process appeared to proceed very much like batch distillation of the components (Wood et al., 1960).

DERIVATION OF THE DROPLET EQUATIONS

The derivation of ordinary differential equations describing the evaporation of a single droplet will be carried out in two steps. First, the transport equations for the gas phase will be solved to generate expressions for the fluxes of heat and mass from the droplet. Then these fluxes will be used in making volume, mass, and energy balances on a droplet to produce differential equations describing changes in its radius, concentrations, and temperature, respectively.

Flux Models

The fluxes of heat and mass from a droplet might be determined by solving exactly the transient equations for coupled heat and mass transfer through the gas with time dependent conditions at the moving gas-liquid interface. However, this exact problem cannot be solved analytically, and numerical solution is tedious. Moreover, the bulk of experimental evidence on droplet evaporation justifies the use of the pseudo steady state approximation, which does produce an analytic solution. Therefore, the approach will be to solve the pseudo steady state problem, whereby the droplet surface and all boundary conditions are assumed to change only very slowly with time. Several other assumptions which deserve comment are:

1. The gas-liquid interface is at equilibrium. This assumption implies that interfacial resistance is negligible compared with the diffusive resistance of the gas, and it should be good except at low pressures.
2. The effect of surface tension on vapor pressure can be ignored. The correction for a water droplet of radius 0.1 micron at 25°C is only about 1%, and the initial droplet radius is much greater than 0.1 micron.

The Problem. With the assumptions just mentioned, the original problem may be stated as follows: n vapors Ai are transported through an inert gas from a sphere of fixed radius r. The mole fractions of the vapors at radial position ξ are given by $y_i(\xi)$, the mole fraction of inert by $y_{n+1}(\xi)$, and the gas temperature by $T(\xi)$. At the surface of the sphere ($\xi = r$) the concentrations and temperature are maintained constant at y_i^* and t, while at $\xi = \infty$ they have the constant values y_{iB} and T_B. An additional requirement is that there is no net flux of inert at the surface $\xi = r$.

The transport equations for this problem are (Bird et al., 1960)

$$\frac{dy_i}{d\xi} = \sum_{j=1}^{n+1} \frac{1}{C_T D_{ij}} (y_i N_j - y_j N_i) \tag{18}$$

(the Stefan-Maxwell equation), and

$$e = -k \frac{dT}{d\xi} + \sum_{i=1}^{n+1} N_i H'_{Ai} \tag{19}$$

where $N_i = N_i(\xi)$ is the net flux of component i, and $e = e(\xi)$ is the total energy flux. The boundary conditions for Equations (18) and (19) are

$$y_i = y_i^*, \quad T = t \quad \text{at} \quad \xi = r \tag{20}$$

and

$$y_i = y_{iB}, \quad T = T_B \quad \text{at} \quad \xi = \infty\,. \tag{21}$$

Mass Flux. Equation (18) cannot be solved as it stands, so it will be rewritten in the approximate form

$$N_i = -C_T D_{im} \frac{dy_i}{d\xi} + y_i \sum_{j=1}^{n+1} N_j \tag{22}$$

where D_{im} is the effective binary diffusivity of component i with respect to the mixture (Bird et al., 1960). Now, since the system is at steady state, the rate of transfer of component i through any sphere ξ = constant will be a constant. Then if J_i is the flux at $\xi = r$, we have

$$N_i(\xi) = \frac{r^2 J_i}{\xi^2} \tag{23}$$

and (22) can be rewritten

$$J_i = -\frac{C_T D_{im}}{r^2} \xi^2 \frac{dy_i}{d\xi} + y_i \sum_{i=1}^{n+1} J_i \tag{24}$$

Substituting $\xi = 1/\eta$, (24) is transformed to

$$\frac{dy_i}{d\eta} = \frac{r^2}{C_T D_{im}} (J_i - y_i \bar{J}) \tag{25}$$

where $\bar{J} = \sum_{j=1}^{n+1} J_j$. This equation is easily integrated to give

$$y_i(\xi) = K \operatorname{Exp}\left(-\frac{\bar{J} r^2}{C_T D_{im}} \frac{1}{\xi}\right) + \frac{J_i}{\bar{J}} \tag{26}$$

The condition as $\xi = \infty$ may be used to evaluate K, the constant of integration. Then, application of the condition at $\xi = r$ yields

$$y_i^* = \left(y_{iB} - \frac{J_i}{\bar{J}}\right) \operatorname{Exp}\left(-\frac{\bar{J} r}{C_T D_{im}}\right) + \frac{J_i}{\bar{J}} \tag{27}$$

Solving for J_i

$$J_i = \bar{J} \left[\frac{y_i^* \operatorname{Exp}\left(\dfrac{\bar{J} r}{C_T D_{im}}\right) - y_{iB}}{\operatorname{Exp}\left(\dfrac{J r}{C_T D_{im}}\right) - 1} \right], \quad i = 1, \ldots n + 1 \tag{28}$$

Equation (28) holds for each of the vapors $i = 1, \ldots n$ and for the inert $i = n + 1 \equiv I$. But, since there is no net flux of inert from the droplet,

$$J_I = \bar{J} \quad \frac{y_I^* \operatorname{Exp}\left(\dfrac{\bar{J} r}{C_T D_{Im}}\right) - y_{IB}}{\operatorname{Exp}\left(\dfrac{J r}{C_T D_{Im}}\right) - 1} = 0 \tag{29}$$

Then we must have

$$\mathrm{Exp}\left(\frac{\bar{J}r}{C_T D_{Im}}\right) = \frac{y_{IB}}{y_I^*} \tag{30}$$

Let

$$C = \frac{y_{IB}}{y_I^*} = \frac{1 - \sum_{i=1}^{n} y_{iB}}{1 - \sum_{i=1}^{n} y_i^*} \tag{31}$$

Then, from (30),

$$\bar{J} = \frac{1}{r} C_T D_{Im} \ln(C) \tag{32}$$

Using this expression to eliminate $\bar{J}$, Equation (28) becomes

$$J = \frac{C_T D_{Im}}{r} \ln(C) \left[\frac{y_i^* \,\mathrm{Exp}\left(\frac{D_{Im}}{D_{im}} \ln C\right) - y_{iB}}{\mathrm{Exp}\left(\frac{D_{Im}}{D_{im}} \ln C\right) - 1} \right]$$

or

$$J_i = \frac{C_T D_{Im}}{r} \ln(C) \left[\frac{y_i^* \, C^{D_{Im}/D_{im}} - y_{iB}}{C^{D_{Im}/D_{im}} - 1} \right] \tag{33}$$

For the droplet the boundary conditions become

$$y_{iB} = \frac{P_{Ai}}{P_T}$$

and (using Raoult's law)

$$y_i^* = \frac{x_i \, P^*_{Ai}(t)}{P_T}$$

where

$$P^*_{Ai}(t) = \mathrm{Exp}(u_i - v_i/t) \tag{34}$$

is the vapor pressure of pure component i at the droplet temperature. The final expression for the flux of i from the droplet is*

$$J_i = \frac{1}{r} \frac{C_T D_{Im}}{P_T} \ln(C) \left[\frac{x_i \, P^*_{Ai}(t) \, C^{D_{Im}/D_{im}} - P_{Ai}}{C^{D_{Im}/D_{im}} - 1} \right] \tag{35}$$

where

$$C = \frac{P_T - \sum_{i=1}^{n} P_{Ai}}{P_T - \sum_{i=1}^{n} x_i P^*_{Ai}(t)} \tag{36}$$

Some Observations on the Mass Flux Model. For the case of a single vapor $D_{im} = D_{Im}$, and (35) reduces to

$$J_1 = \frac{1}{r} C_T D_{1m} \ln\left(\frac{P_T - P_{A1}}{P_T - P^*_{A1}(t)}\right) \tag{37}$$

Note that, according to (32), $C = 1$ corresponds to zero total flux, while $\bar{J}$ is positive for $C > 1$. Letting $C \to 1$ in Equation (35) gives a linear model for mass transfer

$$J_i = \frac{1}{r} \frac{C_T D_{im}}{P_T} [x_i P^*_{Ai}(t) - P_{Ai}] \tag{38}$$

which also comes from solving Equation (22) without the convection term. Then, if $\bar{J} = 0$ Equation (38) shows that the flux of the ith component will be zero if the partial pressures $x_i P^*_{Ai}$ and P_{Ai} are equal. However, according to (35), when the total flux is positive and $x_i P^*_{Ai} = P_{Ai}$ there will yet be a positive flux of i from the droplet. This augmentation effect is due to the convection of component i by the other vapors leaving the droplet and is especially important in predicting the correct behavior of the droplet near its boiling point. For example, the droplet can never exceed its boiling point, since as this point is approached $\sum_{i=1}^{n} x_i P^*_{Ai} \to P_T$, and $C \to \infty$, so that all the fluxes J_i approach infinity.

Finally, note that summing Equation (35) over all i yields the identity $\bar{J} = \bar{J}$ only for the case where all the D_{im} are equal, which is the only case for which Equation (22) holds exactly. When the diffusivities are not equal, Equation (22) only approximates the Stefan-Maxwell Equation (18) and this may be the reason for the apparent inconsistency of the solution (35).

Energy Flux. If E is the energy flux at $\xi = r$, then, reasoning as before,

$$e(\xi) = \frac{r^2 E}{\xi^2} \tag{39}$$

and Equation (19) can be rewritten

$$E = -\frac{k}{r} \xi^2 \frac{dT}{d\xi} + \sum_{i=1}^{n} J_i H'_{Ai}(T) \tag{40}$$

The enthalpies may be expressed as

$$H'_{Ai}(T) = H'_{Air} + C'_{pAi}(T - T_r) \tag{41}$$

where H'_{Air} is the enthalpy at the reference temperature T_r. Then Equation (40) becomes

$$E = -\frac{k}{r} \xi^2 \frac{dT}{d\xi} + \sum_{i=1}^{n} J_i \,[H'_{Air} + C'_{pAi}(T - T_r)] \tag{42}$$

This equation has the same form as (24), and its solution is

$$T(\xi) = K \,\mathrm{Exp}\left(-ar\frac{1}{\xi}\right) - \frac{b}{a} \tag{43}$$

where

$$a = \frac{r}{k} \sum_{i=1}^{n} J_i \, C'_{pAi} \tag{44}$$

and

$$b = \frac{r}{k} \left[\sum_{i=1}^{n} J_i \, H'_{Air} - T_r \sum_{i=1}^{n} J_i \, C'_{pAi} - E \right] \tag{45}$$

Application of boundary conditions (20) and (21) yields

$$t = \left(T_B - \frac{b}{a}\right) \mathrm{Exp}(-a) - \frac{b}{a}$$

or

$$b = a \frac{T_B - t \, e^a}{e^a - 1} \tag{46}$$

Substituting for b from (45) we get for E

$$E = \sum_{i=1}^{n} J_i (H'_{Air} - T_r \, C'_{pAi}) - \frac{k}{r} a \frac{T_B - t \, e^a}{e^a - 1}$$

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* Similar flux expressions can be derived for the analogous planar and cylindrical problems, though in the latter cases both boundaries must be finite.

or

$$E = \sum_{i=1}^{n} J_i H'_{Ai}(t) + \frac{a}{e^a - 1} \frac{k}{r} (t - T) \qquad (47)$$

where for the droplet we have set T_B equal to the gas temperature T.

Some Observations on the Energy Flux Model. Equation (47) shows that the total energy flux from the droplet is the sum of the total enthalpy leaving with the vapors plus the rate of heat conduction from the droplet corrected for the effect of mass transfer. The correction factor $a/(e^a - 1)$ is less than unity so that the effect of mass transfer is to decrease the rate of heat transfer.* If there is no mass transfer ($a = 0$) the correction factor is unity, and Equation (47) reduces to

$$E = \sum_{i=1}^{n} J_i H'_{Ai}(t) + \frac{k}{r} (t - T) \qquad (48)$$

Volume, Mass and Energy Balances

In the derivations which follow, the temperature t and concentrations x_i will be assumed to be uniform over the volume of the droplet. Lumping of the temperature has been justified by El Wakil et al. (1954) for ratios of liquid conductivity/gas conductivity greater than about six, a condition satisfied by most gas-liquid systems. On the other hand, lumping of the concentrations implies that diffusion inside the droplet is either very rapid or nonexistent.† Actually, diffusion in liquids is relatively slow so the concentrations will be uniform only when they remain constant with time. But this is a special circumstance where the fraction of i in the total vapor flux $J_i/\overline{J}$ is equal to x_i the fraction of i in the droplet, for all i. This condition is not met in general, and the assumption of uniform concentrations will lead to higher evaporation rates for some species and lower rates for others. The reason for making the assumption is that a simple analytic expression could not be found to describe diffusion in the droplet. However, the resulting model is of sufficient utility to justify this approach.

Volume Balance. Assuming there is no thermal expansion and no volume change due to mixing, the change in volume of a droplet will equal minus the total volume of liquid vaporized, or

$$\frac{DV_d}{D\theta} = -4\pi r^2 \sum_i mv_i J_i \qquad (49)$$

where mv_i is the molar volume of liquid i. Substituting $V_d = \frac{4\pi}{3} r^3$, (49) yields

$$\frac{Dr}{D\theta} = -\sum_i mv_i J_i \qquad (50)$$

Mass Balance. First, note that the total number of moles in a droplet, N_d, is related to V_d by

$$V_d = \sum_i x_i N_d mv_i$$

$$= N_d \sum_i x_i mv_i$$

or

$$N_d = \frac{V_d}{(mv)_m} \qquad (51)$$

where $(mv)_m$ stands for the molar average of the mv_i. Now a mass balance on the ith component yields

$$\frac{D}{D\theta} (N_d x_i) = -4\pi r^2 J_i$$

or

$$N_d \frac{Dx_i}{D\theta} + x_i \frac{DN_d}{D\theta} = -4\pi r^2 J_i \qquad (52)$$

Substituting for N_d and using

$$\frac{DN_d}{D\theta} = -4\pi r^2 \sum_j J_j \qquad (53)$$

Equation (52) becomes

$$\frac{V_d}{(mv)_m} \frac{Dx_i}{D\theta} - x_i 4\pi r^2 \sum_j J_j = -4\pi r^2 J_i$$

which may be solved for $Dx_i/D\theta$ to give

$$\frac{Dx_i}{D\theta} = \frac{3}{r} (mv)_m \sum_j J_j \left(x_i - \frac{J_i}{\sum_j J_j} \right) \qquad (54)$$

Energy Balance. In making the energy balance on a droplet, radiation effects will be neglected, and the kinetic energy of the vapors leaving the droplet will be assumed negligible. The first assumption has been justified for small droplets by Hottel et al. (1955), who showed that radiation effects decrease rapidly with droplet size and can be safely ignored when the droplet radius is less than about 200 microns. The second assumption is not necessarily a good one since the kinetic energy term varies inversely with the droplet radius. However, comparison of the energy terms involved shows that the kinetic energy term can be safely omitted.

With these assumptions, the energy balance may be written

$$\frac{DE_d}{D\theta} + 4\pi r^2 E + W = 0 \qquad (55)$$

where E_d is the droplet energy, E is the energy flux from the droplet, and W is the work done by the droplet. If energy changes due to mixing are small then

$$E_d = \sum_i N_d x_i E_i(t)$$

or

$$E_d = \sum_i N_d x_i [H_i(t) - P_T mv_i] \qquad (56)$$

Differentiating gives

$$\frac{DE_d}{D\theta} = \sum_i \frac{D}{D\theta} (N_d x_i) [H_i(t) - P_T mv_i] + N_d \sum_i x_i \frac{DH_i}{D\theta} \qquad (57)$$

But

$$\frac{D}{D\theta} (N_d x_i) = -4\pi r^2 J_i$$

and

$$\frac{DH_i}{D\theta} = C_{pi} \frac{Dt}{D\theta}$$

so that (57) may be written

$$\frac{DE_d}{D\theta} = -4\pi r^2 \sum_i J_i [H_i(t) - P_T mv_i] + N_d \sum_i x_i C_{pi} \frac{Dt}{D\theta}$$

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* This effect was noted some time ago by Godsave (1952).

† The effect of internal circulation has been shown to be negligible for small droplets (Harriot, 1962).

and

$$\frac{DE_d}{D\theta} = -4\pi r^2 \sum_i J_i \left[H_i(t) - P_T m v_i\right] + N_d (C_p)_m \frac{Dt}{D\theta} \tag{58}$$

Now, the term W[*] is equal to minus the work done by the gas in expanding against the diminishing droplet, that is,

$$W = -P_T\left(-\frac{DV_d}{D\theta}\right) = -P_T 4\pi r^2 \sum_i J_i m v_i \tag{59}$$

Equations (58), (59), and (47) for $DE_d/D\theta$, W, and E, respectively, are combined in the energy balance (55) to give

$$-4\pi r^2 \sum_i J_i\left[H_i(t) - P_T m v_i\right] + N_d (C_p)_m \frac{Dt}{D\theta} + 4\pi r^2 \left[\sum_i J_i H'_{Ai}(t) + \frac{a}{e^a - 1}\,\frac{k}{r}\,(t - T)\right] - P_T 4\pi r^2 \sum_i J_i m v_i = 0$$

Solving for $Dt/D\theta$ yields

$$\frac{Dt}{D\theta} = \frac{4\pi r^2}{(C_p)_m N_d}\left[\frac{a}{e^a - 1}\,\frac{k}{r}\,(T - t) - \sum_i J_i\left(H'_{Ai}(t) - H_i(t)\right)\right] \tag{60}$$

But

$$H'_{Ai}(t) - H_i(t) = H'_{Air} + C'_{pAi}(t - T_r) - H_{ir} - C_{pi}(t - T_r) = \lambda_{ir} + (C'_{pAi} - C_{pi})(t - T_r)$$

so (60) can be written

$$\frac{Dt}{D\theta} = \frac{3(mv)_m}{r(C_p)_m}\left[\frac{a}{e^a - 1}\,\frac{k}{r}\,(T - t) - \sum_i J_i\left(\lambda_{ir} + (C'_{pAi} - C_{pi})(t - T_r)\right)\right] \tag{61}$$

Summary of the Droplet Equations

$$\frac{Dx_i}{D\theta} = \frac{3}{r}\,(mv)_m \sum_j J_j \left(x_i - \frac{J_i}{\sum J_j}\right), \quad i = 1, \ldots n \tag{62}$$

$$\frac{Dr}{D\theta} = -\sum_i m v_i J_i \tag{63}$$

$$\frac{Dt}{D\theta} = \frac{3}{r}\,\frac{(mv)_m}{(C_p)_m}\left[\frac{a}{e^a - 1}\,\frac{k}{r}\,(T - t) - \sum_i J_i\left(\lambda_{ir} + (C'_{pAi} - C_{pi})(t - T_r)\right)\right] \tag{64}$$

where

$$J_i = \frac{1}{r}\,\frac{D_{Im}}{RT}\ln(C)\left[\frac{x_i P^*_{Ai}(t)\, C^{D_{Im}/D_{im}} - P_{Ai}}{C^{D_{Im}/D_{im}} - 1}\right] \tag{65}$$

$$C = \frac{P_T - \sum_i P_{Ai}}{P_T - \sum_i x_i P^*_{Ai}(t)} \tag{66}$$

$$P^*_{Ai}(t) = \mathrm{Exp}(u_i - v_i/t) \tag{67}$$

$$a = \frac{r}{k}\sum_i J_i C'_{pAi} \tag{68}$$

ANALYSIS OF THE MODEL

The ordinary differential Equations (62) to (64) which describe the evaporation of a droplet have the form

$$\begin{aligned} \frac{dx_i}{d\theta} &= \frac{1}{r^2}\,X_i(x_j, t) \\ \frac{dr^2}{d\theta} &= R(x_j, t) \\ \frac{dt}{d\theta} &= \frac{1}{r^2}\,T(x_j, t) \end{aligned} \tag{69}$$

Thus, the equations are homogeneous in r, and the signs of the various derivatives are determined only by x_i and t. This fact suggests the use of a concentration-temperature phase diagram for analysis of droplet behavior. Therefore, consider a two-component system with the $t - x_1$ phase plane of Figure 1. Curves A, B, and C of Figure 1 are obtained by setting, respectively, the derivatives of x_1, r and t equal to zero. Curve A for $x_1' = 0$ intersects the boiling point curve $t_{BP}(x_1)$ at zero concentration of the more volatile component and approaches zero temperature as $x_1 \to P_{A1}/(P_{A1} + P_{A2})$. It fails to exist for $x_1 \geqq P_{A1}/(P_{A1} + P_{A2})$. Curve B for $r' = 0$ is analogous to the constant dew point temperature obtained for a droplet containing a single pure liquid; in fact, the intersection b of curves A and B corresponds to the dew point of the gas at the given partial pressures P_{Ai}. Curve C, on which $t' = 0$, also has an analog in the single component case, namely, the constant wet-bulb temperature. For this reason, curve C will be referred to as the wet-bulb curve.

It is evident from the signs of the derivatives of x_1 and t and the slopes of curves A and C that a droplet will always move toward the pseudo stationary point a, where

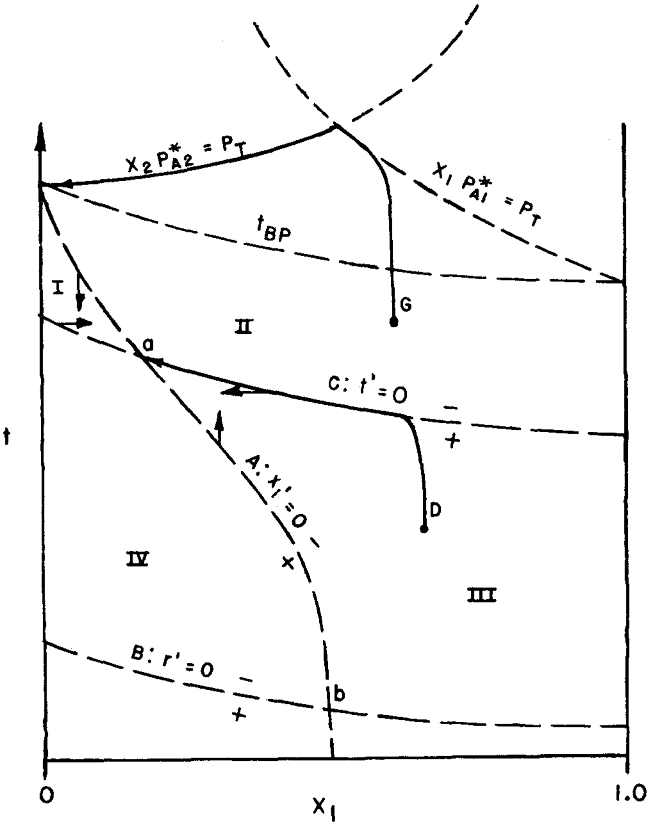

Fig. 1. Analysis of the model in the temperature-concentration phase plane.

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[*] The work term is usually negligible. It is included here to show that it cancels out of the final equation.

both x_1' and t' are zero. Droplets starting in regions I or III will stay in these regions as they approach point a, while droplets in regions II or IV may cross into regions I or III before reaching a. Now, for an unsaturated gas the point a will lie above curve B, so that $r' < 0$ at the pseudo stationary point and the droplet must always evaporate, that is, $r \to 0$. If the gas is saturated, points a and b will coincide to give a truly stationary point where r', x_1' and t' all are zero. In this case if the droplet reaches the stationary point while r is still greater than zero, then the droplet will not evaporate. For a supersaturated gas point a will lie below curve B in the region of positive r', and again the droplet may not evaporate. Note, also that unless $P_{A1} = 0$ a droplet of pure component 2 will not remain pure but will experience some condensation of component 1 as it approaches point a. A similar statement can be made for droplets of pure component 1. Finally, from Equations (65) and (66) we see that the sum $\sum_i J_i \lambda_i(t) \propto \ln(C)$ goes to infinity as $t \to t_{BP}$ at a fixed concentration, so that for any gas temperature T there is always a wet-bulb temperature $t < t_{BP}$ for which Equation (64) gives $t' = 0$. This is not true for models which predict finite fluxes at $t = t_{BP}$, and such models allow the droplet temperature to exceed the liquid boiling point.

As an example of such a model, consider using Equation (37), which describes the flux of a single component, to represent the fluxes in the multicomponent case, that is,

$$J_i = \frac{C_T D_{im}}{r} \ln \left[\frac{P_T - P_{Ai}}{P_T - x_i P^*_{Ai}(t)} \right], \quad i = 1, \ldots n \tag{70}$$

With this model the individual fluxes become infinite as their respective vapor pressures $x_1 P^*_{A1}$ and $x_2 P^*_{A2}$ approach the total pressure P_T. But since the sum of their vapor pressures must approach P_T first, the curves representing $x_1 P^*_{A1}(t) = P_T$ and $x_2 P^*_{A2}(t) = P_T$ always lie above the boiling point curve, as shown in Figure 1. The result is that the wet-bulb temperature, and hence the droplet temperature, cannot be guaranteed to remain below the liquid boiling point. A typical droplet trajectory calculated using Equation (70) for the case of a warm gas appears as curve G in Figure 1.

The behavior of a multicomponent droplet with $n > 2$ is analogous to the two-component case, only much more difficult to visualize.

Method of Integration

Equations (62) to (64) were integrated using a fourth-order Runge-Kutta routine and a variable step size. The step size h was determined by dividing the maximum of the derivatives at the beginning of each step into a prescribed increment δ or

$$h = \delta / \text{MAX} \left(|C_r r'|, |C_t t'|, |C_x x_i'| \right) \tag{71}$$

where C_r, C_t, and C_x are suitable weighting factors. Then, if the equations were linear, we would expect

$$\begin{aligned} |\Delta r| &= |r'|\, h < \delta / C_r \\ |\Delta t| &= |t'|\, h < \delta / C_t \\ |\Delta x_i| &= |x_i'|\, h < \delta / C_x \end{aligned} \tag{72}$$

where Δ indicates the change in a variable for the step. Of course the equations are highly nonlinear, so that the relations (72) will hold only approximately. Therefore, the procedure used was to set h according to (71), perform the integration for that step, and then check to see that

$$\delta_{\max} = \text{MAX} \left(|C_r \Delta r|, |C_t \Delta t|, |C_x \Delta x_i| \right) < 1.2\delta \tag{73}$$

If (73) was not satisfied h was reduced by the factor $\delta/\delta_{\max}$ ($< 1/1.2$), and the step was repeated. With weights of $C_r = C_x = 1$ and $C_t = 5$ temperature controlled the integration during the initial heat up of the droplet and the radius controlled thereafter. This procedure for setting h does not lead to highly accurate results, but it does allow the integration to be completed in a reasonable time.

In addition, problems were encountered at several points in the calculation which necessitated some modification of the above scheme. First, it was found that as the droplet conditions approached very close to the wet-bulb curve (see trajectory D of Figure 1) the integration would diverge greatly. The divergence was due to the droplet temperature crossing curve C of Figure 1, which would cause it to begin oscillating wildly. This behavior was easily avoided by decreasing the step size by an order of magnitude when the temperature started to oscillate. But this increased the number of steps to an unacceptable level, so further improvement was necessary. To speed up the calculation, the droplet temperature was set equal to the wet-bulb temperature, and the integration was completed along the wet-bulb curve. In other words, for this part of the calculation only Equations (62) and (63) for x_i' and r' were integrated, and the temperature was obtained by setting $t' = 0$ in Equation (64). This procedure speeded up the integration considerably and produced only small relative errors in the results. Another problem was encountered as the radius approached the singular point $r = 0$. To ensure that r would remain positive, h was maintained less than $0.9r/|r'|$. The integration was terminated when $r < 0.05\delta$, where $\delta = 0.005$ for most calculations.

Case I—A Two-Component Droplet

We consider here a droplet comprised of heptane and octane which evaporates into a mixture of air plus heptane and octane vapors at a total pressure of one atmosphere. The droplet initially has a radius of 500μ, a temperature of 300°K and mole fractions of 0.52 heptane and 0.48 octane. The physical data (obtained from the usual sources) are presented in the Appendix in Table 1.

The behavior of a droplet at two representative gas conditions is shown in Figures 2a to 2d. At the low gas temperature of Figure 2a the droplet cools down to the wet-bulb curve before approaching the pseudo stationary point. The age profiles of Figure 2b illustrate in an alternate way the changes in temperature and concentration as the radius falls to zero. Figures 2c and 2d exhibit the more usual behavior obtained at higher gas temperatures. Here the droplet heats up to the wet-bulb curve and then approaches a pseudo stationary point which lies very close to $x_1 = 0$. The temperature profile of Figure 2d shows some inflection as the wet-bulb curve is approached but then continues to rise to the pseudo stationary point. Comparison of Figures 2b and 2d shows how much faster the droplet evaporates at the higher temperature. Finally, note that in each case the radius squared varies almost linearly with time once the temperature has become stabilized. Thus, the calculated results are compatible with the experimentally observed D-squared law.

Case II—A Three-Component Droplet

This case is identical to the two-component system except for the addition of a third component, nonane, to the droplet and the gas. The initial mole fractions are 0.35 for heptane and octane and 0.30 for nonane. The physical data are presented in the Appendix in Table 2.

The behavior of a three-component droplet evaporating at reasonable gas conditions is shown in Figure 3. As in the two-component case, the droplet temperature shows some inflection as it nears the wet-bulb condition and then continues to rise to the pseudo-stationary point. Again the variation of r^2 verifies the D-squared law. In addition, from the changes in mole fractions shown in Figure 3, it appears that initially the lightest component, heptane, evaporates most rapidly, resulting in increases in the mole fractions of both octane and nonane. Thus when much of the heptane has evaporated octane begins to behave as the light component, and, eventually, the droplet becomes almost pure nonane. This behavior is analogous to a batch distillation of the three components and therefore verifies the observations of Wood et al. (1960).

TABLE 1. DATA FOR CASE I

$r^0 = 500\mu$ $\qquad$ $t^0 = T_r = 300°\text{K}$
$P_T = 1 \text{ atm}$ $\qquad$ $\theta^0 = 130 \text{ sec}^*$
$k = 11.48\ [(C_p)_m{}^0\ (r^0)^2]/[\theta^0\ (mv)_m{}^0]$
$D_{Im} = 43.7\ [Rt^0\ (r^0)^2]/[P_T\ (mv)_m{}^0]$
$(C_p)_m{}^0 = 57.7 \dfrac{\text{cal}}{\text{g-mole °C}}$ $\qquad$ $C'_{pI} = 7.0 \dfrac{\text{cal}}{\text{g-mole °C}}$
$(mv)_m{}^0 = 154.4 \dfrac{\text{cc}}{\text{g-mole}}$

i	1	2
Ai	n-C_7H_{16}	n-C_8H_{18}
$x_i{}^0$	0.52	0.48
u_i	11.0	11.4
$\dfrac{v_i}{t^0}$	13.7	15.13
$\dfrac{D_{im}}{D_{Im}}$	1.0	1.0
$\dfrac{C_{pi}}{(C_p)_m{}^0}$	0.874	1.1365
$\dfrac{C'_{pAi}}{C'_{pI}}$	5.807	6.608
$\dfrac{mv_i}{(mv)_m{}^0}$	0.952	1.052
$\dfrac{\lambda_{ir}}{(C_p)_m{}^0\ t^0}$	0.441	0.468

* The mean holding time θ^0 pertains to an application of droplet evaporation, and its choice in no way affects the present calculations.

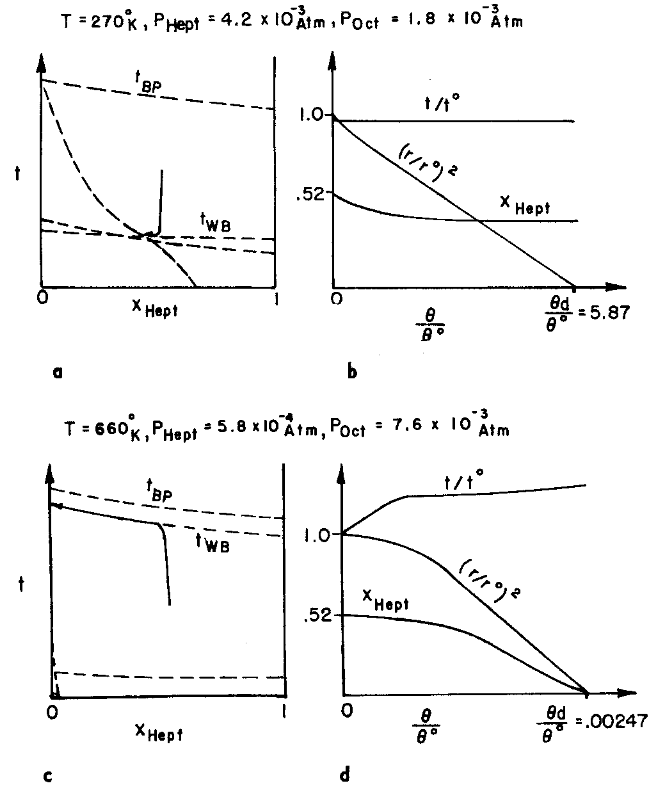

Fig. 2. Results for a two-component droplet (Case I).

TABLE 2. DATA FOR CASE II

$^0 = 500\mu$ $\qquad$ $t^0 = T_r = 300°\text{K}$
$P_T = 1 \text{ atm}$
$k = 10.73\ [(C_p)_m{}^0\ (r^0)^2]/[\theta^0\ (mv)_m{}^0]$
$D_{Im} = 43.7\ [Rt^0\ (r^0)^2]/[P_T\ (mv)_m{}^0]$
$(C_p)_m{}^0 = 58.1 \dfrac{\text{cal}}{\text{g-mole °C}}$ $\qquad$ $C'_{pI} = 7.0 \dfrac{\text{cal}}{\text{g-mole °C}}$
$(mv)_m{}^0 = 162.8 \dfrac{\text{cc}}{\text{g-mole}}$

i	1	2	3
Ai	n-C_7H_{16}	n-C_8H_{18}	n-C_9H_{20}
$x_i{}^0$	0.35	0.35	0.30
u_i	11.0	11.4	11.7
$\dfrac{v_i}{t^0}$	13.7	15.13	16.52
$\dfrac{D_{im}}{D_{Im}}$	1.0	1.0	1.0
$\dfrac{C_{pi}}{(C_p)_m{}^0}$	0.867	1.004	1.1505
$\dfrac{C'_{pAi}}{C'_{pI}}$	5.807	6.608	7.409
$\dfrac{mv_i}{(mv)_m{}^0}$	0.903	1.007	1.105
$\dfrac{\lambda_{ir}}{(C_p)_m{}^0\ t^0}$	0.392	0.416	0.434

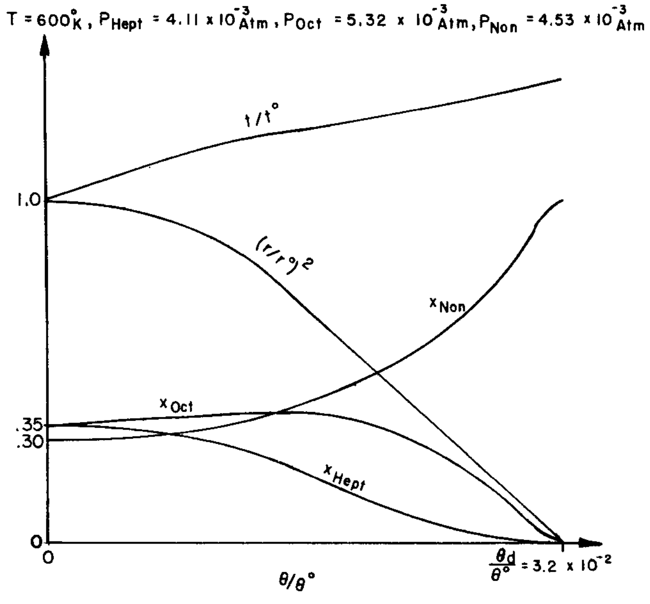

Fig. 3. Results for a three-component droplet (Case II).

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NOTATION

a = mass transfer group defined by Equation (68)
a' = mass transfer group defined by Equation (17)
C = ratio of inert concentration in the bulk gas to inert concentration of the droplet surface
C_i = mole fraction of component i in the particle
C_T = total gas concentration
C_{pi} = molar heat capacity of the ith component of the liquid
C'_{pAi} = molar heat capacity of the ith component of the gas
d = droplet diameter
D_{ij} = binary diffusivity of gas i with respect to gas j
D_{im} = effective binary diffusivity of gas i with respect to the gas mixture
e = total energy flux at position ξ
E = energy flux from a droplet
E_d = total energy of a droplet
D_i = molar energy of component i in the droplet
h_G = droplet heat transfer coefficient
h = step size
H_i = molar enthalpy of the ith component of the liquid
H'_{Ai} = molar enthalpy of the ith component of the gas
i = index permuted over $i = 1, \ldots n$
J_i = molar flux of component i from the droplet
$\overline{J}$ = total molar flux of all components from the droplet
k = mean thermal conductivity of the gas
k_G = droplet mass transfer coefficient
mv_i = volume per mole for the ith component in the liquid
n = number of components in the liquid
N_d = total moles in a droplet
N_i = moles of component i in a droplet, or molar flux at position ξ
N_{Nu} = Nusselt number
N_{Sh} = Sherwood number
P_{Ai} = partial pressure of the ith component of the gas
P^*_{Ai} = equilibrium vapor pressure of pure liquid A_i
q = heat flux from a droplet
r = radius of a droplet
R = gas law constant
t = droplet temperature
t_{BP} = boiling point of the droplet liquid
t_{WB} = wet-bulb temperature of a droplet
T = temperature of the gas
T_r = reference temperature
u_i = parameter in the expression for $P^*_{Ai}(t)$
v_i = parameter in the expression for $P^*_{Ai}(t)$
V_d = volume of a droplet
x_i = mole fraction of component i in a droplet
y_i = mole fraction of component i in the gas

Greek Letters

ϵ = droplet evaporation constant
θ = droplet age
λ_i = molar latent heat of vaporization of component i

Subscripts

$)_{Ai}$ = of the ith component in the gas
$)_B$ = in the bulk gas
$)_d$ = of the droplet
$)_i$ = of the ith component in the liquid
$)_I$ = of the inert
$)_r$ = at the reference temperature T_r
$)_s$ = of the solid
$)_T$ = the sum total
$)_v$ = of the vapor
$(\ )_m$ = the mean molar value

Superscripts

$)^0$ = initial value ($\theta = 0$)
$)^*$ = at the interface
$)'$ = in the gaseous state, or the time derivative

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