

On the evaporation of a fluid into a gas

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BY APPLYING the general balance equations of a mixture with an interface, a free-boundary problem is posed which describes the evaporation of a pure substance in a gas (air, for instance).

Stosując ogólne równanie bilansu do mieszaniny z powierzchnią międzyfazową, sformułowano zagadnienie powierzchni swobodnej opisujące proces parowania czystej substancji w atmosferze gazowej.

Применяя общие уравнения баланса к смеси с межфазовой поверхностью, сформулирована задача свободной поверхности, описывающая процесс испарения чистой субстанции в газовой атмосфере.

1. Introduction

RECENTLY a model describing the phase transition in a classical fluid binary mixture has been proposed (see [1]). In such a model the system is supposed to be made up of a liquid and vapour phase which are both mixtures of the same two substances separated by an interface that, in turn, is a binary mixture itself. The general equilibrium and evolution equations of this system are determined.

The case in which the interface is non-permeable with respect to one of the two constituents of the mixture is particularly interesting. In this case one of the constituents is found in just one phase. The class of systems we are considering permits us to study such phenomena as the evaporation of dilute mixtures or fluids in the presence of a second gas (for instance the evaporation of water in the presence of air).

In this paper we take into account the latter case; more precisely, we examine a system which is made up of a pure liquid phase and of a gaseous phase that, in turn, is a mixture of the vapour of the same substance and of the another gas. The evolution equations of such a system are obtained by supposing that the concentration of one constituent in the liquid phase vanishes in the equation derived in [1] (Sect. 2).

By employing the procedures we have already applied in [2], in order to study a pure substance, in Sect. 3 approximate equations are determined which supply a reasonable mathematical model for the system we are concerned with.

Section 4 is devoted to some physical considerations that we can summarize as follows: the evaporation temperature on the interface is not determined but it depends on the concentrations of the constituents in the gaseous phase. The study of this dependence, in the particular case of water evaporation in the presence of air, makes evident the facts that 1) the evaporation temperature decreases when the air concentration increases on the interface; 2) the advancing interface is governed by a Stefan-like condition, which is similar

to those found in the evaporation and melting of a pure substance; however, the latent heat is not constant because the temperature is not determined on the interface; 3) when the gases in the mixture are both monoatomic or biatomic it is possible to deduce all the thermodynamical fields starting from the concentration and temperature fields.

2. The balance equations

The study of the evaporation phenomenon or sublimation of a substance in the air leads to analyze a system which is made up of a (liquid or solid) pure phase and an air and vapour mixture separated by a surface with an interface. The general equations describing such a system have been discussed in [1] together with the corresponding equilibrium conditions.

In this paper an initial examination of dynamics of this system is carried out by supposing that the following hypotheses are verified for the duration of the process: a) the phenomenon exhibits plane symmetry; b) the pressure is much less than its critical value; c) the interface has no material characteristics.

The aforesaid hypotheses lead us to the following approximations:

- i) the fields depend on the temporal coordinate t and on just one spatial coordinate x ;
- ii) the pure phase is not compressible;
- iii) the mixture is made up of perfect gases;
- iv) the mixture density is negligible with respect to that of the pure phase.

In the sequel we shall refer to the evaporation case, but all these considerations could also be applied to sublimation.

In the liquid the balance equations of mass, momentum and energy assume the following form:

$$(2.1) \quad \begin{aligned} v &= 0, \\ p_x &= 0, \\ \vartheta_t &= a^- \vartheta_{xx}, \end{aligned}$$

where v is the particle velocity, p and ϑ represent the pressure and temperature fields and a^- is the liquid thermal diffusivity.

The gaseous phase will be treated in the framework of the classical theory (see [3]). This means that balance laws for mass, momentum and energy are assumed for the mixture as a whole, whereas the presence of two different constituents is described as follows:

- a new balance law for the concentration ⁽¹⁾ of one constituent is considered;
- a diffusive flux in the energy balance law is introduced.

We are thus led to the system

$$(2.2) \quad \begin{aligned} \rho_t + (\rho v)_x &= 0, \\ \rho(v_t + v v_x) &= h_x, \\ \rho(v_t + v v_x) &= -p_x, \\ \rho(\epsilon_t + v \epsilon_x) &= -p v_x + k^+ \vartheta_{xx} + \mathcal{L}_x, \end{aligned}$$

⁽¹⁾ The concentration of a constituent is defined as the ratio of its density to its total value.

where ρ denotes the total mass density of the mixture, ν is the vapour concentration, v is the mean velocity of the mixture particles, h_x is the relative mass flux of the vapour, p , ϑ and ϵ are the pressure, temperature and specific internal energy, k^+ is the thermal conductivity and \mathcal{L} is the diffusive flux.

Both the relative mass and energy fluxes have to be expressed as functions of ρ , ν , ϑ and their respective spatial derivatives (see [4]) by suitable constitutive equations.

Two remarks are worth mentioning at this point. If we introduce the velocity u of the vapour particles, the equation (2.2)₂ reduces to the continuity equation for the vapour provided we assume

$$(2.3) \quad h = -\rho\nu(u-v).$$

Consequently, the constitutive equation for h supplies the relative velocity $u-v$.

Moreover, it is a classical result of thermodynamics [3] that the flux \mathcal{L} can be expressed in the form

$$(2.4) \quad \mathcal{L} = -\rho\nu\mu(u-v),$$

where μ is the reduced chemical potential of the vapour and is independent of the spatial fields derivatives.

To the system (2.1), (2.2) we have to add the jump conditions on the interface. If \dot{s} is the advancing velocity of the interface and we suppose the continuity of the temperature field, taking into account (2.3) and (2.4), the jump conditions reduce to

$$(2.5) \quad \begin{aligned} -\rho^-\dot{s} &= \rho^+(v-\dot{s}) \equiv J, \\ -\rho^-\dot{s} &= \rho^+\nu(u-\dot{s}), \\ \llbracket v \rrbracket J + \llbracket p \rrbracket &= 0, \\ \llbracket \frac{1}{2}(v-\dot{s})^2 + \epsilon + \frac{p}{\rho} \rrbracket J - \llbracket k\vartheta_x \rrbracket + \nu\rho^+\mu(u-v) &= 0. \end{aligned}$$

From (2.5)_{1,2} we deduce $\nu\rho^+(u-v) = (1-\nu)J$; the energy jump equation (2.5)₄ can be put in the form

$$(2.6) \quad \llbracket \frac{1}{2}(v-\dot{s})^2 + \epsilon + \frac{p}{\rho} + (1-\nu)\mu \rrbracket J = \llbracket k\vartheta_x \rrbracket.$$

The thermodynamic laws require that the dissipation principle must be satisfied together with the balance equations (2.1), ..., (2.6) in every process. Application of this principle leads us to known restrictions on the constitutive equations inside the two phases and to the following inequality on the interface:

$$\vartheta \llbracket \eta \rrbracket J \geq \llbracket k\vartheta_x \rrbracket$$

(η is the specific entropy). By eliminating $\llbracket k\vartheta_x \rrbracket$ between this last relation and (2.6) we arrive at the dissipation inequality in the form

$$\llbracket \frac{1}{2}(v-\dot{s})^2 + \psi + \frac{p}{\rho} + (1-\nu)\mu \rrbracket J \leq 0$$

in which the specific free energy $\psi = \epsilon - \vartheta\eta$ has been introduced.

From now on the following further hypothesis will be supposed to be satisfied:

v) during the process there is no dissipation on the interface.

This hypothesis is the same as supposing that the jump relation is verified

$$(2.7) \quad \left\| \left\| \frac{1}{2}(v - \dot{s})^2 + \psi + \frac{P}{\varrho} + (1 - \nu)\mu \right\| \right\| = 0$$

besides the other jump conditions.

In the approximation iv), from Eqs. (2.5)₁ and (2.5)₂, we derive the following expressions of v and u on the interface

$$(2.8) \quad v = \frac{\varrho^-}{\varrho^+} \dot{s}, \quad u = -\frac{\varrho^-}{\varrho^+ \nu} \dot{s}$$

which permits us to express the remaining conditions (2.5) in terms of the advancing velocity of the interface \dot{s} alone. Simple calculations lead us to the equations

$$(2.9) \quad \begin{aligned} \llbracket P \rrbracket &= -\frac{(\varrho^-)^2}{\varrho^+} \dot{s}, \\ \frac{1}{2} \varrho^- \left(\frac{\varrho^-}{\varrho^+} \right)^2 \dot{s}^3 + \varrho^- \left[\llbracket \epsilon \rrbracket + \frac{P^+}{\varrho^+} + (1 - \nu)\mu \right] \dot{s} &= k^- \vartheta_x^- - k^+ \vartheta_x^+, \\ \frac{1}{2} \left(\frac{\varrho^-}{\varrho^+} \right)^2 \dot{s}^2 + \llbracket \psi \rrbracket + \frac{P^+}{\varrho^+} + (1 - \nu)\mu &= 0. \end{aligned}$$

In conclusion, the system describing the evaporation of a liquid in the air is made up of Eq. (2.1) at the points of the liquid phase, by Eqs. (2.2) at the points of the air-vapour mixture and by the jump conditions (2.8)–(2.9) on the interface. In the sequel this set of the equations will be called the system S .

3. Non-dimensional form of the balance equations

The system S describes in an exact way the liquid evaporation in the air provided the conditions i), ..., v) are satisfied. Following the procedure which was already adopted in [2], in this section the order of all the terms appearing in the equations will be evaluated in order to attain an approximate form of the system.

Let $\bar{\varrho}^+$ be the vapour density at the atmospherical pressure and evaporation temperature ϑ_v , and let us introduce the parameter $\alpha = \bar{\varrho}^+ / \bar{\varrho}^- \ll 1$. If X^- is the dimension of the region initially occupied by the liquid, the characteristic time of thermal phenomena is $T = (X^-)^2 / a^-$ so that the rate $U^- = X^- / T$ can be supposed to be comparable with the advancing velocity of the interface. The relations (2.8) show that the velocities u and v in the vapour-air phase are much greater than \dot{s} and they suggest a comparison of their values to the quantity $U^+ = U^- / \alpha$; this is equivalent to introducing the reference length $X^+ = X^- / \alpha$ in the mixture.

From the previous considerations we derive the following definitions for dimensionless variables and fields.

$$(3.1) \quad \hat{t} = \frac{t}{T}, \quad \hat{x} = \begin{cases} \frac{x}{X^-}, & 0 \leq x \leq s(t), \\ \frac{s(t)}{X^-} + \frac{x-s(t)}{X^+}, & x \geq s(t), \end{cases}$$

$$\rho = \frac{\rho^+}{\rho^+}, \quad p = \frac{p}{\rho^+ c^- \Theta}, \quad \theta = \frac{\vartheta - \vartheta_0}{\Theta}, \quad \dot{s} = \frac{\dot{s}}{U^-}, \quad \hat{v} = \frac{v}{U^+}, \quad \hat{u} = \frac{u}{U^-},$$

where Θ is the difference between the temperature values at the initial time and on the boundary of the system. To complete the scheme of the dimensionless variables, different thermodynamical potentials have to be defined (internal energy, free energy and chemical potential). We shall assume that all the variations of these quantities are of the same order of the product $c^- \Theta$ and therefore, we define the dimensionless potentials by the following ratios:

$$(3.2) \quad \hat{\varepsilon} = \frac{\varepsilon}{c^- \Theta}, \quad \hat{\psi} = \frac{\psi}{c^- \Theta}, \quad \hat{\mu} = \frac{\mu}{c^- \Theta}.$$

In the new variables (3.1), (3.2) by imitting the hat for semplicity, system S assumes the form

Liquid phase

$$p = p(t), \\ \theta_t = \theta_{xx}.$$

Mixture

$$\rho_t + (\rho v)_x = 0, \\ \rho(v_t + v v_x) = -[\rho v(u-v)]_x, \\ p_x = -A \rho(v_t + v v_x), \\ \rho(\varepsilon_t + v \varepsilon_x) = -p v_x + \alpha k \theta_{xx} - [v \rho \mu(u-v)]_x.$$

Interface

$$v = -\frac{\dot{s}}{\rho^+}, \quad u = -\frac{\dot{s}}{\rho^+ \nu}, \\ [[p]] = -A \frac{\dot{s}^2}{\rho^+}, \\ \frac{1}{2} A \frac{\dot{s}^3}{\rho^{+2}} + \left[[[\varepsilon]] + \frac{p^+}{\rho^+} + (1-\nu)\mu \right] \dot{s} = \theta_x^- - \alpha k \theta_x^+, \\ \frac{1}{2} A \frac{\dot{s}^2}{\rho^{+2}} + [[\psi]] + \frac{p^+}{\rho^+} + (1-\nu)\mu = 0.$$

The number $A = U^+ / c^- \Theta$ we have introduced into the system (3.3) expresses the order of the ratios of kinetic energy, pressure force work and heat per unit mass in the mixture. Under the hypotheses of this paper, A assumes extremely small values (for instance in the case of water, it is of the order of 10^{-13}) and therefore they can be neglected.

In such an approximation, the pressure is continuous and uniform in the whole system and it assumes the external value p . The system (3.3) reduces to the form

Liquid phase

$$\theta_t = \theta_{xx}.$$

Mixture

$$\rho_t + (\rho v)_x = 0, \\ \rho(v_t + v v_x) = -[\rho v(u-v)]_x, \\ \rho(\varepsilon_t + v \varepsilon_x) = -p v_x + \alpha k \theta_{xx} - [v \rho \mu(u-v)]_x.$$

Interface

$$v = -\frac{\dot{s}}{\varrho^+}, \quad u = -\frac{\dot{s}}{\varrho^+\nu},$$

$$\left[[\varepsilon] + \frac{p^+}{\varrho^+} + (1-\nu)\mu \right] \dot{s} = \theta_x^- - \alpha k \theta_x^+,$$

$$[[\psi]] + \frac{p^+}{\varrho^+} + (1-\nu)\mu = 0.$$

4. Some considerations concerning the system (3.4)

Equation (3.4) define a complex free boundary problem with unknowns represented by two functions $s(t)$ and $l(t)$ (which assign the interface and external surface position), by the fields $\theta(x, t)$ in each phase and by $\nu(x, t)$, $v(x, t)$, $\varrho(x, t)$ in the mixture.

In this section we confine ourselves to making evident some interesting physical characteristics of the system we are faced with.

The condition (3.4)_a supplies a relation between the values that the fields assume on the interface. According to the approximations ii), iii), the liquid and the mixture phase free energies are respectively expressed by the constitutive equations

$$(4.1) \quad \psi^-(\theta) = (\theta^* + \theta) [1 - \ln(\theta^* + \theta)] - \varepsilon_0 + (\theta^* + \theta)\eta_0,$$

$$\psi^+(\theta, \varrho, \nu) = [c\nu + c_A(1-\nu)] (\theta^* + \theta) [1 - \ln(\theta^* + \theta)] + \frac{R}{c^-m} \nu(\theta^* + \theta) \ln \varrho \nu$$

$$+ \frac{R}{c^-m} (1-\nu) (\theta^* + \theta) \ln \varrho (1-\nu).$$

In Eqs. (4.1) m and m_A are the molecular masses of the evaporating substance and of the mixture; R is the universal gas constant $c = c^+/c^-$, $c_A = \hat{c}/c^-$ are the rates of the specific heats of the vapour, liquid and second gas phases. The remaining constitutive equations can be derived from Eqs. (4.1) and the well-known thermodynamical relations that, in terms of the chosen dimensionless variables, can be written as

$$(4.2) \quad \varepsilon = \psi + \theta\eta, \quad p = \varrho^2 \frac{\partial \psi}{\partial \varrho}, \quad \eta = -\frac{\partial \psi}{\partial \theta}, \quad \mu = \frac{\partial \psi}{\partial \nu}.$$

The constitutive equations (4.1) and (4.2) permits us to put Eq. (3.4)₈ in the form

$$(4.3) \quad p = A \frac{m_A \nu + m(1-\nu)}{m_A \nu} (\theta^* + \theta)^{-\gamma} e^{-\frac{\delta}{\theta^* + \theta}},$$

where A , γ and δ are constants. The external pressure being fixed, Eq. (4.3) supplies a relation $\nu = \nu(\theta)$ between the temperature θ and concentration ν on the interface. In particular, at ordinary pressure ($p = 1$), the evaporation temperature corresponding to a given concentration ν is obtained by intersecting the curve

$$(4.4) \quad y = A(\theta^* + \theta)^{-\gamma} e^{-\frac{\delta}{\theta^* + \theta}}$$

with the straight lines

$$(4.5) \quad y = \frac{m_A \nu}{m_A \nu + m(1-\nu)},$$

In Fig. 1 the curve (4.4) is represented together with the straight lines (4.5) for different values of ν under the assumption that the physical parameters refer to the water evaporation in the air. The figure shows, in agreement with experience, that the evaporation temperature decreases together with the vapour concentration on the interface.

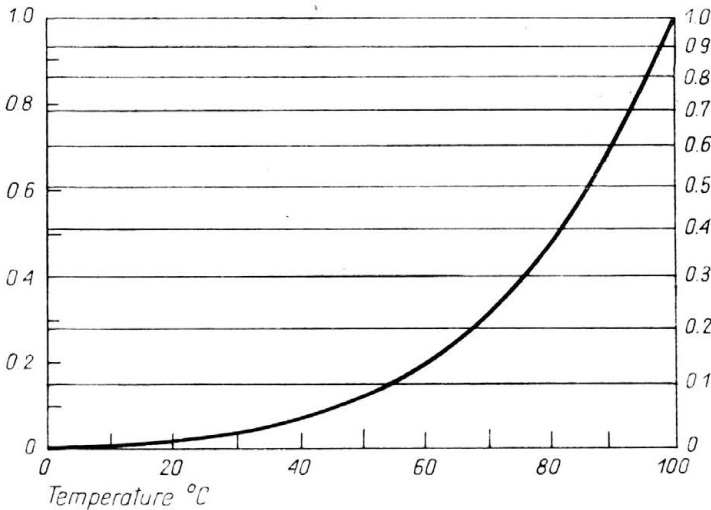


FIG. 1.

If we define the latent heat

$$\lambda = (\theta^* + \theta) [\eta]$$

the condition (3.4)₈ assumes the form

$$(4.6) \quad [\varepsilon] + \frac{p}{\rho^+} + (1-\nu)\mu = \lambda$$

and therefore (3.4)₇ can be written as

$$\lambda \dot{s} = \theta_x^- - \alpha k \theta_x^+.$$

This relation is formally similar to the Stefan condition that we have already deduced in the case of liquid evaporation. However, there is a substantial difference between these two cases. In fact, in the former case λ is constant whereas in the latter case it depends on the unknown value of temperature on the interface.

We suppose that the whole system is constrained between a fixed plane $x = 0$, on the liquid phase side, and a moving plane $x = l(t)$ on the mixture side. The task to determine the curves $x = s(t)$ (interface), $x = l(t)$ (free surface) and the fields $\theta(x, t)$, $\rho(x, t)$, $\nu(x, t)$, $v(x, t)$ is entrusted to the system (3.4) equipped with suitable initial and boundary conditions.

In particular cases it is possible to reduce the whole problem to the study of temperature and concentration fields. In order to prove this, we observe that the energy balance equation in the mixture can be written in the form

$$(4.7) \quad (\rho \varepsilon)_t + [(\rho \varepsilon + p) v]_x = (\alpha k \theta_x + L)_x,$$

where ρ and ε are expressed by the equations

$$(4.8) \quad \rho = \frac{m m_A c^-}{R} \frac{p}{[m_A v + m(1-v)] (\theta^* + \theta)},$$

$$\varepsilon = [c v + c_A(1-v)] (\theta^* + \theta),$$

which can be deduced from Eqs. (4.1) and (4.2), whereas L is the dimensionless energy flux to which we have assigned a constitutive law that, owing to Eqs. (4.8), has the general form $L = L(\theta, v, \theta_x, v_x)$.

If the two gases in the mixture are both monoatomic or biatomic, then the specific heats c and c_A are inversely proportional to the molecular masses m and m_A . In this hypothesis the energy $E = \rho \varepsilon$ and enthalpy $H = \rho \varepsilon + p$ per unit volume are constant and Eq. (4.7) leads us to the following equations for v :

$$(4.9) \quad v = \frac{\alpha k \theta_x + L + f}{H},$$

where f is a time function that we must determine starting from the interface data.

Relations (4.8)₁ and (4.9) can be introduced into the mass and concentration balance equations; simple calculation lead us to the following system of nonlinear parabolic equations in the unknowns θ and v

$$(4.10) \quad H[m_A v + m(1-v)] \theta_t + H(m_A - m) (\theta^* + \theta) v_t + (\alpha k \theta_x + L + f) [(m_A v + m(1-v) (\theta^* + \theta))]_x$$

$$= [m_A v + m(1-v)] (\theta^* + \theta) (\alpha k \theta_x + L)_x$$

$$H v_t + (\alpha k \theta_x + L + f) v_x = \frac{HR [m_A v + m(1-v)] (\theta^* + \theta)}{m m_A c^- p} \left(\frac{L}{\mu} \right)_x.$$

With the temperature field we have to associate the initial data as well as the values at $x = 0$ and $x = l(t)$. We shall suppose that the initial concentration v_0 and the boundary concentration and chemical potential are given on $l(t)$.

Finally, we need a further equation in order to determine the free boundary $l(t)$; such an equation is supplied by the global mass balance that can be written

$$s(t) + \int_{s(t)}^{l(t)} \rho(v(x, t), \theta(x, t)) dx = \text{const}$$

(see [2]), where the function $\rho(v, \theta)$ is expressed by Eqs. (4.8).

In conclusion, the temperature and concentration fields $\theta(x, t)$, $v(x, t)$, the interface $s(t)$ and the free boundary $l(t)$ represent the unknowns of the following system:

$$(4.11) \quad \theta_t = \theta_{xx}, \quad 0 < x < s(t), \quad t > 0,$$

$$H[m_A v + m(1-v)] \theta_t + H(m_A - m) (\theta^* + \theta) v_t$$

$$+ (\alpha k \theta_x + L + f) [(m_A v + m(1-v) (\theta^* + \theta))]_x = [m_A v + m(1-v)] (\theta^* + \theta) (\alpha k \theta_x + L)_x,$$

$$s(t) < x < l(t), \quad t > 0,$$

$$\begin{aligned}
 (4.11) \quad & H\nu_t + (\alpha k \theta_x + L + f)\nu_x = \frac{HR[m_A\nu + m(1-\nu)](\theta^* + \theta)}{mm_A c^- p} \left(\frac{L}{\mu} \right)_x, \\
 & \theta(0, t) = \theta_1(t), \quad \theta(l(t), t) = \theta_2(t), \\
 & \nu(l(t), t) = \nu_2(t), \quad \mu(\nu(l(t), t), \theta(l(t), t)) = \mu_2(t), \quad t > 0, \\
 & \theta(x, 0) = \theta_0(x), \quad 0 \leq x \leq l(0), \\
 & \nu(x, 0) = \nu_0(x), \quad s(t) \leq x \leq l(0), \\
 & f(\nu, \theta) \equiv [\psi] + \frac{b}{\rho^+} + (1-\nu)\mu = 0, \\
 & \lambda \dot{s} = \theta_x^- - \alpha k \theta_x^+, \\
 & s(t) + \int_{s(t)}^{l(t)} \rho(\nu(x, t), \theta(x, t)) dx = \text{const}, \quad t \geq 0, \quad s(0) = t_0, \quad l(0) = l_0.
 \end{aligned}$$

Once the fields $\nu(x, t)$ and $\theta(x, t)$ have been obtained, it is possible to evaluate the remaining fields by resorting to the constitutive equations and the relation (4.9).

The equations represent a complex nonlinear problem and it seems to us that it is not possible to solve it by means of the known methods of analysis.

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