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International Journal of Heat and Mass Transfer 46 (2003) 1687–1692

International Journal of
HEAT and MASS
TRANSFER

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On the non-stationary evaporation kinetics. II. Stability

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Received 11 June 2001

Abstract

A stability analysis of the one-dimensional Oberbeck–Boussinesq equations has been done. It is shown, that the increase of the evaporation rate is result of the instability of the natural convection flow. Velocity parameter of this flow is obtained on the basis of experimental data.

Keywords: Evaporation kinetics; Stability; Natural convection; Stephan flow

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1. Introduction

In the first paper [1] it was demonstrated that in the case of evaporation of liquid (H_2O, CH_3OH, C_2H_5OH, i-C_3H_7OH) in gaseous phase of an inert gas (N_2, He, Ar) a Stephan flow occurs [2] and the evaporation rate has both components: a diffusive component and a convective one. The mathematical model (one-dimensional Oberbeck–Bousinesq equation [3,5]) of the process is:

$$\begin{aligned}
&\frac{\partial v}{\partial t} + v\frac{\partial v}{\partial z} = -\frac{1}{\rho_0}\frac{\partial p}{\partial z} + \vartheta\frac{\partial^2 v}{\partial z^2} - \frac{g\alpha c}{\rho_0},\\
&\frac{\partial c}{\partial t} + v\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2}; \quad \alpha = \frac{\rho_V - \rho_0}{\rho_V};\\
&t = 0, \quad v = c = 0; \qquad (1)\\
&z = 0, \quad v = -\frac{D(1-\alpha)}{c_0^*}\left(\frac{\partial c}{\partial z}\right)_{z=0}, \quad c = c^*;\\
&z = l, \quad v = 0, \quad \frac{\partial c}{\partial z} = 0;
\end{aligned}$$

where t (s) is the time, z (m) is the vertical coordinate oriented normally to the liquid surface ($z = 0$).

The analysis of [1] takes into consideration that the thickness of the diffusion boundary layer upon a non-stationary diffusion $\delta = \sqrt{Dt_0}$ is greater than the depth of the gaseous phase, $l = 0.257$ m.

The comparison of the theoretical results of [1] and the experimental data, published in [4], indicated that the relationship related the rate of the non-stationary diffusion (J, kg/m^{2}s) is zero about the t large values, i.e.

$$t > \frac{l^2}{D}, \quad Q = \int_0^t J\,\mathrm{d}t = \text{const}, \quad (\delta > l). \qquad (2)$$

In the former case, this can be explained by the convective transport as a result of a Stephan flow and by a natural convection contribution. The second situation may be attributed to the saturation of gaseous phase by the liquid vapours due to limited thickness l of the gas phase. The effect of the natural convection may be occurs as a result of random perturbations and their growth should transform the system into a new stable state. This needs a specific investigation of the stability of the model (1), where the main process depends on the Stephan flow, while the perturbations lead to a natural convection.

2. Stability analysis

The stability of the evaporation process described by the model (1) will be investigated by means of

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doi:10.1016/S0017-9310(02)00468-4

Nomenclature

c	concentration in volume (kg/m^3)
c^*	concentration at interface (kg/m^3)
D	diffusivity (m^2/s)
g	gravity (m^2/s)
J	evaporation rate (kg/m^2 s)
l	depth of the gas phase (m)
p	pressure (kg/m s^2)
Q	amount of the evaporation liquid (kg/m^2)
t	time (s)
t_0	characteristic time (s)
u_0	characteristic velocity (m/s)
v	velocity (m/s)
z	coordinate (m)
α	$\rho_v - \rho_0/\rho_v$
ϑ	kinematic viscosity (m^2/s)
π	3.14
ρ_0	density of the gas (kg/m^3)
ρ_v	density of the vapours (kg/m^3)

perturbations of the velocity (v'), pressure (p') and the concentration (c'). Their superposition on the main process leads to

$$v + v', \quad p + p', \quad c + c', \tag{3}$$

where (3) satisfies the model (1). The result of that are two sets of equations:

$$\begin{aligned}
&\frac{\partial v}{\partial t} + v\frac{\partial v}{\partial z} = \vartheta\frac{\partial^2 v}{\partial z^2},\\
&\frac{\partial c}{\partial t} + v\frac{\partial c}{\partial z} = D\frac{\partial^2 c}{\partial z^2};\\
&t = 0, \quad v = c = 0;\\
&z = 0, \quad v = -\frac{D(1-\alpha)}{c_0^*}\left(\frac{\partial c}{\partial z}\right)_{z=0}, \quad c = c^*;\\
&z = l, \quad v = 0, \quad \frac{\partial c}{\partial z} = 0,\\
&\frac{\partial v'}{\partial t} + v'\frac{\partial v'}{\partial z} + v\frac{\partial v'}{\partial z} + v'\frac{\partial v}{\partial z}\\
&\quad = -\frac{1}{\rho_0}\left(\frac{\partial p}{\partial z} + \frac{\partial p'}{\partial z}\right) + \vartheta\frac{\partial^2 v'}{\partial z^2} - \frac{\alpha g}{\rho_0}(c + c')
\end{aligned} \tag{4}$$

and

$$\begin{aligned}
&\frac{\partial c'}{\partial t} + v'\frac{\partial c'}{\partial z} + v\frac{\partial c'}{\partial z} + v'\frac{\partial c}{\partial z} = D\frac{\partial^2 c'}{\partial z^2};\\
&z = 0, \quad v' = c' = 0;\\
&z = 0, \quad v' = -\frac{D(1-\alpha)}{c_0^*}\left(\frac{\partial c'}{\partial z}\right)_{z=0}, \quad c' = 0;\\
&z = l, \quad v' = 0.
\end{aligned} \tag{5}$$

The dimensionless variables of (4) may be introduced as:

$$t = t_0 T, \quad z = lZ, \quad v = u_0 V, \quad c = c^* C, \tag{6}$$

so the new form of the sets of equations becomes:

$$\begin{aligned}
&\frac{\partial V}{\partial T} + \frac{u_0 t_0}{l}V\frac{\partial V}{\partial Z} = \frac{\vartheta t_0}{l^2}\frac{\partial^2 V}{\partial Z^2},\\
&\frac{\partial C}{\partial T} + \frac{u_0 t_0}{l}V\frac{\partial C}{\partial Z} = \frac{D t_0}{l^2}\frac{\partial^2 C}{\partial Z^2};\\
&T = 0, \quad V = C = 0;\\
&Z = 0, \quad V = -\frac{D(1-\alpha)c^*}{c_0^* l u_0}\left(\frac{\partial C}{\partial Z}\right)_{z=0}, \quad C = 1;\\
&Z = 1, \quad V = 0, \quad \frac{\partial C}{\partial Z} = 0.
\end{aligned} \tag{7}$$

The characteristic velocity of the flow as a result of the Stephan flow is determined from the boundary condition at the interface ($z = 0$):

$$\frac{D(1-\alpha)c^*}{c_0^* l u_0} \sim 1, \quad u_0 = \frac{D(1-\alpha)c^*}{c_0^* l} \sim 10^{-6}\ \text{m/s}. \tag{8}$$

This allows to determine also the orders of magnitudes of the other parameters in (7):

$$\frac{u_0 t_0}{l} \sim 10^{-2}, \quad \frac{v t_0}{l} \sim \frac{D t_0}{l^2} \sim 1. \tag{9}$$

It is clear that from (7) and (9) neglecting the convective terms may perform the solution of (4):

$$v\frac{\partial v}{\partial z} \sim v\frac{\partial c}{\partial z} \sim 0. \tag{10}$$

The solution of (4) with respect to the concentration (upon the condition (10)) can be obtained by Laplace transformation [6] in the form:

$$c = c^* \sum_{n=0}^{\infty}(-1)^n\left[\operatorname{erfc}\frac{2nl + z}{2\sqrt{Dt}} + \operatorname{erfc}\frac{(2n+2)l - z}{2\sqrt{Dt}}\right]. \tag{11}$$

Thus,

$$\left(\frac{\partial c}{\partial z}\right)_{Z=0} = -\frac{c^*}{\sqrt{\pi D t}}\left[1 + 2\sum_{n=1}^{\infty}(-1)^n \exp\left(-\frac{n^2 l^2}{Dt}\right)\right] \tag{12}$$

and the velocity of the Stephan flow is

$$v(0,t) = (1-\alpha)\frac{c^*}{c_0^*}\sqrt{\frac{D}{\pi t}}\left[1+2\sum_{n=1}^{\infty}(-1)^n \exp\left(-\frac{n^2 l^2}{Dt}\right)\right]. \tag{13}$$

The solution of (5) will be derived in the form of "normal" perturbations:

$$\begin{aligned} v' &= v_1(z,t)\exp(-\lambda t),\\ p' &= p_1(z,t)\exp(-\lambda t),\\ c' &= c_1(z,t)\exp(-\lambda t), \end{aligned} \tag{14}$$

where v_1, p_1, and c_1 are amplitudes of the perturbations.

The problem concerning the determination of v_1, p_1, and c_1 is an eigenvalue problem, where λ is the eigenvalue while v_1, p_1, and c_1 are the eigenfunctions. The solution will be derived in the form of "neutral" perturbations, whose amplitudes neither attenuate nor grow with the time, i.e. eigenfunctions at $\lambda = 0$. Thus, from (4) and (5) it becomes that:

$$\begin{aligned} & v_1\frac{\partial v_1}{\partial z} + v\frac{\partial v_1}{\partial z} + v_1\frac{\partial v}{\partial z}\\ &\quad = -\frac{1}{\rho_0}\left(\frac{\partial p}{\partial z}+\frac{\partial p_1}{\partial z}\right) + \vartheta\frac{\partial^2 v_1}{\partial z^2} - \frac{g\alpha}{\rho_0}(c+c_1),\\ & v_1\frac{\partial c_1}{\partial z} + v\frac{\partial c_1}{\partial z} + v_1\frac{\partial c}{\partial z} = D\frac{\partial^2 c_1}{\partial z^2};\\ & t=0, \quad v_1 = c_1 = 0;\\ & z=0, \quad v_1 = -\frac{D(1-\alpha)}{c_0^*}\left(\frac{\partial c_1}{\partial z}\right)_{Z=0}, \quad c_1 = 0;\\ & z=l, \quad v_1 = 0. \end{aligned} \tag{15}$$

The solution of (15) will be performed by means of dimensionless variables:

$$\begin{aligned} & t = t_0 T, \quad z = l_1 Z_1, \quad v = u_1 V, \quad v_1 = u_1 V_1, \quad c = c^* C,\\ & c_1 = c^* C_1, \quad p = \rho_0 u_1^2 P, \quad p_1 = \rho_0 u_1^2 P_1. \end{aligned} \tag{16}$$

The substitution of (16) into (15) leads to:

$$\begin{aligned} & \frac{u_1^2\rho_0}{l_1 g\alpha c^*}\left(V_1\frac{\partial V_1}{\partial Z} + V\frac{\partial V_1}{\partial Z} + V_1\frac{\partial V}{\partial Z}\right)\\ &\quad = -\frac{u_1^2\rho_0}{l_1 g\alpha c^*}\left(\frac{\partial P}{\partial Z}+\frac{\partial P_1}{\partial Z}\right) + \frac{\vartheta u_1\rho_0}{l_1^2 g\alpha c^*}\frac{\partial^2 V_1}{\partial Z^2} - C - C_1,\\ & \frac{u_1 l_1}{D}\left(V_1\frac{\partial C_1}{\partial Z} + V\frac{\partial C_1}{\partial Z} + V_1\frac{\partial C}{\partial Z}\right) = \frac{\partial^2 C_1}{\partial Z^2};\\ & T=0, \quad V_1 = C_1 = 0;\\ & Z=0, \quad V_1 = -\frac{D(1-\alpha)c^*}{u_1 l_1 c_0^*}\left(\frac{\partial C_1}{\partial Z}\right)_{z=0}; \quad C_1 = 0;\\ & Z=1, \quad V_1 = C_1 = 0. \end{aligned} \tag{17}$$

It is possible to suggest that in (17) the process is limited by the natural convection and the velocity at the interface, i.e.

$$\frac{\vartheta u_1\rho_0}{l_1^2 g\alpha c^*} = 1, \quad \frac{D(1-\alpha)c^*}{u_1 l_1 c_0^*} = 1. \tag{18}$$

This permits to define the characteristic parameters (the velocity and the thickness of the boundary layer) and their orders of magnitudes:

$$\begin{aligned} u_1 &= D(1-\alpha)\frac{c^*}{c_0^*}\sqrt[3]{\frac{g\alpha c_0^*}{D(1-\alpha)\vartheta\rho_0}} \sim 10^{-3}\ \text{m/s},\\ l_1 &= \sqrt[3]{\frac{(1-\alpha)\vartheta\rho_0 D}{\alpha g c_0^*}} \sim 10^{-4}\ \text{m}. \end{aligned} \tag{19}$$

The expressions (19) permit to define the order of magnitude of the dimensionless parameters of (17) too:

$$\frac{u_1^2\rho_0}{l_1 g c^*} \sim 10^{-2}, \quad \frac{u_1 l_1}{D} \sim 10^{-2}. \tag{20}$$

This allows to express (17) in a zero-order approximation with respect to the small parameters (20):

$$\begin{aligned} & \frac{\partial^2 V_1}{\partial Z_1^2} = C + C_1,\\ & \frac{\partial^2 C_1}{\partial Z_1^2} = 0;\\ & Z_1 = 0, \quad \left(\frac{\partial C_1}{\partial Z}\right)_{Z=0} = -V_1(0,T), \quad C_1 = 0;\\ & Z_1 = 1, \quad V_1 = C_1 = 0. \end{aligned} \tag{21}$$

The concentration $c = c^* C$ in (21) varies within a layer with thickness of $\delta \sim 10^{-2}$ m (see (6)), while the concentration $c_1 = c^* C_1$ varies within the rage defined by a layer of depth $l \sim 10^{-4}$. Thus, the form of (24) allows to introduce for the surface concentration $C = 1$.

The solution of (24) concerning C_1 may be obtained with accuracy defined by an arbitrary function $V_1(0,T)$:

$$C_1 = (1 - Z_1)V_1(0,T). \tag{22}$$

The solution concerning the velocity can be obtained in a similar manner:

$$\begin{aligned} V_1 = {} & \frac{1}{2}Z_1^2 + V_1(0,T)\left(\frac{Z_1^2}{2} - \frac{Z_1^3}{6}\right) - \left[\frac{1}{2} + \frac{4}{3}V_1(0,T)\right]Z_1\\ & + V_1(0,T). \end{aligned} \tag{23}$$

3. Comparison with experimental data

The velocity $V_1(0,T) = v_1(0,t)/u_1$ cannot be determined theoretically by (22) and (23) upon the assumptions of the linear theory of stability. However, it is possible to establish it from experimental data.

If suppose, that the velocity of disturbance $v_1(0,t)$ differs from the velocity of the main flow only the individual effects scales, and it could be obtain it:

$$v_1(0,t) = \gamma(1-\alpha)\frac{c^*}{c_0^*}\sqrt{\frac{D}{\pi t}}\left[1+2\varepsilon\sum_{n=1}^{\infty}(-1)^n\exp\left(-\frac{n^2 l_1^2}{Dt}\right)\right]. \tag{24}$$

Introduction of Eq. (24) in the boundary condition at $z = 0$ leads to:

$$\left(\frac{\partial c_1}{\partial z}\right)_{z=0} = -\gamma\frac{c^*}{\sqrt{\pi D t}}\left[1+2\varepsilon\sum_{n=1}^{\infty}(-1)^n\exp\left(-\frac{n^2 l_1^2}{Dt}\right)\right], \tag{25}$$

where $l_1 = \beta l$, while the parameters β, γ and ε should be obtained from experimental data.

The mass transfer rate upon evaporation depends on both the diffusion and the convective transports through the liquid–gas interface:

$$\begin{aligned} J &= -D\left(\frac{\partial c}{\partial z}+\frac{\partial c_1}{\partial z}\right)_{z=0} + c^*(v+v_1)_{z=0} \\ &= -\frac{D\rho_0}{c_0^*}\left(\frac{\partial c}{\partial z}+\frac{\partial c_1}{\partial z}\right)_{z=0}. \end{aligned} \tag{26}$$

The introduction of (12) and (25) into (26) leads to:

$$\begin{aligned} J &= \frac{\rho_0 c^*}{c_0^*}\sqrt{\frac{D}{\pi t}}\left[1+2\sum_{n=1}^{\infty}(-1)^n\exp\left(-\frac{n^2 l^2}{Dt}\right)\right] \\ &\quad + \gamma\frac{\rho_0 c^*}{c_0^*}\sqrt{\frac{D}{\pi t}}\left[1+2\varepsilon\sum_{n=1}^{\infty}(-1)^n\exp\left(-\frac{n^2\beta^2 l^2}{Dt}\right)\right]. \end{aligned} \tag{27}$$

Taking into account that

$$\rho^* = \rho_0 + \alpha c^* = c_0^* + c^*, \tag{28}$$

it is possible to find the amount of the evaporated liquid through (27):

$$\begin{aligned} Q &= \int_0^{t_0} J\,\mathrm{d}t \\ &= A\left[(1+\gamma)\sqrt{t} + \sum_{n=1}^{\infty}(-1)^n\int_0^{t_0}\frac{1}{\sqrt{t}}\exp\left(-\frac{n^2 l^2}{Dt}\right)\mathrm{d}t \right. \\ &\quad \left. + \varepsilon\gamma\sum_{n=1}^{\infty}(-1)^n\int_0^{t_0}\frac{1}{\sqrt{t}}\exp\left(-\frac{n^2\beta^2 l^2}{Dt}\right)\mathrm{d}t\right], \end{aligned} \tag{29}$$

where

$$A = 2\frac{\rho_0 c^*}{c_0^*}\sqrt{\frac{D}{\pi}}. \tag{30}$$

The experimental data concerning evaporations of various liquids in [4] permit the determination of the values of β, γ and ε. During the calculation of the sums in (29) been three to four terms was required for the first sum and six to eight terms for the second sum.

Figs. 1–6 show the comparison of the values of Q determined through (29) and the experimental data of

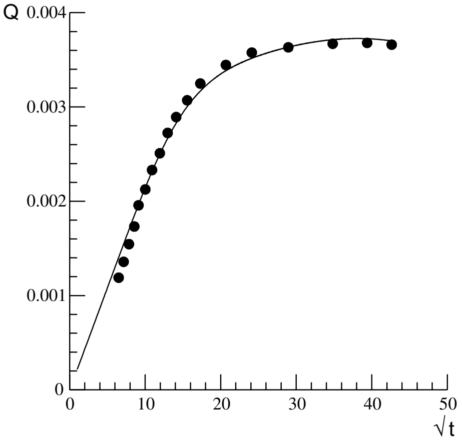

Fig. 1. Evaporation in system H_2O–N_2.

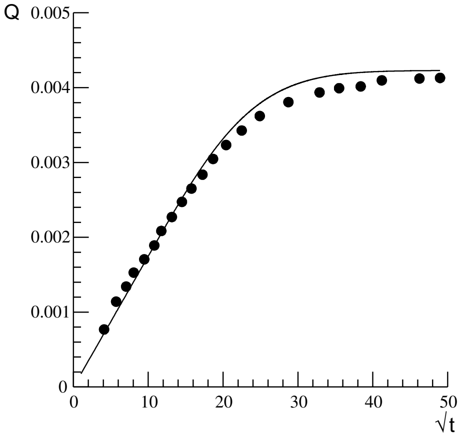

Fig. 2. Evaporation in system H_2O–He.

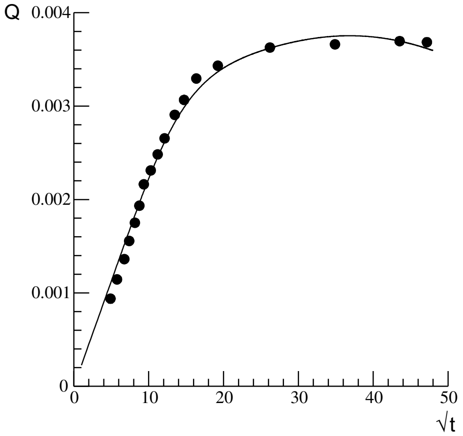

Fig. 3. Evaporation in system H_2O–Ar.

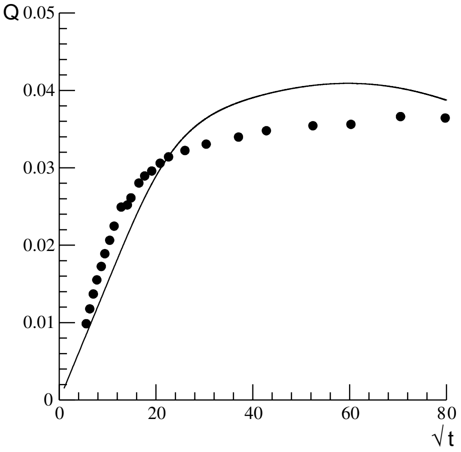

Fig. 4. Evaporation in system CH_3OH–Ar.

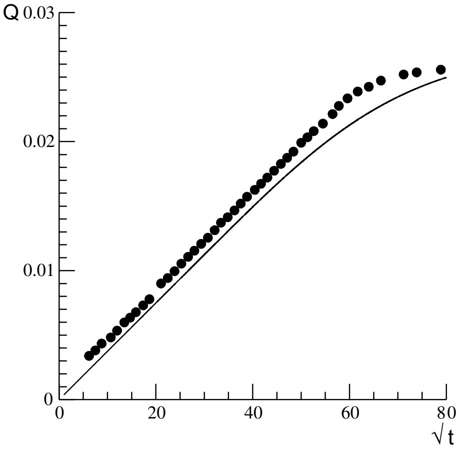

Fig. 5. Evaporation in system C_2H_5OH–Ar.

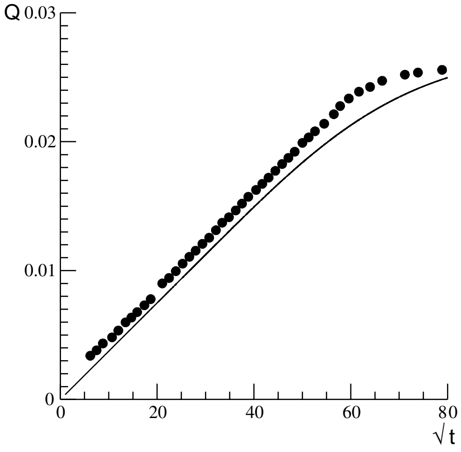

Fig. 6. Evaporation in system C_3H_7OH–Ar.

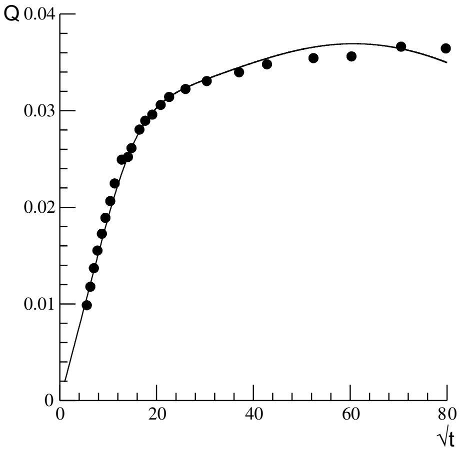

Fig. 7. Evaporation in system CH_3OH–Ar ($\gamma = 2.4$; $\beta^2 = 0.049$; $\varepsilon = 3.08$).

Table 1
Characteristic parameters of the gas–liquid system (20°)

Parameters	Systems					
	H_2O/N_2	H_2O/He	H_2O/Ar	CH_3OH/Ar	C_2H_5OH/Ar	iC_3H_7OH/Ar
$D \times 10^5$ (m^2/s)	2.41	8.86	2.57	0.98	1.00	0.846
ρ_0 (kg/m^3)	1.16	0.16	1.66	1.66	1.66	1.66
c^* (kg/m^3)	0.0142	0.0143	0.0161	0.142	0.0995	0.0939
c_0^* (kg/m^3)	1.13	0.162	1.66	1.48	1.57	1.63
$A_e \times 10^4$ (kg/m^2 $s^{1/2}$)	2.051	1.633	2.190	19.47	3.963	3.287
$A \times 10^4$ (kg/m^2 $s^{1/2}$)	0.954	1.94	0.961	5.92	4.28	1.57
β	0.332	0	0.332	0.332	0	0
γ	1.70	0	1.7	1.7	0	0
ε	2.40	0	2.40	2.40	0	0
$\rho_0/c_0^*c_0^*$	1.02	1.02	1.02	1.12	1.05	1.04
α	−0.555	0.778	−1.216	−0.246	0.133	0.335

[4]. The corresponding values of β, γ and ε are available in Table 1.

The effect of the Stephan flow is determined by the ratio ρ_0/c_0^*, which values are shown in Table 1. The results obtained show, that the Stephan flow is the largest at the evaporation of CH_3OH.

The values of Q from (29) at $\beta = 0.221$; $\gamma = 2.4$; $\varepsilon = 3.08$ for evaporation of CH_3OH are shown in Fig. 7.

4. Conclusions

The results developed here indicate that the evaporation rate from a stagnant liquid into a gaseous layer having a limited depth is controlled by the rate of the non-stationary diffusion between both surfaces. The concentrations of the vapours at the liquid surface is practically constant, while the upper boundary of the gaseous layer is impermeable for the vapours (i.e. diffusion flux is zero). This effect is augmented by the contribution of a convective transport in the gaseous pash. The later contributes both the Stephan flow and the natural convection. The Stephan flow occurs due the phase transition at the interface, while the natural convection is provoked by the loss of stability of the entire process as a result of the growth of small perturbations. The latter leads to a self-organization of the system and a formation of dissipative structures.

It can be seen from Table 1 that in the cases when the vapours of the liquid are weightier than the inert gas (H_2O/He, C_2H_5OH/Ar, *i*-C_3H_7OH/Ar) the process is stable ($\beta = \gamma = \varepsilon = 0$) and the rate of the evaporation could be determined from the non-stationary diffusion rate (increased with 2–5% by the Stephan flow effect—ρ_0/c_0^*).

The process is unstable when the vapours are lighter then gas. In these conditions a natural convection is appeared as a result of the instability. Thus the evaporation rate ($\gamma = 1.70$) is essentially increased which is 2.7 times larger than the diffusion rate.

It is important to note, that the parameters of the dissipative structure (as a result of instability) are equal ($\beta = 0.332$, $\gamma = 1.7$, $\varepsilon = 2.4$) for different liquid gas systems (H_2O/N_2, H_2O/Ar, CH_3OH/Ar). The deviation of the system CH_3OH/Ar could be a result from experimental errors.

Acknowledgements

The work was completed with the financial support of the National Science Fund, Ministry of Education and Science, Republic of Bulgaria, Contract MM-1102/2001.

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