Non-equilibrium evaporation/condensation model

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A new mathematical model for non-equilibrium evaporation/condensation including boiling effect is proposed. A simplified differential-algebraic system of equations is obtained. It is designed to solve both systems of equations with and without the boiling effect. Numerical calculations of ammonia-water systems with various initial conditions, which correspond to evaporation and/or condensation of both components, have been performed. It is shown that, although the system evolves quickly towards a quasi equilibrium state, it is necessary to use a non-equilibrium evaporation model to calculate accurately the evaporation/condensation rates, and consequently all the other dependent variables.

Keywords: non-equilibrium evaporation; condensation; boiling; phase transition.

1. Introduction

The problem of phase transition, and in particular evaporation/condensation, is one of the most important problems of modern technology. There are numerous applications of this process in industry, for example, in refrigeration and chemical industry.

It is very common to use an equilibrium evaporation model which assumes that the concentrations of species in the gas phase are always at saturated conditions [Makeyev et al., 1981] and [Zverev and Smirnov 1989]. This approach is not only conceptually questionable - indeed if the gas is at saturated condition there is no evaporation or condensation - but sometimes it can lead to significant numerical errors, such as the obtention of negative con-

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centrations in complex computer simulations. Therefore, for industrial problems, for example the modelling of an absorption refrigeration cycle, it is paramount to develop and use non-equilibrium evaporation/condensation model \cite{Remorov2005,Chernark1995,Chernak1989,Ivenchenko1987,Ytrehus1996,Young1991,Wang2005,Wang2006,Krishnaswami2006}.

In the work of Ivenchenko 1987 the moment method was applied to solve the problem of evaporation/condensation of a spherical droplet immersed in a vapour-gas mixture. Calculating the moments from the collision integrals he proposed a new procedure which allows the use of collision integrals in the Boltzmann form. He obtained an analytical formula for the time dependence of the droplet radius for any Knudsen number.

The kinetic theory of droplet evaporation has been developed by Chernark 1995. He studied the evaporation/condensation of a single aerosol particle suspended in a non-equilibrium gas mixture. In his earlier work together with Margilevsky \cite{Chernak1989} he developed a linear theory of mass and heat transfer for aerosol particle evaporation.

The condensation and evaporation of a single liquid droplet for an arbitrary Knudsen number have been studied analytically by Young \cite{Young1991,Young1993} who developed a new system of equations describing evaporation/condensation of a small liquid droplet. His theory is valid for polyatomic gases and, apart from the evaporation/condensation coefficients, contains no additional empirical constants.

The continued development of diesel and rocket engines generated a significant interest in the understanding of aerosol behaviour. A good comprehensive review about equilibrium and non-equilibrium droplet evaporation models has been written by Miller et al. \cite{Miller1998}. These authors argued that the Langmuir-Knudsen law \cite{Knudsen1915,Knudsen1934} should be used for general gas-liquid flow calculations because it incorporates the realistic non-equilibrium evaporation/condensation behaviour prevailing in many practical situations while not requiring more computational effort than other equilibrium models.

Comprehensive theoretical research in the field of film condensation in micro-channels have been performed by Wang and Rose \cite{Wang2005,Wang2006}. Their model is based on fundamental principles and takes into account surface tension, vapour shear stress and gravity. The effect of a channel geometry was investigated for different types of cross-sections. They found that there is a significant heat-transfer enhancement by surface tension towards the channel entrance.

This paper is organised as follows. In \S2 the main assumptions are introduced and the framework for the derivation of a novel approach is discussed. Section \S3 is focused on the extension of the model to the boiling situation. The work is completed by the derivation of an analytical solution of a simplified system and the numerical
solution of a differential-algebraic system in §4. The Conclusions are presented in §5.

2. Mathematical model

The main assumptions for the model are:

- There is thermal equilibrium between the two phases. Namely, the gas temperature is equal to the liquid temperature, $T_g = T_l = T$.
- There is mechanical equilibrium between the two phases, that is the gas and liquid pressures are equal. The pressure gradient due to gravity can be neglected.
- The gas phase is considered as an ideal gas.
- The liquid phase is assumed to be incompressible.
- The Stefan flux is neglected.
- The detailed bubble generation mechanism is neglected in the boiling model.
- The zero-dimensional approach is used.

2.1. Non-equilibrium evaporation/condensation model

Let us consider a container which contains both liquid and gas phases. For the sake of simplicity, let us assume that there is only one chemical species in the volume. The generalisation to the multicomponent mixture is straightforward.

If the temperature of the liquid is less than the boiling temperature, $T < T_b$, evaporation will only occur at the interphase surface. By contrast to evaporation, condensation can take place not only at the liquid-gas interphase, but at all surfaces including the surfaces of the chamber. Furthermore, it is assumed that phase transitions can only take place at the liquid surface.

In the case of equilibrium, the molecular flux which leaves the liquid surface is balanced by the molecular flux coming to the liquid from the gas phase. Evaporation occurs if the molecular flux leaving the liquid surface is greater than the flux coming from the gas phase. Conversely, condensation takes place when the molecular flux from the liquid surface is less than the flux coming from the gas phase. Thus,

$$ S_{ev} = \dot{N}_{l \to g} - \dot{N}_{g \to l}, $$

here $S_{ev}$ is the total evaporation/condensation molar rate (e.g. mol s$^{-1}$). It is positive for evaporation, negative for condensation, and zero at saturated (equilibrium) conditions. $\dot{N}_{l \to g}$ and $\dot{N}_{g \to l}$ are respectively the molecular fluxes from liquid to gas and from gas to liquid. From the gas molecular theory [Schroeder 1999], it is well-known that

$$ \dot{N}_{g \to l} = \frac{\xi_g U_m}{A} \Gamma A, $$

(2)
here $A$ is the area of the interphase surface where evaporation/condensation takes place, $U_m$ is the average molecular velocity and $\xi_g$ is the molar volumic concentration of the component in the gas phase. $\Gamma$ is an accommodation coefficient, which represents the fact that not all the gas molecules which hit the liquid surface penetrate the liquid. In fact, a significant part of them bounces back into the gas phase. It is therefore obvious, that $\Gamma$ must be positive and not more than unity, $\Gamma \in [0 : 1]$. If $\Gamma = 1$, all the gas molecules which hit the liquid surface penetrate into the bulk of the liquid, and if $\Gamma = 0$, there is no phase transition at all.

Generally, $\Gamma$ can be a function of temperature, pressure and the chemical composition of the liquid phase [Smirnov and Kulchitski 1997,Remorov and Bardwell 2005,Morita 2003]. In this paper, for the sake of simplicity, it is assumed that $\Gamma$ is constant. The value of $\Gamma$ can be evaluated using the experimental data obtained from a dynamic evaporation experiment.

Using gas molecular theory [Schroeder 1999] the average molecular velocity can be expressed as

$$ U_m = \left( \frac{8R_u T}{\pi W} \right)^{0.5} ,$$

(3)

here $R_u$ is the universal gas constant, $T$ is the temperature of the system and $W$ is the molecular weight of a component.

The molecular flux which leaves the liquid surface is determined by the internal state of the liquid, namely, its temperature, pressure, etc. It does not depend on the concentration of the component in the gas phase. In some sense the liquid “does not know” whether it is at equilibrium conditions or not. Thus, using the fact that at equilibrium the two fluxes (in and out of the liquid) are balanced, the following relation can be written

$$ \dot{N}_{l \rightarrow g} = \dot{N}_{g \rightarrow l}^{eq} = \frac{\xi_g^{eq} U_m}{4} \Gamma A ,$$

(4)

where $\dot{N}_{l \rightarrow g}$ is the molecular flux from gas to liquid at saturation, and $\xi_g^{eq}$ is the concentration of the component in the gas phase at saturation.

Thus, substituting (2) and (4) into (1) and using (3) for the average molecular velocity, one gets:

$$ S_{ev} = \Gamma A \left( \frac{R_u T}{2\pi W} \right)^{0.5} \left( \xi_g^{eq} - \xi_g \right).$$

This is the well-known Hertz-Knudsen’s formula [Knudsen 1915,Knudsen 1934,Smirnov and Kulchitski 1997] - except that the original formula was written in terms of pressures.

In the case of a multicomponent mixture, the above formula can be generalised for each component $i$ as

$$ S_{ev,i} = \Gamma_i A \left( \frac{R_u T}{2\pi W_i} \right)^{0.5} \left( \xi_g^{eq,i} - \xi_{g,i} \right),$$

(5)
From (5), it is easy to find that there are three possible situations:

1) the evaporation of the \(i\)-th component occurs if \(\xi_{gi} < \xi_{eqi}\),
2) the condensation of the \(i\)-th component takes place if \(\xi_{gi} > \xi_{eqi}\),
3) the equilibrium (saturation) for the \(i\)-th component takes place if \(\xi_{gi} = \xi_{eqi}\).

It is worth noticing that in order to derive (5), the assumptions mentioned at the beginning of this chapter have not been used. Therefore, formula (5) is quite general and can be used even if some of the above assumptions are not satisfied. The main assumption in deriving (5) is that the molecules velocity distribution in the gas phase is Maxwellian so that (3) is satisfied.

2.2. Species balance equation

If the system is closed with a constant volume, the budget equations for \(i\)-th species are given by

- **Gas phase**

\[
\frac{d(\alpha \xi_{gi})}{dt} = \frac{S_{ev,i}}{V},
\]

where \(\alpha\) is the gas volume fraction, \(V\) the total volume of the chamber, and \(S_{ev,i}\) the total evaporation rate of the \(i\)-th component. The constant volume assumption is made as it holds for absorption refrigeration cycles and for refrigeration applications in general.

- **Liquid phase**

\[
\frac{d((1 - \alpha) \xi_{li})}{dt} = - \frac{S_{ev,i}}{V},
\]

2.3. Energy balance equation

The energy conservation equation for a constant volume vessel in terms of temperature can be written as (the detailed derivation is given in appendix A)

\[
\left[\alpha \sum_{i=1}^{n} \xi_{gi} c_{pgi} + (1 - \alpha) \sum_{i=1}^{n} \xi_{li} c_{pli}\right] \frac{dT}{dt} - \alpha \frac{dP}{dt} + \sum_{i=1}^{n} \Delta h_i \frac{S_{ev,i}}{V} = -\dot{Q},
\]

where \(c_{pgi}\) and \(c_{pli}\) are the molar heat capacity at constant pressure for the \(i\)-species for respectively the gas and liquid phase. \(\Delta h_i\) is the molar latent enthalpy for the \(i\)-species. \(\dot{Q}\) is the rate of heat transfer from the surroundings to the system and is given by

\[
\dot{Q} = \lambda A_w (T_w - T),
\]

where \(T\) is the temperature of the system, \(T_w\) is the temperature of the wall, \(\lambda\) is the heat transfer rate coefficient, and \(A_w\) is the surface area for heat transfer to the calorimeter.
2.4. Equations of state

In order to simplify the model, it is assumed that the liquid phase is incompressible and the vapour phase behaves as an ideal gas. In this case for the vapour phase the following equation is satisfied

\[ P = R_u T \sum_{i=1}^{n} \xi_{g_i}. \] (10)

The volume of the liquid phase is given by

\[ \sum_{i=1}^{n} \xi_{l_i} \bar{V}_{l_i} = 1. \] (11)

where \( \bar{V}_{l_i} \) is the partial molar volume of the \( i \)-th species, which is assumed to be constant.

2.5. Phase equilibria relation

In order to complete the evaporation/condensation model, (5), it is necessary to express the concentration of the components at the saturation condition, \( \xi_{eq_i} \) as functions of the temperature and composition of the liquid phase. For condensable species, Raoult’s law [Smith et al., 2005] is used

\[ y_i P = p_i(T)x_i, \] (12)

where \( p_i(T), x_i \) and \( y_i \) are respectively the vapour pressure, mole fraction in the liquid phase and mole fraction in the gas phase of the \( i \)-th species. The temperature dependence of the vapour pressure is given by Antoine’s equation [Smith et al., 2005]

\[ \ln (p_i(T)) = D_i - B_i T + T_a. \] (13)

where \( D_i, B_i, \) and \( T_a \) are material dependent empirical constants, that are well-tabulated.

Using, (12) together with the ideal gas equation (10), and the definitions of mole fractions in gas and liquid phase, \( y_i, x_i \), it can be shown that

\[ \xi_{eq_i} = \frac{1}{R_u T} \exp \left( D_i - \frac{B_i}{T + T_a} \right) \frac{\xi_{l_i}^{eq}}{\sum_{i=1}^{n} \xi_{l_i}^{eq}}. \] (14)

Thus, the relation between the concentrations of a component in the gas and liquid phases is obtained.

3. Boiling evaporation model

The previous evaporation model [8], (11) and (14) was developed using the assumption that there is no boiling. In case when boiling takes place additional consideration is required.
By definition at boiling evaporation takes place not only at the surface of the liquid but also in the bulk of the liquid. To model this phenomenon, additional bulk evaporation source terms \( S_{b\,ev,i} \) must be introduced. These terms describe the evaporation rate in the bulk of liquid. Thus, to take into account boiling in \((6), (7)\) and \((8)\) the term \( S_{ev,i}/V \) must be substituted by \((S_{ev,i} + S_{b\,ev,i})/V\).

There are now \( n \) new variables, \( S_{b\,ev,i} \) \( i = 1...n \) that have been introduced in our system. Therefore, it is necessary to add \( n \) relations to close the system. During boiling, bubbles are generated within the liquid bulk. They contain a mixture of saturated gases. Therefore, it is reasonable to suggest that the evaporation rate of a component is proportional to the component concentration at saturation in the gas phase:

\[
\begin{align*}
S_{b\,ev,1} &= \xi_{eq}^g_1 \\
S_{b\,ev,2} &= \xi_{eq}^g_2 \\
\vdots & \quad \vdots \\
S_{b\,ev,n} &= \xi_{eq}^g_n 
\end{align*}
\]

(15)

It is easy to see that the above relation consists of \( n - 1 \) equations, consequently, one more relation is needed to close the system.

From our point of view, it is consistent to suggest that the total bulk evaporation rate is proportional to the difference between the saturated pressure \( P_{eq} \) and current pressure \( P \) in the system

\[
S_{b\,ev,t} = \sum_{i=1}^{n} S_{b\,ev,i} \sim (P_{eq} - P)\mathcal{H}(P_{eq} - P),
\]

here \( S_{b\,ev,t} \) is the total bulk evaporation rate. \( \mathcal{H} \) is the Heavyside function with \( \mathcal{H}[0] = 0 \). If boiling is in a developed stage, bubbles are generated in the whole bulk of the liquid. Therefore, it is natural to assume that the total bulk evaporation rate is proportional to the volume of boiling liquid. Thus,

\[
S_{b\,ev,t} = \sum_{i=1}^{n} S_{b\,ev,i} = \zeta(T, P, \xi_{li})V_i(P_{eq} - P)\mathcal{H}(P_{eq} - P),
\]

(16)

here the correction factor \( \zeta(T, P, \xi_{li}) \) has been introduced, which, in general, can be a function of the temperature, pressure, and liquid composition. For the sake of simplicity, it is assumed that \( \zeta \) is constant in our model. Generally, the value of \( \zeta \) or its dependence on other parameters can be found from an experiment.

After substituting the ideal gas equation \((10)\) and the expression for the liquid volume \( V_i = (1 - \alpha)V \) in formula \((16)\), it is found that

\[
\sum_{i=1}^{n} S_{b\,ev,i} = \zeta R_a T (1 - \alpha)V \left( \sum_{i=1}^{n} \xi_{g_i}^q(T) - \sum_{i=1}^{n} \xi_{g_i} \right).
\]

(17)

Owing to the nature of boiling, the bulk evaporation rate of each component must take a non-negative value.
For a complete boiling model a condition for boiling is needed. It is well-known that boiling takes place when the saturated pressure of the mixture is larger than the pressure in the system, \( P_{eq} > P \). Using the equation for ideal gas (10), the boiling condition can be written as

\[
\sum_{i=1}^{n} \xi_{eqi} > \sum_{i=1}^{n} \xi_{gi}.
\] (18)

4. Numerical results

4.1. Numerical results for a constant wall temperature

All numerical results in the following sections are related to the behaviour of a two component ammonia/water system. This kind of binary system is chosen owing to its importance for the refrigeration industry.

Using the following characteristic scales based on the vessel properties:

\[
\begin{align*}
L_e &= V^{1/3} \\
T_e &= T_{in} \\
t_e &= \frac{R_{w}}{A_{w} \lambda}, \\
m_e &= \frac{R^{3} T_{in} (A_{w} \lambda)^{2} V_{2} / 3 }{
\end{align*}
\] (19)

the system of equations (6), (7), (8), (10), (11) and (14) can be written in the dimensionless form:

\[
\begin{align*}
\frac{d(\tilde{\xi}_{eqi})}{dt} &= \tilde{S}_{ev,i}^{} + \tilde{S}_{ev,i}^b \\
\frac{d((1-\alpha)\tilde{\xi}_{li})}{dt} &= -\tilde{S}_{ev,i}^{} - \tilde{S}_{ev,i}^b \\
\left[ \alpha \sum_{i=1}^{n} \tilde{\xi}_{gi} \tilde{c}_{gi}^p + (1-\alpha) \sum_{i=1}^{n} \tilde{\xi}_{li} \tilde{c}_{li}^p \right] \frac{d\tilde{T}}{dt} - \alpha \frac{dP}{dt} + n \sum_{i=1}^{n} \Delta \tilde{h}_{i}(\tilde{S}_{ev,i} + \tilde{S}_{ev,i}^b) &= (\tilde{T}_{w} - \tilde{T}) \\
\tilde{P} &= \tilde{T} \sum_{i=1}^{n} \tilde{\xi}_{gi} \\
\sum_{i=1}^{n} \tilde{\xi}_{li} \tilde{V}_{li} &= 1 \\
\tilde{S}_{ev,i} &= \tilde{S}_{ev,i} \\
\tilde{\xi}_{eqi} &= \tilde{\xi}_{eqi} \\
\tilde{\xi}_{li} &= \tilde{\xi}_{li} \\
\tilde{S}_{ev,1}^b / \tilde{S}_{ev,2}^b &= \tilde{\xi}_{eqi} / \tilde{\xi}_{g2} \\
\sum_{i=1}^{n} \tilde{S}_{ev,i}^b &= \tilde{T}(1-\alpha) \left( \sum_{i=1}^{n} \tilde{\xi}_{eqi}^b (\tilde{T}) - \sum_{i=1}^{n} \tilde{\xi}_{g2i}^b \right) \mathcal{H} \left[ \sum_{i=1}^{n} \tilde{\xi}_{eqi}^b (\tilde{T}) - \sum_{i=1}^{n} \tilde{\xi}_{g2i}^b \right]
\end{align*}
\] (20)

This is a set of differential-algebraic equations (DAE). DAE are encountered in a number of scientific disciplines in particular in equilibrium chemistry. The mathe-
mathematical background for these equations and the different numerical methods used for solving them are presented and analysed in [Brenan et al., 1995]. Based on these methods we have developed an in-house code to solve the equation set (20).

4.1.1. Initial conditions

It is easy to see that in our systems of equation (20), there are \( 2n + 2 \) first derivatives. Namely:

\[
\frac{d\tilde{\xi}_g}{dt}, \quad \frac{d\tilde{\xi}_l}{dt}, \quad \frac{d\alpha}{dt}, \quad \frac{d\tilde{T}}{dt}
\]

Therefore, for a two component system \( (n = 2) \), it is necessary to provide our systems with 6 initial conditions.

Thus, to complete the problem the following initial conditions must be specified:

\[
\tilde{\xi}_g(0) = \tilde{\xi}_{g0}, \quad \tilde{\xi}_l(0) = \tilde{\xi}_{l0}, \quad \alpha(0) = \alpha_0, \quad \tilde{T}(0) = \tilde{T}_0
\]

It is necessary to note that the equation of state for the liquid must be always satisfied. Therefore, only the concentration of one component can be specified arbitrarily in the range \([0 : 1/\tilde{V}_l]\), the other must be calculated from the liquid state equation (11). In all the cases considered in this paper the initial concentration of ammonia in liquid phase is fixed, and \( \tilde{\xi}_l = 3 \times 10^4 \text{ mol m}^{-3} \). From the above consideration it is obvious that the initial concentration of water in the liquid phase is fixed, and taken as \( \tilde{\xi}_l = 2.11 \times 10^4 \text{ mol m}^{-3} \). This value was calculated from (11) using the values for the specific volumes of both liquids given in Table 2.

The initial value for gas volume fraction, \( \alpha_0 \) is also fixed for all calculations in this paper and \( \alpha_0 = 0.5 \). The reason for this is that this value represents the volume of gas/liquid and does not have any significant effect on the behaviour of the system. Unless it is very close to the limiting values 0 and 1, which correspond to one component system with liquid or gas respectively. In this paper these two cases when the two phase system becomes a one phase system corresponding to a complete evaporation or condensation are not considered. The initial temperature is also fixed for all considered cases, and \( T_0 = 335 \text{ K} \).

Thus, only the initial concentrations of both components in the gas phase will be varied together with the wall temperature of the system.

Generally, the initial conditions for the concentrations in the gas phase can be written as

\[
\xi^0_{g1} = a_1 \xi_{eq}(T_0), \quad \xi^0_{g2} = a_2 \xi_{eq}(T_0),
\]

where \( a_1 \) and \( a_2 \) are non-negative constants.

For our numerical calculations the following five cases are considered.

1. Evaporation of both components, \( \tilde{\xi}^0_{g1} = 0.5 \tilde{\xi}_{g1}(\tilde{T}_0), \quad \tilde{\xi}^0_{g2} = 0.5 \tilde{\xi}_{g2}(\tilde{T}_0) \). In this case, both initial concentrations are less than the equilibrium concentrations, therefore, the boiling condition (18) is satisfied. Thus, boiling takes place during the whole evaporation process.

2. Evaporation of one component and condensation of the other component (without boiling), \( \tilde{\xi}^0_{g1} = 1.6 \tilde{\xi}_{g1}(\tilde{T}_0), \quad \tilde{\xi}^0_{g2} = 0.4 \tilde{\xi}_{g2}(\tilde{T}_0) \). In this case one of the initial concentration is less than the equilibrium concentration, and the initial concentration of the second component is more than the equilibrium value. Therefore, initially, one component evaporates and the other con-
denses during the process. It is easy to see that these initial conditions do not satisfy inequality (18). Therefore, there is no boiling.

(3) Evaporation of one component and condensation of the other component (with boiling), $\xi^0_{g1} = 0.4\xi_{eq}^g(\hat{T}^0)$, $\xi^0_{g2} = 1.6\xi_{eq}^g(\hat{T}^0)$. Inequality (18) is satisfied, so there is boiling. Interestingly, in this case, the first component (ammonia) evaporates in the bulk because of boiling and at the surface. The second component (water) evaporates in the bulk but condenses at the surface. Therefore, the total rate of evaporation of the second component can be positive or negative.

(4) Condensation of both components, $\xi^0_{g1} = 1.5\xi_{eq}^g(\hat{T}^0)$, $\xi^0_{g2} = 1.5\xi_{eq}^g(\hat{T}^0)$.

In this case the concentrations of both components are higher than the equilibrium concentrations. Therefore, both components condensate during the whole process.

(5) Both components are initially in equilibrium: $\xi^0_{g1} = \xi_{eq}^g(\hat{T}^0)$, $\xi^0_{g2} = \xi_{eq}^g(\hat{T}^0)$.

These initial conditions do not satisfy inequality (18), therefore there is no boiling.

4.1.2. Characteristic times

In the considered problems there are two characteristic times, namely: i) a characteristic time related to evaporation/condensation, $\tau_{ev}$, ii) a characteristic time related to heating up/cooling, $\tau_h$. Typically the evaporation characteristic time is much smaller than the heating evaporation time, $\tau_{ev} \ll \tau_h$.

After a relatively long period of time, $t \gg \tau_{ev}$, the initial concentrations of the components are ‘forgotten’ and the behaviour of all the considered cases is almost identical. The behaviour of the system is determined mostly by the wall temperature or consequently, by the heat flux into the system. By contrast, for a short period of time, $t \sim \tau_{ev}$, the initial concentrations are very important but the influence of the wall temperature (heat flux) is negligible.

Accordingly, two sets of calculations are performed and discussed in this paper: one set of calculations is done for a short time $t_f = 0.2$ s and a second set is done for a long time, $t_f = 6 \times 10^3$ s.

It is reasonable to distinguish two types of equilibria, a) concentration equilibrium, and b) thermal equilibrium. For the concentration equilibrium the concentration of the component is equal, or almost equal, to the saturated concentration at the current temperature. The external heat flux is not zero, so the system can gain or lose internal energy. It is obvious that the system can be in concentration equilibrium in one component while simultaneously an other component can have a phase transition. By contrast, when there is a thermal equilibrium, the external heat flux is zero but the concentration of one component is not equal to the saturated value. Therefore, evaporation/condensation of the component takes place.

If the system is in concentration equilibrium in all components and simultaneously in thermal equilibrium, then the system is in a total equilibrium, or just in an
equilibrium. In this situation all processes are stopped, and the system will remain in such a state for an indefinite time.

### 4.2. Numerical results for cases with short period of calculation

It is possible to show that for a short period, \( t \sim \tau_{ev} \) the influence of the wall temperature (external heat flux) is not significant. Therefore for all the calculations in this subsection, one value of the wall temperature has been used, \( T_w = 270 \text{ K} \).

In Fig. 1 profiles of temperature, pressure and gas volume fraction are presented for all five cases under consideration. It can be seen that all the profiles display a monotonic behaviour.

In case 1 when the two components evaporate continuously with boiling, temperature decreases because of evaporation, whereas pressure and gas volume fraction increase. In case 2 ammonia (first component) condenses and water (second component) evaporates without boiling, the temperature increases in time while pressure and gas volume ratio are reduced. In this case there are two competing processes: the condensation of ammonia and the evaporation of water. In case 3 there is evaporation of ammonia and condensation of water with boiling. It is worth emphasising that while there is boiling in the system, simultaneously water condenses on the interface surface. The temperature reduces in time whereas the pressure and gas
volume fraction increase. In case 4 both components condense. The temperature increases in time owing to the condensation of both components whereas the pressure and gas volume fraction is reduced. In case 5 the initial concentrations are at equilibrium and therefore all the variables remain constant. Although, the external heat flux is not zero, as the wall temperature is different from the initial temperature of the mixture, its influence is not significant for such short times.

It is worth noting, that the pressures for all 5 cases do not approach the same value. This is because for all 5 cases the initial conditions for the gas concentrations do not approach the same value. This is because for all 5 cases the initial conditions for the gas concentrations

In Fig. 2 the gas (a) and liquid (b) concentrations of ammonia are presented. The gas concentrations of ammonia and water do not approach a single value as the mixture temperatures are different in each case.

All the evaporation rates (surface evaporation rate, bulk evaporation rate and total evaporation rate) of ammonia are presented in Fig. 3. As expected, all evaporation rate profiles monotonically approach zero, which corresponds to the concentration equilibrium state. The bulk evaporation rate is positive for both components only for the two cases 1 and 3 where boiling takes place.
4.3. Numerical results for cases with a large time calculation

In the case of a large time of calculation ($t \sim \tau_h$) the initial conditions for the gas concentrations are not so significant. For such long time lags the external heat flux starts to play a significant role. Here, as opposed to what happened in the previous subsection, the initial conditions for the gas concentrations are fixed and the wall temperature is varied in order to investigate the system dependence on the external heat flux. Namely three cases are considered:

1) heating, $T_w = 400$ K. In this case the external heat flux is positive, and the internal energy of the system is increasing in time,

2) cooling, $T_w = 270$ K. The external flux is negative which causes a decrease in the internal energy

3) equilibrium, $T_w = 335$ K. In this thermal equilibrium the external heat flux is zero and the system is in an equilibrium state.

The initial conditions for the gas concentrations for all the cases in this subsection correspond to the concentration equilibrium. They are fixed: $\tilde{\xi}_{g1}^0 = \xi_{g1}(\tilde{T}^0)$, $\tilde{\xi}_{g2}^0 = \xi_{g2}(\tilde{T}^0)$. In Fig. 4 the temperature, pressure and gas volume evolutions as functions of time are presented for the large time calculations.

The temperature of the system rises in time in the case of heating as the exter-
nal flux is positive. It approaches the wall temperature. The pressure also rises as a consequence of heating, and the gas volume fraction increases as a consequence of evaporation. In the case of cooling, the external heat flux is negative. Therefore, in contrast to the previous case, temperature, pressure and gas volume fraction decrease during the process. In the case of thermal equilibrium all the dependent variables remain constants and the external heat flux is zero.

The concentrations of ammonia in both phases are shown in Fig. 5. Owing to evaporation the gas concentration of ammonia is increasing and the liquid concentration is decreasing as would be expected.

In the case of cooling, the gas concentration of ammonia decreases and the liquid concentration of ammonia increases in time. For water, both concentrations in gas and liquid phases decrease.

All the evaporation rates for ammonia are plotted in Fig. 6. In the heating case there is boiling, so the bulk evaporation rate is not zero. Whereas for the equilibrium and cooling cases the bulk evaporation rates are zero.

It can be inferred from the plots that the ratio of the calculation periods for the long and short cases is equal to $3 \times 10^4$. Thus, for the values of the parameters we used, the system reaches a concentration quasi-equilibrium state after a very short period of time (in our case it is approximately 0.1 s). After that it evolves relatively
slowly to thermal equilibrium.

5. Conclusions

The main achievements of the work presented in this paper are:

- A novel mathematical model of non-equilibrium evaporation/condensation, including boiling, has been developed.
- A new relationship (16) to close the system of equations with boiling has been proposed. It has been shown that this equation well describes the behaviour of the physical system. It only requires an additional parameter which can be obtained from an experiment.
- A numerical code for the numerical solution of the differential-algebraic system has been developed. It was designed to solve both systems of equations with and without boiling and to switch from one regime to another, depending on the boiling condition (18).
- Numerical calculations of an ammonia-water system with different initial conditions corresponding to evaporation and/or condensation of both components, and wall temperature have been performed.
- It has been shown that, although the system quickly evolves to a quasi concentration equilibrium state (the differences between actual and equilibrium concentrations are rather small) it is necessary to use the non-
Fig. 6. Ammonia evaporation rates: (a) at the surface, (b) in the bulk, and (c) the total evaporation rate as function of temperature for the long period of calculation, $t \sim \tau_h$.

equilibrium evaporation model, Eqs. (5), (15) and (17) to calculate the evaporation/condensation rates as well as all the other dependent variables accurately.

Appendix

A. Derivation of the energy equation

According to the 1st law of thermodynamics the increase of the total internal energy of the system is equal to $Q$ the heat input (or output) by the surroundings to the system or in terms of rates:

$$\frac{dU}{dt} = \dot{Q}.$$  \hfill (A.1)

It is assumed that the rate of heat transfer from the surroundings to the system is given by

$$\dot{Q} = \lambda A_w (T_w - T),$$

where $T$ is the temperature of the system, $T_w$ the temperature of the wall, $\lambda$ the heat rate transfer coefficient, and $A_w$ the surface area for the heat transfer to the calorimeter. The total internal energy of the system can be written as

$$U = H - PV = H_g + H_l - PV,$$
where $H_g$ is the total enthalpy of the vapour phase and $H_l$ the total enthalpy of the liquid phase. Substituting this into the energy balance (A.1), one can find if $V$ is constant:

$$\frac{dH_g}{dt} + \frac{dH_l}{dt} - V \frac{dP}{dt} = \dot{Q},$$

Using the well-known thermodynamic relation, Smith et al., 2005

$$dH_k = C_{p_k}dT + V_k \left[ 1 - \frac{T}{V_k} \left( \frac{\partial V_k}{\partial T} \right) \right] dP + \sum_{i=1}^{n} H_{ki} dN_{ki},$$

here the subscript $k = g, l$ stands for the gas or liquid phase, the following relation is obtained

$$(C_{pg} + C_{pl}) \frac{dT}{dt} + \left\{ V_g \left[ 1 - \frac{T}{V_g} \left( \frac{\partial V_g}{\partial T} \right) \right] + V_l \left[ 1 - \frac{T}{V_l} \left( \frac{\partial V_l}{\partial T} \right) \right] \right\} \frac{dP}{dt} + \sum_{i=1}^{n} (H_{gi} - H_{li}) \frac{dN_{gi}}{dt} - V \frac{dP}{dt} = \dot{Q},$$

where $C_{pg}$ is the overall heat capacity of the vapour phase, $C_{pi}$ is the overall heat capacity of the liquid phase, $N_{gi}$ the number of moles of $i$-th species in the vapour phase, $N_{li}$ is the number of moles of $i$-th species in the liquid phase, $H_{gi}$ is the partial molar enthalpy of the $i$-th species in the vapour phase, and $H_{li}$ the partial molar enthalpy of the $i$-th species in the liquid phase. Using the species balance equation leads to

$$(C_{pg} + C_{pl}) \frac{dT}{dt} + \left\{ V_g \left[ 1 - \frac{T}{V_g} \left( \frac{\partial V_g}{\partial T} \right) \right] + V_l \left[ 1 - \frac{T}{V_l} \left( \frac{\partial V_l}{\partial T} \right) \right] \right\} \frac{dP}{dt} + \sum_{i=1}^{n} (H_{gi} - H_{li}) \frac{dN_{gi}}{dt} - V \frac{dP}{dt} = \dot{Q},$$

For an ideal gas $\frac{\partial V_g}{\partial T} = \frac{V_g}{T}$, so the first square brackets disappears. For the liquid phase the isobaric thermal expansivity, $(\frac{\partial V_l}{\partial T})/V_l$, is small and can be neglected. Therefore, the equation can be considerably simplified

$$(C_{pg} + C_{pl}) \frac{dT}{dt} - \alpha V \frac{dP}{dt} + \sum_{i=1}^{n} \Delta H_i S_{ev,i} = \dot{Q},$$

Substituting in the previous equation the following relations

$$C_{pg} = \sum_{i=1}^{n} N_{gi} c_{pg,i} = \alpha V \sum_{i=1}^{n} \xi_{gi} c_{pg,i},$$
$$C_{pi} = \sum_{i=1}^{n} N_{li} c_{pi,i} = (1 - \alpha) V \sum_{i=1}^{n} \xi_{li} c_{pi,i},$$

where $c_{pg,i}$ and $c_{pi,i}$ are the molar heat capacity of the $i$-th species in gas and liquid phase respectively, then dividing by $V$, it becomes

$$\left[ \alpha \sum_{i=1}^{n} \xi_{gi} c_{pg,i} + (1 - \alpha) \sum_{i=1}^{n} \xi_{li} c_{pi,i} \right] \frac{dT}{dt} - \alpha \frac{dP}{dt} + \sum_{i=1}^{n} \Delta H_i \frac{S_{ev,i}}{V} = \frac{\dot{Q}}{V}. \quad (A.2)$$
B. Parameter estimation

The values for the various physical properties that were used in the model are summarised in Tables [1] and [2] [Reid et al., 1987; Vargaftik 1975; Forsythe 2003; EngineeringToolBox].

Table 1. Parameters for Antoine’s equation (13).

| Species   | \( D_i \) [-] | \( B_i \) K   | \( T_i^a \) K |
|-----------|----------------|---------------|---------------|
| Ammonia   | 22.40          | 2363.24       | -22.62        |
| Water     | 23.50          | 3992.51       | -38.48        |

The heat of vaporisation was estimated using the Clausius-Clapeyron equation [Smith et al., 2005]

\[
\frac{\Delta h_i}{R_u} \approx \frac{d \ln(p_i(T))}{d(1/T)} = \frac{B_i}{(1 + T_i^a/T)^2}.
\]

All other parameters used to calculate characteristic scales, are summarised here: \( V = 10^{-3} \) m³, \( A_w = 6 \times 10^{-2} \) m², \( A = 10^{-1} \) m², \( \lambda = 25 \) J m⁻²s⁻¹K⁻¹. In all the calculations the time step was fixed. For the short period calculations \( \Delta t = 10^{-3} \) s, while for the long period calculations \( \Delta t = 10^{-2} \) s.

In the current model three empirical coefficients have been used. Namely: two accommodation coefficients \( \Gamma_1 \) and \( \Gamma_2 \), and one correction factor, \( \zeta \) for total bulk evaporation rate at boiling Eq. (17). For an accurate modelling, the values for these coefficients should be estimated from experiments, which is beyond the scope of this paper. For our calculations the following values \( \Gamma_1 = \Gamma_2 = 10^{-1} \) and \( \zeta = 10^{-1} \) mol s m⁻²kg⁻¹ have been used.

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