

A model for mass and heat transfer in an aerosol cloud

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Abstract

In mathematical models for heavy gas clouds dispersing in the atmosphere, two-phase dynamics is usually modelled using assumptions of homogeneous equilibrium. This implies that the mixture of liquid droplets and gas is homogeneous and in thermodynamic equilibrium at all times. This paper discusses a more rigorous approach for modelling the thermodynamical aspects of heavy gas dispersion. A model is presented for the evaporation and condensational growth of a monodisperse binary droplet population, including also the influence of air entrainment. The model evaluates the thermodynamical evolution of a five-component aerosol mixture, consisting of two-component droplets and a three-component gas. The model has been applied for evaluating two-phase ammonia clouds released in both dry and moist air. The numerical results show the influence on contaminant concentration of the droplet size, the atmospheric moisture and the non-ideality of a liquid solution.

1. Introduction

This study was part of work in developing mathematical models for estimating the atmospheric dispersion of accidental hazardous releases. Releases of liquefied toxic or flammable gases may take place in aerosol form, consisting of vapour and liquid droplets of the released species together with entrained humid air. This has been demonstrated in several laboratory and field-scale experiments (for instance, [1–4]). Aerosol phenomena may have a significant influence on the temperature and density evolution of the source term, and on the subsequent heavy gas dispersion. In particular, the deposition of substance liquid droplets may, under certain conditions, cause a substantial decrease of concentration (for instance, [5]).

Since the early 1970s, numerous mathematical models have been presented for the dispersion of heavier-than-air clouds, and considerable progress has been made both

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theoretically and experimentally; for reviews the reader is referred to [6–9]. However, two-phase dynamics are either ignored or treated in a very simple way, whether these models are fairly simple integral (or box) models, or more complex three-dimensional fluid models. Practically all of these models rely on the homogeneous equilibrium assumptions, implying that the liquid is uniformly distributed in the cloud and that the liquid and the gas are at a uniform temperature and in thermodynamical equilibrium. However, no convincing justification has been presented up to now on the validity of the assumptions of homogeneous equilibrium; neither have the limits of applicability of this model been determined.

The purpose of this paper is to present the basic assumptions and the mathematical structure of a more general non-equilibrium model. The homogeneous equilibrium model is the limiting case of the aerosol model presented, when the cloud is well mixed, and the droplet–gas equilibration processes are rapid compared to the rate at which other processes occur. This study is closely related to cooperative papers by the present authors and the UKAEA Consultancy Services [10, 11], in which the limits of applicability of the homogeneous equilibrium assumptions have been tested in more detail. These investigations have shown that the simpler model does indeed provide a good description for some envisaged release situations, and guidance is given on where the homogeneous equilibrium model is not likely to be adequate.

Physically, the composition and temperature of the gas around the droplets is constantly changing due to the condensation and evaporation processes, and to entrainment. For instance, the evaporation of contaminant tends to cool the gas and increase the concentration of contaminant vapour in the gas. The changes in the composition and temperature of the gas in turn have an influence on the behaviour of the droplets.

Here we do not consider in detail the modelling of the mass and heat transfer processes from the droplet surface into the surrounding gas, as this has been the topic of earlier papers. The quasistationary evaporation or condensation of droplets has been addressed in detail by Kukkonen et al. [12], Kulmala and Vesala [13], Vesala and Kukkonen [14] and Vesala and Kulmala [15], see also Kulmala et al. [16]. Vesala [17] has discussed the validation of various mass flux and droplet temperature equations against laboratory-scale experimental data. Vesala and Kulmala [15] have addressed the validation of the mass and heat transfer models used in this study, although without the inclusion of entrainment. We assume here that the mass fluxes of the two evaporating or condensing species are known, and proceed to model the consequent mass and heat balances between the droplet population and the gaseous mixture. In other words, the model allows for the entrainment of humid air into the aerosol cloud.

Mathematical models for droplet vaporisation and condensation have recently been developed also by Hewitt and Pattison [18], with the aim of incorporating the aerosol model into a heavy gas dispersion model. Woodward and Papadourakis [19] have presented a two-phase jet model, including a description of droplet vaporisation.

Most of the heavier-than-air cloud field experiments have focused on the dispersion of gaseous clouds. However, there are some experiments with two-phase effects, e.g. the Desert Tortoise, Eagle and Goldfish series [9]. In particular, the Desert Tortoise

series was designed to study the dispersion of two-phase ammonia clouds. It was reported that two-phase effects had a dominating influence on the temperature and spreading behaviour of the cloud, and the extent of the heavy cloud dispersion regime [1]. Recently, Nolan et al. [3], Moodie and Ewan [2] and Johnson [20] have studied two-phase source terms on the laboratory scale. Johnson [20] has presented results on the deposition of contaminant liquid versus liquid superheat for six substances. Nolan et al. [3] and Moodie and Ewan [2] have also presented measurements on droplet characteristics, including size and number concentration.

The model here presented treats the gas phase mass fluxes and the amount of entrained air as input variables for which appropriate correlations can be adopted. We utilize in the numerical computations the entrainment data from the heavier-than-air cloud dispersion model DRIFT [21].

We do not attempt here an experimental testing of the model presented against the above experiments. However, we have illustrated the model predictions by evaluating two-phase ammonia clouds released in both dry and moist air. The main objective has been to show the influence on the evolution of contaminant concentration of the most important thermodynamic variables. We disregard depletion of liquid due to deposition for the sake of a clear thermodynamic interpretation of numerical results, although it would surely be an important process at larger droplet sizes.

2. Theory

2.1. Statement of the problem

Consider a system consisting of binary (two-component) droplets in the continuum regime together with the surrounding gas (such as air) and the vapours of species forming the droplet. In the following we refer to the gaseous phases of the two condensing or evaporating species simply as “the vapours”, and to the mixture of air and the two vapours as “the surrounding gas”, or “the gas”. The total mass of humid air within the system is time-dependent, while the total mass of contaminant is assumed to be constant, i.e., the deposition of droplets and the contaminant vapour is neglected. We refer to the system of droplets and gas as “the cloud”.

The droplets are assumed to contain no impurities. They are also assumed to be spherical and falling freely. They are assumed to be well mixed; the validity of this assumption has been studied in detail by Vesala [22]. The gas is assumed to behave as an ideal gas. The total number of droplets is constant, i.e., the coagulation of droplets is neglected. The total pressure is assumed to be equal to atmospheric pressure at all times. Finally, the droplet population is assumed to be monodisperse and uniformly distributed in the gas.

In the following, we derive equations for the rate of change of quantities related to (i) the droplet population (the total mass of the droplets, the droplet composition and the droplet temperature) and (ii) the gas (the gas temperature, the droplet number concentration and the gas composition, i.e., the partial vapour pressures in the gas).

2.2. Change of quantities related to the droplet population

The change of the total mass of a droplet

The droplet evaporation or condensation rate is described by means of the mass and heat fluxes from the droplet into the surrounding gas. In the following, the two condensing or evaporating species are denoted with the subscripts 1 and 2. In a steady state the mass fluxes are constant according to the equation of continuity, and the quasisteady change of the droplet mass m_d is by definition equal to the sum of the mass fluxes of species 1 and 2 from the droplet surface into the gas

$$\frac{dm_d}{dt} = I_1 + I_2. \quad (1)$$

The positive radial direction has been chosen to be into the droplet (i.e., condensation corresponds to a positive mass flux). Generally, the mass fluxes depend on the droplet radius, the total gas pressure, the droplet and gas temperatures, the mole fractions of the vapours just above the droplet surface and far from it, and the diffusivities of vapours in the gas mixture.

The change of the droplet composition

In order to determine the mass fluxes the composition of the droplet must be known. A direct consequence of the definition of the mass fluxes ($I_i = dm_i/dt$, $i = 1, 2$) is that the change of the mass fraction x_i of species i in the droplet can be written as

$$\frac{dX_i}{dt} = \frac{d}{dt} \left[\frac{m_i}{m_1 + m_2} \right] = \frac{I_i - x_i(I_1 + I_2)}{m_d}, \quad (2)$$

where m_i is the mass of species i within the droplet.

The change of the droplet temperature

In order to determine the mass fluxes the droplet temperature must also be known. An equation for the quasisteady droplet temperature can be derived using energy conservation. The time rate of change of the total droplet enthalpy H_d due to condensation and evaporation is

$$\frac{dH_d}{dt} = h_{1l} I_1 + h_{2l} I_2 + m_d \bar{c}_d \frac{dT_d}{dt}, \quad (3)$$

where h_{1l} is the liquid specific enthalpy of species i for the liquid mixture, \bar{c}_d is the average specific heat capacity of the droplet and T_d is the droplet temperature. The first two terms on the right-hand-side of Eq. (3) represent changes of the liquid phase enthalpies of species 1 and 2 in the droplet, and the third term represents the change of the total droplet enthalpy due to the change in the droplet temperature.

The formation of a real solution occurs with a release or an absorption of heat, which is given by the excess enthalpy; this is taken into account in the value of the liquid specific enthalpy in Eq. (3). The correlations for the partial mixing enthalpies of

ammonia and water for the low temperature range are given by Vesala and Kukkonen [14]. The average specific heat capacity of the droplet can be estimated by assuming that it is a mass fraction average of the pure component values (contaminant liquid and liquid water). For more detailed correlations for mixture specific heat capacities, the reader is referred to [23].

The heat flux Q from the gas into the droplet is given by

$$Q = h_{v1}I_1 + h_{v2}I_2 + 4\pi ak(T_g - T_a), \quad (4)$$

where h_{vi} is the vapour specific enthalpy of species i , a is the droplet radius, k is the thermal conductivity of the gas and T_g is the temperature of the gas. The first two terms on the right-hand-side of Eq. (4) represent the enthalpies carried by the vapour molecules of the condensing or evaporating species, and the third term represents thermal conduction from the gas into the droplet.

Noticing that $dH_d/dt = Q$ yields

$$\frac{dT_a}{dt} = \frac{L_1I_1 + L_2I_2 + 4\pi ak(T_g - T_a)}{m_d \bar{c}_d}, \quad (5)$$

where $L_i = h_{vi} - h_{li}$ is the heat of vaporisation for species i , and the vapour specific enthalpy is evaluated at the droplet temperature. Kulmala and Vesala [13] have discussed alternative methods for modelling the droplet temperature, also taking into account the temperature dependencies of the vapour phase enthalpies.

2.3. Change of quantities related to the gas

Eqs. (1)–(5) form a complete set of equations for describing the evolution of a single droplet in an infinite volume of gas, with no entrainment. Assume that the gas temperature and the partial vapour pressures vary sufficiently slowly in a sphere with a radius considerably greater (say, ten times the droplet radius) than the droplet radius, but smaller than half of the mean droplet distance. Then the single droplet model can be extended to a monodisperse droplet population [24].

We have generalised this concept for an aerosol cloud with air entrainment. In the following, the gas temperature and the partial vapour pressures in the gas are allowed to change due to the mutual influence of evaporating or growing droplets, and the entraining humid air. It is assumed that the entrained air will be sufficiently rapidly distributed uniformly into the cloud.

The change of the gas temperature

The temperature of the gas changes due to the thermal conduction between the droplets and the gas and due to the entrainment of air, i.e.,

$$\frac{dT_g}{dt} = \left(\frac{dT_g}{dt}\right)_{tc} + \left(\frac{dT_g}{dt}\right)_{ent}. \quad (6)$$

The change of the gas temperature due to thermal conduction is

$$\left(\frac{dT_g}{dt}\right)_{tc} = \frac{N \left(L_1 I_1 + L_2 I_2 - m_d \bar{c}_d \frac{dT_a}{dt} \right)}{\bar{c}_g m_g} \quad (7)$$

where N is the number of droplets, \bar{c}_g is the average specific heat capacity of the gas and m_g is the mass of gas. Eq. (5) was used in deriving this equation. The average specific heat capacity of the gas is estimated by assuming that it is the mass fraction average of the pure component values (contaminant vapour, water vapour and dry air).

The temperature change of the gas due to the entrainment of air is

$$\left(\frac{dT_g}{dt}\right)_{ent} = \frac{(T_{amb} - T_g) \bar{c}_{amb} G_{ent}}{\bar{c}_g m_g}, \quad (8)$$

where T_{amb} is the temperature of the ambient gas and \bar{c}_{amb} is the average specific heat capacity of the ambient gas. \bar{c}_{amb} was estimated by assuming it to be a mass fraction average of the pure component values (dry air and water vapour). The quantity G_{ent} is defined as the mass flux of air into the gas cloud,

$$G_{ent} = \frac{dm_{g,ent}}{dt}, \quad (9)$$

where $m_{g,ent}$ is the mass of entrained air.

Finally, combining results (7) and (8) gives

$$\frac{dT_g}{dt} = \frac{N \left(L_1 I_1 + L_2 I_2 - m_d \bar{c}_d \frac{dT_a}{dt} \right) + (T_{amb} - T_g) \bar{c}_{amb} G_{ent}}{\bar{c}_g m_g}. \quad (10)$$

The change of the droplet number concentration

The droplet number concentration is defined as the number of droplets in a unit volume of the cloud. Using the ideal gas law for writing the cloud volume gives

$$C_N = \frac{Np}{nRT_g}, \quad (11)$$

where p is the total pressure, n is the number of moles in the gas and R is the universal gas constant. As the total number of droplets and the total pressure are constant, differentiation of this equation gives

$$\frac{dC_N}{dt} = -\frac{C_N}{T_g} \frac{dT_g}{dt} - \frac{C_N}{n} \frac{dn}{dt}. \quad (12)$$

The total amount of moles in the gas changes due to the evaporation and condensation processes, and entrainment of air.

$$\frac{dn}{dt} = \left(\frac{dn}{dt}\right)_{e/c} + \left(\frac{dn}{dt}\right)_{ent} = -N\left(\frac{I_1}{M_1} + \frac{I_2}{M_2}\right) + \frac{G_{ent}}{\bar{M}_{amb}}, \tag{13}$$

where M_i is the molar mass of species i and \bar{M}_{amb} is the average molar mass of the ambient air, defined as

$$\bar{M}_{amb} = X_{amb,1}M_1 + X_{amb,2}M_2 + X_{amb,air}M_{air}, \tag{14}$$

where $X_{amb,i}$ and $X_{amb,air}$ are the mole fractions of species i and dry air in the ambient air, and M_{air} is the molar mass of dry air. In this study the mole fraction of contaminant vapour in the ambient air is assumed to be negligible.

Finally, combining the above results gives

$$\frac{dC_N}{dt} = -\frac{C_N}{T_g} \frac{dT_g}{dt} + \frac{C_N N}{n} \left(\frac{I_1}{M_1} + \frac{I_2}{M_2}\right) - \frac{C_N G_{ent}}{n \bar{M}_{amb}}. \tag{15}$$

On the right-hand-side of Eq. (15), the first term is due to the change in the cloud volume caused by the temperature change of the gas, the second term is due to the change in the number of gas molecules caused by evaporation and condensation, and the third term is due to the change in the cloud volume caused by entrainment.

The change of the partial vapour pressures

The partial vapour pressure p_i of species i is given by

$$p_i = \frac{n_i}{n} p, \tag{16}$$

where n_i is the amount of vapour moles of species i . Differentiation of this equation gives

$$\frac{dp_i}{dt} = \frac{p}{n} \frac{dn_i}{dt} - \frac{n_i p}{n^2} \frac{dn}{dt}. \tag{17}$$

The total amount of species i in the gas changes due to evaporation and condensation processes and entrainment, i.e.,

$$\frac{dn_i}{dt} = -N \frac{I_i}{M_i} + \frac{X_{amb,i} G_{ent}}{\bar{M}_{amb}}. \tag{18}$$

Finally, combining Eqs. (17) and (18), and using Eq. (13), one obtains for species 1

$$\frac{dp_1}{dt} = \frac{N}{n} \left(\frac{I_1}{M_1}(p_1 - p) + \frac{I_2}{M_2}p_2\right) + \frac{(p_{amb,1} - p_1)G_{ent}}{\bar{M}_{amb}n}. \tag{19}$$

The equivalent equation for species 2 is found by interchanging subscripts “1” and “2” in Eq. (19).

2.4. The influence of the convective mass and heat transfer

If the droplet is moving with respect to the surrounding gas, the rates of mass and heat transfer are increased due to forced convection. We have applied semi-empirical methods for estimating the effect of convection due to free fall. The purely diffusive mass fluxes are multiplied by the droplet Sherwood number, and the thermal conductivity of the gas mixture, which corresponds to the purely conductive heat flux, is multiplied by the droplet Nusselt number [25, 12]. To evaluate these dimensionless factors, the terminal settling velocity of the droplet is computed from standard equations [26].

3. The numerical model

We have written a computer program – AERCLOUD (AERosol CLOUD) – for solving the above equations. The coupled differential Eqs. (1), (2), (5), (10), (15) and (19) are solved using the NAG-library FORTRAN-routine D02EBF [27], which applies the variable-order, variable-step Gear Method. The numerical error of the solution was set to be smaller than 0.1%.

For the numerical results of this study the mass fluxes were evaluated from the uncoupled (the vapours diffuse as though independent) equations derived by Kulmala and Vesala [13], and the thermal diffusion was neglected. The computer program also includes the exact, coupled expressions [28, 29, 14], as alternative computational procedures. However, their use requires a substantial amount of computational time, as a set of two non-linear algebraic equations has to be solved. The importance of the diffusion coupling for ammonia–water droplets in the air has been analyzed by Vesala [17] and by Vesala and Kulmala [15], and has been found to be of minor importance.

Finally, various physicochemical properties of ammonia–water mixtures are required for the model computations. The data were adopted from the literature [30–34, 23], and summaries of the required correlations have been reported by Vesala [17], Kukkonen et al. [12], Vesala et al. [35] and Vesala and Kukkonen [14]. In estimating the mass flux of water we have used the binary diffusion coefficient of water in air, although in the numerical computations of this study the cloud initially consists mainly of ammonia vapour. However, the numerical results show that the resulting inaccuracy is negligible.

4. Results and discussion

4.1. General considerations

We have illustrated the model predictions by evaluating two-phase ammonia clouds released in dry and moist air. The numerical test cases are identical to those in the paper [10], which presents a comparison of the model AERCLOUD and the thermodynamical submodel of the heavy cloud dispersion program DRIFT [21].

We shall use predictions on the mass of entrained air from the code DRIFT. An aerosol cloud is modelled with the same initial content using the code AERCLOUD, importing air into it at the time-dependent rate given by DRIFT. In this way we need not couple the model AERCLOUD explicitly to a heavy gas dispersion model. The DRIFT model relies on the homogeneous equilibrium assumption.

This test relies on DRIFT's predictions for mixing rates being at least approximately correct. It is therefore important to note that mixing rates are to first order determined by the cloud slumping rate and atmospheric turbulence and that aerosol effects are secondary for the mixing process. It is also important to note that the dilution rates predicted by DRIFT compare very favourably with field and wind-tunnel experiments on both gas and aerosol clouds (including ammonia and hydrogen fluoride cases), as has been demonstrated by Jones et al. [36], Jones et al. [37], and Webber et al. [38]. We can therefore confidently exclude this possible source of an erroneous result.

It is important to distinguish between vaporisation and condensation, and deposition phenomena. The prime objective here is to examine the vaporisation and condensation processes, and so we shall ignore deposition in the following, however large the droplets. The gravitational settling velocities of 10, 100 and 1000 μm ammonia droplets in dry air are about 0.01, 0.5 and 5 m/s, respectively.

In fact deposition can be handled in exactly the same way as air entrainment: in this case it is a sink of contaminant which will change the molar concentrations in the cloud. If deposition is rapid compared to air entrainment then it will all happen close to the source; if it happens on the same time scale, then any conclusions about the competing rates of equilibration and entrainment will also apply when deposition is present.

The mathematical model makes assumptions about homogeneity of the cloud; we are assuming homogeneity, or at least an approximately self-similar global inhomogeneity. However, equilibrium is regarded as the most questionable part of the homogeneous equilibrium assumption; in the instantaneously released cloud flow considered here, there is evidence (see for example [39] for a discussion of the Thorney Island Trial data) that the strong frontal gravity current vortices mix the cloud reasonably well, at least in the early stages where aerosol effects are likely to be most important.

The convective fluxes of mass and heat increase the purely diffusive mass transfer and the purely conductive heat transfer substantially for large droplets. The expressions for the convective fluxes are not valid for very high droplet number concentrations. We therefore believe it prudent to make estimates using two model options: including and excluding convective mass and heat transfer.

4.2. Selection of cases

We have made predictions for instantaneous releases of a pure ammonia cloud into both dry and humid air. A summary of the initial and ambient conditions for the cases chosen is shown in Table 1.

Liquid and vapour deposition were neglected, and we assumed that there is no heat transfer from the ground into the cloud. The ambient temperature was taken to be

Table 1
A summary of the cases selected for the numerical results

Case	Ambient air relative humidity (%)	Solution in liquid phase	Contaminant liquid fraction
01	0.00	—	85
02	0.00	—	60
03	0.00	—	30
11	99.99	Ideal	85
12	99.99	Ideal	60
13	99.99	Ideal	30
21	99.99	Interactions	85
22	99.99	Interactions	60
23	99.99	Interactions	30

+15 °C, the Pasquill-class was D, the average wind velocity at a height of 10 m was 2 m/s, and the roughness length was 6 mm.

The total mass of contaminant was taken to be 10 000 kg, which is roughly two or three times the mass of the initial gas cloud in the Thorney Island field experiments [40]. The flashing has been assumed to have taken place, and therefore the pressure is atmospheric and the initial contaminant temperature is equal to the boiling point of ammonia (–33 °C). The initial contaminant liquid fraction by mass was assumed to be 30, 60 or 85%. The value of 85% corresponds approximately to the largest possible liquid fraction after flashing has taken place, and the values of 30 and 60% correspond to cases where part of the released ammonia has been stored in vapour form.

In order to illustrate the effects of atmospheric moisture, we have included the case of dry air and that of 99.99% relative humidity; this is effectively the maximum humidity short of introducing fog. Two options were used for the interactions of ammonia and water in liquid phase: assuming an ideal solution and allowing for the actual interactions. Ammonia and water behave attractively in liquid phase, and the activity coefficients are therefore smaller than unity; respectively, the partial mixing enthalpies are negative [14, 41]. For an ideal solution, the activity coefficients are equal to unity and the partial mixing enthalpies vanish.

4.3. Numerical results

We have evaluated cases 01, 11, 21 and 23 in more detail. The droplet size regime considered ranges from 1 µm to 1000 µm. The curves including and excluding the convective mass and heat transfer have been marked in the figures with “ventilation” and “no ventilation”, respectively. The droplets consist initially of pure ammonia; ammonia then vaporises and water vapour condenses onto the droplet surface.

Fig. 1 shows the evolution of the droplet radius for case 21, for the initial droplet radius values of 1000, 700, 500, 300 and 100 µm. The evaporation of droplets is qualitatively similar to the evaporation of a single ammonia droplet in humid air [14]. Two effects of the condensation of water vapour can be seen, particularly for the

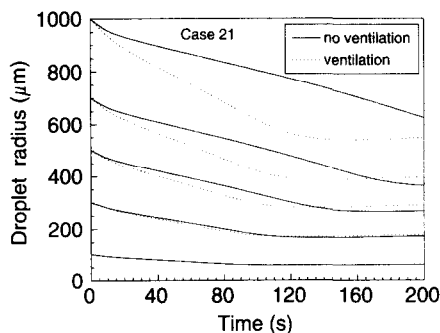


Fig. 1. Droplet radius vs. time for case 21. The curves are shown for five different initial droplet radii, using two model options: including and excluding convective mass and heat transfer.

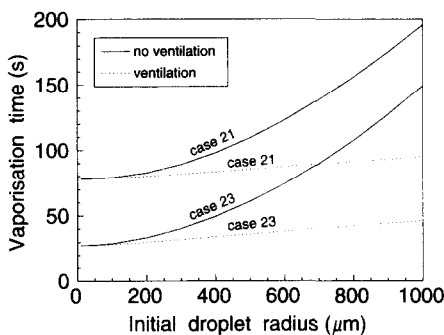


Fig. 2. The ammonia vapourisation times for cases 21 and 23, for initial droplet radii from 10 to 1000 µm.

curves with ventilation. (i) At small elapsed times latent heat released by the condensing water vapour tends to raise the droplet temperature and therefore enhances the vaporisation of ammonia. (ii) At larger elapsed times the concentration of ammonia in the droplet decreases with increasing water amount. For a large dilution, the mole fraction of ammonia and the activity coefficient are small, which reduces the evaporation rate of ammonia. These effects can also be seen for the curves with no ventilation, although not so clearly.

The vaporisation of ammonia is more efficient for a ventilated droplet, and a nearly pure water droplet is formed earlier, compared to a non-ventilated droplet. For some of the curves it is actually seen that the droplets are slowly growing at large elapsed times, due to water vapour condensation.

Fig. 2 presents a comparison of the vaporisation times of ammonia in two cases, 21 and 23. The vaporisation time has been defined here as the time by which 80% of the liquid ammonia within the droplet has been vaporised. This choice of definition may need some clarification. For high values of the relative humidity, ammonia

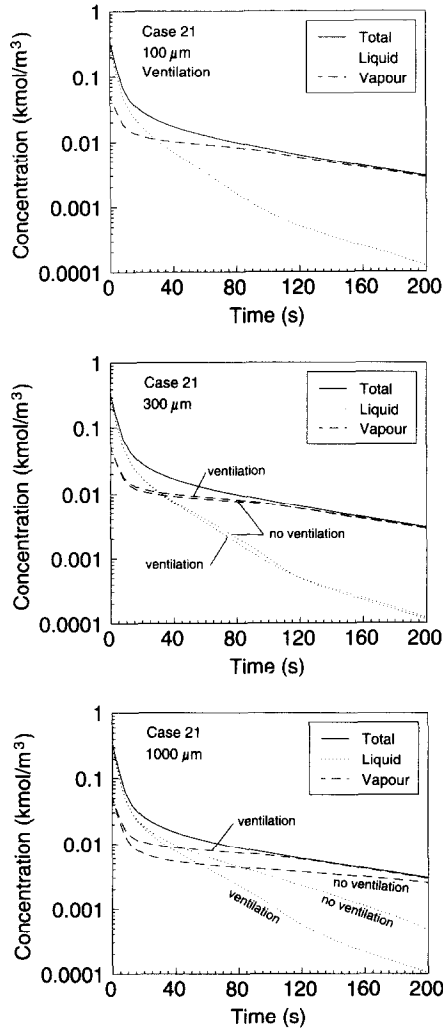


Fig. 3a–c. The contaminant molar concentration vs. time for case 21, for three values of the initial droplet radius (100, 300 and 1000 μm). The curves are shown for liquid, vapour, and total concentrations. For an initial droplet radius of 100 μm, the curves including and excluding droplet ventilation are indistinguishable.

vaporisation is strongly suppressed at large elapsed times by the condensation of liquid water, which eventually constitutes most of the mass within the droplets. The times of vaporisation of, for instance, 95% or 99% of the liquid ammonia would therefore be strongly dependent on processes within a very dilute droplet. The 80% vaporisation time is better representative for the behaviour of the major fraction of contaminant.

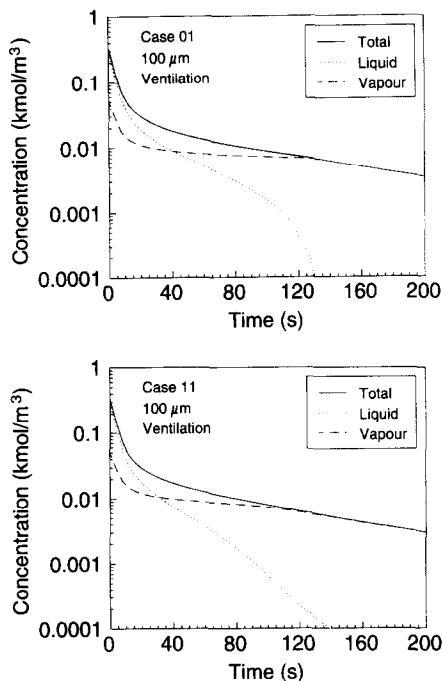


Fig. 4a–b. The contaminant molar concentration vs. time for cases 01 and 11, for an initial droplet radius of 100 μm. The curves are shown for liquid, vapour and total concentrations.

Fig. 2 shows clearly the enhancement of ammonia vaporisation due to the convective mass and heat transfer; the magnitude of this effect increases with the initial droplet radius. For case 23 a smaller fraction of ammonia is initially in liquid form, and the droplet number concentration within the cloud is therefore smaller, compared to case 21. A smaller droplet number concentration causes a more rapid vaporisation of contaminant, as the cloud will be less cold and the vapour pressure of contaminant in the cloud will be smaller.

Figs. 3a–c show the liquid, vapour and total concentration of ammonia versus time for case 21. The curves are shown for three values of the initial droplet radius, including and excluding droplet ventilation. The total concentration of contaminant is almost identical for these three figures, as the numerical tests were designed so that the entrainment of air versus time is the same by definition. The slight differences of the total concentration are due to differences in cloud volume, caused by temperature changes.

Figs. 3a–c show that the ammonia liquid is almost completely vaporised during 200 s in all three cases. The influence of droplet ventilation decreases with decreasing initial droplet radius, and for a droplet radius of 100 μm (or smaller), the influence of ventilation on the contaminant vaporisation is negligible. As already stated earlier, ventilation enhances the vaporisation of ammonia at small elapsed times; the corresponding behaviour is also seen in the contaminant vapour curves.

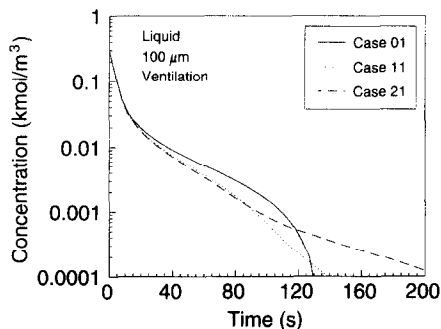


Fig. 5. The molar concentration of contaminant liquid vs. time for cases 01, 11 and 21. The initial droplet radius is 100 μm .

Figs. 3a–c show that the influence of the initial droplet size on the vaporisation rate of ammonia is fairly small, unless the droplet radius is of the order of a few hundred micrometres or larger. One reason for this phenomenon is that the evaporation–condensation process within a cloud is self-controlling, with a negative feedback. For instance, consider the vaporisation of fairly small droplets. The vaporisation of contaminant is more efficient (compared to large droplets), which causes a lower cloud temperature and a larger contaminant vapour pressure in the cloud. This in turn reduces the rate of vaporisation. For large droplets, the changes in the gas properties due to vaporisation are smaller, which tends to allow a correspondingly more efficient vaporisation.

Finally, we illustrate the influence on contaminant vaporisation of atmospheric moisture and the solution effects in liquid phase. Figs. 4a–b show the liquid, vapour and total concentration of ammonia versus time for the cases 01 and 11, for the initial droplet radius of 100 μm . The respective curves for case 21 have already been presented in Fig. 3a. As defined in Table 1, case 01 is a release of two-phase ammonia cloud into dry air, case 11 is the respective release in moist air, assuming an ideal solution of ammonia and water in liquid phase, and case 12 is identical to case 11 except that non-ideality of solution was properly taken into account. In all three cases 85% of contaminant is initially in liquid form.

For comparison purposes, the contaminant liquid concentration curves have been redrawn in Fig. 5. Again the results show that the influence of ambient moisture is to increase the rate of vaporisation at small elapsed times, and suppress it at larger times. The solution effects have only a slight influence on vaporisation at small elapsed times, while at larger times they decrease even further the rate of ammonia vaporisation.

5. Conclusions

In the currently-used heavier-than-air cloud dispersion models two-phase dynamics is commonly treated using the homogeneous equilibrium assumptions. However, no

convincing justification has yet been presented for their validity, and the limits of applicability of this model have not been determined. We have presented a more rigorous non-equilibrium model for evaluating the thermodynamical behaviour of two-phase clouds.

This approach considers the actual phase composition of the cloud, as binary (two-component) droplets together with the surrounding gas. The mass and heat transfer processes from the droplets into the surrounding gas are then modelled in detail. The rates of these processes are strongly dependent on the rates of diffusion and thermal conduction in the gas. For large droplets the ventilation of droplets due to their free fall is also an important factor, as it causes enhancement of mass and heat transfer by forced convection. The droplets and the gas are not generally in thermal equilibrium, and the deviation from equilibrium is determined by the rates at which mass and heat can be transported in the mixture.

The thermodynamical non-equilibrium effects in a two-phase cloud have two essential consequences: (i) the thermodynamical behaviour of the mixture is different, in particular the temperature and density evolution, and (ii) the deposition of contaminant liquid may cause a decrease of concentration. Our prime objective here was to examine the vaporisation and condensation processes, and we have therefore ignored deposition. However, the deposition of droplets is surely an important process in some conditions; clearly, deposition is highly sensitive to droplet size.

The model was applied for evaluating instantaneous releases of a pure ammonia cloud into dry and into humid air. Numerical results show the influence of the initial droplet radius, the atmospheric moisture and the non-ideality of liquid solution on the evolution of contaminant concentration. Entrainment is not calculated explicitly but the rate of imported air is assumed to be known, and was derived from the heavier-than-air cloud model DRIFT.

Ammonia liquid was almost completely vaporised during 200 s in the considered cases. The ventilation of droplets substantially enhances the vaporisation of ammonia for large droplets; however, its influence decreases with decreasing droplet radius. For an initial droplet radius of 100 μm or smaller, the influence of droplet ventilation on the contaminant vaporisation was found to be negligible in the cases considered.

The influence of the initial droplet size was found to be fairly small, unless the droplet radius was a few hundred micrometers or larger. One reason for this behaviour is that the evaporation–condensation process within a cloud is self-controlling. For instance, smaller droplets are vaporised more efficiently, causing a lower cloud temperature and a larger contaminant vapour pressure in the cloud; this in turn reduces the rate of vaporisation. In contrast, the more slowly vaporising larger droplets cause smaller changes in gas properties, with less suppression of vaporisation. The influence of the initial droplet size is therefore smaller than would be expected if one considered only the numerical results from single-droplet evaporation theory. Clearly, the influence of the initial droplet size on the cloud properties might be much larger if the deposition of droplets were to be allowed for in the computations.

The condensation of water onto the surface of the ammonia droplets has two consequences: (i) it enhances the vaporisation of ammonia due to the release of latent

heat, and (ii) on the other hand it suppresses ammonia vaporisation due to the dilution of the droplet. The net effect of these competing processes is that initially ammonia is more efficiently vaporised, and at larger elapsed times the rate of vaporisation is decreased, compared with the corresponding case with no ambient humidity.

The solution effects of ammonia and water in liquid phase only have a slight influence on ammonia vaporisation at small elapsed times, while at larger times they even further decrease the rate of ammonia vaporisation. The reason is that for highly dilute mixtures the activity coefficient of ammonia is much less than unity; physically, ammonia molecules are effectively attracted by the liquid water molecules in a dilute mixture.

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Nomenclature

a	droplet radius (m)
c	specific heat capacity ($J/(kg\ K)$)
C_N	droplet number concentration ($1/m^3$)
G	mass flux (kg/s)
h_{ij}	specific enthalpy of species j , phase i (J/kg)
H	total enthalpy (J)
I	mass flux (kg/s)
k	thermal conductivity ($J/(s\ m\ K)$)
L	specific latent heat of vaporisation (J/kg)
m	mass (kg)
M	molar mass ($kg/kmol$)
n	number of moles
N	number of droplets
p	pressure (Pa)
Q	heat flux (J/s)
R	universal gas constant ($J/(mol\ K)$)

<i>T</i>	temperature (K)
<i>t</i>	time (s)
<i>V</i>	volume (m ³)
<i>x</i>	mass fraction
<i>X</i>	mole fraction

Subscripts

<i>a</i>	droplet surface
air	air
amb	ambient
e/c	evaporation or condensation
cl	cloud
d	droplet
ent	entrainment
g	gas
tc	thermal conduction
1, 2	condensing or evaporating species

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