

THEORY

UDM THERMODYNAMICS

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This report describes the thermodynamics module included in the Unified Dispersion Model (UDM). UDM invokes the thermodynamics module while solving the dispersion equations in the downwind direction. The module describes the mixing of the released pollutant with moist air, including possible water-vapour and heat transfer from the substrate to the cloud. The module calculates the phase distribution and vapour temperature. Additional droplet equations may be solved to determine the droplet trajectories, droplet mass and droplet temperature. Rainout of the liquid pollutant occurs if the droplet size is sufficiently large.

Reference to part of this report which may lead to misinterpretation is not permissible.





No.	Date	Reason for Issue	Prepared by	Verified by	Approved by
1	1999	PHAST 6.0	Witlox		
2	Aug 2005	SAFETI 6.5	Witlox	Harper	
3	Nov 2009	Phast 6.6	Harper		
4	Sep 2017	Phast 8.0	Witlox		
5	Dec 2020	Generalised multiple aerosol algorithm	Witlox	Harper	
6	May 2021	Apply new template	D. Vazier		

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ABSTRACT

This report describes the thermodynamics module included in the Unified Dispersion Model (UDM). UDM invokes the thermodynamics module while solving the dispersion equations in the downwind direction. The module describes the mixing of the released pollutant with moist air, and may take into account water-vapour and heat transfer from the substrate to the cloud. The module calculates the phase distribution [pollutant (vapour, liquid), water (vapour, liquid, ice)], vapour and liquid cloud temperature, and cloud density. Thus separate water (liquid or ice) and pollutant (liquid) aerosols may form.

The liquid pollutant in the aerosol is considered to consist of spherical droplets and additional droplet equations may be solved to determine the droplet trajectories, droplet mass and droplet temperature. Rainout of the liquid pollutant occurs if the droplet size is sufficiently large.

The UDM includes the following types of thermodynamic models:

- 1) Equilibrium model (no reactions). Thermal equilibrium is assumed, which implies that the same temperature is adopted for all components in the cloud (vapour and liquid). The equilibrium model determines the phase distribution and the mixture temperature. Separate droplet equations are solved to determine the droplet trajectories (and the point of rainout).

The released pollutant is normally modelled as a single 'pseudo-component'. For 'multi-component modelling' the model has been generalised to allow the mixing of moist air with a pollutant consisting of a mixture of non-reactive chemicals (including possibly air and water). Each of the pollutant components may occur in both liquid and vapour phase. Two methods have been implemented:

- a) The first method presumes a single aerosol including possibly both pollutant and water. It is based on phase equilibrium calculations using the new multi-component property system XPRP.
 - b) The second method allows for non-interacting multiple aerosols, with ideal mixing presumed of the components within each aerosol. It is based on the multi-component method developed by Witlox (1993).
- 2) Non-equilibrium model (no reactions). This model allows the temperature of the droplet (liquid pollutant) to be different to the temperature of the other components in the cloud. The non-equilibrium model determines the phase distribution of the water and the vapour temperature. Additional droplet equations are solved to determine the droplet trajectories (and point of rainout), droplet mass and droplet temperature. The released pollutant is always modelled as a single 'pseudo-component'
 - 3) Equilibrium model (release of HF). The same temperature is adopted for all components in the cloud (vapour and liquid). The model includes the effect of HF polymerisation and fog formation.

The model includes the capability to model solid phase CO₂. Solid properties (density, enthalpy, vapour pressure) are applied below the triple point temperature and the formation of solid CO₂ modelled based on the enthalpy of fusion.

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1 INTRODUCTION

The Unified Dispersion Model UDM invokes the thermodynamics model while incrementally solving the dispersion equations in the downwind direction. The thermodynamic model calculates the following data:

- phase distribution [pollutant (vapour, liquid), water (vapour, liquid, ice)]
- vapour cloud temperature T_{vap} (K)
- cloud density ρ_{cld} (kg/m³)
- cloud volume V_{cld} (m³) for instantaneous dispersion, or volumetric flow rate $A_{\text{cld}}U_{\text{cld}}$ (m³/s) for steady-state dispersion

The Unified Dispersion Model (UDM) includes a two-phase thermodynamics model for mixing of moist air with the released pollutant. In the case of ground-level dispersion, the model may take into account water-vapour and heat transfer from the substrate to the cloud.

The mixture consists of dry air, water and pollutant. The pollutant may occur both in liquid and vapour phase. Water may consist of vapour, liquid and/or ice. Separate water (liquid or ice) and pollutant (liquid) aerosols may form.

The liquid pollutant in the aerosol is considered to consist of spherical droplets and additional droplet equations may be solved to determine the droplet trajectories, droplet mass and droplet temperature. Rainout of the liquid pollutant will only occur if the droplet size is sufficiently large. Also note that only the liquid pollutant will rainout (non-vapour water remains in the cloud).

The UDM includes the following types of thermodynamic models:

1. Equilibrium model (no reactions)

The simplest approach is to assume that the initial flash results in a vapour/liquid aerosol in thermal equilibrium at atmospheric pressure. Thus the same temperature T_{vap} is adopted for all components in the cloud (vapour and liquid). The mixing process is assumed to be at the saturated condition with respect to the released liquid for as long as there is some proportion of the released material in the liquid phase in the cloud. This may result in low cloud temperatures as air is mixed into the cloud while liquid still remains. In calculating the condensation of water, the vapour phase is assumed to be saturated with respect to water, neglecting any interaction with other components.

The equilibrium model determines the phase distribution [pollutant (liquid, vapour), water (liquid, vapour, ice)] and the mixture temperature. Separate droplet equations for pollutant droplet position and speed are solved to determine the droplet trajectories (and the point of rainout). Note that the droplet equations don't affect the dispersion results, and only determine the point of rainout.

For PHAST6.4, the released pollutant was always modelled as a single 'pseudo-component'. For PHAST6.5, the model has been generalised to allow for the mixing of moist air with a multi-component pollutant consisting of a mixture of non-reactive chemicals (including possibly air and water). Each of the pollutant components may occur in both liquid and vapour phase. Two methods have been implemented:

- a) The first method presumes a single aerosol (for both pollutant and water), and is based on phase equilibrium calculations using the new multi-component property system XPRPⁱ.
- b) The second method allows for multiple aerosols. Ideal mixing is presumed between the components within each liquid aerosol, and no interaction is assumed between the different aerosols. It is based on the multi-component method developed by Witlox (1993)ⁱⁱ for implementation into HGSYSTEM. This method allows for both cases of a single two-component aerosol (with ideal mixing between the two components), and a number of separate non-interacting one-component aerosols.

2. Non-equilibrium model (no reactions)

In this model the released pollutant is always modelled as a single 'pseudo-component', and the model allows the temperature T_d of the droplet (liquid pollutant) to be different of the temperature T_{vap} of the other components in the cloud [vapour pollutant, water (vapour, liquid, ice), air]. This allows the liquid temperature to decrease as the droplets evaporate, thereby developing a temperature driving force for heat conduction to the drop. The temperature decreases until a balance is achieved between heat gain by convection, conduction, and radiation, and heat loss by evaporation. At the same time, the driving force for mass transfer is decreased by the accumulation of evaporated vapour in the plume, but is increased when air is added by entrainment. In the limit, when either the driving force for mass transfer or the driving force for heat transfer goes to zero, the non-equilibrium model reduces to the special case of the equilibrium model. This is a theoretically more correct approach.

The non-equilibrium model determines the phase distribution of the water (vapour, liquid, ice) and the vapour temperature. Additional droplet equations are solved to determine the droplet trajectories (and point of rainout), droplet mass and droplet temperature. Thus the droplet equations do affect the dispersion results before rainout.

3. Equilibrium model (HF)

This is a model specifically developed for the release of HF pollutant. The model assumes the same temperature T_{vap} for all components in the cloud (vapour and liquid), and it includes the effect of HF polymerisation and fog formation.

The plan of this report is as follows. First the model parameters are given, and the initial composition and enthalpies are calculated. Subsequently the above models are described (equilibrium model, non-equilibrium model, HF) and the droplet equations are given. Finally the overall thermodynamics algorithm is given.

1.1 Solid CO₂

CO₂ at atmospheric pressure is below its triple point pressure (5.1 bar), and exists as either a solid or vapour. THRM has been extended to model this behaviour, and uses solid rather than liquid properties. For temperatures to the left of the solid vapour pressure curve, solid properties are used. Thus the following solid properties are applied in THRM:

- saturated vapour pressure and saturated vapour temperature
- solid enthalpy and heat of fusion
- solid density

See XPRP Theory for details on the implementation of solid CO₂ properties.

As CO₂ cannot exist as a liquid at atmospheric pressure, one should read 'solid' rather than 'liquid' in the theory below (i.e. solid fraction, solid enthalpy, etc.)

The component must be called 'carbon dioxide' and have the correct CAS (124389). Solid phase modelling is not enabled for any mixture containing CO₂. Neither does it apply for the single aerosol (SA) multi-component method.

2. MODEL PARAMETERS, AND INITIAL STATE PRIOR TO MIXING

The model parameters are given as follows.

1. Material properties

- dry air (see Appendix A. Air and water material properties)
 - * molecular weight $M_a = 28.966$, kg/kmole
 - * specific vapour enthalpy $h_a(T)$, J/kg
- water (see Appendix A. Air and water material properties)
 - * molecular weight $M_w = 18.01$, kg/kmole
 - * specific enthalpies of vapour $h_{wv}(T)$, liquid $h_{wl}(T)$ and ice $h_{wi}(T)$, J/kg
 - * saturated vapour pressure $P_v^w(T)$, Pa
 - * freezing point $T_{\text{freeze}} = 273.15\text{K}$
- data for each component α within the released material (pollutant; data obtained from DIPPR property database):
 - * molecular weight M_α , kg/kmole
 - * specific enthalpies of vapour $h_v^\alpha(T)$ and liquid $h_L^\alpha(T)$, J/kg
 - * saturated vapour pressure $P_v^\alpha(T)$, Pa
 - * (needed for HGSYSTEM method only) compounds $\alpha = n_{\beta-1}+1, n_{\beta-1}+2, \dots, n_\beta$ are known to potentially form aerosol β ($\beta=1, 2, \dots, M$; $0 = n_0 < n_1 < n_2 < \dots < n_M = N$); aerosol $\beta=1$ includes the liquid water (compound $\alpha=1$).

2. Release material (pollutant)¹:

- temperature T_{pol}° , K (from discharge calculations)
- release liquid pollutant mass fraction $\eta_{\text{pol,L}}^\circ$ (from discharge calculations)

¹ The pollutant vapour/cloud composition and pollutant enthalpy can be determined from the pollutant temperature using an isothermal flash (special case of no air added). Liquid fraction is only required to be specified in the case of a single pollutant component at its boiling temperature. Alternatively to input of pollutant temperature (or liquid mass fraction), one could consider as input the pollutant enthalpy (and using an isenthalpic flash).

- pollutant composition: mole fraction g_α ($\alpha=0,1,\dots,N$); in addition to possibly dry air and water it is assumed that the pollutant consists of $N-1$ compounds ($N \geq 1$); $\alpha=0,1$ are taken to correspond to dry air and water, respectively.
- mass m_{pol} , kg or kg/s

3. Wet air

- temperature T_a , K
- pressure P_a , Pa
- relative humidity r_h
- mass m_{wa} (kg or kg/s); $m_{wa} = m_a + m_{wv}^a$ with
 - * m_a the dry-air mass
 - * $m_{wv}^a = y_{wv}^a m_{wa} / M_{wa}$ the water-vapour in the wet air; here $y_{wv}^a = r_h P_v^w(T_a) / P_a$ is the mole fraction of water vapour in the air; furthermore $M_{wa} = y_w^a M_a + (1 - y_w^a) M_w$ is the molecular mass of the wet air (kg/kmole)

4. Substrate:

- substrate temperature T_{gnd} , K
- heat added from the substrate to the cloud q_{gnd} , J or J/s
- mass of water-vapour added from the substrate to the cloud m_{wv}^{gnd} , kg or kg/s

From the above it follows that the total cloud mass m_{cld} is given by

$$m_{cld} = m_a + m_w + m_{pol}, \quad m_w = m_{wv}^a + m_{wv}^{gnd} \quad (1)$$

The enthalpy of the total cloud H_{cld} (J or J/s) is the sum of the enthalpies of the component before mixing and the heat transferred from the substrate,

$$H_{cld} = H_{pol} + H_{wa} + H_{gnd} + q_{gnd} \quad (2)$$

where the pollutant enthalpy H_{pol} , the wet-air enthalpy H_{wa} , and the enthalpy of the water-vapour added from the ground are given by

$$\begin{aligned} H_{pol} &= [1 - \eta_{pol,L}^0] m_{pol} h_{pol,v}(T_o) + \eta_{pol,L}^0 m_{pol} H_{pol,L}(T_o) \\ H_{wa} &= m_a h_a(T_a) + m_{wv}^a h_{wv}(T_a) \\ H_{gnd} &= m_{wv}^{gnd} h_{wv}(T_{gnd}) \end{aligned} \quad (3)$$

Here $h_{pol,v}$, $h_{pol,L}$, h_a , h_{wa} are the specific enthalpies (J/kg) for pollutant vapour, pollutant liquid, dry air and water vapour, respectively.

3. PHASE DISTRIBUTION AND TEMPERATURE

3.1 Equilibrium model

This model assumes thermal equilibrium at the atmospheric pressure. Thus the same temperature T_{vap} is adopted for all components in the cloud (vapour and liquid). The equilibrium model determines the phase distribution [pollutant (liquid, vapour), water (liquid, vapour, ice)] and the mixture temperature, by imposing phase equilibrium calculations for given cloud enthalpy H_{clid} and given pressure P_a .

3.1.1 Single aerosol (XPRP method)

The first method for applying the equilibrium model presumes a single aerosol for all liquid components (including both pollutant and water). It is based on phase equilibrium calculations using the new multi-component property system XPRP.

This method determines the phase distribution (liquid, vapour) and the mixture temperature by imposing phase equilibrium calculations for given cloud enthalpy H_{clid} and given pressure P_a .

The advantage of this method is that it does allow for non-ideal mixing within the aerosol. The disadvantage of the method is that it not allows for separate aerosol classes (always single aerosol assumed), and it also does not allow for ice formation.

3.1.2 Multiple aerosols (HGSYSTEM method)

The equilibrium model is based on the two-phase multi-component algorithm developed by Witloxⁱⁱ. The advantage of this method is that it allows for separate aerosols. The disadvantage is that ideal liquid mixing is currently always assumed within the individual aerosols.

The mixture components are indicated below by α with

- $\alpha=0$ corresponding to dry air (from ambient moist air and possibly from pollutant; always assumed to be vapour)
- $\alpha=1$ corresponding to water (from ambient moist air and possibly from pollutant; vapour, liquid or ice)
- $\alpha=2-N$ corresponding to remaining pollutant components (vapour or liquid)

Unknowns

The basic unknown variables are as follows:

1. Mole fraction of vapour for component α : $y_{\alpha v}$ ($\alpha = 1, 2, \dots, N$)
2. Mole fraction of aerosol for component α : $y_{\alpha n}$ ($\alpha = 1, 2, \dots, N$)
3. Mole fraction L_β of each aerosol ($\beta=1, 2, \dots, M$)
4. Total mole fraction of non-vapour: L
5. Mixture temperature (K): T

Equations

The above unknowns must satisfy the following equations

1. Conservation of molar flow for components ($\alpha = 1, 2, \dots, N$)

$$y_\alpha = y_{\alpha v} + y_{\alpha n} \quad (4)$$

2. Raoult's law for each compound ($\alpha=n_{\beta-1}+1, n_{\beta-1}+2, \dots, n_\beta; \beta=1, 2, \dots, M$)

$$y_{\alpha v} = \min \left\{ y_\alpha, (1-L) \frac{y_{\alpha n} P_v^\alpha(T_m)}{L_\beta P_a} \right\} \quad (5)$$

Application of the above law implies that each aerosol β ($\beta=1, \dots, M$) is assumed to be an ideal liquid solution of its constituent components $\alpha=n_{\beta-1}+1, n_{\beta-1}+2, \dots, n_\beta$. It states that in the presence of aerosol β , the ratio of the mole fraction

$y_{\alpha v}/(1-L)$ of the compound α in the vapour and the mole fraction $y_{\alpha n}/L_{\beta}$ of the component α in the liquid solution β equals the ratio $P_v^{\alpha}(T_m)/P_a$ of the partial vapour pressure of compound α in the vapour and the total vapour pressure. For a one-compound aerosol ($y_{\alpha n}=L_{\beta}$; $\alpha=n_{\beta}=n_{\beta-1}+1$), Raoult's law reduces to Dalton's law

$$y_{\alpha v} = \min \left\{ y_{\alpha}, (1-L) \frac{P_v^{\alpha}(T_m)}{P_a} \right\}$$

Thus Dalton's law states that the mole fraction of the compound in the vapour equals the ratio of the partial pressure of compound α in the vapour and the total pressure. The reader is referred to, for example, McCain (1989) for further details of Raoult's and Dalton's laws.ⁱⁱⁱ

3. The amount of each aerosol is the sum of its liquid compounds:

$$L_{\beta} = \sum_{\alpha=n_{\beta-1}+1}^{n_{\beta}} y_{\alpha n} \quad (6)$$

4. The total amount of liquid is the sum of all individual aerosols:

$$L = \sum_{\beta=1}^M L_{\beta} \quad (7)$$

5. The overall enthalpy balance of the cloud equates the enthalpy H_{cld} of the individual components prior to mixing [see Equation (2)] to the total enthalpy $H_{\text{cld}}(T)$ after mixing,

$$\begin{aligned} H_{\text{cld}} &= \sum_{\alpha=0}^N H_{\alpha} = \sum_{\alpha=0}^N \{m_{\alpha} h_{\alpha}\} = & (8) \\ &= m_a h_a(T) + m_{wv} h_{wv}(T) + m_{wn} h_{wn}(T) + \sum_{\alpha=2}^N \{m_{cv} h_{cv}(T) + m_{cL} h_{cL}(T)\} \end{aligned}$$

Aerosol criterion

The unknowns $y_{\alpha v}$ and $y_{\alpha n}$ can be eliminated as unknowns using Equations (4) and (5),

$$y_{\alpha v} = \left\{ 1 + \frac{L_{\beta}}{(1-L)} \frac{P_a}{P_v^{\alpha}(T)} \right\}^{-1} y_{\alpha}, \quad \alpha = n_{\beta-1} + 1 \dots, n_{\beta}; \beta = 1, \dots, M \quad (9)$$

$$y_{\alpha n} = \left\{ 1 + \frac{(1-L) P_v^{\alpha}(T)}{L_{\beta} P_a} \right\}^{-1} y_{\alpha}, \quad \alpha = n_{\beta-1} + 1 \dots, n_{\beta}; \beta = 1, \dots, M \quad (10)$$

Insertion of Equation (10) into (6), leads to the equation

$$F_{\beta}(L_{\beta}; L, T) = \sum_{\alpha=n_{\beta-1}+1}^{n_{\beta}} \left\{ \frac{y_{\alpha} P_a / P_v^{\alpha}(T)}{1 - L + L_{\beta} P_a / P_v^{\alpha}(T)} \right\} = 1, \quad \beta = 1, \dots, M \quad (11)$$

Note that the function $F(L_{\beta}, L, T)$ monotonically decreases with increasing L_{β} . Aerosol formation requires that the equation $F(L_{\beta}, L, T)=1$ has a positive root L_{β} . Thus the criterion for formation of aerosol β ($L_{\beta} > 0$) is $F(0, L, T) > 1$, or equivalently,

$$S[\beta, T] = 1 - \sum_{\alpha=n_{\beta-1}+1}^{n_{\beta}} \left\{ y_{\alpha} \frac{P_a}{P_v^{\alpha}(T)} \right\} < L \quad \Leftrightarrow \quad L_{\beta} > 0, \quad \beta = 1, \dots, M \quad (12)$$

Analytical evaluation of L_{β} ($n_{\beta}-n_{\beta-1}=1,2$)

As stated by Witloxⁱⁱ, multiplication of Equation (11) with each denominator $1 - L + L_{\beta} P_a / P_v^{\alpha}(T)$, $\alpha = n_{\beta-1}+1, \dots, n_{\beta}$, leads to a polynomial equation for L_{β} of order $n_{\beta} - n_{\beta-1}$, which can be solved analytically for $n_{\beta} - n_{\beta-1} = 1, 2, 3$. If there is only a single 2-component aerosol, $j=1$, $L=L_1$ and Equation (11) leads to a square equation for L , which can be easily solved.

For $n_{\beta} - n_{\beta-1} = 1$, Equation (11) can be rewritten as a linear equation in L_{β} with the following analytical solution

$$L_{\beta} = y_{\alpha} - (1 - L) \frac{P_v^{\alpha}(T)}{P_a}, \quad \text{if } n_{\beta} - n_{\beta-1} = 1 \text{ where } \alpha = n_{\beta} \quad (13)$$

For $n_{\beta} - n_{\beta-1} = 2$, Equation (11) can be rewritten as a square equation

$$L_{\beta}^2 + bL_{\beta} + c = 0 \quad (14)$$

where b,c are defined by

$$\begin{aligned} b &= (1 - L)(r_{\alpha 1} + r_{\alpha 2}) - (y_{\alpha 1} + y_{\alpha 2}) \\ c &= (1 - L) \{ (1 - L) r_{\alpha 1} r_{\alpha 2} - (y_{\alpha 1} r_{\alpha 2} + y_{\alpha 2} r_{\alpha 1}) \} \end{aligned} \quad (15)$$

with

$$\alpha 1 = n_{\beta-1}, \quad \alpha 2 = n_{\beta}, \quad r_{\alpha 1} = P_v^{\alpha 1}(T) / P_a, \quad r_{\alpha 2} = P_v^{\alpha 2}(T) / P_a \quad (16)$$

The root to Equation (14) satisfying $L_{\beta} \uparrow (y_{\alpha 1} + y_{\alpha 2})$ for $P_v^{\alpha 1}(T) \downarrow 0$ and $P_v^{\alpha 2}(T) \downarrow 0$ (i.e. components $\alpha 1$ and $\alpha 2$ are 100% liquid for very low temperature equals

$$L_{\beta} = -\frac{1}{2}b + \sqrt{\frac{1}{4}b^2 - c}, \quad \text{if } n_{\beta} - n_{\beta-1} = 2 \quad (17)$$

Algorithm for evaluation of phase distribution and cloud enthalpy

An analytical algorithm² for solving the above equations was formulated by Witloxⁱⁱ for both cases of a single two-component aerosol (with ideal mixing between the two components), and a number of separate non-interacting one-component aerosols. Below this algorithm has been generalised to allow for any number separate aerosols, and any number of components in each aerosol. See Witloxⁱⁱ for details on the analytical solutions.

Using the above equations, the phase distribution and cloud enthalpy can be set as follows for given temperature T:

1. Following Equation (12), set order of possible aerosol appearance, by ordering $S[\beta, T]$ in ascending order: $S[\beta_1, T] \leq S[\beta_2, T] \leq \dots \leq S[\beta_M, T]$. Thus aerosol β_1 forms first, and aerosol β_M forms last.
2. Set number of liquid aerosols present (NAEROS), amount of each aerosol, L_{β} ($\beta = \beta_1, \dots, \beta_{\text{NAEROS}}$), and mole fraction L of total fog,
 - 2.1. Initialise loop: $L=0$, NAEROS=0
 - 2.2. Loop over all aerosols: $j=1, M$
 - 2.2.1. If $S[\beta_j, T] \geq L$, then "Aerosol j does not form, go to step 3"
 - 2.2.2. Otherwise aerosol j forms. Set NAEROS= j. Presuming that aerosol β_1, \dots, β_j form only, set aerosol L_{β} ($\beta = \beta_1, \dots, \beta_{\text{NAEROS}}$) and set total fog L as follows:

²This analytical solution was implemented only up to Phast version 8.2*. Following this it was generalised as described in this section.

- If ($j=1$ and $n_\beta - n_{\beta-1} = 1, 2$) then use analytical logic for 2-component aerosol
- Elseif (aerosol β_1, \dots, β_j all contain one component) use analytical logic
- Else Initialise outer iteration loop for L and solve $f(L) = L - \sum L_\beta = 0$ iteratively [lower limit $L=0$, upper limit $L = \sum_{\alpha=n_0+1}^{n_j} y_\alpha$], where L_β in inner iteration loop is set as follows:
 - If $n_\beta - n_{\beta-1} = 1$, use analytical solution [Equation (13)]
 - Elseif $n_\beta - n_{\beta-1} = 2$, use analytical solution [Equation (17)]
 - Else solve Equation (11) numerically [lower limit $L_\beta = 0$, upper limit $L_\beta = \sum_{\alpha=n_{\beta-1}+1}^{n_\beta} y_\alpha$]
- Endif

3. Set mixture vapour and liquid mole fraction, $y_{\alpha v}, y_{\alpha l}$, [$\alpha = 1, \dots, N$], from Equations (9) and (10).
4. Convert back to mass fractions; set liquid-water/ice for $T > 0 / T < 0^3$
5. Set right-hand side $H_{\text{cid}}(T)$ of enthalpy equation (8)

³ If the solution of the above algorithm results in a mixing temperature T equal to the freezing point $T = T_{\text{freeze}}$, the liquid water mass equals $m_{\text{wL}} = [H_{\text{cid}} - H_{\text{cid}}(T_{\text{fr}})] / h_{\text{w}}^{\text{fus}}$. Here $H_{\text{cid}}(T_{\text{fr}})$ is the right-hand side of Equation (8) evaluated immediately below the freezing point (assuming all water is ice). Furthermore $h_{\text{w}}^{\text{fus}} = h_{\text{wl}}(T_{\text{fr}}) - h_{\text{wl}}(T_{\text{fr}})$ is the heat of fusion of water (J/kg). The ice water mass is subsequently set as $m_{\text{wi}} = m_{\text{wt}} - m_{\text{wL}}$.

3.2 Non-equilibrium model

In this model the released pollutant is always modelled as a single 'pseudo-component'. The non-equilibrium model assumes the temperature T_d of the droplet (liquid pollutant) to be different to the temperature T_{vap} of the other components in the cloud [vapour pollutant, water (vapour, liquid, ice), air]. The non-equilibrium model determines the phase distribution of the water (vapour, liquid, ice) and the vapour temperature.

Unknowns

The basic unknown variables are as follows:

1. Mole fraction of water vapour y_{wv}
2. Mole fraction of aerosol for water: y_{wn}
3. Total mole fraction of non-vapour: L
4. Vapour temperature (K): T

Equations

The above unknowns must satisfy the following equations

1. Conservation of molar flow of water

$$y_w = y_{wv} + y_{wn} \quad (18)$$

2. Dalton's law for mole fraction of water vapour

$$y_{wv} = \min \left\{ y_a, (1-L) \frac{P_v^w(T_m)}{P_a} \right\} \quad (19)$$

3. The amount of total aerosol is the sum of those for the components

$$L = y_{wn} + y_{pol,L} \quad (20)$$

4. The overall enthalpy balance of the cloud equates the enthalpy H_{clid} of the individual components prior to mixing [see Equation (2)] to the total enthalpy $H_{clid}(T)$ after mixing,

$$H_{clid} = m_a h_a(T) + m_{wv} h_{wv}(T) + m_{wn} h_{wn}(T) + m_{pol,v} h_{pol,v}(T) + m_{pol,L} h_{pol,L}(T_d) \quad (21)$$

Evaluation of phase distribution and cloud enthalpy

Using the above equations, the phase distribution of the water and cloud enthalpy can be set as follows for given temperature T

1. Find the phase distribution of the water:
 - 1.1. If $y_w/(1-y_{cl}) < P_v^w(T)/P_a \rightarrow y_{wv} = y_w, y_{ws}=y_{wL} = 0$ [no fog]. Goto step 3
 - 1.2. Set y_{wv} from solving Dalton's law $y_{wv} / [1-(y_w-y_{wv})-y_{pol,L}] = P_v^w(T)/P_a$
2. Set right-hand side $H_{clid}(T)$ of enthalpy equation (21).

3.3 Equilibrium model (HF)

In case of the release of HF, the UDM adopts a two-phase equilibrium model including the effect of HF polymerisation and fog formation. The formulation is derived from the HGSYSTEM HF-thermodynamics model described by a report by Witlox^{iv}. For further details the reader is referred to the latter report.

The thermodynamics of mixing of HF with moist air is based on a model developed by Schotte^{v,vi}. The UDM model assumes the released pollutant to be pure HF⁴. The thermodynamics for HF is complex because of formation of HF polymers, depolymerisation of the gas to the monomer state HF (endothermic reaction), and exothermic reaction of HF with water vapour. Following mixing of the HF with the moist air a mixture forms consisting of the following components:

- vapour consisting of HF monomer (HF), HF dimer (HF)₂, HF hexamer (HF)₆, HF octamer (HF)₈, HF•H₂O complex, water and dry air
- an aqueous liquid HF fog consisting of water and HF monomer

The HF thermodynamics model determines the composition of the above mixture and the mixture temperature.

Unknowns

1. Mole fractions of HF monomer, HF dimer, HF hexamer, HF octamer, HF•H₂O complex, water, air in vapour mixture: $y_{11}, y_{12}, y_{16}, y_{18}, y_{cmp}, y_w, y_a$
2. Molar flow of vapour (kmole or kmole/s): Q_{vap}^{mol}
3. In case of presence of liquid:
 - mole fraction of HF in liquid HF/H₂O fog: x
 - molar flow of fog (kmole or kmole/s): Q_{liq}^{mol}
4. Mixture temperature (K): T

Equations

The above unknowns must satisfy the above equations:

1. Conservation of equivalent (based on all HF monomer) molar flow of HF, water and dry air (equivalent molar flow before mixing = equivalent molar flow after mixing):

$$Q_{HF}^{mol} = [y_{11} + 2y_{12} + 6y_{16} + 8y_{18} + y_{cmp}] Q_{vap}^{mol} + x Q_{liq}^{mol} \quad (22)$$

$$Q_w^{mol} = [y_w + y_{cmp}] Q_{vap}^{mol} + (1-x) Q_{liq}^{mol} \quad (23)$$

$$Q_a^{mol} = y_a Q_{vap}^{mol} \quad (24)$$

Here Q_{HF}^{mol} , Q_w^{mol} , Q_a^{mol} are the molar flows of HF (based on all HF monomer), water and air (kmole or kmole/s). These data can easily be calculated from the mass composition of the mixture [masses $m_c = m_{HF}, m_w, m_a$ of HF, water and air (kg or kg/s)] and the molecular weights M_{HF}, M_w, M_a of HF monomer, water, air (kg/kmole).

2. Sum of molar fractions of all components in the vapour mixture must be one:

$$y_{11} + y_{12} + y_{16} + y_{18} + y_{cmp} + y_w + y_a = 1 \quad (25)$$

3. Peng-Robinson equations of state for HF dimer, HF hexamer, HF octamer, and HF•H₂O complex [see Schotte^{vi}]:

$$y_{12}(f_1, T) = \frac{K_2(T) f_1^2}{\Phi_1 P} \quad (26)$$

$$y_{16}(f_1, T) = \frac{K_6(T) f_1^6}{\Phi_1 P} \quad (27)$$

⁴ Note that the HGSYSTEM model described by Witlox^{iv} also allows for the presence of water and inert gas in the released pollutant.

$$y_{18}(f_1, T) = \frac{K_8(T) f_1^8}{\Phi_1 P} \quad (28)$$

$$y_c(f_1, T) = \frac{K_c(T) f_1 P_{wt}}{\Phi_1 P} \quad (29)$$

Here the fugacity $f_1 = y_{11}$, the fugacity coefficient $\Phi_1 \cong 1$, the total vapour pressure $P = P_a$ (ambient pressure), and $P_{wt} = y_w P$ is the true partial pressure (excluding HF•H₂O complex) of water in the vapour. Furthermore $K_2(T)$, $K_6(T)$, $K_8(T)$, $K_c(T)$ are the equilibrium constants associated with the reactions for the formation of HF dimer, hexamer, octamer and complex respectively. These are defined as a function of temperature by Schotte^{vi}.

4. In the presence of liquid fog, the partial vapour pressures of HF (including HF•H₂O complex) and water (including HF•H₂O complex) are set as a function of x and T from empirical expressions $p_w(x, T)$, $p_{HF}(x, T)$ given by Equations (1) and (2) in Schotte^v.

In the absence of fog and with all HF assumed to be HF monomer, the partial pressures of the water and HF are given by $(Q_w^{mol}/Q_{tot}^{mol})P$ and $(Q_{HF}^{mol}/Q_{tot}^{mol})P$, respectively. In the presence of fog, the amounts of HF and water in the vapour are smaller than in the presence of fog, and the partial vapour pressures must also be correspondingly smaller. Thus the following equations apply in the presence of liquid fog ($Q_{liq}^{mol} > 0$):

$$y_w + y_{cmp} = \frac{P_w}{P} = \min \left\{ \frac{p_w(x, T)}{P}, \frac{Q_w^{mol}}{Q_{tot}^{mol}} \right\} \quad (30)$$

$$y_{11} + y_{12} + y_{16} + y_{18} + y_{cmp} = \frac{P_{HF}}{P} = \min \left\{ \frac{p_{HF}(x, T)}{P}, \frac{Q_{HF}^{mol}}{Q_{tot}^{mol}} \right\} \quad (31)$$

6. The overall enthalpy balance of the cloud equates the enthalpy H_{cld} of the individual components prior to mixing [see Equation (2)] to the total enthalpy after mixing,

$$H_{cld} = H_{HF} + H_w + H_a \quad (32)$$

where H_{HF} , H_w , H_a of HF are the enthalpies of HF (including water in fog and HF in HF•H₂O), water (excluding fog; including water in HF•H₂O) and air. See Witlox^{iv} for full expression of these enthalpies.

Solution algorithm for phase distribution and mixture temperature

In case of absence of a fog, it follows from the above that there are 9 equations [Equations (20)-(29), and Equation (32)] for the 9 unknowns [y_{11} , y_{12} , y_{16} , y_{18} , y_{cmp} , y_w , y_a , Q_{vap}^{mol} , T]. In the presence of a fog, there are two additional equations [Equations (30), (31)] for the two additional unknowns (x , Q_{liq}^{mol}). See the report by Witlox^{iv} for full details of the algorithm for determining the unknowns for both cases of the presence of the fog and the absence of a fog.

4. DROPLET MODEL

4.1 Introduction

The liquid pollutant in the aerosol is considered to consist of spherical droplets, surrounded by a mixture of air and evaporated vapour. The trajectory of a single drop (with a cloud-averaged drop size varying with downwind distance) is followed, representing the path of the centre of a cloud of drops. Rainout is taken to be centred at the point of grounding of this trajectory and rainout is uniform over the pool.

Evaporation and condensation are treated by either the non-equilibrium model or the equilibrium model as described in the previous section. With either evaporation model option, we also calculate droplet trajectories. When the droplet trajectories touch the ground, rain-out is modelled as occurring, and all remaining liquid in the cloud is assumed to rain out. Distributed rainout could be modelled, but at the expense of making subsequent pool spread modelling more complex. The rained-out pool is assumed to spread from this point of rain-out.

The horizontal component of drop velocity is set equal to the horizontal component of the cloud⁵. The vertical component of the droplet velocity is dominated early in the response by drag, which keeps the drops near the centre of the plume. Later, as the vertical component of the relative velocity decreases, drop buoyancy dominates, and the drops can move further away from the plume centre-line. Vapour evaporating from the drops is added to the plume. Upon rainout, the mass, momentum and enthalpy of the rained-out liquid is subtracted from the plume.

This treatment is a non-equilibrium approach, since the drop temperature is determined through an unsteady-state energy balance rather than through a flash calculation. Typically, the drop temperature falls below the gas temperature. For some discharge conditions, the driving force for evaporation becomes negative so that condensation occurs. When the driving force approaches zero the non-equilibrium model's predictions approach those of the equilibrium model.

For smaller size droplets, the difference in temperature between liquid and vapour phases becomes less, and the solution becomes numerically more difficult to compute. There is a minimum individual droplet mass of 10^{-12} kg below which the equilibrium model will be used⁶.

The droplet modelling described hereafter is only applied to those releases which contain an initial aerosol, i.e. Droplet trajectory, droplet energy balance and rainout are not modelled for an initial pure vapour cloud that condenses to form an aerosol. The thermodynamics of such clouds are governed by the equilibrium model described in the previous section.⁷

4.2 Number of drops

The number of drops⁸

$$N_d = \frac{\eta_{pol,L}^o m_{pol}}{m_d} \quad (33)$$

where m_{pol} is the total discharge rate (kg/s) for a continuous release, or the total mass (kg) discharged for an instantaneous release; $\eta_{pol,L}^o$ is the mass fraction of liquid condensable pollutant initially in the cloud. The mass m_d and volume V_d of an individual droplet are:

$$m_d = \rho_{pol,L} V_d, \quad V_d = \frac{4\pi}{3} r_d^3 \quad (34)$$

where $\rho_{pol,L}$ is the liquid density and r_d the droplet radius.

The number of drops, N_d , remains constant until the drop size becomes low ($< \sim 5 \mu\text{m}$), and the numerical integration slows. At this point, droplet clustering is used to speed the solution. The drop size is increased to 15-20 μm and N_d is decreased correspondingly. This may be repeated several times until the drops totally evaporate or rain out. Clustering does not appreciably affect the droplet trajectories or rainout predictions since such small drops behave similarly⁹.

⁵This is not applicable to the initial phase of energetic expansion for an instantaneous release

⁶ For a propane droplet at its boiling point, this corresponds to approximately a 15 μm diameter

⁷ This feature should be generalised to account for any scenario which results in the formation of an aerosol from a pure vapour cloud e.g. aerosol \rightarrow vapour \rightarrow aerosol

⁸ For instantaneous cloud N_d is total number of drops in the cloud. For a continuous cloud N_d is the total number of released drops per second.

⁹ JUSTIFY – To verify by UDM runs with varying cut-off diameter that this is indeed the case

4.3 Droplet variables and equations

The set of variables which are integrated is:

x_d	droplet horizontal position (m)
z_d	droplet vertical position (m)
u_{dx}	droplet horizontal velocity (m/s)
u_{dz}	droplet vertical velocity (m/s) ¹⁰
m_d	droplet mass (kg/drop)
T_d	droplet temperature (K)

The initial values for the variables at the point of release are found as follows:

- The initial droplet position equals the release position of the jet¹¹
- The initial droplet speed equals the release speed of the jet
- The initial droplet temperature equals the mixture temperature of the jet
- The initial droplet mass is found from the initial droplet diameter $d_d = 2 r_d$ using Equation (34). The initial droplet diameter is obtained from the PHAST discharge model; see 0 for further details.

These variables can be found by relating the droplet speed to the droplet position, and imposing momentum, mass and heat balances for a single droplet. Thus the following system of ordinary differential equations is integrated to obtain droplet trajectories, evaporation rate, and temperature¹².

- *Droplet horizontal and vertical position:*

$$\frac{dx_d}{dt} = u_{dx} \quad , \quad \frac{dz_d}{dt} = u_{dz} \quad (35)$$

- *Droplet horizontal and vertical momentum*

Initial phase of energetic expansion for pressurised instantaneous release

For the initial phase of energetic expansion ($0 < t < t_{end}-t_0$) for a pressurised instantaneous release, the droplet velocity is chosen to be proportional to the cloud expansion velocity dR/dt ,

$$\begin{bmatrix} u_{dx} \\ u_{dz} \end{bmatrix} = r_{d,exp} \frac{dR}{dt} \begin{bmatrix} \cos(\theta_{d,exp}) \\ \sin(\theta_{d,exp}) \end{bmatrix} \quad (36)$$

with $r_{d,exp} = 0.8$ a parameter, and $\theta_{d,exp}$ the average drop-out angle. See the section on instantaneous energetic expansion in the UDM theory manual for further details and meaning of variables.

Note that the above are analytically solved to give x_d and z_d at each step rather than being solved numerically. Using dR/dt as given in the UDM theory manual¹³:

$$\begin{bmatrix} x_d \\ z_d \end{bmatrix} = \begin{bmatrix} x_d^o \\ z_d^o \end{bmatrix} + r_{d,exp} R_o \left(t^{3/8} - t_o^{3/8} \right) \begin{bmatrix} \cos(\theta_{d,exp}) \\ \sin(\theta_{d,exp}) \end{bmatrix} \quad (37)$$

¹⁰ In the new PHAST6.5 formulation $m_d u_{dz}$ is integrated instead of u_{dz} .

¹¹ JUSTIFY. For instantaneous releases initial $x_d = x_{cloud}^{init} + W_{eff}/2 \times \cos(\theta)$, where θ is the release angle. As release angle should not be used, I have assumed $\theta = 0$. For instantaneous expansion cases, $\theta =$ average dropout angle and similar logic applies for $z_d (= z_{cloud}^{init} + H_{eff}/2 \times \sin(\theta))$. This logic has been kept.

¹² CORRECTED. In UDM v2 the independent variable was cloud arc length, and time based droplet derivatives were transformed (incorrectly) by dividing by u_d (in fact u_{cloud} should have been used). This correction is no longer needed as the independent variable in v3 UDM is time

¹³ CHECK. So $(z_d - z_d^o) / (x_d - x_d^o) = \tan(\theta)$ during the instantaneous expansion phase

Continuous release, or period after energetic expansion for instantaneous release

The horizontal component u_{dx} of drop velocity is set equal to the horizontal component u_x of the plume.

$$\frac{dx_d}{dt} = u_{dx} = u_x \quad (38)$$

The following equation expresses conservation of droplet vertical momentum^{14,15,16},

$$m_d \frac{d u_{dz}}{dt} = -u_{dz} \frac{dm_d}{dt} + F_{body} + F_{drag} \quad (39)$$

The first term in the right-hand side of Equation (39) represents the loss of momentum because of droplet evaporation. The second term is the buoyancy force F_{body} for the droplet (density ρ_{cl} , volume V_d) in the plume (density ρ_{cl})¹⁷,

$$F_{body} = (\rho_{cl} - \rho_{pol,L}) g V_d \quad (40)$$

The third term is the drag force F_{drag} defined by

$$F_{drag} = \frac{1}{2} C_{Dd}(\text{Re}) \rho_{cl} \pi r_d^2 |u_z - u_{dz}| (u_z - u_{dz}) \quad (41)$$

Here C_{Dd} is the drag coefficient of the drop (-) determined by the following standard correlation^{18,vii},

$$\begin{aligned} C_{Dd} &= 0.44 && \text{for } \text{Re} > 985 \\ &= 24 \frac{1 + 0.15 \text{Re}^{0.687}}{\text{Re}} && \text{for } 2 < \text{Re} < 985 \\ &= 24 \frac{1 + 3(\text{Re}/16) + [9 \text{Re}^2 \log(2 \text{Re})] / 160}{\text{Re}} && \text{for } 0.1 < \text{Re} < 2 \\ &= 24 / \text{Re} && \text{for } 0 < \text{Re} < 0.1 \end{aligned} \quad (42)$$

where C_{Dd} is restricted to a maximum value of $C_{dmax}=100$ and the Reynolds number Re is defined by

$$\text{Re} = \frac{2 r_d |u_z - u_{dz}| \rho_{cl}}{\mu_{a,pol}(T_m)} \quad (43)$$

Here $\mu_{a,pol}$ is the dynamic viscosity of the material in air (kg/m/s) at the mean temperature $T_m = (T_{vap} + T_d)/2$.

¹⁴ CODE corrected - In old code term $-\pi r_d^2 (dm_d/dt) u_{dz}$ was used instead of $-(dm_d/dt) u_{dz}$. For most cases this results in only a small error.

¹⁵ For droplets with diameter $2r_d < 10^{-5}$ m, equation is modified to $m_d (du_{dz}/dt) = F_{body} (2r_d/10^{-5})$, thus resulting in zero vertical acceleration for $r_d \downarrow 0$. Note that in this range droplet clustering is carried out as previously noted. This allows the drops to continue settling at their previous rate and smoothes drop trajectories. Even so, the vertical momentum of droplets tends to change readily as the plume nears the ground, which gives a desirable simulation of turbulence keeping the drops in suspension.

¹⁶ CORRECTED. Prior to PHAST 6.5 the evaporation term was incorrectly omitted from this equation for the equilibrium model (V17348), [so $m_d du_{dz}/dt = F_{body} + F_{drag}$] and therefore the integrated variable was u_{dz} rather than $m_d u_{dz}$.

¹⁷ CODE corrected/changed. The old code used $F_{body} = (\rho_v - \rho_{cl}) g V_d$, $F_{drag} = 0.5 C_{Dd}(\text{Re}) \rho_v \pi r_d^2 |u_{dv}| u_{dv}$, $\text{Re} = 2r_d |u_{dv}| \rho_v / \mu_{ac}(T_m)$. Here the vapour density ρ_v was adopted to be the cloud density ($\rho_v = \rho_{cl}$) for droplet inside plume and the ambient density ($\rho_v = \rho_a$) for droplet outside plume. Error was made in the code in determining whether cloud has moved outside the cloud (W_{eff} partly used rather than H_{eff}). In new description always ρ_{cl} is used instead of ρ_v .

¹⁸ JUSTIFY - Not clear where this formula comes from; $C_{Dd} = 0.44$ corresponds to Newton's law, the formula for $2 < \text{Re} < 985$ is suggested by Schiller and Nauman, and the formula $C_{Dd} = 24/\text{Re}$ for $\text{Re} < 0.1$ corresponds to Stokes law. See Clift et al.^{vii} for the standard drag curve and an overview of proposed correlations for this curve. Suggest to modify existing curve from the 'best' of Clift. If Re is plotted against C_{Dd} the region $0.1 < \text{Re} < 2$ is clearly discontinuous.

Droplet evaporation rate¹⁹:

$$\frac{dm_d}{dt} = -A_d K_g \rho_{pol,v} C' \ln \left(\frac{1 - y_g}{1 - \frac{y_s}{T_d / T_{vap}}} \right) \quad (44)$$

The above equation states that the droplet evaporation is proportional to the droplet surface area $A_d = 4\pi r_d^2$.

The term $\rho_{pol,v}$ (kg/m³) serves to convert mole fractions to concentration, and it is the vapour density of the pure condensable pollutant at the vapour cloud temperature T_{vap} and the ambient pressure P_a ; $\rho_{pol,v} = \rho_{pol,v}(T_{vap}, P_a)$ is set using a DIPPR formula (also valid for non-ideal gases).

The logarithmic term in Equation (44) is introduced to correct for the Stefan flow (Newbold and Amundson, 1973)^{viii}. When the argument to the logarithmic term is > 1 evaporation occurs, and when it is < 1 condensation occurs. In the logarithmic term $y_s = P_v(T_d)/P_a$ is the equilibrium mole fraction of condensable pollutant on the droplet surface, and y_g the mole fraction of condensable pollutant in the gas phase around the droplets; $y_g=0$ for droplet evaporation in pure air.

The correction constant C' (-) is made up of two terms, a term for Stefan flow which accounts for enhanced evaporation at high mass flux, and a correction for the temperature gradient on the diffusion coefficient as described by Barrett and Clement^{ix}

$$C' = C_s \cdot C_t \quad (45)$$

$$C_s = 1 + \frac{P_v^{pol}(T_m) + y_g P_a}{2 P_a} \quad (46)$$

$$C_t = \frac{(2 - \mu) (T_{vap} - T_d)}{T_{vap}^{\mu-1} (T_{vap}^{2-\mu} - T_d^{2-\mu})} \quad (47)$$

where μ varies with composition. According to Vesala et al.^x in most cases $1.6 < \mu < 2$, so we used $\mu = 1.8$.

The mass transfer coefficient K_g (m/s) is calculated from a Sherwood number correlation,

$$K_g = \frac{Sh D_{a,pol}(T_m)}{r_d} \quad (48)$$

where $D_{a,pol}$ is the diffusivity (m²/s) of the drop (liquid pollutant) into the surrounding medium.

The dimensionless Sherwood number Sh for evaporating droplets is defined to be the ratio of the total mass transfer to purely diffusive transfer, and is chosen to be defined by the following empirical relation

$$Sh = (a + b Re^{1/2} Sc^{1/3}) / (1 + B_m) \quad (49)$$

Here the Reynolds number Re is defined by Equation (43), and the Schmidt number Sc is given by

$$Sc = \frac{\mu_{a,pol}(T_m)}{\rho_a D_{a,pol}(T_m)} \quad (50)$$

Furthermore B_m is the mass transfer number using the vapour heat capacity $C_{pv}^c(T_m)$ of condensable pollutant at the mean temperature T_m ,

¹⁹ JUSTIFY. In the code the 2nd term in the denominator of the log argument is multiplied by the ambient pressure in atmospheres.

$$B_m = \frac{C_{pv}^{pol}(at T_m) (T_{vap} - T_d)}{h_{fg}(T_d)} \quad (51)$$

It is noted that the empirical relation (49) for the Sherwood number is a hybrid of the correlation of Fuchs (1959)^{xi} [recommended by Davies (1978)^{xii}],

$$Sh = 1 + 0.276 Re^{1/2} Sc^{1/3} \quad (52)$$

and of the correlation recommended by Eisenklam et al. (1967)^{xiii}:

$$Sh(1 + B_m) = 1.0 + 0.8 Re^{1/2} \quad (53)$$

The evaluation of the empirical parameters a, b in Equation (49) is discussed below.

- *Energy balance by heat conduction and evaporation or condensation:*

$$u_d \frac{dT_d}{ds} = \frac{A_d h (T_{vap} - T_d) + \frac{dm_d}{dt} h_{fg}(T_d) + A_d \sigma_r \varepsilon (T_{atm}^4 - T_d^4)}{m_d C_{pL}(T_d)} \quad (54)$$

The three terms in numerator of the right-hand side of the above equation represent heat conduction, evaporative heat loss and radiation energy, respectively. In these terms h is the heat transfer coefficient (W/m²/K), h_{fg} the heat of vaporisation (J/kg) at T_d, σ_r = 5.67x10⁻⁸ W/m²/K⁴ the Stephan-Boltzmann constant, and ε the droplet emissivity (-).

The heat transfer coefficient h is calculated from a Nusselt number correlation,

$$h = \frac{Nu k(T_{vap})}{r_d} \quad (55)$$

where k is the thermal conductivity of the gas (W/m/K) at the vapour temperature T_{vap}.

Following Fuchs (1959)^{xi} and Eisenklam, et al. (1967)^{xiii}, similarity of mass transfer (Sherwood number) and heat transfer is used (Nusselt Number) to give the following hybrid of the empirical correlations of Fuchs and Eisenklam for the Nusselt number [cf. Equation (49)]

$$Nu = \frac{a + b Re^{1/2} Pr^{1/3}}{1 + B_m} \quad (56)$$

where the Prandtl number is defined by Pr = C_{pv}(T_m)μ(T_m)/k(T_m).

The empirical parameters a, b in Sherwood correlation (49) and the Nusselt correlation (56) are obtained by sequentially using decoupled experiments:

- First use experiments for the evaporation of a single drop in still air such as the data of Ranz and Marshall (1952)^{xiv} for water drops shown in

Figure 1. The drop area is seen to decrease linearly in time, consistent with theory. These tests establish that a= 1.03 in the Sherwood and Nussel correlations to match the water data most closely. That is, the diffusivity reported in the literature and used in our model is within 3% of the value needed to fit Ranz and Marshall's test data. Consequently, we take a= 1.0, and accept an error in diffusivity of around ± 3-5%.

- Use single droplet evaporation experiments with constant wind speeds and ambient temperature to set b = 0.32 in the Sherwood and Nussel correlations. This is larger than the value of 0.276 given by Fuchs (1959)^{xi}, but 0.32/(1+B_m) is near 0.276 for Ranz and Marshall's water and benzene data shown in

Figure 2. This is confirmed against a much larger body of data cited by Eisenklam et al. (1967)^{xiii} shown in Figure 3. Our correlation is accurate at low Reynolds number but is slightly low at high Reynolds number.

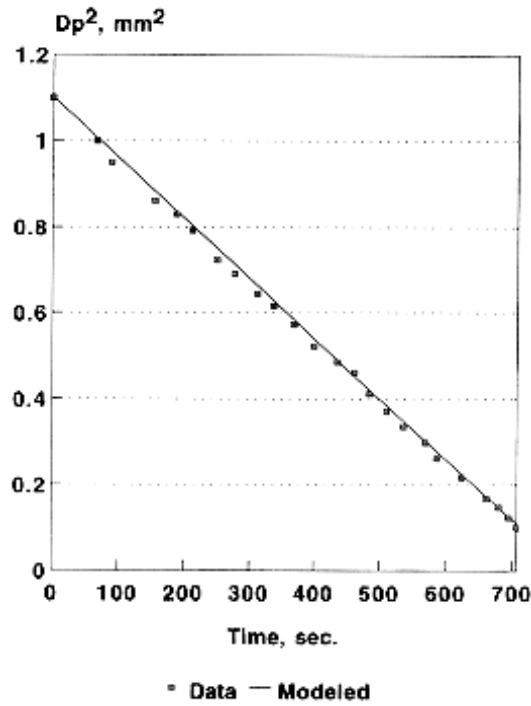


Figure 1. Comparison of model predictions for evaporation of a single drop of water in still air: experimental data by Ranz and Marshall^{xiv}

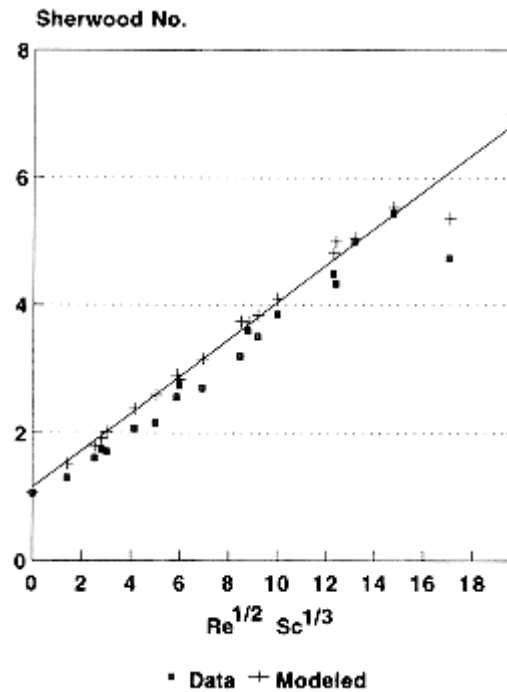


Figure 2. Comparison of Sherwood number correlation (49) in model with experimental values for benzene and water evaporating in air: experimental data by Ranz and Marshall^{xiv}

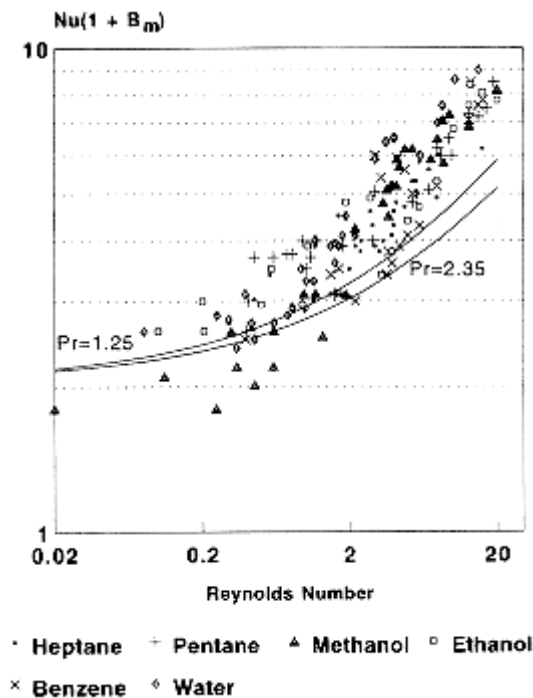


Figure 3. Comparison of Nusselt number correlation (56) in model with experimental values found by various investigators: experimental data summarised by Eisenklam et al.^{xiii}

5. OVERALL THERMODYNAMICS ALGORITHM

The thermodynamics model is invoked while incrementally solving the dispersion equations in the downwind direction. In case of the non-equilibrium model, input data supplied by the dispersion model include the liquid pollutant mass and the

liquid pollutant (droplet) temperature. After each incremental step, the UDM uses the thermodynamic model to calculate the cloud temperature T , the cloud density ρ_{cld} , and the cloud volume V_{cld} (instantaneous) or cloud volumetric flow rate $A_{\text{cld}}U_{\text{cld}}$ (continuous)

These calculations are done as follows by the thermodynamics model:

1. Set total cloud enthalpy H_{cld} (sum of enthalpies of individual components before mixing) from Equation (2)
2. Set mass and mole fractions of dry air, water and pollutant
3. Use Brent root solver to solve enthalpy equation (8) or (21) for temperature T , and determine phase distribution
4. Set specific volumes (m^3/kg) for liquid v_{liq} , vapour v_{vap} and cloud v_{cld} :

$$\begin{aligned} v_{\text{liq}} &= \eta_{\text{ws}} / \rho_{\text{ice}} + \eta_{\text{wL}} / \rho_{\text{wL}} + \eta_{\text{pol,L}} / \rho_{\text{pol,L}} (T_{\text{d}}) \\ v_{\text{vap}} &= [(\eta_{\text{a}} + \eta_{\text{wv}}) / (\rho_{\text{a}} T_{\text{a}} / T_{\text{vap}})] + [\eta_{\text{pol,v}} / \rho_{\text{pol,v}} (T_{\text{vap}})] \\ v_{\text{cld}} &= v_{\text{vap}} + v_{\text{liq}} \end{aligned}$$

5. Set cloud density (kg/m^3): $\rho_{\text{cld}} = 1 / v_{\text{cld}}$
6. Set cloud volume $V_{\text{cld}} = v_{\text{cld}} * m_{\text{cld}}$ (instantaneous, m^3) or volumetric flow rate $A_{\text{cld}} U_{\text{cld}} = v_{\text{cld}} * m_{\text{cld}}$ (steady-state, m^3/s)

6. FUTURE DEVELOPMENTS

Further developments to THRM are currently envisaged as follows:

1. At present solid effects are account for only for the water from the ambient air (ice), and for CO₂ when the released component is pure CO₂. Otherwise the current formulation always presumes liquid aerosols. The formulation could first be extended to include solid thermodynamics for other one-component materials, as is now currently done for CO₂ (with properties obtained from DIPPR). Subsequently, although this would be more complex, it could be further generalised to account for solid effects when the released material is a mixture.
2. At present the complex HF thermodynamics (polymerisation, aqueous fog formation) is only accounted for when the released material is pure HF. It could be further generalised if the released material is not pure HF (e.g. when it also contains water and/or an inert gas). The thermodynamics model could also be further generalised to account for reactions for other released materials (e.g. for phosphoric pentoxide to react with the water in the air to form phosphoric acid).

APPENDICES

Appendix A. Air and water material properties

The latest version of the UDM thermodynamics module allows for application of both DIPPR (added option) and non-DIPPR (original option) for air and water properties.

A.1 Non-DIPPR (default option)

These data are taken from J.A.Goff, "Transactions of the American Society of Heating and Ventilation Engineers" Vol.55 (1949) pp459-484. They include

- specific enthalpies (J/kg) of the dry air, the water vapour in the air and condensed water (liquid for >°C and ice for temperature <°C): $h_a(T)$, $h_{wv}(T)$, $h_{wL}(T)$, $h_{ws}(T)$
- saturated vapour pressure of water: $p_v^w(T)$

Specific enthalpies

The specific enthalpy calculation uses a simple interpolation or extrapolation from established data, as follows:

temperature (°C)	enthalpy of dry air (kcal/kg)	enthalpy of water vapour (kcal/kg)	enthalpy of ice (kcal/kg)	enthalpy of liquid water (kcal/kg)
-90	-21.641	561.38	-117.79	
-80	-19.23	565.64	-114.25	
-70	-16.823	569.9	-110.54	
-60	-14.418	574.17	-106.64	
-50	-12.0132	578.43	-102.58	
-40	-9.6093	582.7	-98.34	
-30	-7.2065	586.96	-93.92	
-20	-4.8046	591.22	-89.34	
-10	-2.4027	595.49	-84.57	
0	0	599.77	-79.64	0.02
10	2.4021	604.18		10.06
20	4.8052	608.68		20.06
30	7.2096	613.27		30.04
40	9.614	617.95		40.03
50	12.0195	622.78		50.01
60	14.4264	627.74		60
70	16.8348	632.87		69.99
80	19.2447	638.2		80.01
90	21.657	644.18		90.05

The enthalpies at the reference temperature $T_{ref} = 298.16K = 25C$ are determined during initialisation, and these values are used as reference values. Conversion from kcal to Joule is carried out (1 kcal = 4186.8 J).

Saturated vapour pressure of water

The following formula is adopted for the saturated vapour pressure (Pa) of water, $P_v^w(T)$

$$P_v^w = P_a 10^{s(T)}$$

Here $s(T)$ is given for $T > T_{freeze} = 273.15$ by

$$s(T) = \frac{-7.90298(r-1) + 5.02808 * \log(r) - 1.3816 \{ 10^{11.344 * (1-1/r)} - 1 \} + 0.0081328 * \{ 10^{-3.49149(r-1)} - 1 \}}{T_{boil}^w / T = 284.15/T}$$

and for $T < T_{freeze}$ by

$$s(T) = -9.09718(r-1) - 3.56654 * \log(r) +$$

$$r = r(T) = \frac{0.876793(1-1/r) - 2.21988}{T_{freeze} / T}$$

Atmospheric density

The atmospheric density ρ_a at a height z is calculated from the atmospheric temperature T_a , pressure p_a and humidity r_h at that height. The ideal-gas equation is used assuming the wet air to consist of dry-air and water vapour. The adopted equation is therefore:

$$\rho_a = \frac{M_w r_h P_v^w(T_a)}{(RT_a)} + \frac{M_a [P_a - r_h P_v^w(T_a)]}{(RT_a)}$$

where R is the gas constant, $P_v^w(T_a)$ is the vapour pressure of water in the air, M_a the molecular weight of dry air, and M_w the molecular weight of water.

A.2 DIPPR (added option)

DIPPR formulas are applied for both air and water properties, with enthalpies derived from the DIPPR specific heat:

Air and water vapour enthalpies

1. specific enthalpy (J/kg) of the dry air, $h_a(T)$
2. specific enthalpy (J/kg) of the water vapour, $h_{wv}(T)$

Saturated vapour pressure of the water

The saturated vapour pressure (P_a) of the water, $P_v^w(T)$ is set as:

- the vapour pressure for solid-vapour equilibrium for $T < T_{freeze} = 273.15K$ (ice)
- the vapour pressure for liquid-vapour equilibrium, $T > T_{freeze}$ (liquid water)

The vapour pressure function can be shown to be continuous at $T = T_{freeze}$.

Non-vapour enthalpy of water

The specific enthalpy (J/kg) of the non-vapour water, $h_{wn}(T)$ is set as follows:

$$\begin{aligned} h_{wn}(T) &= h_{wL}(T) \quad , \quad \text{for } T > T_{freeze} \quad (\text{liquid}) \quad (57) \\ &= h_{wL}(T_{freeze}) - \Delta h_{w,fus} - \int_T^{T_{freeze}} C_{Ps}^{DIPPR}(\tau) d\tau \quad , \quad \text{for } T < T_{freeze} \quad (\text{ice}) \end{aligned}$$

The DIPPR specific heat of ice $C_{Ps}^{DIPPR}(T)$ can be shown to decay virtually linear between the temperatures $T_{freeze} = 273.15K$ (0C) and $T_o = 183.15K$ (-90C). Therefore it is approximated by

$$C_{Ps}(T) \approx C_{Ps}^{DIPPR}(T_{freeze}) - \alpha_{ice} [T_{freeze} - T] \quad , \quad \text{for } T < T_{freeze} \quad (58)$$

with

$$\alpha_{ice} = \frac{C_{Ps}^{DIPPR}(T_{freeze}) - C_{Ps}^{DIPPR}(T_o)}{T_{freeze} - T_o} \quad (59)$$

Thus the integral in the above equation is evaluated as

$$\int_T^{T_{freeze}} C_{Ps}^{DIPPR}(\tau) d\tau \approx C_{Ps}^{DIPPR}(T_{freeze}) [T_{freeze} - T] - \frac{1}{2} \alpha_{ice} (T_{freeze} - T)^2 \quad (60)$$

Ambient density

The atmospheric density ρ_a at a height z is calculated from the atmospheric temperature T_a , pressure p_a and humidity r_h at that height, as follows:

- First the composition of the air is set:
 - o water mole fraction = $r_h P_v^w(T_a)/P_a$. Here the appropriate water vapour pressure is used.
 - o dry air mole fraction = $1 - r_h P_v^w(T_a)/P_a$
- Subsequently the ambient vapour density is determined using the new property system for the mixture of the above given composition of water and dry air; see the XPRP theory manual for detailsⁱ.

Appendix B. Properties of released material

B.1 DIPPR properties

Most properties of the released material (pollutant) are obtained by the UDM directly from the DIPPR database:

- molecular mass M_c , kg/kmole
- boiling point $T_{\text{boil}}^{\text{pol}}$, K
- critical temperature $T_{\text{crit}}^{\text{pol}}$, K
- vapour and liquid specific heat, $C_{p,v}^{\text{pol}}$ and $C_{p,L}^{\text{pol}}$, J/kg/K [thermodynamics]
- vapour and liquid enthalpy, $h_{\text{pol},v}$ and $h_{\text{pol},L}$, J/kg [thermodynamics]
- heat of vaporisation, h_{fg} , J/kg [enthalpy balance; droplets]
- saturated vapour pressure function P_v^{pol} [droplets]
- material vapour density $\rho_{\text{pol},v}$ (of condensable pollutant), kg/m³ [droplets]
- material liquid density $\rho_{\text{pol},L}$, kg/m³ [droplets]
- thermal vapour conductivity k , W/m/K [heat transfer coefficient for droplet energy balance]
- solubility in water f_s , kg/kg [dissolution in water for pool model]

B.2 Other properties

Additional pollutant properties are required for the heat/water-vapour substrate transfer equations and the droplet equations (droplet drag coefficient, droplet evaporation). These are the binary diffusivity $D_{a,\text{pol}}$ of the pollutant in air (m²/s), and the dynamic vapour viscosity $\mu_{a,\text{pol}}$ of the pollutant in air (kg/m /s).

Binary diffusivity $D_{a,\text{pol}}$

The UDM requires the evaluation of the diffusivity $D_{a,\text{pol}}$ as a function of temperature T for a binary gas system consisting of the released material (pollutant) and air. Several empirical correlations exist for the diffusivity in low-pressure binary gas systems. The adopted formula is that of Wilke and Lee^{xv}. This formula uses the pollutant properties (from DIPPR) M_{pol} , $T_{\text{boil}}^{\text{pol}}$, $\rho_L^{\text{pol}}(T_{\text{boil}}^{\text{pol}})$, and the ambient properties $M_a = 28.966$ kg/kmole, $T_{\text{boil}}^a = 84.3$ K, $\rho_L^a(T_{\text{boil}}^a) = 955.4$ kg/m³. The formula is given by

$$D_{a,\text{pol}} = \frac{\left(3.03 - \frac{0.98}{\sqrt{M_{a,\text{pol}}}} \right) 10^{-4} T^{1.5}}{P_a \sqrt{M_{a,\text{pol}}} \sigma_{a,\text{pol}}^2 \Omega_d(T^*)}$$

where

- dimensionless temperature $T^* = kT / \epsilon_{a,\text{pol}}$; here $\epsilon_{a,\text{pol}} = [\epsilon_a \epsilon_{\text{pol}}]^{1/2}$, with $\epsilon_a/k = 1.15 T_{\text{boil}}^a$, $\epsilon_{\text{pol}}/k = 1.15 T_{\text{boil}}^{\text{pol}}$
- molar mass (kg/kmole): $M_{a,\text{pol}} = 2 / [M_a^{-1} + M_c^{-1}]$
- characteristic scaling length: $\sigma_{a,\text{pol}} = [\sigma_a + \sigma_{\text{pol}}]/2$; here $\sigma_a = 1.18 [V_b^a]^{1/3}$, $\sigma_{\text{pol}} = 1.18 [V_b^{\text{pol}}]^{1/3}$ with liquid molar volumes at normal boiling point (m³/kmol) defined by $V_b^{\text{pol}} = M_{\text{pol}}/\rho_L^{\text{pol}}$, $V_b^a = M_a/\rho_L^a$
- the collision integral:
 $\Omega_d(T) = 1.06036 T^{-0.15610} + 0.19300 e^{-0.47635T} + 1.03587 e^{-1.52996T} + 1.76474 e^{-3.89411T}$

Dynamic vapour viscosity $\mu_{a,\text{pol}}$

The formula for the dynamic vapour viscosity $\mu_{a,\text{pol}}$ of the pollutant in air as function of the temperature T is taken from Fleischer (1980)^{xvi}. This formula uses the pollutant properties (from DIPPR) m_{pol} , $T_{\text{boil}}^{\text{pol}}$, $T_{\text{crit}}^{\text{pol}}$, $P_{\text{crit}}^{\text{pol}}$ and $P_v^{\text{pol}}(T)$. The formula is given by

$$\mu_{a,\text{pol}} = \frac{\gamma_a M_a^{1/2} \mu_a + \gamma_{\text{pol}} M_{\text{pol}}^{1/2} \mu_{\text{pol}}}{\gamma_a M_a^{1/2} + \gamma_{\text{pol}} M_{\text{pol}}^{1/2}}$$

Here $\gamma_{\text{pol}} = 0.5 P_v^{\text{pol}}[\min(T, T_{\text{boil}})]/P_a$ and $\gamma_a = 1 - \gamma_{\text{pol}}$. Furthermore the dynamic viscosity of the air μ_a and the dynamic viscosity of the pollutant μ_{pol} are given by

$$\mu_a = 1.458 \times 10^{-6} \frac{T^{1.5}}{T + 110.4}$$

$$\begin{aligned} \mu_{pol} &= \beta T_r^{0.965}, & T_r < 1 \\ &= \beta T_r^{0.71+0.29/T_r}, & T_r > 1 \end{aligned}$$

with β and the reduced temperature T_r defined by

$$\begin{aligned} T_r &= T / T_{crit}^{pol} \\ \beta &= 10^{-7} \frac{3.5 M_{pol}^{1/2} [P_{crit}^{pol} / P_a]^{2/3}}{[T_{crit}^{pol}]^{1/6}} \end{aligned}$$

Specific heat of vapour cloud

For the equilibrium model, the specific heat C_p^{cld} is evaluated at the cloud temperature T_{vap} (vapour temperature T_{vap} = pollutant liquid temperature), and is given by

$$C_p^{cld} = \eta_{pol,L} C_{pL}^{pol} + \eta_{pol,v} C_{pv}^{pol} + \eta_a C_p^a + \eta_{wv} C_{pv}^w + \eta_{wL} C_{pL}^w + \eta_{wi} C_{pi}^w$$

where $\eta_{pol,L}$, $\eta_{pol,v}$, η_a , η_{wv} , η_{wL} , η_{wi} and C_{pL}^{pol} , C_{pv}^{pol} , C_p^a , C_{pv}^w , C_{pL}^w , C_{pi}^w are the mass fractions and specific heat of pollutant vapour, dry air, water vapour, water liquid and ice, respectively.

For the non-equilibrium model the specific heat is evaluated at the vapour temperature T_{vap} . The specific heat of the vapour cloud C_p^{cld} (J/kg) excludes the liquid pollutant,

$$C_p^{cld} = \frac{\eta_{pol,v} C_{pv}^{pol} + \eta_a C_p^a + \eta_{wv} C_{pv}^w + \eta_{wL} C_{pL}^w + \eta_{wi} C_{pi}^w}{\eta_{pol,v} + \eta_a + \eta_{wv} + \eta_{wL} + \eta_{wi}}$$

Note that the droplet energy balance takes into account heat transfer from the vapour cloud to the liquid pollutant droplet.

Appendix C. Errors and warnings in UDM thermodynamics module THRM

Below information on errors/warnings/messages are given, which can currently be produced by the UDM thermodynamics module THRM.

Error messages:

1 "Cloud temperature calculation failed with enthalpy"

The thermodynamics module THRM provides the dispersion model UDM with cloud phase distributions, cloud temperatures, cloud densities and cloud volumetric flow-rates/volumes. This is described in detail in the UDM technical reference manual. The calculations involve an iterative technique, which can occasionally fail or not find a solution to the required calculation accuracy. Under these circumstances it is recommended that the user:

- i) Selects equilibrium thermodynamics. This is a somewhat simpler more robust thermodynamic approach, and/or
- ii) Disables heat transfer from the substrate

5 "Cannot do a fixed liquid fraction MA flash"

Currently, the MA flash method requires known temperature and pressure to determine the initial state. It cannot as yet find the initial state for mixtures by iterating temperature to find a specified liquid fraction. Temperature is always given as input to THRM in case of linked models, but for user-defined sources the users needs to specify temperature rather than liquid fraction for mixtures.

6 "Sum of mass fractions calculated by HMIXEQ does not equal one"

Mass is not being conserved in the solution.

Warning messages

1002 "Zero vapour enthalpy at temperature ___"

The thermodynamics module THRM provides the dispersion model UDM with cloud phase distributions, cloud temperatures, cloud densities and cloud volumetric flow-rates/volumes. This is described in detail in the UDM technical reference manual. The calculations involve an iterative technique, which can occasionally fail or not find a solution to the required calculation accuracy. Under these circumstances it is recommended that the user:

- iii) Selects equilibrium thermodynamics. This is a somewhat simpler more robust thermodynamic approach, and/or
- iv) Disables heat transfer from the substrate

NOMENCLATURE

a	coefficient in empirical correlations for Sherwood and Nusselt numbers (-)
A_d	droplet surface area, m^2
b	coefficient in empirical correlations for Sherwood and Nusselt numbers (-)
B_m	mass/heat transfer number in correlations for Sherwood/Nusselt numbers (-) [$B_m = C_{pm} (T_{vap} - T_d) / h_{fg}$]
C'	correction factor for Stefan flow (-)
C_{Dd}	drag coefficient of drop (-)
C_p^a	atmospheric specific heat capacity, J/kg/K
C_p^{cld}	vapour heat capacity of cloud mixture, J/kg/K
C_{pL}^{pol}	liquid heat capacity of condensable pollutant, J/kg/K
C_{pv}^{pol}	vapour heat capacity of condensable pollutant, J/kg/K
$D_{a,pol}$	diffusivity of the drop (released pollutant) into the surrounding medium, m^2/s
g	gravitational acceleration m/s^2
H_α	enthalpy of component α , J or J/s; $\alpha = cld$ (total cloud), $\alpha = pol,v$ (pollutant vapour), pol,L (pollutant liquid), wa (dry air), wv (water vapour), wn (non-vapour water)
h_α	specific enthalpy of component α , J/kg; $\alpha = cld$ (total cloud), $\alpha = pol,v$ (pollutant vapour), pol,L (pollutant liquid), wa (dry air), wv (water vapour), wn (non-vapour water)
l_{dz}	vertical component of droplet momentum [$l_{dz} = m_d u_{dz}$], kg m/s or kg/m/s ²
k	thermal conductivity of the gas, W/m/K
K_g	mass transfer coefficient, $kg/m^2/s^2$
M_a	molecular weight of dry air, kg/kmol
M_c	molecular weight of pollutant, kg/kmol
M_w	molecular weight of water, kg/kmol
m_{cld}	mass in plume (instantaneous release, kg) or mass rate in plume (continuous release, kg/s)
m_α	mass of component α , kg or kg/s; $\alpha = pol,v$ (pollutant vapour), pol,L (pollutant liquid), wa (dry air), wv (water vapour), wn (non-vapour water)
m_d	droplet mass, kg
m_{wv}^{gnd}	water-vapour added from the substrate, kg or kg/s
Nu	Nusselt Number [$Nu = h r_d / k$], (-)
P_a	atmospheric pressure, Pa
P_v^{pol}	saturated vapour pressure of released pollutant
Pr	Prandtl number [$Pr = C_{pv} \mu / k$] (-)
q_{gnd}	heat transfer rate from ground to cloud, J or J/s
R	gas constant, J/K/kmole

r_d	drop radius, m
Re	Reynolds number based on the relative velocity of the drops, (-) [$Re = 2r_d \rho_{cld} u_{dv} / \mu(T_m)$]
Sc	dimensionless Schmidt number for mass transfer [$Sc = \mu(T_m) / [\rho_a D_{12}(T_m)]$], (-)
Sh	dimensionless Sherwood number for evaporating droplets (ratio of total mass transfer to purely diffusive transfer) [$Sh = K_g r_d / D_{12}$], (-)
t	time, s
T_o	initial temperature of released material, K
T_a	ambient temperature, K
T_d	temperature of drops, K
T_{gnd}	substrate temperature, K
T_m	average of droplet and vapour temperature [$T_m = (T_{vap} + T_d) / 2$], K
T_{vap}	temperature of vapour phase of the cloud, K
u_{dx}, u_{dz}	horizontal and vertical components of drop velocity, m/s
u_d	absolute droplet velocity [$u_d = (u_{dx}^2 + u_{dz}^2)^{1/2}$], m/s
u_x, u_z	horizontal and vertical components of cloud speed, m/s
x	horizontal downwind distance, m
y	crosswind distance, m
y_g	mole fraction of condensable pollutant in the gas phase around the droplets [$y_g = 0$ for droplet evaporation in pure air] (-)
y_s	equilibrium mole fraction of condensable pollutant on the droplet surface, [$y_g = P_v(T_d) / P_a$], (-)
z	vertical height, m

Greek letters

$\mu_{a,pol}$	dynamic vapour viscosity of material in air, kg/m/s
$\nu_{a,pol}$	kinematic vapour viscosity of material in air, m ² /s
ρ_a	density of ambient air, kg/m ³
ρ_{cld}	density of plume, kg/m ³
$\rho_{pol,v}$	vapour density of condensable pollutant, kg/m ³
$\rho_{pol,L}$	liquid density of released material, kg/m ³
θ_d	angle of drop trajectory to horizontal, rad.



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