2. THERMODYNAMICAL DESCRIPTIONS IN HGSYSTEM

CONTENTS

2. THERMODYNAMICAL DESCRIPTIONS IN HGSYSTEM

There are two thermodynamical descriptions for fluids available in HGSYSTEM:

1. A *multi-compound, two-phase model* which calculates the two-phase liquid-vapour state of a mixture. The user can specify the mixture composition, choosing compounds as available in the HGSYSTEM database program DATAPROP. This thermodynamical description is quite general, but does *not* include the effect of any chemical reactions. The two-phase model is also sometimes called the *aerosol* model. It is described in full detail in Chapter 2.A.

   All HGSYSTEM models using this thermodynamical model need specific physical properties, like saturated vapour pressures, liquid densities, specific heats and so on, for all specified compounds in the mixture. It is strongly recommended to generate these properties using the database program DATAPROP and transfer the results to HGSYSTEM to be used via a link file. For details on this, see the DATAPROP chapter and Chapter 4 in the HGSYSTEM User's Manual. HGSYSTEM models using this aerosol model are: SPILL, AEROPLUME, HEGABOX and HEGADAS. LPOOL does use the compound properties as generated by DATAPROP but its pool description does not need a full thermodynamical model.

2. A *hydrogen fluoride (HF) chemistry and thermodynamical* model. This model is suitable for mixtures of HF, water and an inert ideal gas. It includes the effect of chemical reactions (reaction of HF and water, polymerisation of HF) and gives a full thermodynamical description based on the empirical relations of the so-called Schotte model. This very specific model is available because originally HGSYSTEM was developed to simulate the dispersion of HF releases only. The HF chemistry and thermodynamical model is discussed in full detail in Chapter 2.B. HGSYSTEM contains several HF-specific models: HFSPILL (only pure HF) and HFPLUME. Other models can optionally use the HF-model: HEGABOX and HEGADAS. LPOOL can use the physical properties of HF but does not need the full HF chemistry and thermodynamics.

The following two chapters (2.A and 2.B) give detailed descriptions of each of the two thermodynamical models mentioned above.

2.A. THE MULTI-COMPOUND, TWO-PHASE MODEL

2.A.1. Introduction

In accidental releases, the released pollutant often does *not* consist of a single inert gas in the vapour phase, but it consists of a mixture of inert gases and possibly water with possible accompanying aerosols. Following mixing of the pollutant with the moist air additional aerosol formation may occur.

This chapter discusses the standard HGSYSTEM two-phase thermodynamics model, new in HGSYSTEM version 3.0 as compared with version 1.0 (NOV90), that allows for a multi-compound pollutant and takes into account effects of possible aerosol formation. This chapter also discusses the implementation of this thermodynamic model into the HGSYSTEM dispersion models.

Thermodynamic Model

Following mixing of the pollutant with the moist air, the mixture is assumed to be in thermodynamic equilibrium, and the compounds contained in the mixture are assumed not to react with each other or to (de)polymerise.

Non-ideal liquid solutions (see below for details) and reactions with water (for example needed for ammonia and SO_3) are not taken into account. Concerning the mathematical description of aerosols the following possibilities for a pollutant compound are considered.

1. The compound has a *very low boiling point*. In this case the compound is always in the vapour phase and does not form part of an aerosol. Examples: oxygen, nitrogen, etc.

2. The compound has a *very high boiling point*. In this case the compound is always in the liquid phase and does not evaporate. Example: H_2SO_4 aerosol upon release of pollutant consisting of propane and H_2SO_4.

3. The compound may be present in both vapour and liquid phase. The following types of aerosols can be distinguished (see for example [1] for details).

    a. The compound forms a single, separate aerosol (individual droplets), which does not interact with possible aerosols for other pollutant compounds. For this case the amount of aerosol formation can be calculated using *Dalton's law*. This law states that in the presence of an aerosol, the mole fraction of the compound in the vapour equals the ratio of the partial vapour pressure for the compound and the total vapour pressure. Example: separate propane and water aerosols upon release of (cold) propane in humid air.

b. The compound forms a so-called *ideal liquid solution* with a number of other compounds. The vapour and liquid mole fractions for each compound in the aerosol can be derived via *Raoult's law*. This law states that in the presence of an aerosol, the ratio of the mole fraction of the compound in the vapour and the mole fraction of the compound in the aerosol equals the ratio of the partial vapour pressure for the compound and the total vapour pressure. Ideal solutions will usually be formed for compounds which have a similar chemical structure. Example: single propane/butane aerosol upon release of a pollutant consisting of propane and butane

c. The compound forms a *non-ideal liquid solution* with a number of other compounds. In this case Raoult's law as stated above is not applicable.

While the aerosol formation for an ideal solution can be determined via Raoult's law from individual saturated vapour-pressure functions for each individual compound, the determination of the aerosol formation for an non-ideal solution involves much more empiricism. In literature this is usually determined by means of one of the following two methods:

- By means of *generalisation of Dalton's law* by adding an empirical parameter called the 'convergence pressure'. The value of this convergence pressure is purely empirically determined and depends on the precise composition of the mixture, i.e. the amount of each compound present in the mixture.
- By means of a *Peng-Robinson equation of state* of the mixture, which involves empirical binary interaction coefficients between the compounds.

The reader is referred to [1] for further details.

It is clear from the above that the determination of the aerosol formation for a non-ideal liquid solution requires a massive amount of empiricism, and is therefore not practical for implementation into HGSYSTEM.

However, it is believed that for most practical release scenarios either one of the above cases a and b should enable sufficient accurate dispersion predictions.
Therefore non-ideal liquid solutions will not be taken into account, and *ideal liquid* solutions are assumed in HGSYSTEM.

Implementation of thermodynamic model in HGSYSTEM

The above thermodynamic model is complex and requires a large number of physical properties for each of the compounds. Thus the development of the HGSYSTEM property database program DATAPROP is required, which generates the required pollutant properties to each of the HGSYSTEM models.

See the HGSYSTEM User's Manual chapter on DATAPROP for use of the database program. Technical details of DATAPROP (only useful for expert users) can be found in [2]. In [2] it is also discussed how new compounds can be added to DATAPROP. Users are advised not to change the DATAPROP database without first consulting the HGSYSTEM developers.

Outside the thermodynamic routines within the HGSYSTEM dispersion models, averaged properties are adopted for the pollutant, whereas within the thermodynamic routines properties for each of the individual pollutant compounds are required (specific heats, heat of vaporisation, saturated vapour pressure, etc.).

Outline of this chapter

The outline for the rest of this chapter is as follows.

Paragraph 2.A.2 describes the new theoretical thermodynamics model. A set of thermodynamic equations for the unknown thermodynamic quantities is derived, and the criteria for aerosol formation is defined.

Paragraph 2.A.3 discusses the algorithm for solving these equations for both the general case, the specific case of a series of one-compound aerosols and the specific case of a single two-compound aerosol. It also discusses the implementation of the thermodynamic model into the HGSYSTEM dispersion models.

2.A.2. Thermodynamics model

This paragraph describes the two-phase thermodynamics model for mixing of moist air with a pollutant consisting of a number of ideal non-reactive fluids and water. In case of ground-level dispersion (HEGADAS and HEGABOX but not AEROPLUME)), the model may take into account water-vapour transfer and heat transfer from the substrate to the cloud.

The mixture is assumed to consist of dry air and a number of non-reactive compounds. Each of the compounds may occur both in liquid and vapour phase. Water may consist of liquid water and/or ice.

It is assumed that the liquid in the mixture is composed of a number of non-interacting aerosols and that each compound forms part of not more than one of these aerosols. If an aerosol consists of more than one compound, the aerosol is assumed to be an ideal liquid solution of its constituent compounds.

Paragraph 2.A.2.1 describes the model parameters that are required as input to the thermodynamics model.

Paragraph 2.A.2.2 lists the basic unknown thermodynamic variables in the model and derives the thermodynamic equations for these variables.

In paragraph 2.A.2.3 the criterion is determined for aerosol formation.

2.A.2.1. Model parameters

The model parameters are as follows:

1. Pollutant (original release) data:
    - Mole fraction of pollutant in mixture, y_{pol}.

    - Mole fraction of each compound in the pollutant, η_α ($\alpha = 0,...,N$).
      In addition to possibly dry air and water it is assumed that the pollutant consists of N - 1 compounds ($N > 2$); $\alpha = 0, 1$ are taken to correspond to dry air and water, respectively.

    - Pollutant enthalpy, H_{pol} (J/kmole).
      Enthalpies are taken to be zero at 0 °C, with unmixed gaseous compounds.
      The pollutant enthalpy H_{pol} can be calculated from the pollutant temperature and the pollutant composition by imposing thermodynamic equilibrium to the initial pollutant state.
      See the end of paragraph 2.A.3.2 and Chapter 7.A, Appendix 7.A.D. for details (HEGADAS and HEGABOX).

   The above data uniquely define the amount of pollutant in the mixture, the pollutant composition and the pollutant enthalpy.

2. Ambient data:
    - humidity r_H (-).

- ambient temperature T_a (°C).

The above data uniquely define the composition of the air (mole fractions of dry air and water) and the enthalpy H_{air}^{wet} of the moist air (Joule/kmole of moist air).

3. Substrate data:
   - mole fraction y_{w3} of water vapour added from substrate (-)
   - heat added from the substrate, H_e (J/kmole)
   - substrate temperature T_s (°C)

The data y_{w3} and T_s uniquely define the amount and enthalpy of the water vapour added to the mixture. These parameters only apply to HEGADAS and HEGABOX.

4. Properties of each compound in the mixture.
   Dry air (α=0):
   - molecular weight m^a (kg/kmole)
   - specific heat $C_p{}^a$ (J/kmole/K)
   - Other compounds (α = 1,2,...,N; α = 1 is chosen to correspond to water)
     - molecular weight m^α (kg/kmole)
     - specific heats $C_p{}^{\alpha v}$, $C_p{}^{\alpha l}$ (J/kmole/K) for vapour and liquid
     - heat of condensation $H^\alpha{}_{cond}$ (J/kmole)
     - coefficients in the formula defining the saturated vapour pressure of the compound $P_v{}^\alpha(T_m)$ as function of the mixture temperature T_m. This (Wagner) equation is given in the description of the GASDATA input block, SPECIES keyword, for each model using the two-phase thermodynamical model.
     - in addition for water only (α = 1): specific heat of ice, C_p^{wi} (J/kmole/K), and heat of fusion, H_{fus}^{w} (J/kmole)

Furthermore compounds $\alpha = n_{\beta-1}+1, n_{\beta-1}+2, ..., n_\beta$ are known to potentially form aerosol β ($\beta = 1, 2, ..., M$; $0 = n_0 < n_1 < n_2 < ..... < n_M = N$). Notice that aerosol $\beta = 1$ includes the liquid water (compound $\alpha = 1$).

The values of specific heats, heats of condensation and fusion are assumed to correspond with values at standard atmospheric pressure (1 atmosphere) and at an appropriately chosen reference temperature. The specific heat values for typical temperatures between -50 °C and 50 °C and pressures 'close' to 1 atmosphere are not expected to differ considerably from these values.

5. Total vapour pressure P.
   This pressure equals the ambient atmospheric pressure, which for a pressurised release equals the pressure immediately following the depressurisation of the pollutant at the point of release.

The above mentioned parameters uniquely define the composition of the mixture (mole fractions y_α ($\alpha = 0, 1, ..., N$) and the total enthalpy of the mixture, H_{tot} (J/kmole).

2.A.2.2. Basic thermodynamic unknowns and equations

The unknown thermodynamic variables are as follows:

1. mole fraction $y_{\alpha v}$ of *vapour* for each mixture compound ($\alpha = 1, ..., N$) (-)

2. mole fraction $y_{\alpha n}$ of *liquid* for each mixture compound ($\alpha = 1, ..., N$) (-)

3. mole fraction liquid L_β of each aerosol ($\beta = 1, ..., M$) (-)

4. total mole fraction of liquid, L (-)

5. mixture temperature T_m (°C)

The above unknowns must satisfy the following equations:

1. *Conservation of molar flow for each compound*

$$y_\alpha = y_{\alpha v} + y_{\alpha n} \qquad (1)$$

2. *Raoult's law for each compound*

$$y_{\alpha v} = \min\left\{ y_\alpha, \left[\left(\frac{y_{\alpha n} \cdot (1-L)}{L_\beta} \right) \cdot \left(\frac{P_v^\alpha(T_m)}{P} \right) \right] \right\} \qquad (2)$$

Application of the above law implies that each aerosol β (β = 1,..,M) is assumed to be an ideal liquid solution of its constituent compounds $\alpha = n_{\beta\text{-}1}+1,.., n_\beta$.

Raoult's law states that in the presence of aerosol β, the ratio of the mole fraction $y_{\alpha v}/(1\text{-}L)$ of the compound α in the vapour and the mole fraction $y_{\alpha n}/L_\beta$ of the compound α in the liquid solution β equals the ratio $P_v^\alpha(T_m)/P$ of the saturated vapour pressure of compound α in the vapour and the total vapour pressure.

For a one-compound aerosol ($y_{\alpha n} = L_\beta$; $\alpha = n_\beta = n_{\beta\text{-}1} + 1$), Raoult's law reduces to Dalton's law $y_{\alpha v}/(1\text{-}L) = P_{v\alpha}(T_m)/P$.
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, [1] for further details of Raoult's and Dalton's laws.

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

$$L_\beta = \sum_{\alpha=n_{\beta-1}+1}^{n_\beta} y_{\alpha n} \qquad (\beta = 1,..., M) \qquad (3)$$

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

$$L = \sum_{\beta=1}^{M} L_\beta \qquad (4)$$

5. *Conservation of energy:*

$$H_{tot} = \sum_{\alpha=0}^{N} H_\alpha = y_{pol} \cdot H_{pol} + (1 - y_{pol} - y_{w3}) \cdot H_{air}^{wet} + H_e + y_{w3} \cdot C_p^{wv} \cdot T_s \qquad (5)$$

where the post-mixing enthalpy of compound α (α = 0, 1,..., N) is given by

$$H_\alpha = y_\alpha \cdot C_p^a \cdot T_m \qquad \text{(dry air, } \alpha = 0\text{)}$$

$$y_{\alpha v}\cdot C_p^{wv}\cdot T_m + y_{\alpha n}\cdot (C_p^{wl}\cdot T_m - H_{cond}^{w}) \qquad \text{(water with } T_m > 0\ °\text{C}, \alpha = 1)$$

(6)

$$y_{\alpha v}\cdot C_p^{wv}\cdot T_m + y_{\alpha n}\cdot (C_p^{wi}\cdot T_m - H_{cond}^{w} - H_{fus}^{w}) \qquad \text{(water with } T_m < 0\ °\text{C. } \alpha = 1)$$

$$y_{\alpha v}\cdot C_p^{\alpha v}\cdot T_m + y_{\alpha n}\cdot (C_p^{\alpha l}\cdot T_m - H_{cond}^{\alpha}) \qquad (\alpha = 2,...,N)$$

Dry air corresponds with $\alpha = 0$ and water with $\alpha = 1$.

Equation (5) expresses that the total post-mixing enthalpy H_{tot} equals the sum of the pollutant enthalpy, the enthalpy of the ambient moist air, the heat added from the substrate and the enthalpy of the water-vapour added from the substrate.

2.A.2.3. Criterion for aerosol formation

The thermodynamic equations (1), (2), (3), (4) and (5) are to be solved for the thermodynamic unknowns $y_{\alpha v}$, $y_{\alpha n}$ (α = 1,..., N), L_β (β=1,..., M), L and T_m.
The unknowns $y_{\alpha v}$ and $y_{\alpha n}$ can be eliminated as unknowns using Equations (1) and (2),

$$y_{\alpha v} = \left\{1+\frac{L_\beta}{1-L}\cdot\frac{P}{P_v^\alpha(T_m)}\right\}^{-1}\cdot y_\alpha \qquad (\alpha = n_{\beta-1}+1,...,n_\beta;\ \beta = 1,...,M) \qquad (7)$$

$$y_{\alpha n} = \left\{1+\frac{1-L}{L_\beta}\cdot\frac{P_v^\alpha(T_m)}{P}\right\}^{-1}\cdot y_\alpha \qquad (\alpha = n_{\beta-1}+1,...,n_\beta;\ \beta = 1,...,M) \qquad (8)$$

Insertion of equation (8) into (3) leads to the equation $F_\beta(L_\beta;L,T_m) = 1$ for L_β, with the function $F_\beta(L_\beta;L,T_m)$ defined by

$$F_\beta(L_\beta;L,T_m) = \sum_{\alpha=n_{\beta-1}+1}^{n_\beta}\left[\frac{y_\alpha\cdot\left(\dfrac{P}{P_v^\alpha(T_m)}\right)}{1-L+L_\beta\cdot\left(\dfrac{P}{P_v^\alpha(T_m)}\right)}\right] \qquad (9)$$

The function $F_\beta(L_\beta;L,T_m)$ monotonously decreases with increasing values of L_β. Aerosol formation requires that the equation $F_\beta(L_\beta;L,T_m) = 1$ has a positive root L_β. Thus the criterion for formation of aerosol β is $F_\beta(0;L,T_m) > 1$, or equivalently,

$$S[\beta;T_m] \overset{\text{def}}{=} 1-\sum_{\alpha=n_{\beta-1}+1}^{n_\beta}\left[y_\alpha\left(\frac{P}{P_v^\alpha(T_m)}\right)\right] < L \iff L_\beta > 0 \qquad (\beta = 1,...,M) \qquad (10)$$

If the above condition $S[\beta;T_m] < L$ is satisfied, the equation $F_\beta(L_\beta;L,T_m) = 1$ has precisely one positive root L_β.
Note that according to formula (9), multiplication of the equation $F_\beta(L_\beta;L,T_m) = 1$ with each denominator $[1-L+L_\beta \cdot P/P_v^\alpha(T_m)]$, $\alpha = n_{\beta-1}+1,.., n_\beta$ leads to a polynomial equation for L_β of the order $(n_\beta - n_{\beta-1})$.
This equation can be solved analytically for $n_\beta - n_{\beta-1} = 1$, 2 and 3.
For higher orders equation (9) can be solved, without transformation to a polynomial, using the non-linear algebraic equations solver NAESOL [3]. This is used in the AEROPLUME and SPILL implementation of the aerosol model.

Thus the overall equation for L_β ($\beta = 1,..., M$) is given by

$$\begin{array}{lll} F_\beta(L_\beta;L,T_m) = 1, & \text{if } S[\beta;T_m] < L & (L_\beta > 0;\ \text{aerosol formation}) \\ L_\beta = 0 & \text{if } S[\beta;T_m] \geq L & (\text{no aerosol formation}) \end{array} \qquad (11)$$

The thermodynamic equations (7), (8), (11), (4) and (5) are to be solved for the thermodynamic unknowns $y_{\alpha v}$, $y_{\alpha n}$ ($\alpha = 1,..., N$), L_β ($\beta = 1,..., M$), L and T_m.

Elimination of $y_{\alpha v}$ and $y_{\alpha n}$ ($\alpha = 1,..., N$) using equations (7) and (8) leads to the reduced set of equations (11), (4)and (5) for L_β ($\beta = 1,..., M$), L and T_m.

2.A.3. Solution algorithm

This paragraph describes the solution algorithm with which the thermodynamic equations described in paragraph 2.A.2 are solved.

Paragraph 2.A.3.1 contains the solution algorithm for the general problem, paragraph 2.A.3.2 discusses the solution algorithm for the specific case of separate one-compound aerosols (absence of multi-compound aerosols), whereas paragraph 2.A.3.3 discusses the solution algorithm for the specific case of a single two-compound aerosol. Paragraph 2.A.3.4 discusses the implementation of the thermodynamics solution algorithm into the dispersion model.

2.A.3.1. General problem

This paragraph describes the algorithm for solving the equations (7), (8), (11), (4) and (5) for the thermodynamic unknowns $y_{\alpha v}$, $y_{\alpha n}$ ($\alpha = 1,..., N$), L_β ($\beta = 1,..., M$), L and T_m.

It is this *general algorithm* which is used in AEROPLUME and SPILL. Note that HEGADAS and HEGABOX use less general algorithms as discussed below (paragraphs 2.A.3.2 and 2.A.3.3).

For details on how AEROPLUME uses the thermodynamical model, see Chapter 5.A., paragraphs 5.A.3 and 5.A.7. The SPILL implementation of the aerosol model is identical to the AEROPLUME one (only slightly more dry air is added for numerical reasons).

The algorithm below is formulated in terms of four convergence control parameters, these are

- the absolute convergence tolerance ε_T for the mixture temperature T_m,
- the absolute convergence tolerance ε_L for the liquid fraction L,
- the maximum number i_{max} of outer iteration steps for T_m,
- the maximum number k_{max} of inner-most iteration steps for L.

The subsequent steps in the thermodynamic routine are as follows:

1. Assume that no fog forms: set $y_{\alpha n} = 0$, $y_{\alpha v} = y_\alpha$ ($\alpha = 1,..., N$), $L_\beta = 0$ ($\beta = 1,..,M$), L = 0 and determine T_m from equation (5).

2. Initialise the outer iteration loop for evaluation of T_m (i is number of iterations, T_m^i is estimate of T_m after i iterations): i = 0, $T_m^i = T_m$.

3. Carry out the next outer iteration step i+1 for the temperature T_m:

   a) Order $S[\beta;T_m^i]$ in ascending order ($\beta = 1,..,M$): $S[\beta_1;T_m^i] < S[\beta_2;T_m^i] < .... < S[\beta_M;T_m^i]$. According to equation (11) aerosol β_j can only be present if the aerosols $\beta_1,.., \beta_{j-1}$ are also present (j = 1,..,M). Thus aerosol β_1 forms 'first' and aerosol β_M forms 'last'.

   b) Initialise inner iteration loop for evaluation of L [aerosols β_1, β_2, .., β_j have been established to be present at temperature T_m^i, and L_j is the value for L assuming the presence of aerosols $\beta_1,.., \beta_j$ only]: j = 0, $L_j = 0$.

   c) Establish if aerosol β_{j+1} is present by carrying out the next inner iteration j+1 for the liquid fraction L:

      1. If $S[\beta_{j+1};T_m^i] > L_j$, than according to equation (11) aerosols $\beta_{j+1},..., \beta_M$ do *not* form at temperature T_m^i ($L_\beta = 0$ for $\beta = \beta_{j+1},.., \beta_M$): set $L = L_j$ and go to Step d)

2. If $S[\beta_{j+1};T_m^i] < L_j$, than according to equation (11) aerosol β_{j+1} *does* form at temperature T_m^i; calculate the aerosol formation (L_{j+1}, β_1,.., β_{j+1}) assuming the presence of aerosols β_1,.., β_{j+1} only:

   (a) Initialise the inner-most iteration loop: $k = 0$, $L^k = L_j$, $L = L^k$.

   (b) $k = k+1$; set L_β for $\beta = \beta_1$,.., β_{j+1} from $F_\beta(L_\beta;L,T_m^i)=1$, which using equation (9) can be transformed into a polynomial equation in L_β of order $(n_\beta - n_{\beta-1})$.
   In the general case this equation need not be transformed, but can be solved directly using the NAESOL solver [3]. This method is followed in SPILL and AEROPLUME.

   (c) Set L from L_β ($\beta = \beta_1,..,\beta_{j+1}$) using equation (4), $L^k = L$.

   (d) Check for convergence (three cases):

   - If $k < k_{max}$ and $|L^k - L^{k-1}| > \varepsilon_L$ (no convergence): go to (b) (carry out next inner-most iteration for L).

   - If $k = k_{max}$ and $|L^k - L^{k-1}| > \varepsilon_L$ (no convergence within maximum number of inner-most iterations): stop thermodynamic calculations and produce error message.

   - If $|L^k - L^{k-1}| < \varepsilon_L$ (convergence): $j = j+1$, $L_j = L^k$, $L = L_j$.

   (e) If $j < M$ establish if aerosol β_{j+1} is present: go to start of Step c).

d) Set $y_{\alpha v}$, $y_{\alpha n}$ from L_β ($\beta = 1,..,M$), L, T_m^i using Equations (7) and (8).

e) Set T_m from $y_{\alpha v}$, $y_{\alpha n}$ using equation (5); $i = i+1$; $T_m^i = T_m$.

f) Check for convergence of temperature T_m (three cases):

- If $i < i_{max}$ and $|T_m^i - T_m^{i-1}| > \varepsilon_T$ (no convergence): go to Step a) (carry out next iteration for temperature).

- If $|T_m^i - T_m^{i-1}| < \varepsilon_T$ (convergence): *end of thermodynamic calculations.*

- If $i = i_{max}$ and $|T_m^i - T_m^{i-1}| > \varepsilon_T$ (no convergence within i_{max} iterations), and if assuming $T_m < 0$ °C, equation (5) leads to $T_m > 0$ °C and if assuming $T_m > 0$ °C, equation (5) leads to $T_m < 0$ °C, than ice is partially melted. Set for this case $T_m = 0$ °C and set L, $y_{\alpha v}$, $y_{\alpha n}$ ($\alpha = 1,..., N$) as described in Steps a), b), c) and d): *end of thermodynamic calculations*.

2.A.3.2. Case of separate one-compound aerosols

In this paragraph the special case is considered for the mixture consisting of *non-interacting one-compound aerosols* (individual droplets).

This case is available in HEGADAS and HEGABOX. AEROPLUME and SPILL use the general case as described in paragraph 2.A.3.1.

Following the notation of paragraph 2.A.2, M = N, $L_\alpha = y_{\alpha n}$ ($\alpha = 1,..., N$), $n_\beta = \beta$ ($\beta = 1,..., N$). Furthermore Raoult's law given by equation (2) reduces to Dalton's law,

$$y_{\alpha v} = \min\left\{ y_\alpha, (1-L)\cdot\frac{P_v^\alpha(T_{m)}}{P} \right\} \qquad (\alpha = 1,...,N) \qquad (12)$$

and it follows from Equations (1), (12) and (4) that the total mole fraction of aerosol can be expressed by

$$L = 1 - \frac{A}{(1-B)} \qquad (13)$$

where A is the total mole fraction in the *mixture* of those compounds for which an aerosol does not form ($y_{\alpha n} = 0$), and where B is total mole fraction in the *vapour* of those compounds for which an aerosol does form ($y_{\alpha n} > 0$),

$$A = y_0 + \sum_{\alpha=1,...,N;y_{\alpha n}=0} y_\alpha$$
$$B = \sum_{\alpha=1,...,N;y_{\alpha n}>0} \frac{P_v^\alpha(T_m)}{P} \qquad (14)$$

Solution to Thermodynamic Equations

The equations (1), (12), (13) and (5) for $y_{\alpha v}$, $y_{\alpha n}$ ($\alpha = 1,..., N$), L, T_m are solved by means of the following algorithmic steps in the thermodynamic routine (ε_T = convergence tolerance for mixture temperature T_m, i_{max} = maximum number of iterations for T_m):

1. Assume that no fog forms: set $y_{\alpha n} = 0$, $y_{\alpha v} = y_\alpha$ ($\alpha = 1,..., N$), $L = 0$ and determine T_m from equation (5).

2. Initialise the outer iteration loop for evaluation of T_m (i is number of iterations, $T_m^{\,i}$ is estimate of T_m after i iterations): $i = 0$, $T_m^{\,i} = T_m$.

3. Carry out the next outer iteration i+1 for the temperature T_m:

    a) Order $S[\alpha;T_m^{\,i}] = 1 - y_\alpha \cdot P/P_v^{\alpha}(T_m^{\,i})$ in ascending order ($\alpha = 1,...,N$): $S[\alpha_1;T_m^{\,i}] < S[\alpha_2;T_m^{\,i}] < .... < S[\alpha_N;T_m^{\,i}]$.
    Note from equation (10) that aerosols 'first' form for compound α_1 and 'last' form for compound α_N.

    b) Initialise the inner iteration loop for evaluation of L [aerosols for compounds $\alpha_1,...,\alpha_j$ do form at temperature $T_m^{\,i}$.
    L_j, A and B are the values for L, A and B from Equations (13) and (14) assuming the presence of aerosols for compounds $\alpha_1,...,\alpha_j$ only]: $j = 0$, $L_j = 0$, $A = 1$, $B = 0$.

    c) Establish if aerosol α_{j+1} is present at temperature $T_m^{\,i}$ by carrying out the next inner iteration j+1 for the liquid fraction L:

        1. If $S[\alpha_{j+1};T_m^{\,i}] > L_j$ than aerosols for compounds $\alpha_{j+1},...,\alpha_N$ do *not* form ($y_{\alpha n} = 0$ for $\alpha = \alpha_{j+1},.., \alpha_N$): set $L = L$ and go to Step d).

        2. If $S[\alpha_{j+1};T_m^{\,i}] < L_j$, than aerosol for compound α_{j+1} *does* form:

            - increment j: $j = j+1$, $A = A - y_{\alpha j}$, $B = B + P_v^{\alpha j}(T_m^{\,i})/P$, $L_j = 1 - A/(1 - B)$, $L = L_j$.

            - if $j < N$ carry out next iteration: go to Step c).

    d) Set $y_{\alpha v}$, $y_{\alpha n}$ ($\alpha = 1,...,N$) from L and $T_m^{\,i}$ using Equations (1) and (12)

    e) Set T_m from $y_{\alpha v}$, $y_{\alpha n}$, L using equation (5); $i = i+1$; $T_m^{\,i} = T_m$

    f) Check for convergence of temperature T_m (three cases):

        - If $i < i_{max}$ and $|T_m^{\,i} - T_m^{\,i-1}| > \varepsilon_T$ (no convergence): go to Step a) (carry out next iteration for temperature).

- If $|T_m^{\,i} - T_m^{\,i-1}| < \varepsilon_T$ (convergence): *end of thermodynamic calculations.*

- If $i = i_{max}$ and $|T_m^{\,i} - T_m^{\,i-1}| > \varepsilon_T$ (no convergence within i_{max} iterations), and if assuming $T_m < 0$ °C equation (5) leads to $T_m > 0$ °C and if assuming $T_m > 0$ °C equation (5) leads to $T_m < 0$ °C , than ice is partially melted. Set for this case $T_m = 0$ °C and set L, $y_{\alpha v}$, $y_{\alpha n}$ ($\alpha = 1,...,N$) as described in Steps a), b), c), and d): *end of thermodynamic calculations.*

<u>Order of Aerosol Formation During Mixture Cooling</u>

Assume that during temperature cooling of a mixture with given constant composition $y_0, y_1,.., y_N$ ($\alpha = 0$ corresponds to dry air) aerosols for compounds $\alpha = 1,.., N$ form successively at the temperatures $T_1, T_2,.., T_N$ (with $T_1 > T_2 > .. > T_N$).
Thus compound 1 condenses first and compound N condenses last.

Consider a temperature T with $T_{j-1} > T > T_j$ ($j = 2,..,N$), i.e. aerosols $\alpha = 1,..,j-1$ are present and compounds $\alpha = j,..,N$ occur in vapour phase only. Following Equations (13) and (14), L is given by

$$L = 1 - \frac{\left\{1 - \sum_{\alpha=1}^{j-1} y_\alpha\right\}}{\left\{1 - \sum_{\alpha=1}^{j-1} \frac{P_v^\alpha(T)}{P}\right\}} \qquad T_{j-1} > T > T_j \tag{15}$$

At the temperature T_j onset of formation of aerosol j starts.

Thus following equation (10), $S[j;T_j] = 1 - y_j \cdot P/P_v^j(T_j) = L$, or equivalently, using the above equation (15),

$$y_j \cdot \left\{1 - \sum_{\alpha=1}^{j-1} \frac{P_v^\alpha(T)}{P}\right\} = \left(\frac{P_v^j(T)}{P}\right) \cdot \left\{1 - \sum_{\alpha=1}^{j-1} y_\alpha\right\} \tag{16}$$

Above equation (16) defines the temperature T_j at which aerosol j forms.

Note that for j=1, this equation reduces to Dalton's law $y_1 = P_v^1(T_1)/P$, defining the onset of condensation of the first compound within the mixture (formation of first aerosol).

For j = N with absence of air ($y_0 = 0$), equation (16) reduces to

$$\sum_{\alpha=1}^{N} \frac{P_v^{\alpha}(T)}{P} = 1 \qquad \text{(for } y_0 = 0\text{, no dry air)} \qquad (17)$$

defining the onset of condensation of the last compound within the mixture.

The temperature T will stay equal to the temperature T_N until all vapour has been condensed (L = 1). For temperature $T < T_N$, the mixture will be pure liquid.

Initial Pollutant State

Applying the above discussion to the initial pollutant (prior to mixing), it follows from equation (17) and (14) that B = 1 in the expression (13) for the liquid fraction L at the temperature T_N.

Thus the thermodynamic problem is ill conditioned if all compounds do occur in two phases. To avoid associated numerical problems 0.01% of dry air is added to the initial pollutant in order to force the presence of at least one compound in the pure vapour phase.
This holds for the general version of the algorithm (paragraph 2.A.3.1) as well. Dry air is added in all HGSYSTEM modules using the aerosol thermodynamical model. In SPILL 0.1% dry air is added for numerical reasons.

For HEGADAS and HEGABOX, input to the thermodynamic model is either the temperature T_{pol} or the enthalpy H_{pol} of the pollutant prior to mixing with the air. If $T_{pol} \approx T_N$ the user is advised not to prescribe T_{pol} but H_{pol}.
The calculation of H_{pol} should be based on equation (6) using the known value of T_{pol} and the amount of liquid present for each pollutant compound.
The latter liquid fractions could be derived either from flash calculations or by imposing thermodynamic equilibrium to the initial pollutant state (i.e. by imposing equations (1-5), with $y_{pol} = 1$, $H_e = 0$, $y_{w3} = 0$).

Note that for AEROPLUME and SPILL, the user does not have to give this input to the thermodynamical model as the data is calculated by the model from reservoir (or stack) conditions as given by the user.

For a pollutant consisting of a single compound (N = 1) the above situation arises if the temperature of the pollutant equals the boiling temperature of the pollutant. Thus in this case the user needs to know the amount of liquid fraction in the pollutant, in order to evaluate the pollutant enthalpy.

2.A.3.3. Case of single two-compound aerosol

In this paragraph the special case is considered of the mixture consisting of *one two-compound aerosol* (ideal solution; compounds α =1, 2). All other compounds occur in vapour phase only (compounds α = 3,..,N).

Thus following the notation of paragraph 2.A.3.2.: M = 1, L_1 = L, n_1 = 2, $y_{\alpha n}$=0 (α=3,..,N), $y_{\alpha v}$=y_α (α = 3,..,N).

This case is available in HEGADAS and HEGABOX. Note that SPILL and AEROPLUME have the general case available as discussed in paragraph 2.A.3.1.

The 6 remaining unknowns to be evaluated are $y_{\alpha v}$, $y_{\alpha n}$ (α = 1,2), L and T_m.

The 6 governing equations for these unknowns are equations (7), (8), (11) and (5). Using formula (9), equation (11) can be rewritten as a square equation for L,

$$q_1 q_2 L^2 - (r_1 q_2 + r_2 q_1) L - (1 + r_1 + r_2) = 0 \tag{18}$$

where the auxiliary parameters q_α, r_α (α = 1,2) are given by

$$\begin{aligned} q_\alpha(T_m) &= \left(\frac{P}{P_v^\alpha(T_m)} \right) - 1 \\ r_\alpha(T_m) &= y_\alpha \cdot \left(\frac{P}{P_v^\alpha(T_m)} \right) - 1 \end{aligned} \tag{19}$$

where $-1 < r_\alpha \leq q_\alpha$.

The root to equation (18) satisfying $L \rightarrow y_1 + y_2$ for $P_v^\alpha(T_m) \rightarrow 0$ (i.e. compounds α = 1,2 are 100% liquid for very low temperatures), equals

$$L = \frac{\left([r_1 q_2 + r_2 q_1] + \{ [r_1 q_2 + r_2 q_1]^2 + 4[q_1 q_2][1 + r_1 + r_2] \}^{1/2} \right)}{[2 q_1 q_2]}$$

or, written alternatively (20)

$$L = \frac{2[1 + r_1 + r_2]}{\left(-[r_1 q_2 + r_2 q_1] + \{ [r_1 q_2 + r_2 q_1]^2 + 4[q_1 q_2][1 + r_1 + r_2] \}^{1/2} \right)}$$

Solution to Thermodynamic Equations

The equations (7), (8), (20) and (5) for $y_{\alpha v}$, $y_{\alpha n}$ ($\alpha = 1,2,...,N$), L, T_m are solved by means of the following algorithmic steps in the thermodynamic routine (ε_T = convergence tolerance for mixture temperature T_m, i_{max} is maximum number of iterations for T_m):

1. Assume that no fog forms: set $y_{\alpha n} = 0$, $y_{\alpha v} = y_\alpha$ ($\alpha = 1,...,N$), L = 0 and determine T_m from equation (5).
   If $[1+r_1+r_2] < 0$ (aerosol does not form): *end of thermodynamic calculations*.

2. Initialise the iteration loop for the evaluation of T_m (i is number of iterations, T_m^i is estimate of T_m after i iterations): i = 0, $T_m^i = T_m$.

3. Carry out the iteration loop for the temperature T_m:

   a. Set $L = L(T_m^i)$ from equation (20). Set $y_{\alpha v}$, $y_{\alpha n}$ ($\alpha = 1,2$) from Equations (7) and (8).

   b. Set T_m from $y_{\alpha v}$, $y_{\alpha n}$, L using equation (5); i = i+1; $T_m^i = T_m$.

   c. Check for convergence of temperature T_m (three cases):

      - If $i < i_{max}$ and $|T_m^i - T_m^{i-1}| > \varepsilon_T$ (no convergence): go to Step a. (carry out next iteration for temperature).

      - If $|T_m^i - T_m^{i-1}| < \varepsilon_T$ (convergence): *end of thermodynamic calculations*.

      - If $i = i_{max}$ and $|T_m^i - T_m^{i-1}| > \varepsilon_T$ (no convergence within i_{max} iterations), and if assuming $T_m < 0$ °C, equation (5) leads to $T_m > 0$ °C and if assuming $T_m > 0$ °C, equation (5) leads to $T_m < 0$ °C , than ice is partially melted. Set for this case $T_m = 0$ °C and set L, $y_{\alpha v}$, $y_{\alpha n}$ ($\alpha = 1,...,N$) as described in Step a.

2.A.3.4. Implementation of thermodynamics into dispersion model

This paragraph discusses the implementation of the thermodynamics solution algorithm into the HGSYSTEM dispersion models.

Paragraph 2.A.2.1 outlined the parameters required as input to the thermodynamic model. These input parameters are obtained as follows:

1. User-specified parameters.

The user is required to input to the dispersion model:

- the pollutant composition (mole fractions η_α, $\alpha = 1,...,N$)
- pollutant temperature T_{pol} or alternatively, pollutant enthalpy H_{pol} (*only for HEGADAS and HEGABOX*)
- ambient humidity r_H, ambient temperature T_a, ambient pressure P
- ground temperature T_s (*only for HEGADAS and HEGABOX*).

For model-specific information on input parameters, see the relevant chapter in the HGSYSTEM User's Manual.

2. Properties generated by the property database program DATAPROP.

Based on the user-specified pollutant composition, the physical property database program DATAPROP is used to calculate the required pollutant properties. See DATAPROP chapter in the HGSYSTEM User's Manual for more information on how to use DATAPROP.

3. Solution parameters generated by dispersion program.

The pollutant molar fraction y_{pol}, the heat H_e and the water vapour y_{w3} added from the substrate are a function of downwind distance and are generated by the dispersion model as input to the thermodynamic routine. The latter two apply only to HEGADAS and HEGABOX.
These variables are calculated internally by the dispersion model by solving ordinary differential equations in the downwind direction, i.e. by solving empirical entrainment, heat-transfer and water-vapour transfer equations.

For details on how AEROPLUME uses the thermodynamical model, see Chapter 5.A., paragraphs 5.A.3 and 5.A.7.

In the HEGADAS and HEGABOX dispersion model the thermodynamics model is required to evaluate from the above input parameters the mixture temperature T_m (°C), the mixture volume V_m (m^3/kmole) and the mixture density ρ_m (kg/m^3). V_m and ρ_m are set as follows

$$V_m = \left(R \cdot \frac{(T_m + 273.15)}{P} \right) \cdot (1 - L)$$

$$\rho_m = \frac{1}{V_m} \cdot \sum_{\alpha=0}^{N} (m^\alpha \cdot y_\alpha) \qquad (21)$$

where R is the universal gas constant.

2.A.4. References

1. McCain, W.D., '*The properties of petroleum fluids*', 2nd Edition, Penwell Publishing Company, Tulsa, Oklahoma, 1990.

2. Witlox, H.W.M., '*Two-phase thermodynamic model for mixing of a non-reactive multi-component pollutant with moist air*', Shell Research Limited, Thornton Research Centre, TNER.93.022, 1993.

3. Scales, L.E., '*NAESOL - A Software toolkit for the solution of nonlinear algebraic equation systems; User Guide - Version 1.5*', Shell Research Limited, Thornton Research Centre, TRCP.3661R, 1994.

2.A.5. Notation

C_p^{α}	specific heat at constant pressure of compound α (J/kmole/K) - compound a = 0 (dry air): C_p^{a} - compound a = 1 (water): liquid, C_p^{wl}, vapour, C_p^{wv} - compounds a = 2,..,N: liquid, $C_p^{\alpha l}$, vapour $C_p^{\alpha v}$
$F_\beta(L_\beta;L,T_m)$	function defined by equation (9)
H^{w}_{cond}	heat of condensation of water (J/kmole)
H^{α}_{cond}	heat of condensation of compound (J/kmole)
H_e	heat added from the substrate (J/kmole)
H^{w}_{fus}	heat of fusion of water (J/kmole)
H_{pol}	pollutant enthalpy (J/kmole)
H_{tot}	total mixture enthalpy (J/kmole)
H^{wet}_{air}	enthalpy of moist air (J/kmole)
H_α	enthalpy of compound α after mixing of pollutant/moist air (J/kmole)
L	mole fraction of liquid in mixture (-)
L_β	mole fraction of liquid compound β in mixture (-)
P	total pressure (atm)
$P_v^{\alpha}(T_m)$	saturated vapour pressure of compound α at temperature T_m (°C) (atm)
R	universal gas constant (= 0.082057 atm·m^3/kmole/K)
r_H	relative humidity of the ambient air (-)
$S(\beta;T_m)$	function defined by equation (10)
T	temperature (K)
T_a	ambient temperature (°C)
T_m	mixture temperature (°C)
T_{pol}	pollutant temperature (°C)

y_{pol}	mole fraction of pollutant in mixture (-)
y_{α}	mole fraction of compound α in mixture (-)
$y_{\alpha n}$	mole fraction of liquid (non-vapour) phase of compound α in mixture (-)
$y_{\alpha v}$	mole fraction of vapour phase of compound α in mixture (-)
η_{α}	mole fraction of compound α in (released, original) pollutant (-)

2.B. THE HYDROGEN FLUORIDE MODEL

2.B.1. Introduction

The HGSYSTEM software package consists of a number of programs capable of modelling the release and dispersion of hydrogen fluoride (HF). The thermodynamics and chemistry adopted in these programs to describe the mixing of air with HF is based on a model developed by Schotte [1,2]. This Schotte model assumes the pollutant to be 100% HF.
The thermodynamics and chemistry for HF is complex because of formation of HF polymers, de-polymerisation of the gas to the monomer state HF (endothermic reaction), and exothermic reaction of HF with water vapour.

In accidental HF releases, the released pollutant is often *not* 100% pure HF, but may also consist of water and/or a mixture of hydrocarbons.

This chapter 2.B describes a thermodynamics and chemistry model for mixing of moist air with a pollutant consisting not only of HF, but also possibly water and possibly an additional mixture of non-reactive chemicals. This additional inert mixture will be indicated by 'N-gas'. N-gas is assumed to be in a pure vapour phase and is considered to be an ideal gas with known specific heat and molecular weight; it may be, for example, nitrogen, air, hydrocarbon or a mixture of ideal gases.

Following *mixing* of the *pollutant* with *moist air* a mixture forms at any downwind cross-section, consisting of the following mixture components:

- A vapour mixture, consisting of HF monomer (HF), HF dimer $(HF)_2$, HF hexamer $(HF)_6$, HF octamer $(HF)_8$, $HF \bullet H_2O$ complex, water, N-gas and air.

- An aqueous HF fog, that is, a liquid fog consisting of water and HF monomer.

Although the model described in this chapter was formulated for a pollutant containing HF, it can also be used to simulate the thermodynamics of a mixture of wet gas (ideal gas, water) and moist air (water, dry air).

The thermodynamical model does not include the effects of ambient fog, rain or snow. Neither does it take deposition of liquid fog from the cloud into account.

2.B.2. Thermodynamics model

This paragraph describes the thermodynamics and chemistry model for the mixing of moist air with a pollutant consisting of HF, water and N-gas. A set of thermodynamic equations for the unknown thermodynamic quantities is derived.

2.B.2.1. Model Parameters

In the thermodynamic model the following data are assumed to be known quantities (input):

1. The mixture composition defined by

   - Pollutant mole fraction, y_{pol} (mole/mole of mixture)

   - Water in pollutant, η_w (mole/mole of pollutant)

   - N-gas in pollutant, η_N (mole/mole of pollutant)

   - Relative ambient humidity, r_H (fraction; $0 \leq r_H \leq 1$)

   - Ambient temperature, T_a (°C)

   The mole fractions y_{pol}, η_w, η_N are defined to be *equivalent* mole fractions based on *all* HF being in the monomer state.
   The ambient data r_H, T_a are needed to determine the enthalpy of the air and the mole fraction of water in the air.
   The parameters y_{pol}, η_w, η_N, r_H, T_a uniquely define the equivalent *molar flows* M_{HF}, M_w, M_N, M_a of HF, water, N-gas and dry air respectively.
   Without loss of generality, M_{tot} ($M_{tot} = M_{HF} + M_w + M_N + M_a$) is taken to be equal to 1.

2. Pollutant enthalpy, H_{pol} (Joule/kmole of pollutant)

3. Heat added from the substrate, H_e (Joule/kmole of mixture)
   Heat transfer from the substrate to the dispersing cloud can be caused by both natural convection and forced convection.

4. Specific heat C_p^N (J/kmole/K) of N-gas

2.B.2.2. Thermodynamic unknowns and equations

The thermodynamic state after the mixing of pollutant with moist air is defined by the following unknown quantities (output):

- Molar fractions of HF-monomer, HF-dimer, HF-hexamer, HF-octamer, HF-complex, water, N-gas, air in vapour mixture (y_{11}, y_{12}, y_{16}, y_{18}, y_c, y_w, y_N, y_a) and molar flow of vapour (M_{vap}; kmole/s): 9 unknowns

- Molar fraction HF in liquid H_2O/HF fog (denoted by x, dimensionless) and molar flow of fog (denoted by L; kmole/s): 2 unknowns (unknowns in presence of fog only)

- Mixture temperature T_m (°C)

The above unknowns must satisfy the following equations:

1. *Conservation of equivalent molar flow* for HF, water, N-gas and dry air (equivalent molar flow before mixing = equivalent molar flow after mixing):

$$M_{HF} = (y_{11} + 2y_{12} + 6y_{16} + 8y_{18} + y_c)\cdot M_{vap} + x\cdot L \tag{1}$$

$$M_w = (y_w + y_c)\cdot M_{vap} + (1 - x)\cdot L \tag{2}$$

$$M_N = y_N\cdot M_{vap} \tag{3}$$

$$M_a = y_a\cdot M_{vap} \tag{4}$$

2. *Sum of molar fractions* of all components in vapour mixture must be 1:

$$y_{11} + y_{12} + y_{16} + y_{18} + y_c + y_w + y_N + y_a = 1 \tag{5}$$

3. *Peng-Robinson equations* of state for HF dimer, HF hexamer, HF octamer, and HF•H_2O complex (see [2])

$$y_{12}(f_1,T_m) = K_2(T_m)\cdot(f_1)^2/(\Phi_1\cdot P) \tag{6}$$

$$y_{16}(f_1,T_m) = K_6(T_m)\cdot(f_1)^6/(\Phi_1\cdot P) \tag{7}$$

$$y_{18}(f_1,T_m) = K_8(T_m)\cdot(f_1)^8/(\Phi_1\cdot P) \tag{8}$$

$$y_c(f_1,y_w,T_m) = K_c(T_m)\cdot f_1\cdot P_{wt}/(\Phi_1\cdot P) \tag{9}$$

where the fugacity $f_1 = \Phi \cdot y_{11} \cdot P$ (in atm), the (dimensionless) fugacity coefficient $\Phi_1 \approx 1$, the total (ambient) vapour pressure P is taken to be 1 atm and $P_{wt} = y_w \cdot P$ is the true partial pressure (excluding $HF{\bullet}H_2O$ complex) of water in the vapour.

$K_2(T_m)$, $K_6(T_m)$, $K_8(T_m)$, $K_c(T_m)$ are equilibrium constants associated with the reactions for the formation of $(HF)_2$, $(HF)_6$, $(HF)_8$, $HF{\bullet}H_2O$, respectively, and are defined as function of the temperature T_m by Schotte [2]. See paragraph 2.B.6 for the functional shape of these constants.

4. In the presence of liquid fog (L > 0), the partial vapour pressures of HF (including $HF{\bullet}H_2O$ complex) and water (including $HF{\bullet}H_2O$ complex) are set as a function of x and T_m from empirical expressions $p_w(x,T_m)$, $p_{HF}(x,T_m)$ given by equations (1) and (2) in Schotte [2].
   These expressions consist of different formulae for x < 0.4738 and x > 0.4738. In the HEGADAS formulation these expressions are smoothed (identical to the smoothing carried out in the program HFPLUME) to arrive at functions $p_w(x,T)$, $p_{HF}(x,T)$ which are everywhere continuous and differentiable. See [3], figure 1 for these curves at 26 °C.

   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 $(M_w/M_{tot}) \cdot P$ and $(M_{HF}/M_{tot}) \cdot P$, respectively.
   In the *presence* of fog, the amounts of HF and water in the vapour are smaller than in the absence of fog, and the partial vapour pressures must also be correspondingly smaller. Thus the following equations apply in the presence of liquid fog (L > 0):

$$y_w + y_c = P_w/P = \min\left\{\frac{p_w(x,T_m)}{P}, \frac{M_w}{M_{tot}}\right\} \tag{10}$$

$$y_{11} + y_{12} + y_{16} + y_{18} + y_c = P_{HF}/P = \min\left\{\frac{p_{HF}(x,T_m)}{P}, \frac{M_{HF}}{M_{tot}}\right\} \tag{11}$$

5. *Conservation of energy*: the total enthalpy H_{tot} following mixing of the pollutant with the moist ambient air, equals the sum of the enthalpy of the pollutant, the enthalpy of the moist air and the heat H_e added from the substrate

$$H_{tot} = H_{HF} + H_w + H_N + H_a = y_{pol} \cdot H_{pol} + (1 - y_{pol}) \cdot H_{air}^{wet} + H_e \tag{12}$$

where the post-mixing enthalpies of HF (including water in fog and HF in $HF{\bullet}H_2O$), water (excluding fog; including water in $HF{\bullet}H_2O$), N-gas, and air are given by

H_{HF} = TERM1 - TERM2

with

$$\text{TERM1} = [M_{HF} - x\cdot L]\cdot\{H^{\Delta HF} + C_p^{HFV}\cdot(T_m - T^*)\} - x\cdot L\cdot\{H_{cond}^{HF} + H_{mix}\} \qquad (13a)$$

$$\text{TERM2} = (1 - x)\cdot L\cdot H_{cond}^{w} - L\cdot C_p^{fog}(x,T_m)\cdot(T_m - T^*)$$

$$H_w = [M_w - (1 - x)\cdot L]\, C_p^{wv}\,(T_m - T^*) \qquad (13b)$$

$$H_N = M_N\cdot C_p^{N}\cdot(T_m - T^*) \qquad (13c)$$

$$H_a = M_a\cdot C_p^{a}\cdot(T_m - T^*) \qquad (13d)$$

with $H_{cond}^{HF}, H_{cond}^{w}$ the heats of condensation of HF and water, H_{mix} the heat of mixing liquid HF with liquid water, $C_p^{HFV}, C_p^{fog}, C_p^{wv}, C_p^{N}, C_p^{a}$ the specific heats of HF-vapour, fog, water-vapour, N-gas and air, respectively.

In the equations above, it is assumed that the enthalpy is zero at the reference temperature T^* with unmixed gaseous components (HF, water, N-gas, air) and all HF in the monomer state; $H_{cond}^{HF}, H_{cond}^{w}$ and H_{mix} are taken at T^*. Following Schotte [2], $T^* = 25$ °C is taken.

In equation (13a), the enthalpy departure $H^{\Delta HF}$ of the HF vapour from the ideal monomeric gas at the final temperature T_m, is given by

$$H^{\Delta HF} = \frac{y_{12}\cdot\Delta H_2 + y_{16}\cdot\Delta H_6 + y_{18}\cdot\Delta H_8 + y_c\cdot\Delta H_c}{y_{11} + 2y_{12} + 6y_{16} + 8y_{18} + y_c} \qquad (14)$$

where ΔH_2, ΔH_6, ΔH_8 and ΔH_c are the enthalpies of association of HF-dimer, hexamer, octamer and complex, respectively (Joule/kmole) at the reference temperature T^*.

2.B.2.3. Enthalpy of Air

In equation (12), the enthalpy H_{air}^{wet} of the moist air (Joule/kmole of moist air) is given by

$$H_{air}^{wet} = [1 - P_w^{amb}/P]\cdot C_p^{a}\cdot(T_a - T^*) + [P_w^{amb}/P]\cdot C_p^{wv}\cdot(T_a - T^*) \qquad (15)$$

with P_w^{amb} the partial vapour pressure of water in the air and with P the total atmospheric pressure (P is always 1 atm in HEGADAS, but can be user-specified in HFPLUME. For consistency of the thermodynamical description, P should be taken (almost equal to) 1 atm).

$P_w^{amb} = r_H\cdot P_V^{w}(T_a)$, with r_H the relative ambient humidity and with $P_V^{w}(T_a)$ the saturated vapour pressure of water (atm) at temperature T_a.

Note that the ratio P_w^{amb}/P equals the mole fraction of water in the moist air.

2.B.2.4. Pollutant Enthalpy

For an evaporating liquid pool (unpressurised release), the pollutant enthalpy H_{pol} in equation (12) corresponds to 100% liquid with the pool temperature T_{liq}. Assuming the liquid to consist of 100% HF, this implies that $H_{pol} = C_p^{HFL} \cdot (T_{liq} - T^*) - H_{cond}^{HF}$ with $T^* = 25$ °C and C_p^{HFL} the specific heat of HF liquid.

For pressurised releases of pollutant containing HF, a flash occurs immediately upon release. The following two cases are distinguished.

1. The pollutant *contains no water*. For this case the model requires as input the pollutant temperature, T_{pol}, and the equivalent mole fraction of liquid HF in the pollutant, η_{HFL}. This data should correspond to the post-flash state and are in HGSYSTEM derived from flash calculations in either the HFPLUME model or the HFFLASH model. The composition of the pollutant vapour is evaluated from equations (1) to (9).

2. The pollutant *contains water*. For this case the model adopts $\eta_{HFL} = 0$ and the model requires as input the pollutant temperature T_{pol} only. The pollutant is assumed to be in thermodynamic equilibrium, and consists of a vapour mixture (HF with enthalpy departure $H_{pol}^{\Delta HF}$ from monomer, N-gas, water) and an aqueous liquid fog (equivalent mole fraction L_{pol} of fog in pollutant; mole fraction x_{pol} of HF in fog). The pollutant composition is evaluated from equations (1) to (11).

For pressurised releases the enthalpy H_{pol} must include the kinetic energy E_{pol}^{kin} (Joule/kmole of pollutant) of the post-flash pollutant; E_{pol}^{kin} given by

$$E_{pol}^{kin} = ½ \cdot m_{pol} \cdot V_{fl}^2 \qquad \text{with } m_{pol} = g_{HF} \cdot m_{HF} + g_w \cdot m_w + g_N \cdot m_N \tag{16}$$

with m_{pol} the mean molecular weight (kg/kmole) of the pollutant, m_α the molecular weight of species α (α can be: HF, w, N for HF, water and N-gas, respectively) and V_{fl} the post-flash velocity (m/s). The pollutant enthalpy is now given by the following formula (compare with equations (12) and (13)),

$$\begin{aligned} H_{pol} = \; & E_{pol}^{kin} + \\ & + \eta_{HFL} \cdot \{C_p^{HFL} \cdot (T_{pol} - T^*) - H_{cond}^{HF}\} + \\ & + \{\eta_N \cdot \{C_p^{N} \cdot (T_{pol} - T^*)\} + \\ & + [\eta_w - (1 - x_{pol}) \cdot L_{pol}] \, C_p^{wv} \cdot (T_{pol} - T^*) + \\ & + [\eta_{HF} - \eta_{HFL} - x_{pol} \cdot L_{pol}] \cdot \{H_{pol}^{\Delta HF} + C_p^{HFV} \cdot (T_{pol} - T^*)\} + \end{aligned} \tag{17}$$

$$
\begin{aligned}
&- x_{pol}\cdot L_{pol}\cdot\{ H^{HF}_{cond} + H_{mix}\} + \\
&- (1 - x_{pol})\cdot L_{pol}\cdot H^{w}_{cond} + \\
&+ L_{pol}\cdot\{ C^{fog}_{p}(x_{pol},T_{pol})\cdot(T_{pol} - T^{*})\}
\end{aligned}
$$

2.B.3. Solution algorithm

In the previous paragraph the set of thermodynamic equations governing the thermodynamics model has been derived, that is, the twelve equations (1-12) in the presence of a liquid fog and the ten equations (1-9), (12) in the absence of a fog.

This paragraph describes the algorithm for solving these equations as it is used in HEGADAS and HEGABOX. The algorithm used in HFPLUME is somewhat different but has been checked to give identical results.

The HEGADAS/HEGABOX algorithm is used to determine the ten unknowns in the absence of a fog (y_{11}, y_{12}, y_{16}, y_{18}, y_c/y_w, y_w, y_N, y_a, M_{vap}, T_m) and twelve unknowns in the presence of a fog (additional unknowns x, L).

The calculations described below are carried out using the model parameters described in paragraph 2.B.2 (y_{pol}, η_w, η_N, r_H, T_a, H_{pol}, H_e, $C_p{}^N$).

Without loss of generality the total molar flow M_{tot} is taken equal to unity. The molar flows before mixing of HF, water, N-gas and air (M_{HF}, M_w, M_N, M_a; $M_{tot} = M_w+M_{HF}+M_N+M_a = 1$) can be expressed in terms of the input parameters as follows:

$$
\begin{aligned}
M_{HF} &= (1 - \eta_w - \eta_N)\cdot y_{pol}\cdot M_{tot} \\
M_w &= \eta_w\cdot y_{pol}\cdot M_{tot} + [P^{amb}_{w}/P]\cdot(1 - y_{pol})\cdot M_{tot} \\
M_N &= \eta_N\cdot y_{pol}\cdot M_{tot} \qquad (18) \\
M_a &= [(P - P^{amb}_{w})/P]\cdot(1 - y_{pol})\cdot M_{tot}
\end{aligned}
$$

with $P^{amb}_{w}/P = r_H\cdot P_V{}^w(T_a)/P$ and P the total atmospheric pressure.

2.B.2.1. Solving the equations

The set of equations is reduced to a set of two (in the absence of liquid fog) or three (with fog) equations for two or three basic unknowns. These unknowns are the molar fraction y_{11} of the HF monomer, the mixture temperature T_m, and (in case of fog) the molar fraction x of HF in the fog. The algorithm for the derivation of the reduced set of equations is as follows.

1. Set y_{12}, y_{16}, y_{18}, y_c/y_w as function of y_{11} and T_m from the Peng-Robinson equations of state (6), (7), (8) and (9).

2. Set M_{vap}, y_w and L.

a In the presence of a liquid fog (L > 0), M_{vap}, y_w, L are set as functions of y_{11}, T_m, x by imposing conservation of the sum of molar flow of air and N-gas (see equations (10), (11), (3-5)), the water vapour pressure relation (equation (10)) and conservation of energy (equation (12)),

$$M_{vap} = [M_a + M_N]/[1 - P_{HF}/P - P_w/P + y_c] \tag{19}$$

$$y_w = [1 + y_c/y_w]^{-1}\cdot \min\left\{\frac{p_{HF}(x,T_m)}{P}, \frac{M_{HF}}{M_{tot}}\right\} \tag{20}$$

$$L = \frac{TERM1}{TERM2 + TERM3} \tag{21}$$

with

$$\begin{aligned}
TERM1 &= H_a + H_N - H_{tot} + M_w \cdot C_p^{wv} \cdot (T_m - T^*) + M_{HF} \cdot \left\{H^{\Delta HF} + C_p^{HFV} \cdot (T_m - T^*)\right\} \\
TERM2 &= (1-x)\cdot\left\{C_p^{wv}\cdot(T_m - T^*) + H_{cond}^{w}\right\} - C_p^{fog}(x,T_m)\cdot(T_m - T^*) \\
TERM3 &= x\cdot\left\{H^{\Delta HF} + C_p^{HFV}\cdot(T_m - T^*) + H_{cond}^{HF} + H_{mix}\right\}
\end{aligned}$$

b In the absence of a liquid fog (L = 0), M_{vap}, y_w are set as functions of y_{11}, T_m.
For $M_{HF} > 0.5$ conservation of HF molar flow (equation (1)) and conservation of water molar flow (equation (2)) is imposed, while for $M_{HF} < 0.5$ conservation of the sum of air, N-gas and water molar flow (see equations (2-5)) and conservation of water molar flow (equation (2)) is imposed:

$$M_{vap} = \begin{cases} M_{HF}/[y_c + y_{11} + 2y_{12} + 6y_{16} + 8y_{18}] & (M_{HF} > 0.5) \\ \\ [M_a + M_N + M_w]/[1 - y_{11} - y_{12} - y_{16} - y_{18}] & (M_{HF} < 0.5) \end{cases} \tag{19*}$$

$$y_w = \begin{cases} \left[1 + \left(1 - \frac{M_w}{M_{HF}}\right)\cdot\frac{y_c}{y_w}\right]^{-1}\cdot\left[y_{11} + 2y_{12} + 6y_{16} + 8y_{18}\right]\cdot\frac{M_w}{M_{HF}} & (M_{HF} > 0.5) \\ \\ \left[1 + \frac{y_c}{y_w}\right]^{-1}\cdot\frac{M_w}{M_{vap}} & (M_{HF} < 0.5) \end{cases} \tag{20*}$$

$$L = 0 \tag{21*}$$

3. Set y_a and y_N from conservation of air and N-gas moles (equations (3-4)):

$$\begin{aligned} y_a &= M_a/M_{vap} \\ y_N &= M_N/M_{vap} \end{aligned} \qquad (22)$$

4. Formulate basic set of equations for basic unknowns: HF-monomer molar fraction y_{11}, the final temperature T_m and (in the presence of fog) the molar fraction x of HF in the fog.

   a In the presence of a liquid fog (L > 0) the equations represent conservation of HF molar flow (equation (1)), conservation of water molar flow (equation (2)), and the HF-vapour pressure relation (equation (11)):

$$M_{HF} = (y_c + y_{11} + 2y_{12} + 6y_{16} + 8y_{18})\cdot M_{vap} + x\cdot L \qquad (I)$$

$$M_w = (y_w + y_c)\cdot M_{vap} + (1 - x)\cdot L \qquad (II)$$

$$y_{11} + y_{12} + y_{16} + y_{18} + y_c = \min\left\{\frac{p_{HF}(x, T_m)}{P}, \frac{M_{HF}}{M_{tot}}\right\} \qquad (III)$$

   The above set of equations is solved iteratively for y_{11}, T and x.

   b In the absence of a liquid fog (L = 0) the equations represent conservation of energy (equation (12)), and the consistency equation of all components in vapour mixture (equation (5); for $M_{HF} > 0.5$) or conservation of HF molar flow (equation (1); for $M_{HF} < 0.5$),

$$H_{tot} = H_{HF} + H_w + H_N + H_a = y_{pol}\cdot H^0_{pol} + (1 - y_{pol})\cdot H^{wet,0}_{air} + H_e \qquad (I^*)$$

$$\begin{aligned} M_{HF} &= (y_c + y_{11} + 2y_{12} + 6y_{16} + 8y_{18})\cdot M_{vap} && M_{HF} < 0.5 \\ y_{11} + y_{12} + y_{16} + y_{18} + y_c + y_w + y_N + y_a &= 1 && M_{HF} > 0.5 \end{aligned} \qquad (II^*)$$

   The above set of equations is solved iteratively for y_{11} and T_m.

2.B.2.2. Evaluation of pollutant enthalpy

For given pollutant temperature T_{pol}, one can evaluate the pollutant enthalpy H_{pol} from equation (17), if one knows $H^{\Delta HF}_{pol}$, x_{pol}, L_{pol}. To this purpose the previous equations are considered for the special case of y_{pol} = 1 (y_a = 0) and the temperature $T_m = T_{pol}$ ($H^{\Delta HF} = H^{\Delta HF}_{pol}$, $x = x_{pol}$, $L = L_{pol}$).

In the presence of fog (L > 0) the equations are solved as follows:

- The unknowns y_{12}, y_{16}, y_{18} and y_c/y_w are set as a function of y_{11} from equations (6), (7), (8) and (9)
- The unknown y_w is determined as function of y_{11} and x from equation (20)
- The unknowns M_{vap} and L are set from equations (1) and (2)
- The unknown y_N is set from equation (3)
- The remaining two unknowns y_{11} and x are set by iteratively solving the equations (5) and (11)

In the absence of fog (L = 0) the equations are solved as follows:

- The unknowns y_{12}, y_{16}, y_{18} and y_c/y_w are set as a function of y_{11} from equations (6), (7), (8) and (9)
- The unknowns M_{vap}, y_w are determined from equations (19*) and (20*)
- The unknown y_N is set from equation (3)
- The remaining unknown y_{11} is set by iteratively solving equation (5) for $M_{HF} > 0.5$ and equation (1) for $M_{HF} < 0.5$.

2.B.2.3. Evaluation of molar mixture volume and mixture density

The algorithm described above has been implemented into the heavy gas dispersion program HEGADAS and in the instantaneous heavy gas release model HEGABOX, to calculate thermodynamic data for given pollutant molar fraction y_{pol} and added heat from the surface H_e. These calculations are carried out by the routine THRMHF, which outputs data required for further HEGADAS dispersion calculations, i.e. the mixture temperature T_m, the molar mixture volume V_m and the molar mixture density ρ_m. The temperature T_m follows from the iterative solution of the HF thermodynamic equations described above. The molar mixture volume V_m and the molar mixture density ρ_m are set as follows.

1. The molar mixture volume V_m, m^3/kmole of mixture, is the ratio of the total volume flow (m^3/s; volume of liquid fog can be neglected) and the total molar flow (kmole/s; vapour and fog). Thus it is seen that

$$V_m = \frac{\left[R \cdot (T_m + 273.15)/P\right] \cdot M_{vap}}{M_{vap} + L} \tag{23}$$

with R = 0.082 atm·m^3/K/kmole being the universal gas constant.
Note that the term between square brackets in the numerator of equation (23) signifies the molar volume (m^3/kmole) of an ideal gas at temperature T_m and pressure P.

2. The mixture density is the ratio of the total mass flow (kg/s; vapour and fog) and total volume flow (m^3/s). Thus it is seen that

$$\rho_m = \frac{m_a \cdot M_a + m_N \cdot M_N + m_w \cdot M_w + m_{HF} \cdot M_{HF}}{\left[R \cdot (T_m + 273.15) / P\right] \cdot M_{vap} + \left[m_w \cdot (1-x) + m_{HF} \cdot x\right] \cdot L / \rho_{fog}} \tag{24}$$

   with m_a = 28.95, m_N, m_{HF} = 20.01, m_w = 18.02 the molecular weights of dry air, N-gas, HF-monomer and water, respectively and ρ_{fog} = 1200 kg/m^3 the density of the fog.

3. The ratio ρ_m/ρ_{amb} of the mixture density ρ_m and the density of the ambient humid air ρ_{amb} is output by the HEGADAS HF-thermodynamics routine. It is set from equation (24) and

$$\rho_{amb} = P \cdot m_{amb} / [R \cdot (T_a + 273.15)] \tag{25}$$

   with m_{amb}, the molecular weight of the humid air (kg/kmole), given by

$$m_{amb} = m_a \cdot [1 - P_w^{amb}/P] + m_w \cdot [P_w^{amb}/P] \tag{26}$$

2.B.4. General trends of HF thermodynamics model

Following implementation of the algorithm as described in paragraph 2.B.2 into the heavy gas dispersion program HEGADAS, a sensitivity analysis has been carried out for a pollutant consisting of HF (liquid or vapour), propane and water. In this limited exercise, fully described in [3], the following results were obtained. These results are given here to give the HGSYSTEM user some feeling for the thermodynamic and chemistry model described in this chapter.

1. Upon mixing of dry HF vapour with moist air, initial cooling resulting from de-polymerisation of HF is diminished because of formation of an aqueous fog and because of heat convection from the ground. For increasing humidity, the fog formation and mixture temperature increase, and the mixture density, molar entrainment and cloud width increase. Dependence of peak concentration on humidity is complex. See [3] for more details.

2. If a part of the HF in the pre-mixed pollutant is liquid, less additional liquid fog forms, the mixture temperature decreases and the mixture density increases. For less than 5% initial liquid, cloud widths and concentrations do not significantly depend on the amount of initial liquid HF.

3. If the pollutant contains an ideal gas in addition to HF, the pollutant will be less polymerised, less additional de-polymerisation occurs upon mixing and the mixture temperature increases. The precise effect of the presence of ideal gas in the pollutant on mixture density depends both on the molecular weight of the ideal gas and the increase in mixture density because of previous cooling. See [3] for more details.

4. If the pollutant contains water in addition to HF, the pollutant contains an initial aqueous fog, less additional fog forms, the mixture temperature decreases and the mixture density increases. For less than 4% initial water, cloud widths and concentrations do not significantly depend on the amount of initial water.

2.B.5. References

1. Schotte, W., '*Fog formation of hydrogen fluoride in air*', Ind. Eng. Chem. Res. vol 26, 300-306, 1987.

2. Schotte, W., '*Thermodynamic model for HF fog formation*', Letter from Schotte to Soczek, E. I. Du Pont de Nemours & Company, Du Pont Experimental Station, Engineering Department, Wilmington, Delawere 19898, 31 August 1988.

3. Witlox, H.W.M., '*Thermodynamics model for mixing of moist air with pollutant consisting of HF, ideal gas and water*, Shell Research Limited, Thornton Research Centre, TNER.93.021, 1993.

2.B.6. Notation

C_p^α specific heat at constant pressure of species α, J/kmole/K

α = HFL: liquid HF

$C_p^{HFL} = C_p^{HFL}(T^0) = 50260 + 68.6T^0$

HFV: gaseous HF, $C_p^{HFV} = 29120$

fog: aqueous fog, C_p^{fog} is as a function of x and T (°C) (equation (24) in [2]),

$C_p^{fog}(x,T) = 75519 + 1.661\cdot T - (58475 - 63.6\cdot T)\cdot x + (35686 + 7.83\cdot T)\cdot x^2$

wl: water liquid, $C_p^{wl} = 75700$

wv: water vapour, $C_p^{wv} = 33690$

N: N-gas,
a: dry air, $C_p^a = 29120$

f_1	fugacity of HF-monomer (after mixing; $f_1 = \Phi \cdot y_{11} \cdot P$) (atm)
H_e	heat added from the substrate to the pollutant/air mixture (Joule/equivalent kmole of mixture)
H_{air}^{wet}	enthalpy of moist air (Joule/kmole of moist air)
H_{cond}^{HF}	heat of condensation of HF monomer at 25 °C (J/kmole) $H_{cond}^{HF} = 30258000$
H_{mix}	heat of mixing of liquid HF and H_2O at 25 °C (J/kmole of HF) $H_{mix} = H_{mix}(x) = 18831000 \cdot (1 - x^2)$
H_{pol}	enthalpy of pollutant (Joule/equivalent kmole of pollutant)
H_{cond}^{w}	heat of condensation of water at 25 °C (J/kmole) $H_{cond}^{w} = 44017000$
H_α	enthalpy (J/kmole) of species α after mixing of pollutant and moist air α can be: tot (total enthalpy), HF (HF; including water in fog and HF in $HF \bullet H_2O$), w (water; excluding fog and including water in $HF \bullet H_2O$), N (N-gas) or a (dry air)
$H^{\Delta HF}$	enthalpy departure (J/equivalent kmole of HF vapour) of HF vapour in pollutant/air mixture from the ideal monomeric gas
$H_{pol}^{\Delta HF}$	enthalpy departure (Joule/equivalent kmole of HF vapour) of HF vapour in the pre-mixed pollutant from the ideal monomeric gas
$K_i(T)$	$K_1(T) = 1$ For $i > 1$, $K_i(T)$ is chemical equilibrium constant at temperature T (Kelvin) for the dimer ($i = 2$), hexamer ($i = 6$), octamer ($i = 8$) formation at temperature T, (atm^{-i+1}). $K_i(T)$ ($i > 1$) is given by equation (5) in [2]: $\ln(K_2) = [53458.697/T - 200.76387]/R$ $\ln(K_6) = [175448.07/T - 579.77837]/R$ $\ln(K_8) = [209734.20/T - 694.02013]/R$

	with the universal gas constant R given by R = 8.3143 J/K/mole
$K_c(T)$	chemical equilibrium constant at temperature T (Kelvin) for the formation of the $HF \bullet H_2O$ complex at temperature T, (atm^{-1}) $K_c(T)$ is given by equation (5) in [2]: $\ln(K_c) = [26220.445/T - 94.989486]/R$
L	total molar flow of aqueous fog (after mixing) (kmole/s)
M_{vap}	total molar flow of vapour (after mixing) (kmole/s) the number of moles after mixing must be equal to the number of moles prior to mixing, if *all* HF is based on HF-monomer: $(y_{11} + 2y_{12} + 6y_{16} + 8y_{18} + 2y_c + y_w + y_N + y_a)\cdot M_{vap} + L = M_{tot}$
M_α	equivalent molar flow of species α after mixing of pollutant and moist air (with *all* HF based on HF monomer) (kmole/s) α can be: tot (total molar flow), HF (HF), w (water), N (N-gas), a (dry air) $M_{tot} = M_{HF} + M_w + M_N + M_a$
P	total (ambient or atmospheric) pressure (atm)
P_{HF}	partial vapour pressure of HF (including $HF \bullet H_2O$) (atm)
$P_V^w(T)$	vapour pressure of water in air at temperature T (atm)
P_w	partial vapour pressure of water (including $HF \bullet H_2O$) (atm)
P_w^{amb}	partial vapour pressure of water in the ambient wet air (before mixing) (atm) $P_w^{amb} = r_H \cdot P_V^w(T_a)$
r_H	relative humidity of the ambient air (-)
T_a	ambient temperature (°C)
T_m	mixture temperature (°C)
T_{pol}	(post-flash) temperature of pre-mixed pollutant (°C)

x	molar fraction of HF (monomer) in aqueous fog (after mixing) (-)
x_{pol}	molar fraction of HF (monomer) in aqueous fog in pre-mixed pollutant (-)
y_{pol}	equivalent molar fraction of pollutant (HF, water, N-gas) in final mixture; *equivalent* fraction means that the fraction is calculated with *all* HF based on HF monomer (-)
y_α	molar fraction of species α in vapour (after mixing) (-) α 11, 12, 16, 18, c, w, N or a (dry air) the sum of these fractions must be 1: $y_{11} + y_{12} + y_{16} + y_{18} + y_c + y_w + y_N + y_a = 1$
ΔH_α	enthalpy of association of HF species α (J/kmole) α can be: 2 (dimer, $\Delta H_2 = -53458000$), 6 (hexamer, $\Delta H_6 = -175448000$), 8 (octamer, $\Delta H_8 = -209734000$) or c ($HF{\bullet}H_2O$, $\Delta H_c = -26220000$)
η_α	equivalent molar fraction of species α in pre-mixed pollutant (-) α can be: HF (total HF), w (water), N (N-gas), HFL (HF liquid; excluding HF in fog), HFV (HF vapour; including HF in fog and in $HF{\bullet}H_2O$), N (N-gas) $\eta_{HF} + \eta_w + \eta_N = 1$, $\eta_{HF} = \eta_{HFL} + \eta_{HFV}$
Φ_1	fugacity coefficient of HF in vapour phase; approximated by $\Phi_1 = 1$ (-)