

HGSYSTEM 3.0

Technical Reference Manual

by

L. Post

TNER.94.059

**Shell Research Limited, Thornton Research Centre,
P.O. Box 1, Chester, United Kingdom**

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Documents

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HGSYSTEM version 3.0

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The LPOOL model was made available by Exxon Research and Engineering Company.

EXECUTIVE SUMMARY

1. Historical background

As a result of many years in-house research, the gas dispersion group at Shell Research Ltd. Thornton (United Kingdom) has developed a package of mathematical models, called HGSYSTEM, to study the atmospheric dispersion of accidental pollutant releases with emphasis on denser-than-air materials. HGSYSTEM can be simulate different dispersion scenarios (jet dispersion, heavy gas dispersion, passive dispersion). The first version of HGSYSTEM was made freely available for use in November 1990. This version, called NOV90 or version 1.0, was prepared by Shell Research Ltd. for *The Industry Cooperative HF Mitigation/Assessment Program, Ambient Impact Assessment Subcommittee* as one component of a wider programme aimed at a better understanding of atmospheric dispersion, including hydrogen fluoride (HF) releases. HGSYSTEM can model the full HF chemistry and thermodynamics. Most of the modules in the HGSYSTEM package can also be used for more general, non-reactive (ideal gas) releases as well. Validation of the HF-related simulations has been done with the well-known Goldfish Test Series. Full documentation to the 1.0 version was given in the HGSYSTEM Technical Reference Manual and User's Manual.

After release of the 1.0 (NOV90) version, a version 1.1 was made available which contained minor changes to solve some program bugs. Several internal versions were also developed.

2. HGSYSTEM 3.0

HGSYSTEM is in wide use for simulation of atmospheric dispersion scenarios for HF and other pollutant releases. It has been assessed against other models and found to rank amongst the best available atmospheric dispersion models in the world. HGSYSTEM sets the standard for HF dispersion calculations. However, a number of topics were open for improvement and generalisation. With financial support of the *American Petroleum Institute, Air Modelling Task Force*, Shell Research has upgraded and updated the existing HGSYSTEM package, resulting in a new release called HGSYSTEM version 3.0. The following major changes have been made to HGSYSTEM 1.0 to obtain HGSYSTEM 3.0:

- The thermodynamical models available in HGSYSTEM have been extended. The full HF chemistry and thermodynamical model is now suitable for mixtures of HF, water and an inert ideal gas. The non-reactive ideal gas description has been extended to multi-compound liquid-vapour mixtures (aerosols).

HGSYSTEM version 3.0

- A database containing physical properties for some 30 compounds has been added to HGSYSTEM. This database is needed when using the new two-phase multi-compound thermodynamical model.
- The PLUME model for pressurised releases has been extended to model jet dispersion of multi-compound, two-phase mixtures and is now called AEROPLUME.
- A new model describing the initial phase of instantaneous releases, HEGABOX, has been added to HGSYSTEM.
- A new model to calculate release rates from pressurised vessels, SPILL, is now available in HGSYSTEM version 3.0.
- The existing evaporating pool model EVAP has been replaced by a better model, LPOOL, for boiling and non-boiling pools and land and water. LPOOL is based on a model developed by Exxon Research and Engineering Company.
- The formulation of the lateral spreading in the heavy gas dispersion model HEGADAS has been reviewed and improved.
- Several options have been added to the time-dependent version of the heavy gas model HEGADAS making it easier to use and to evaluate the results.
- HGSYSTEM now contains three post-processors to generate data for graphical output after a pressurised jet release, steady state heavy gas release and a time-dependent heavy gas release respectively. These post-processors will improve the ease of use of the HGSYSTEM modules.
- Five additional options resulting from work done on HGSYSTEM as sponsored by Martin Marietta Energy Systems Inc (USA) are available to all HGSYSTEM users.
- A new HGSYSTEM 3.0 User's Manual and Technical Reference Manual have been written. These are now up-to-date and their format allows for easy future updating.

3. Modules available in HGSYSTEM 3.0

The following models are available in HGSYSTEM version 3.0:

HGSYSTEM version 3.0

Database program

DATAPROP	generates physical properties used in other HGSYSTEM models
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Source term models

SPILL	transient liquid release from a pressurised vessel
HFSPILL	SPILL version specifically for hydrogen fluoride (HF)
LPOOL	evaporating multi-compound liquid pool model (unpressurised release)

Near-field dispersion models

AEROPLUME	high-momentum jet and elevated plume model
HFPLUME	AEROPLUME version specifically for hydrogen fluoride (HF)
HEGABOX	dispersion of instantaneous heavy gas releases

Far-field dispersion models

HEGADAS	heavy gas dispersion (steady-state and transient version)
PGPLUME	passive Gaussian plume dispersion

Utility programs

HFFLASH	flashing of hydrogen fluoride (HF) from pressurised vessel
POSTHS/POSTHT	post-processing of HEGADAS results (steady state and time-dependent version)
PROFILE	post-processor for concentration contours of air borne plumes
GET2COL	utility for data retrieval

4. Documentation

HGSYSTEM version 3.0 is documented in the following two manuals:

HGSYSTEM version 3.0

HGSYSTEM 3.0 User's Manual

L. Post

Shell Research Limited, Thornton Research Centre, TNER.94.058

1994

HGSYSTEM 3.0 Technical Reference Manual

L. Post (editor)

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The User's Manual is thought to be the main reference document for normal use of the HGSYSTEM modules. It contains all information necessary to run the models and interpret the generated results. The Technical Reference Manual is intended as a source of background information for users who want to know more about the technical/scientific contents of the HGSYSTEM modules.

HGSYSTEM 3.0 Course Notes (TNER.94.060) are also available for use during possible HGSYSTEM training sessions.

HGSYSTEM 3.0 TECHNICAL REFERENCE MODEL

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Chapters 2.A, 2.B and 7.A

HGSYSTEM 3.0 TECHNICAL REFERENCE MANUAL

CONTENTS

1. GENERAL INTRODUCTION	1-1
1.1. Introduction	1-1
1.2. Main new features in HGSYSTEM version 3.0	1-1
2. THERMODYNAMICAL DESCRIPTIONS IN HGSYSTEM	2-1
2.A. THE MULTI-COMPOUND, TWO-PHASE MODEL	2-4
2.A.1. Introduction	2-4
2.A.2. Thermodynamics model	2-6
2.A.2.1. Model parameters	2-7
2.A.2.2. Basic thermodynamic unknowns and equations	2-9
2.A.2.3. Criterion for aerosol formation	2-11
2.A.3. Solution algorithm	2-12
2.A.3.1. General problem	2-12
2.A.3.2. Case of separate one-compound aerosols	2-15
2.A.3.3. Case of single two-compound aerosol	2-19
2.A.3.4. Implementation of thermodynamics into dispersion model	2-20
2.A.4. References	2-22
2.A.5. Notation	2-22
2.B. THE HYDROGEN FLUORIDE MODEL	2-24
2.B.1. Introduction	2-24
2.B.2. Thermodynamics model	2-25
2.B.2.1. Model Parameters	2-25
2.B.2.2. Thermodynamic unknowns and equations	2-25
2.B.2.3. Enthalpy of Air	2-28
2.B.2.4. Pollutant Enthalpy	2-29
2.B.3. Solution algorithm	2-30

2.B.2.1. Solving the equations	2-30
2.B.2.2. Evaluation of pollutant enthalpy	2-32
2.B.2.3. Evaluation of molar mixture volume and mixture density	2-33
2.B.4. General trends of HF thermodynamics model	2-34
2.B.5. References	2-35
2.B.6. Notation	2-35
3. THE SPILL MODEL	3-1
3.1. Introduction	3-2
3.2. The model equations	3-3
3.2.1. Algebraic equations	3-3
3.2.2. Conservation of total reservoir mass	3-4
3.2.3. Conservation of energy	3-6
3.2.4 Conservation of mixture compound α	3-7
3.2.5. Initial conditions	3-8
3.3. Notation	3-9
3.4. References	3-10
4. THE LPOOL MODEL	4-1
4.1. Introduction	4-2
4.2. Differences between LPOOL and LSM90	4-2
4.2.1. Physical properties database	4-2
4.2.2. Updating physical properties	4-2
4.2.3. Input parameters	4-3
4.3. References	4-3
5. PLUME OR JET MODELS IN HGSYSTEM	5-1
5.A. THE AEROPLUME MODEL	5-3
5.A.1. Introduction	5-3
5.A.2. The AEROPLUME code	5-3
5.A.3. Summary of the aerosol algorithm	5-4

HGSYSTEM Technical Reference Manual

5.A.4. The reservoir state calculation	5-6
5.A.5. Calculation of post-flash conditions	5-7
5.A.6. Discharge rate specification	5-13
5.A.7. Plume development model	5-16
5.A.8. References	5-19
5.A.9. Notation	5-20
5.B. DEVELOPMENT OF PLUME AND JET RELEASE MODELS	5-22
5.B.1. Introduction	5-22
5.B.2. The Stages of Plume Development	5-23
5.B.3. Control Volume Analysis: Basic equations of Motion	5-26
5.B.4. External flashing; Flow Establishment; Gaussian profiles	5-31
5.B.5. The Airborne Plume: geometry and shear entrainment	5-34
5.B.6. The Touchdown and Slumped Plume	5-37
5.B.7. Closure Assumptions for the 'Top-Hat' Model	5-40
5.B.8. The Entrainment Function	5-47
5.B.9. The atmosphere model.	5-54
5.B.10. Plume cross-sectional over-lap: curvature limited entrainment	5-54
5.B.11. The HGSYSTEM plume models: algorithmic structure.	5-57
5.B.12. Validation studies, entrainment formulae	5-57
5.B.13. Comparison with models of Wheatley, Raj and Morris, and Havens	5-60
5.B.14. References	5-64
6. THE PGPLUME MODEL FOR FAR-FIELD DISPERSION	6-1
6.1. Introduction	6-2
6.2. Far-field Dispersion: Pasquill/Gifford Models	6-3
6.3. Local versus Integral Average Properties: Near/Far field Matching	6-6
6.4. System Asymptotics: the Limit of Great Dilution	6-11
6.5. Prediction of (Steady) Far-field Dispersion	6-14
6.6. Transient Effects: Releases of Limited Duration	6-14

6.7. Conclusions	6-17
6.8. References	6-18
7. THE HEAVY GAS DISPERSION MODEL HEGADAS	7-1
7.A. TECHNICAL DESCRIPTION OF THE HEGADAS MODEL	7-5
7.A.1. Introduction	7-5
7.A.2. Steady-state model	7-7
7.A.2.1. Wind-speed and concentration similarity profiles	7-7
7.A.2.2. Dispersion variables and effective cloud data	7-8
7.A.2.3. Dispersion equations	7-10
7.A.2.4. Solution to dispersion equations	7-14
7.A.3. Time-dependent model	7-17
7.A.3.1. Introduction	7-17
7.A.3.2. Algorithm for evaluation of concentrations	7-19
7.A.3.3. Dispersion from ground-level source	7-23
7.A.3.3.1. Secondary source	7-23
7.A.3.3.2. Observer source data	7-25
7.A.3.3.3. Concentrations	7-26
7.A.3.4. Dispersion downwind of transition with near-source jet model	7-27
7.A.3.4.1. Transition data	7-27
7.A.3.4.2. Concentrations	7-27
7.A.3.5. Inclusion of along-wind-diffusion effects	7-28
7.A.4. Interfacing with pool-evaporation and near-source jet/plume models	7-34
7.A.4.1. Interface with pool evaporation models	7-34
7.A.4.2. Interface with near-source models	7-34
7.A.5.3. Interface with near-source models (finite-duration release)	7-39
7.A.5. Validation	7-40
7.A.6. Summary and conclusions	7-42
7.A.7. References	7-43

HGSYSTEM Technical Reference Manual

7.A.8. Notation	7-47
Figures	7-50
Appendix 7.A.A - Evaluation of ambient data	7-65
Appendix 7.A.B - Cross-wind diffusion effects	7-68
Appendix 7.A.C - Inclusion of heat and water-vapour transfer from substrate	7-72
Appendix 7.A.D - Evaluation of pollutant enthalpy	7-76
Appendix 7.A.E - Observer position and observer speed	7-79
Appendix 7.A.F - Cloud shape correction for downwind gravity spreading	7-82
7.B. PLUME SPREAD AND AIR ENTRAINMENT FORMULATION	7-86
7.B.1. Introduction	7-86
7.B.2. Plume spread and entrainment in HEGADAS	7-86
7.B.3. Illustration of model changes	7-90
7.B.4. References	7-91
7.C. NEW OPTIONS FOR THE HEGADAS MODEL	7-94
7.C.1. Automated output times in HEGADAS-T	7-94
7.C.1.1. Introduction	7-94
7.C.1.2. Algorithm	7-95
7.C.1.3. Implementation	7-97
7.C.2. Automatic downwind stepsize in HEGADAS-T	7-98
7.C.2.1. Introduction	7-98
7.C.2.2. Algorithm	7-99
7.C.2.3. Implementation	7-101
7.C.3. Surface roughness breakpoints in HEGADAS-T	7-101
7.C.3.1. Introduction	7-101
7.C.3.2. Algorithm	7-103
7.C.3.3. Implementation	7-103
7.C.4. Other new options	7-104
7.C.4.1. Volumetric concentrations in CLOUD input block	7-104

HGSYSTEM Technical Reference Manual

8. THE HEGABOX MODEL	8-1
8.1. Introduction	8-2
8.2. Model description	8-2
8.3. Implementation in HGSYSTEM	8-3
8.3.1. Thermodynamics	8-3
8.3.2. Initial conditions	8-3
8.3.3. Transition to far-field model	8-4
8.4. Model validation	8-6
8.5. References	8-7
9. TECHNICAL DESCRIPTION OF 'MMES' OPTIONS	9-1
9.1. Removal By Dry And Wet Deposition	9-2
9.1.1. Overview of Removal Processes	9-2
9.1.2. Desired Complexity Level in Deposition Algorithms	9-3
9.1.3. Removal by Gravitational Settling and Dry Deposition	9-3
9.1.4. Removal of Particles and Gases by Precipitation and Clouds	9-8
9.2. Plume Lift-Off Module	9-10
9.3. Meteorological Preprocessor	9-12
9.3.1. Background	9-12
9.3.2. Approach to Revised Meteorological Preprocessor	9-13
9.3.3. Description of Revised Meteorological Preprocessor	9-14
9.4. Concentration Fluctuations And Variations With Averaging Time	9-15
9.4.1. Plume Centerline Concentrations at a Given Downwind Distance	9-15
9.4.2. Concentrations at a given Receptor Position	9-18
9.5. Effects Of Buildings And Terrain Obstacles	9-20
9.5.1. Introduction	9-20
9.5.2. Background	9-21
9.5.3. Plume Confinement by Canyons	9-22
9.5.4. Concentrations on Building Faces due to Releases from Vents	9-23



HGSYSTEM Technical Reference Manual

9.5.5. Concentrations on the Building Downwind Face (the Near-Wake) due to Releases from Sources on the Building	9-24
9.5.6. Other Effects of Buildings	9-24
9.6. References	9-25
10. HGSYSTEM VALIDATION	10-1
10.1. Objectives of model evaluation exercise	10-2
10.2. Evaluations with field data from eight sites	10-2
10.2.1. Models to be included	10-2
10.2.2. Description of field data sets	10-2
10.2.3. Model output parameters that were evaluated	10-4
10.2.4. Statistical model evaluation procedures to be used	10-4
10.2.5. Standards for accepting or rejecting model performance	10-5
10.2.6. Results of model evaluation at eight field sites	10-5
10.3. References	10-6

1. GENERAL INTRODUCTION

1.1. Introduction

This Technical Reference Manual gives technical background information for the HGSYSTEM version 3.0 models. To keep this Manual as concise as possible, in general only that information is supplied which is not available in the open scientific literature.

Of course, for every model detailed descriptions of all input parameters is given in the HGSYSTEM User's Manual. Information in the User's Manual should enable the user to run any HGSYSTEM model.

The information in this Technical Reference Manual is intended as supplementary information for those users who want to know more about the 'technical' contents of an HGSYSTEM model.

In this paragraph, an overview of the main new features available in HGSYSTEM version 3.0 is given, as compared to the first public domain release of HGSYSTEM, version 1.0 which is also called the NOV90 version.

1.2. Main new features in HGSYSTEM version 3.0

Compared to the first public domain version of HGSYSTEM (version 1.0 or NOV90), many changes have been made to the separate models. Apart from several minor changes (additional input parameters, removed bugs etc.), the following new *major features* are now available in version 3.0 of HGSYSTEM.

- A new thermodynamical model describing *multi-compound, two-phase fluids* has been implemented. This model is also called the HGSYSTEM aerosol model. It is described in full detail in Chapter 2.A. It is available in all main and non-HF specific HGSYSTEM models.
- To generate the physical compound properties need by the new two-phase model, a *database program* called DATAPROP has been added to HGSYSTEM. DATAPROP generates link files containing all relevant data, for all HGSYSTEM models using the two-phase description.
- The new PLUME version using the new two-phase thermodynamical model is renamed to *AEROPLUME*. AEROPLUME describes near-field jet dispersion for multi-compound, two-phase releases from pressurised vessels. AEROPLUME has a built-in discharge model

to give estimates for release rates, that is, it calculates a source term for the dispersion calculation.

The AEROPLUME implementation in HGSYSTEM is described in detail in Chapter 5.A.

- The *hydrogen fluoride (HF) chemistry and thermodynamical model* has been extended to describe mixtures of HF, water and an inert ideal gas. This model is now available in the HGSYSTEM modules HFPLUME, HEGADAS and the new HEGABOX model. The new HF model is described in full detail in Chapter 2.B.
- A new model describing the initial gravity slumping behaviour for *instantaneous releases* is now available in HGSYSTEM. This model is called HEGABOX. More details are given in Chapter 8.
- A new model calculating the *transient* (time-dependent) *release rate* of a multi-compound, two-phase fluid from a pressurised vessel is now available in HGSYSTEM. This model is called SPILL and can be seen as the counterpart of the HF-specific model HFSPILL. The new SPILL model is discussed in full detail in Chapter 3.
- The EVAP model describing *evaporating liquid pools*, as used in HGSYSTEM 1.0, has been replaced by a completely new model called LPOOL. LPOOL is based on the LSM90 model as made available by Exxon Research & Engineering Company. LPOOL can be used for boiling and non-boiling pools of multi-compound mixtures on land or on water. More information on the LPOOL model is given in Chapter 4.
- The HEGADAS algorithm has been revised to prevent *unrealistic concentration profiles*. A detailed description of these changes is given in Chapter 7.B.
- Several new options have been added to the transient (time-dependent) version of the heavy gas model, HEGADAS-T. These new features are:
 - An algorithm to automatically generate an 'optimal' set of output times. See User's Manual, Chapter on HEGADAS, input block AUTOTIM.
 - A similar algorithm to automatically generate an 'optimal' step size in the downwind direction. See User's Manual, Chapter on HEGADAS, input block CLOUD, parameters XSFACT and XSEPS.
 - The possibility to specify a change in surface roughness at given downwind distances. See User's Manual, Chapter on HEGADAS, input block TRANSIT, parameter ZRS.Technical documentation on these new HEGADAS-T features are given in Chapter 7.C.

HGSYSTEM Technical Reference Manual

- The post-processors for HEGADAS results have been updated and can now be used in 'batch' mode like all other main HGSYSTEM modules. Capabilities for dosage calculations were added. Time-averaging is now done in a better way. These new models are called POSTHS and POSTHT. See the relevant chapter in the HGSYSTEM User's Manual.
- A utility program to generate concentration contours for airborne plumes as calculated by AEROPLUME and PGPLUME, is now available. The utility is called PROFILE. See the relevant chapter in the HGSYSTEM User's Manual.
- The model HFJET, which was a strongly simplified version of the HFPLUME model, is no longer part of HGSYSTEM, as its use is very limited.
- Following work done on a specific HGSYSTEM version by The Earth Technology Corporation, U.S.A., several new options are now available to all users of HGSYSTEM version 3.0. This work was sponsored by Martin Marietta Energy Systems and the added options are therefore available in an MMESOPT input block. The technical descriptions of options are given in Chapter 9. The corresponding input parameters are discussed in the HGSYSTEM 3.0 User's Manual for the relevant models (AEROPLUME, HEGADAS, HEGABOX and HFPLUME). General guidance is given in Chapter 18 of the HGSYSTEM 3.0 User's Manual.

2. THERMODYNAMICAL DESCRIPTIONS IN HGSYSTEM

CONTENTS

2. THERMODYNAMICAL DESCRIPTIONS IN HGSYSTEM	2-1
2.A. THE MULTI-COMPOUND, TWO-PHASE MODEL	2-4
2.A.1. Introduction	2-4
2.A.2. Thermodynamics model	2-6
2.A.2.1. Model parameters	2-7
2.A.2.2. Basic thermodynamic unknowns and equations	2-9
2.A.2.3. Criterion for aerosol formation	2-11
2.A.3. Solution algorithm	2-12
2.A.3.1. General problem	2-12
2.A.3.2. Case of separate one-compound aerosols	2-15
2.A.3.3. Case of single two-compound aerosol	2-19
2.A.3.4. Implementation of thermodynamics into dispersion model	2-20
2.A.4. References	2-22
2.A.5. Notation	2-22
2.B. THE HYDROGEN FLUORIDE MODEL	2-24
2.B.1. Introduction	2-24
2.B.2. Thermodynamics model	2-25
2.B.2.1. Model Parameters	2-25
2.B.2.2. Thermodynamic unknowns and equations	2-25
2.B.2.3. Enthalpy of Air	2-28
2.B.2.4. Pollutant Enthalpy	2-29
2.B.3. Solution algorithm	2-30
2.B.2.1. Solving the equations	2-30
2.B.2.2. Evaluation of pollutant enthalpy	2-32
2.B.2.3. Evaluation of molar mixture volume and mixture density	2-33
2.B.4. General trends of HF thermodynamics model	2-34

2.B.5. References	2-35
2.B.6. Notation	2-35

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, AEROPLOME, 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 a 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} ($\alpha = 0, \dots, N$).

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 ($\alpha=0$):

- molecular weight m^a (kg/kmole)
- specific heat C_p^a (J/kmole/K)
- Other compounds ($\alpha = 1, 2, \dots, N$; $\alpha = 1$ 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_{cond}^α (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 ($\alpha = 1$): specific heat of ice, C_p^{wi} (J/kmole/K), and heat of fusion, H_{fus}^w (J/kmole)

Furthermore compounds $\alpha = n_{\beta-1} + 1, n_{\beta-1} + 2, \dots, n_{\beta}$ are known to potentially form aerosol β ($\beta = 1, 2, \dots, M$; $0 = n_0 < n_1 < n_2 < \dots < n_M = N$). 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} ($\alpha = 0, 1, \dots, N$)) 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 ($\alpha = 1, \dots, N$) (-)
2. mole fraction $y_{\alpha n}$ of *liquid* for each mixture compound ($\alpha = 1, \dots, N$) (-)
3. mole fraction liquid L_{β} of each aerosol ($\beta = 1, \dots, M$) (-)
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

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

2. Raoult's law for each compound

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

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 compounds $\alpha = n_{\beta-1} + 1, \dots, n_{\beta}$.

Raoult's law 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 compound α in the liquid solution β equals the ratio $P_{\alpha}^{\alpha}(T_m)/P$ of the saturated vapour pressure of compound α in the vapour and the total vapour pressure.

For a one-compound aerosol ($y_{\alpha n} = L_{\beta}$; $\alpha = n_{\beta} = n_{\beta-1} + 1$), Raoult's law reduces to Dalton's law $y_{\alpha v}/(1-L) = P_{\alpha}^{\alpha}(T_m)/P$.

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:

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

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

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

5. Conservation of energy:

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

where the post-mixing enthalpy of compound α ($\alpha = 0, 1, \dots, N$) is given by

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

$$y_{av} \cdot C_p^{wv} \cdot T_m + y_{an} \cdot (C_p^{wi} \cdot T_m - H_{cond}^w) \quad (\text{water with } T_m > 0^\circ\text{C}, \alpha = 1) \quad (6)$$

$$y_{av} \cdot C_p^{wv} \cdot T_m + y_{an} \cdot (C_p^{wi} \cdot T_m - H_{cond}^w - H_{fus}^w) \quad (\text{water with } T_m < 0^\circ\text{C}, \alpha = 1)$$

$$y_{av} \cdot C_p^{\alpha v} \cdot T_m + y_{an} \cdot (C_p^{\alpha i} \cdot T_m - H_{cond}^\alpha) \quad (\alpha = 2, \dots, N)$$

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_{av} , y_{an} ($\alpha = 1, \dots, N$), L_β ($\beta = 1, \dots, M$), L and T_m .

The unknowns y_{av} and y_{an} can be eliminated as unknowns using Equations (1) and (2),

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

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

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

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

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,

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

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 $[1 - L + L_\beta \cdot P/P_v^\alpha(T_m)]$, $\alpha = n_{\beta-1} + 1, \dots, n_\beta$ 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 ($\beta = 1, \dots, M$) is given by

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

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

Elimination of $y_{\alpha v}$ and $y_{\alpha n}$ ($\alpha = 1, \dots, N$) using equations (7) and (8) leads to the reduced set of equations (11), (4) and (5) for L_β ($\beta = 1, \dots, M$), 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 $y_{\alpha v}$, $y_{\alpha n}$ ($\alpha = 1, \dots, N$), L_β ($\beta = 1, \dots, M$), 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 $y_{an} = 0$, $y_{av} = y_a$ ($\alpha = 1, \dots, N$), $L_\beta = 0$ ($\beta = 1, \dots, M$), $L = 0$ 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 ($\beta = 1, \dots, M$): $S[\beta_1; T_m^i] < S[\beta_2; T_m^i] < \dots < S[\beta_M; T_m^i]$. According to equation (11) aerosol β_j can only be present if the aerosols $\beta_1, \dots, \beta_{j-1}$ are also present ($j = 1, \dots, M$). Thus aerosol β_1 forms 'first' and aerosol β_M forms 'last'.
 - b) Initialise inner iteration loop for evaluation of L [aerosols $\beta_1, \beta_2, \dots, \beta_j$ have been established to be present at temperature T_m^i , and L_j is the value for L assuming the presence of aerosols $\beta_1, \dots, \beta_j$ 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 $S[\beta_{j+1}; T_m^i] > L_j$, then according to equation (11) aerosols $\beta_{j+1}, \dots, \beta_M$ do *not* form at temperature T_m^i ($L_\beta = 0$ for $\beta = \beta_{j+1}, \dots, \beta_M$): set $L = L_j$ and go to Step d)

2. If $S[\beta_{j-1}; T_m^i] < L_j$, then according to equation (11) aerosol β_{j-1} *does* form at temperature T_m^i ; calculate the aerosol formation ($L_{j-1}, \beta_1, \dots, \beta_{j-1}$) assuming the presence of aerosols $\beta_1, \dots, \beta_{j-1}$ 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 $\beta = \beta_1, \dots, \beta_{j-1}$ 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 ($\beta = \beta_1, \dots, \beta_{j-1}$) using equation (4), $L^k = L$.
- (d) Check for convergence (three cases):
 - If $k < k_{\max}$ and $|L^k - L^{k-1}| > \epsilon_L$ (no convergence): go to (b) (carry out next inner-most iteration for L).
 - If $k = k_{\max}$ and $|L^k - L^{k-1}| > \epsilon_L$ (no convergence within maximum number of inner-most iterations): stop thermodynamic calculations and produce error message.
 - If $|L^k - L^{k-1}| < \epsilon_L$ (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 ($\beta = 1, \dots, M$), 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 $|T_m^i - T_m^{i-1}| > \epsilon_T$ (no convergence): go to Step a) (carry out next iteration for temperature).
- If $|T_m^i - T_m^{i-1}| < \epsilon_T$ (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 $T_m < 0^\circ\text{C}$, equation (5) leads to $T_m > 0^\circ\text{C}$ and if assuming $T_m > 0^\circ\text{C}$, equation (5) leads to $T_m < 0^\circ\text{C}$, than ice is partially melted. Set for this case $T_m = 0^\circ\text{C}$ and set L , $y_{\alpha v}$, $y_{\alpha n}$ ($\alpha = 1, \dots, N$) 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, $M = N$, $L_\alpha = y_{\alpha n}$ ($\alpha = 1, \dots, N$), $n_\beta = \beta$ ($\beta = 1, \dots, N$). Furthermore Raoult's law given by equation (2) reduces to Dalton's law.

$$y_{\alpha v} = \min \left\{ y_{\alpha}, (1-L) \cdot \frac{P_v^\alpha(T_m)}{P} \right\} \quad (\alpha = 1, \dots, N) \quad (12)$$

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

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

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 ($y_{\alpha n} > 0$),

$$A = y_0 + \sum_{\alpha=1, \dots, N; y_{\alpha n}=0} y_{\alpha} \quad (14)$$

$$B = \sum_{\alpha=1, \dots, N; y_{\alpha n}>0} \frac{P_v^\alpha(T_m)}{P}$$

Solution to Thermodynamic Equations

The equations (1), (12), (13) and (5) for $y_{\alpha v}$, $y_{\alpha n}$ ($\alpha = 1, \dots, N$), 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 $y_{\alpha n} = 0$, $y_{\alpha v} = y_{\alpha}$ ($\alpha = 1, \dots, N$), $L = 0$ 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 ($\alpha = 1, \dots, N$): $S[\alpha_1; T_m^i] < S[\alpha_2; T_m^i] < \dots < S[\alpha_N; T_m^i]$.
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 $\alpha_1, \dots, \alpha_j$ 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 $\alpha_1, \dots, \alpha_j$ 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 $\alpha_{j+1}, \dots, \alpha_N$ do *not* form ($y_{\alpha n} = 0$ for $\alpha = \alpha_{j+1}, \dots, \alpha_N$): 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 $y_{\alpha v}$, $y_{\alpha n}$ ($\alpha = 1, \dots, N$) 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 $|T_m^i - T_m^{i-1}| > \epsilon_T$ (no convergence): go to Step a) (carry out next iteration for temperature).

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

Order of Aerosol Formation During Mixture Cooling

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

Thus compound 1 condenses first and compound N condenses last.

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

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

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),

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

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

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

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 $T_{\text{pol}} \approx T_N$ 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 $y_{\text{pol}} = 1$, $H_e = 0$, $y_{w3} = 0$).

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 $\alpha = 1, 2$). All other compounds occur in vapour phase only (compounds $\alpha = 3, \dots, N$).

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

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 $y_{\alpha v}$, $y_{\alpha m}$ ($\alpha = 1, 2$), 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 ,

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

where the auxiliary parameters q_{α} , r_{α} ($\alpha = 1, 2$) are given by

$$q_{\alpha}(T_m) = \left(\frac{P}{P_v^{\alpha}(T_m)} \right) - 1 \quad (19)$$

$$r_{\alpha}(T_m) = y_{\alpha} \cdot \left(\frac{P}{P_v^{\alpha}(T_m)} \right) - 1$$

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 $\alpha = 1, 2$ are 100% liquid for very low temperatures), equals

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

or, written alternatively (20)

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

Solution to Thermodynamic Equations

The equations (7), (8), (20) and (5) for $y_{\alpha v}$, $y_{\alpha n}$ ($\alpha = 1, 2, \dots, N$), 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 $y_{\alpha n} = 0$, $y_{\alpha v} = y_{\alpha}$ ($\alpha = 1, \dots, N$), $L = 0$ 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 $|T_m^i - T_m^{i-1}| > \epsilon_T$ (no convergence): go to Step a. (carry out next iteration for temperature).
- If $|T_m^i - T_m^{i-1}| < \epsilon_T$ (convergence): *end of thermodynamic calculations.*
- If $i = i_{\max}$ and $|T_m^i - T_m^{i-1}| > \epsilon_T$ (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, then ice is partially melted. Set for this case $T_m = 0$ °C and set L , $y_{\alpha v}$, $y_{\alpha n}$ ($\alpha = 1, \dots, N$) 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 , $\alpha = 1, \dots, N$)
- 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_g (*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_c 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 ($^{\circ}\text{C}$), 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

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

$$\rho_m = \frac{1}{V_m} \cdot \sum_{\alpha=0}^N (m^\alpha \cdot y_\alpha)$$
(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 $a = 2, \dots, N$: liquid, $C_p^{\alpha l}$, vapour $C_p^{\alpha v}$
$F_\beta(L_\beta; L, T_m)$	function defined by equation (9)
H_{cond}^w	heat of condensation of water (J/kmole)
H_{cond}^α	heat of condensation of compound (J/kmole)
H_e	heat added from the substrate (J/kmole)
H_{fus}^w	heat of fusion of water (J/kmole)
H_{pol}	pollutant enthalpy (J/kmole)
H_{tot}	total mixture enthalpy (J/kmole)
H_{air}^{wet}	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 (-)
$y_{\alpha\text{li}}$	mole fraction of liquid (non-vapour) phase of compound α in mixture (-)
)	
$y_{\alpha\text{v}}$	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•H₂O 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; $0 \leq r_{\text{H}} \leq 1$)
- 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} ($M_{\text{tot}} = M_{\text{HF}} + M_{\text{w}} + M_{\text{N}} + M_{\text{a}}$) 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 ($^{\circ}C$)

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):

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

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

$$M_N = y_N \cdot M_{vap} \quad (3)$$

$$M_a = y_a \cdot M_{vap} \quad (4)$$

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

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

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

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

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

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

$$y_c(f_1, y_w, T_m) = K_c(T_m) \cdot f_1 \cdot P_w / (\Phi_1 \cdot P) \quad (9)$$

where the fugacity $f_1 = \Phi_1 y_{11} P$ (in atm), the (dimensionless) fugacity coefficient $\Phi_1 \approx 1$, the total (ambient) vapour pressure P is taken to be 1 atm and $P_{w1} = y_w P$ is the true partial pressure (excluding $\text{HF} \cdot \text{H}_2\text{O}$ 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 $(\text{HF})_2$, $(\text{HF})_6$, $(\text{HF})_8$, $\text{HF} \cdot \text{H}_2\text{O}$, 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 $\text{HF} \cdot \text{H}_2\text{O}$ complex) and water (including $\text{HF} \cdot \text{H}_2\text{O}$ complex) are set as a function of x and T_m from empirical expressions $p_w(x, T_m)$, $p_{\text{HF}}(x, T_m)$ 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 $p_w(x, T)$, $p_{\text{HF}}(x, T)$ 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 $(M_w/M_{\text{tot}}) \cdot P$ and $(M_{\text{HF}}/M_{\text{tot}}) \cdot P$, 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 ($L > 0$):

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

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

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_c added from the substrate

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

where the post-mixing enthalpies of HF (including water in fog and HF in $\text{HF} \cdot \text{H}_2\text{O}$), water (excluding fog; including water in $\text{HF} \cdot \text{H}_2\text{O}$), N-gas, and air are given by

$$H_{HF} = \text{TERM1} - \text{TERM2}$$

with

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

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

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

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

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

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], $T^* = 25^\circ\text{C}$ 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

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

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

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

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 $T^* = 25^\circ\text{C}$ 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}^{AHF} 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

$$E_{pol}^{kin} = \frac{1}{2} \cdot m_{pol} \cdot V_{fl}^2 \quad \text{with } m_{pol} = g_{HF} \cdot m_{HF} + g_w \cdot m_w + g_N \cdot m_N \quad (16)$$

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)),

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

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

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 ; $M_{\text{tot}} = M_w + M_{\text{HF}} + M_N + M_a = 1$) can be expressed in terms of the input parameters as follows:

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

with $P_w^{\text{amb}}/P = r_H \cdot P_v^w(T_a)/P$ 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)).

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

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

$$L = \frac{\text{TERM1}}{\text{TERM2} + \text{TERM3}} \quad (21)$$

with

$$\text{TERM1} = H_a + H_N - H_{\text{tot}} + M_w \cdot C_p^{\text{wv}} \cdot (T_m - T^*) + M_{\text{HF}} \cdot \{H^{\Delta\text{HF}} + C_p^{\text{HFV}} \cdot (T_m - T^*)\}$$

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

$$\text{TERM3} = x \cdot \{H^{\Delta\text{HF}} + C_p^{\text{HFV}} \cdot (T_m - T^*) + H_{\text{cond}}^{\text{HF}} + H_{\text{mix}}\}$$

- b In the absence of a liquid fog ($L = 0$), M_{vap} , y_w are set as functions of y_{11} , T_m .

For $M_{\text{HF}} > 0.5$ conservation of HF molar flow (equation (1)) and conservation of water molar flow (equation (2)) is imposed, while for $M_{\text{HF}} < 0.5$ 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:

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

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

$$L = 0 \quad (21^*)$$