MODELLING THE CONSEQUENCE OF HAZARDOUS MULTI-COMPONENT TWO-PHASE RELEASES TO THE ATMOSPHERE

Henk Witlox, Mike Harper, Panos Topalis and Stuart Wilkinson, DNV Software, London, UK
www.dnvsoftware.com

Abstract

A typical hazard analysis of a chemical process installation involves several hazardous materials/streams. Rigorous thermodynamics is a standard feature of models used in process plant design and process simulation. However, models used in hazard and risk assessment frequently make simplistic assumptions. The "pseudo component" approach is often used and the mixture is assumed to have a constant composition throughout the model and to behave like a single component. The actual compositions and properties of the two phases can be very different, affecting the accuracy of the release and dispersion calculations. The current paper discusses more rigorous multi-component modelling for multi-component two-phase flashing releases of hazardous chemicals into the atmosphere. A new multi-component property system has been implemented in the consequence modelling package PHAST and applied to discharge and dispersion models.

The new multi-component property system allows usage of cubic equations of state (Soave-Redlich Kwong and Peng-Robinson), which are most favoured by the industry for mixture calculations. These allow modelling of non-polar and slightly polar mixtures for consequence-analysis purposes. The phase-equilibrium calculations of a multi-component stream produce results for vapour composition, liquid composition, pressure, temperature, enthalpy, entropy and density. Currently the property system allows the following types of flash calculations: isothermal, isentropic, isenthalpic, constant energy and constant vapour fraction. The property and phase equilibrium calculations have been verified and validated by means of comparison against a commercial process simulation package.

The discharge model calculates the expansion from the stagnation conditions to the orifice conditions (isentropic expansion for the release from a vessel, conservation of energy for expansion along a pipe), and the expansion from the orifice conditions to the ambient conditions (conservation of energy). These expansion calculations have been extended to allow usage of the above multi-component property system. It is demonstrated that the new multi-component calculations may significantly affect the vapour and liquid composition of the released pollutant.

The dispersion model includes a thermodynamic model for mixing of a non-reactive multi-component pollutant with moist air, which includes possible water-vapour transfer and/or heat transfer from the substrate to the cloud. Conservation of enthalpy is assumed during the mixing with air. Two methods have been included, i.e. the case for which all components are assumed to form a single aerosol and a case for which separate aerosols form. The new multi-component version of the dispersion model has been tested and verified thoroughly. It is demonstrated that the new multi-component calculations may significantly affect the predicted vapour and liquid composition of the dispersing cloud, and also the predicted temperature, concentration and amount of rainout.

Keywords: two-phase releases, multi-component

1. Introduction

Many accidents involve multi-component two-phase flashing releases of flammable or toxic chemicals into the atmosphere. An assessment of the hazards involves the modelling of the discharge/spillage and subsequent dispersion. In the case of a flammable cloud, ignition may lead to fires or explosions.

Typical release scenarios involve two-phase releases from vessel or pipe work attached to vessels. Consequence

modelling first involves discharge modelling involving expansion from stagnation to orifice conditions, and expansion from orifice conditions to ambient conditions. Secondly a cloud forms which moves in the downwind direction. Two-phase atmospheric dispersion calculations are carried to calculate the cloud concentrations. Rainout may occur, and pool formation/spreading and re-evaporation needs to be modelled.

A typical hazard analysis of a chemical process installation involves several hazardous materials/streams and often these streams are a mixture of two or more chemical substances. Modelling of the behaviour of the mixture requires calculation of mixture thermodynamic properties such as densities, enthalpies, entropies, fugacities and phase equilibrium conditions. Rigorous multi-component (MC) thermodynamics is a standard feature of models used in process plant design and process simulation. However, models used in hazard and risk assessment frequently make simplistic assumptions in order to avoid the use of rigorous multi-component thermodynamics. The "pseudo component" (PC) approach is often used and the mixture is assumed to have a constant composition throughout the model and to behave like a single component. The properties of the mixture are calculated from the component properties with a simple averaging equation. The error from a pseudo-component approach varies according to the component volatility range, the non-ideality of the mixture and the consequence model itself. This will be further demonstrated in the paper for both release and dispersion modelling.
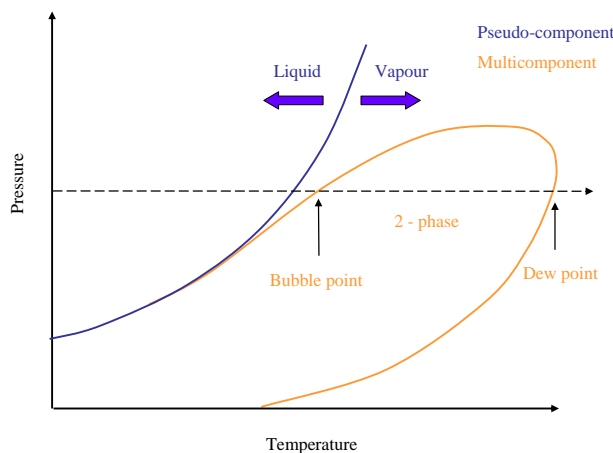

Figure 1. Phase equilibrium curve for PC and MC thermodynamics

Figure 1 illustrates that at a given pressure a mixture might be 2-phase across a range of temperatures, but under PC logic the bubble point and dew point temperatures for a mixture are identical. Thus a 2-phase or 100% liquid mixture may, according to PC logic, be a vapour. Moreover, the liquid phase of the 2-phase mixture will preferentially contain the heavier components, but under PC logic the composition of both phases are identical.

A common justification of the use of simplified thermodynamics is that hazard and risk assessment do not require the same accuracy as process design. In addition rigorous thermodynamics might affect the speed and robustness of the consequence models and significant investment is required to avoid these problems and keep this development under control. However, the industry often makes important decisions based on the results of consequence models and since the recent modelling technology has overcome many of the technical difficulties, this should be made available to the users of consequence models because of the resulting overall benefit: improvement of the accuracy of the risk assessment results.

Section 2 includes a brief review of methods for multi-component phase equilibrium including both 'equations of state' and 'activity coefficient' models. Section 3 summarises a new multi-component property system based on cubic equations. Section 4 describes the application of this system to discharge and dispersion models in multi-component consequence modelling calculations. Section 5 finally summarises the main conclusions and proposed further work.

2.   Methods for multi-component phase equilibrium

The development of calculation methods for multi-component fluid phase equilibrium has been driven largely by the process design industry, and followed different branches due to the diverse nature of the types of mixtures. Below a brief review is given for these methods.

Equations of state

In oil and gas processing, the components are typically hydrocarbons and other light gases (e.g. Nitrogen, Carbon Dioxide etc). Because these components are largely non-polar (or only slightly polar) and because the processing frequently employs high pressures and/or temperatures, any deviations from ideal behaviour are largely associated with volumetric effects. The conventional way of modelling such systems therefore uses equations of state which attempt to model the Pressure-Volume-Temperature behaviour of the fluid.

The equation of state is a significant improvement over the ideal gas law. The Redlich-Kwong (1949) equation was accurate enough for engineering calculations of the vapour phase fugacity coefficients but did not model the material vapour pressure equation. Soave (1972) modified the Redlich Kwong equation by fitting the α-parameter of the equation to vapour pressure data using a generic (material-independent) polynomial. This modification allowed use of the equation of state for calculating fugacity coefficients for both the vapour and the liquid phase. The same equation

can be used for calculating several thermodynamic properties of the vapour and liquid phase for pure materials and multi-component non-polar mixtures. The Peng Robinson (1976) is a modification of the Soave equation presumed to calculate liquid densities slightly more accurately than Soave. The two equations are relatively simple and can be used nearly interchangeably in phase equilibrium algorithms. They are fairly accurate for modelling hydrocarbon mixtures and they can even be used without fitted binary parameters for mixtures of symmetric (not dissimilar) materials.

The cubic equations of state are the most favoured by the industry for mixture calculations especially when there are very few experimental data available. Cubic equations are semi-empirical equations and they have a number of advantages:

- They allow a uniform approach in mixture thermodynamic modelling and predict many properties for both the vapour and liquid phase for multiple components and for a wide range of pressures, temperatures and compositions.

- They can be used to calculate simultaneously Pressure-Volume-Temperature properties (density), fugacity coefficients and other thermodynamic property (enthalpy, entropy, heat capacity) departures from the ideal behaviour.

- They usually have few parameters and do not require very extensive experimental data. Some of the simpler cubic equations (such as Soave(1972) and Peng Robinson(1976)) can even be used without any mixture data (or binary parameters) in some cases. Critical temperature and critical pressure data are the main requirement and most of the equations also use the acentric factor derived from vapour pressure data.

- They are quite easy to solve and there is always an analytical solution.

- Cubic equations usually combine easily component data to calculate mixture data.

- For mixtures, non-cubic equations are not generally more accurate than the cubic ones.

The Soave-Redlich-Kwong and Peng-Robinson equations are universally accepted, and allow a reasonable modelling of non-polar and slightly polar mixtures for consequence analysis purposes. Moreover use of binary interaction parameters can make possible the modelling of hydrocarbon mixtures with H_2 , N_2 and other light components. As a result these methods have been selected for the consequence modelling calculations in this paper.

A disadvantage of the original Soave and Peng Robinson cubic equations is their inability to handle polar mixtures. There has been a drive to extend the equations of state

models to deal with polar mixtures through more complex mixing rules or rules based on Excess Gibbs Free Energy models. See Topalis (1999) for further details on these as well as other recent work on improvement of cubic equations. It is also known (Poling et al, 2000) that the original Soave and Peng Robinson equations are still not accurate enough for liquid density calculations. Generally their performance deteriorates very near the critical point. The liquid density calculation can be improved with volume translation while some new equations, involving switching or crossover functions have been developed to improve accuracy near the critical point. The reader is referred to Poling et al (2000) for further details on these models.

Activity coefficient models

In the chemical industry, the components involved are often highly polar resulting in large interaction energies between molecules. The deviations from ideal behaviour are dominated by these interactions, and so the approach to modelling these systems was through the free energy or activity coefficient models. Activity coefficient models deal only with the liquid phase and are generally applicable within a limited range of pressures (low to moderate) and temperatures. They can be made very accurate for even the most highly polar mixtures by using mixture interaction parameters, but are of limited value without them. The Wilson (Wilson, 1964), NRTL (Renon and Prausnitz 1968) and UNIQUAC equations as well as the associated UNIFAC predictive approach are the most commonly used activity coefficient models.

3.   Multi-component property calculations

This section describes a new multi-component property system (XPRP) allowing for more rigorous multi-component calculations. The structure of the property system is shown in Figure 2.
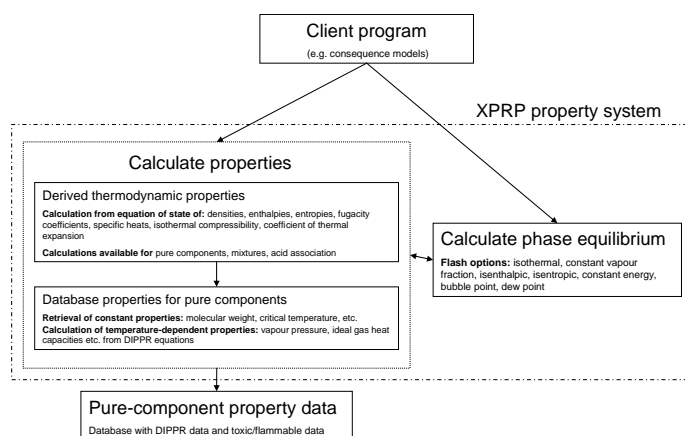

Figure 2: The Structure of the Property System

The property system is invoked by the "client program" (e.g. a consequence model) for the calculation of mixture properties and phase equilibrium. The property system utilises a database of pure-component property data including DIPPR data. This includes both constant component properties (e.g. molecular weight, critical data, melting point, normal boiling point) and temperature-dependent properties (e.g. liquid density, saturated vapour pressure; liquid/vapour heat capacity, viscosity, thermal conductivity, surface tension, ideal gas enthalpy, second virial coefficient). In addition the database contains toxic and flammable data not present in DIPPR.

Evaluation of "simple" properties via mixing rules

When modelling a mixture, the program calculates the values of some "simple" properties, such as the molecular weight and the Lower Flammability Limit, as a composition-based average of the base properties of the individual components. A number of choices for the averaging method, or mixing rule, are available. For constant properties, the mixing rules are applied directly to the property values. For temperature-dependent properties, the mixing rules are applied to the values obtained from the equation for each of the components in the mixture at the specified temperature. The most commonly applied mixing rules are

$$Q_m = \sum_{i=1}^{i=N} y_i Q_i \text{ (ideal)}, \quad \frac{1}{Q_m} = \sum_{i=1}^{i=N} \frac{y_i}{Q_i} \text{ (Le Chatelier)} \quad (1)$$

Where N is the number of mixture components, y_i the mass or mole fraction, Q_i the component property value, and Q_m the mixture property value (at the specified temperature if relevant). The property system contains 'template' sets of methods for calculating properties, which use particular mixing rules for particular properties. The mixing rule accounts for the phase (liquid or or vapour) and may use fractions on a mass or mole basis.

Equations of state

The equations of state are based on the equations for a pure material modified by means of mixing rules to apply to vapour mixtures or to liquid mixtures. There is the choice of the ideal-gas equation, the first-order virial Equation and three cubic equations of state: Redlich-Kwong, Soave-Redlich-Kwong, and Peng-Robinson:

$$Z = \frac{PV}{RT} = 1.0 \text{ (ideal)} \quad (2)$$

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} \text{ (virial)} \quad (3)$$

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b) + ub(V-b)} \text{ (cubic)} \quad (4)$$

Where Z is the compressibility (-), P the absolute pressure (Pa), T the absolute temperature (K), V the molar volume (m³/kmol) and R the gas constant (J/kmol/K). The temperature-dependent second virial coefficient B in the virial equation is derived from DIPPR for pure components and from an ideal mole mixing rule for mixtures. The coefficients $a\alpha$ and b in the cubic equation are determined according to mixing rules,

$$a\alpha = \sum_{i=1}^{N}\sum_{j=1}^{N} y_i y_j (a_i\alpha_i)^{0.5} (a_j\alpha_j)^{0.5} (1-k_{ij}), \quad b = \sum_{i=1}^{N} y_i b_i \quad (5)$$

where y_i, y_j are mole fractions and k_{ij} binary interaction coefficients. The pure component parameters $a_i\alpha_i$ and b_i are derived from standard correlations in the literature according to the Redlich-Kwong, Soave-Redlich-Kwong and Peng-Robinson equations of state (see e.g. Poling et al., 2000). Both the Soave-Redlich-Kwong and Peng-Robinson equation give good results for mixtures of non-polar or slightly polar components. The binary interaction constants k_{ij} must be determined from equilibrium data. For hydrocarbon mixtures the k_{ij} may be taken to be zero. The binary interactions are not very important for bulk phase calculations but may be quite significant in equilibrium *K*-value calculations. Even mixtures that are fairly non-ideal may be successfully treated if specific binary interaction constants are derived from measured equilibrium data.

The above equations were chosen because they can predict the behaviour of fluids over a wide range of conditions, covering the vapour phase and the liquid phase, and covering multi-component fluids (see Section 2).

Derivation of thermodynamic properties from equations of state

Thermodynamic properties for the vapour mixture or the liquid mixture can be derived from the equation of state for the mixture. The basic premise of the equation of state approach is that the same model (same equation of state) should be used to calculate the thermodynamic properties (densities, fugacities, enthalpy departures and entropy departures) for all phases. In the specific case of vapour-liquid equilibrium, the requirement is that the selected equation of state should be able to model adequately both vapour and liquid phase. The reader is referred to the literature (e.g. Reid et al. 1997) for full details on the derivation of these data. Below a brief summary is given:

- The vapour and liquid compressibility and density are first derived from the Equation of state. For liquids, equations of state may not be very accurate at predicting density, so the Costald method is also available, calculating liquid density as the inverse of the molar volume calculated by the Thomson equation.
- Vapour or liquid enthalpy, entropy and fugacity are calculated using standard departure functions as derived from the Maxwell equations.

- Subsequently isothermal compressibility, coefficient of thermal expansion, and specific heat capacities are set using well-known equations.

Calculation of phase equilibrium for a mixture

The general case of phase equilibrium in the flashing of a multi-component stream is shown in Figure 3. A multi-component mixture stream of given molar flow F, overall composition (mole fractions) z, temperature T_0 and pressure P_0 is flashed at a temperature T and a pressure P with exchange of heat Q (which may be zero). This process produces a vapour stream (of molar flow V and composition **y**) and a liquid stream (of molar flow L and composition **x**).
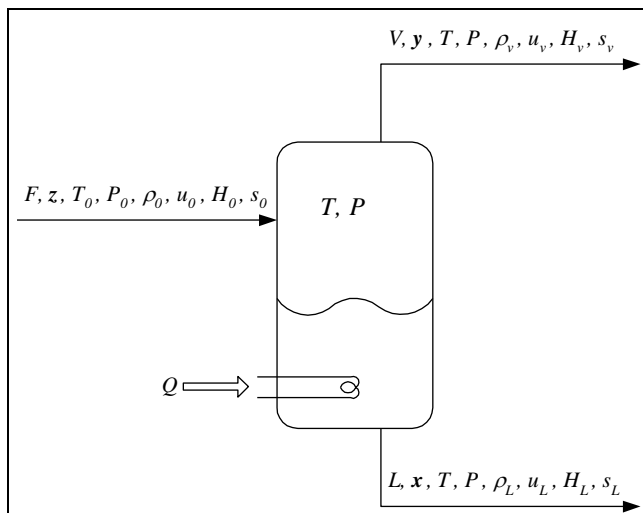

$V, \mathbf{y}, T, P, \rho_v, u_v, H_v, s_v$

$F, z, T_0, P_0, \rho_0, u_0, H_0, s_0$

T, P

Q

$L, \mathbf{x}, T, P, \rho_L, u_L, H_L, s_L$

Figure 3: Equilibrium between vapour and liquid in multi-component flash

Some of the flash conditions are known (e.g. T and P), and the model calculates the remaining conditions (e.g. V, L, **y** and **x**). Five types of flash calculation are performed, with different known and unknown quantities for each type:

1. *Isothermal flash* or flash at specified temperature T and pressure P.
   This is a useful calculation for a variety of situations e.g. in phase identification before a consequence calculation and the calculation of mixed-phase stream thermodynamic properties (enthalpies, entropies).

2. *Isentropic flash* or flash at specified specific entropy s and pressure P.
   This is a reversible adiabatic flash and it can be used in situations usually approximated by a reversible process e.g. an orifice expansion between the bulk of the fluid and the vena contracta.

3. *Isenthalpic flash* or flash at specified specific enthalpy h and pressure P.

This is an irreversible adiabatic flash and it can be used in processes with high degree of irreversibility e.g. in dispersion modelling for the mixing of air with the released pollutant.

4. *Constant Energy flash* or flash at specified energy E and pressure P.
   The energy E is given by the sum of the specific enthalpy (h) and the kinetic energy ($0.5u^2$). This is a generalisation of the isenthalpic flash. The constant energy flash is used in discharge modelling for adiabatic but irreversible expansions, when the kinetic energy cannot be neglected; e.g. expansion from the stagnation point to the pipe orifice and for the expansion from the pipe orifice to the atmosphere.

5. *Constant vapour fraction flash* or flash at specified P & vapour mole fraction (Ψ) or T & Ψ.
   This includes dew/bubble pressures and temperatures. This can also be very useful in phase identification /scenario identification and in a variety of consequence models.

Flash calculations at specified enthalpy and temperature or specified entropy and temperature are also available and they are used as part of other models or algorithms. See Topalis (1999) and Harper et al. (2005) for further details on the solution of the phase-equilibrium and on the verification of the property and phase equilibrium calculations by means of comparison against a commercial process simulation package.

4. Multi-component consequence modelling

This section describes the application of the above multi-component property system for multi-component releases to the atmosphere. To this purpose, the discharge and dispersion models in the consequence modelling package PHAST and the risk analysis package SAFETI are extended in order to allow usage of the above property system.

4.1 Discharge modelling

As shown in Figure 4, the discharge model calculates both the expansion from the initial storage conditions to the orifice conditions, as well as the subsequent expansion from orifice conditions to atmospheric conditions. For a two-phase vessel storage, the leak is usually assumed from the liquid side since this usually poses the most hazards. However, the leak can also be from the vapour side.

Expansion from stagnation to orifice conditions

In the case of the release from a vessel (no attached pipe), the flow rate dm/dt (kg/s) through the orifice is given by

$$\frac{dm}{dt} = C_d\, A_o\, \rho_o\, u_o \ , \ \text{with} \ u_o = \sqrt{2(h(P_{st},T_{st},\eta_{Lst}) - h_o(P_o,T_o,\eta_{Lo}))} \quad (\,6\,)$$

where the subscripts st,o refer to the stagnation and orifice conditions; A_o is the orifice area, ρ the density, u the speed, and h the specific enthalpy, T temperature, P the pressure, η_L the liquid fraction, and C_d the discharge coefficient (<1 because of presence of vena contracta). A multi-component isentropic flash is applied to determine the temperature and liquid fraction at the vessel exit. Herewith optionally a meta-stable liquid assumption can be applied (non-equilibrium), which forces the liquid to remain liquid in the vessel and for which the orifice pressure equals the ambient pressure. For choked vapour or two-phase flow, the orifice pressure P_o is varied to maximise the flow rate.

In the case of the release from a pipe attached to be vessel, conservation of mass, energy and momentum are applied along the pipe. The momentum balance is integrated along the pipe to calculate the total frictional resistance $F_{friction}$ as a function of mass flux through the pipe,

$$F_{friction} = \ 2\left[\frac{dm}{dt}\right]^{-2} \int_{P_{end}}^{P_{start}} \rho \ dP - 2\ln\left(\frac{\rho_{start}}{\rho_{end}}\right) \quad (\,7\,)$$

Here P_{start}, P_{end} are the pressures and ρ_{start}, ρ_{end} the densities at the start and the end of the pipe. Furthermore the frictional force $F_{friction}$ is estimated empirically by the use of a Fanning friction factor, and the mass flux is varied until the above equation is satisfied. At the pipe exit the flow may be choked, with the choke pressure determined from a standard choke criterion. A multi-component constant-energy flash is carried out to determine the temperature and liquid fraction at the pipe exit.
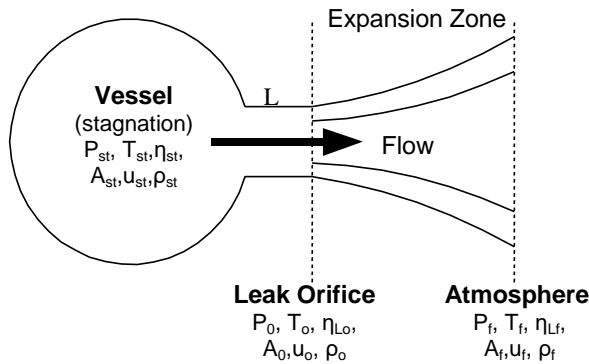

Figure 4.   **Expansion from stagnation to orifice and from orifice to ambient conditions**

Expansion from orifice to ambient conditions

The post-expansion pressure equals the ambient pressure. The model allows application of conservation of mass,

momentum and energy in line with recommendations by Britter (1994,1995) or application of conservation of mass, entropy and energy in line with recommendations by Woodward in Perry's Handbook (1999). The post-expansion temperature and liquid fraction are set by performing a multi-component constant-energy flash. The model also includes a new formulation for the initial droplet size accounting for both effects of mechanical break-up and flashing break-up; see Witlox and Bowen (2002) and Witlox et al. (2005) for details.

4.2   *Dispersion modelling*

The PHAST dispersion model UDM (Witlox and Holt, 1999) invokes a thermodynamics module while solving the dispersion equations in the downwind direction. The module describes the mixing of a multi-component pollutant with moist air, which includes possible water-vapour transfer and/or heat transfer from the substrate to the cloud. It calculates the phase distribution [pollutant (vapour, liquid), water (vapour, liquid, ice)], vapour and liquid cloud temperature, and cloud density. The liquid pollutant in the aerosol is considered to consist of spherical droplets and additional droplet equations may be solved to determine the droplet trajectories, droplet mass and droplet temperature. Rainout of the liquid pollutant occurs if the droplet size is sufficiently large (see Figure 5).
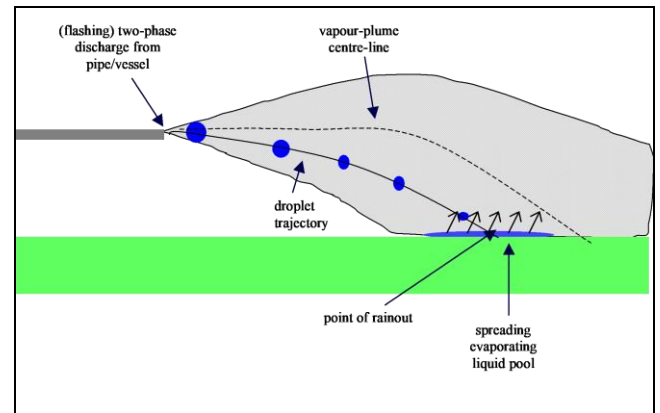

Figure 5.   Downwind cloud dispersion including droplet evaporation and rainout

The thermodynamics module contains an equilibrium model, a non-equilibrium model, and an equilibrium model specific to HF [including the effects of HF polymerisation and fog formation; see Witlox (1993a)].

The equilibrium model (see Figure 6) assumes thermal equilibrium, which implies that the same temperature is adopted for all components in the cloud (vapour and liquid). The equilibrium model determines the phase distribution and the mixture temperature. Separate droplet equations are

solved to determine the droplet trajectories (and the point of rainout). The model has been generalised to allow the mixing of moist air with a multi-component pollutant consisting of a mixture of non-reactive chemicals (including possibly air and water). Each of the pollutant components may occur in both liquid and vapour phase. Two methods have been implemented:

a) Case for which all components are assumed to form a single aerosol (SA method). For this case, the new property system XPRP is used to evaluate the isenthalpic flash.

b) Case for which separate aerosols form, with ideal mixing for all components in an individual aerosol (MA method). For this case Raoult's law is used to determine the vapour and liquid mole fractions in each aerosol. The temperature is evaluated using an isenthalpic flash. It is based on the multi-component method developed by Witlox (1993b) for implementation in the program HEGADAS in HGSYSTEM.

The non-equilibrium model allows the temperature of the droplet (liquid pollutant) to be different from the temperature of the other components in the cloud, and it determines the phase distribution of the water and the vapour temperature. It models the released pollutant as a single 'pseudo-component'. Additional droplet equations are solved to determine the droplet trajectories (and point of rainout), droplet mass and droplet temperature.
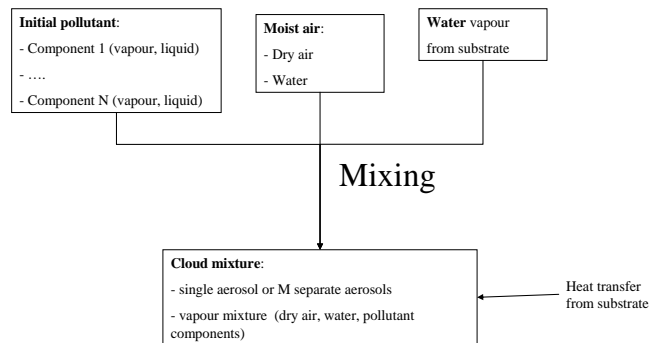

Figure 6. Mixing of multi-component pollutant with moist air

4.3 Examples

Comparison of rigorous multi-component (MC) and pseudo-component (PC) methods

The liquid release of an ethane/butane pollutant (50%/50% mole fraction) is considered with an orifice pressure of 2 bar and orifice temperature just below its bubble point (225K). A constant-energy flash to ambient conditions is carried out to simulate the expansion from orifice to ambient conditions before the onset of mixing with ambient

dry air (at ambient temperature of 293.15K). For this case a single ethane/butane liquid aerosol occurs only.
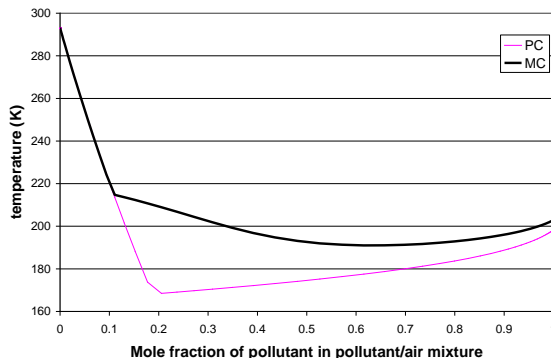
(a)
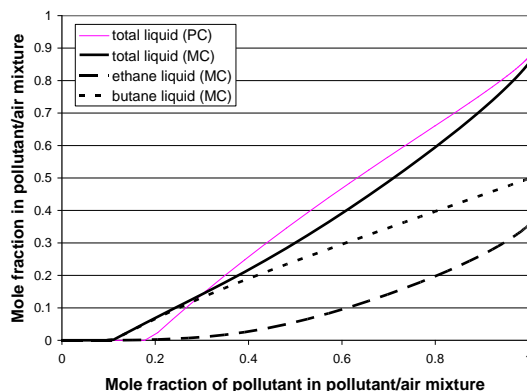
(b)

Figure 7. Mixing of ethane/butane pollutant with dry air (MC versus PC method)

Figure 7 plots mixture temperature and liquid mole fractions (total butane/ethane liquid or ethane, butane only) as function of the pollutant mole fraction y_{pol} in the pollutant/air mixture, with y_{pol} reducing from 1 (corresponding to the initial post-expansion state) to 0 (corresponding to pure air) during mixing with air. The MC method results in initially more vapour formation (less liquid) with the initial vapour in the pollutant almost all consisting of ethane, while for the PC method the composition of both vapour and liquid in the pollutant is assumed to remain identical during mixing (50% ethane, 50% butane). Upon sufficient mixing with air, the liquid disappears less quickly for MC because of the longer prevalence of the butane (Figure 7b). The MC method results in significant less mixture cooling than the PC method (Figure 7a). For both methods discontinuities in temperature slope can be observed at the point at which the final liquid evaporates.

Thus this example illustrates that the PC method may result in significant errors in predictions for temperature, vapour

and liquid composition during discharge and dispersion predictions.

<u>Comparison of Multiple Aerosol (MA) and Single Aerosol (SA) methods</u>

Figure 8 illustrates the MA method (using both UDM and HEGADAS) and SA method (UDM) for the example of mixing of liquid ammonia/butane pollutant (0.5/0.5 mole fraction; initial temperature of 235K) with dry air (at ambient temperature of 293.15K). The SA method assumes a single ammonia/butane aerosol, while the MA method assumes separate ammonia and butane aerosols. Good agreement between the MA methods of UDM and HEGADAS models is confirmed. The MA method results in significant more ammonia vaporisation (less ammonia liquid) and slightly more butane liquid than the SA method. The initial larger vaporisation of ammonia results in more cooling for the MA method than for the SA method. For the MA method two discontinuities in temperature slope can be observed corresponding to the points at which the butane and ammonia aerosols disappear. Temperatures between MA and SA methods are identical after all liquid is disappeared for both methods. For this specific example, it is expected that the MA method will provide a more accurate description of the thermodynamics.
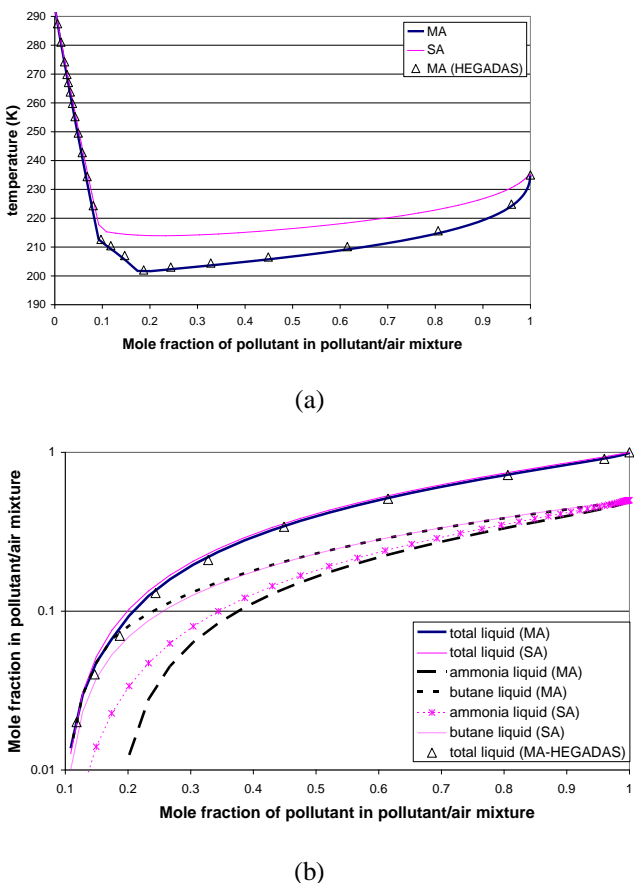

(a)

(b)

Figure 8.   Mixing of ammonia/butane pollutant with dry air (MA versus SA method)

The above examples illustrate that the new multi-component calculations may significantly affect the predicted vapour and liquid composition of the dispersing cloud, and therefore also the predicted cloud temperature and cloud density. This may considerably affect the concentration and amount of rainout predicted by the dispersion model.

5.   Conclusions and future work

In this paper more rigorous multi-component modelling has been discussed for multi-component two-phase flashing releases of hazardous chemicals into the atmosphere, and a review of methods for multi-component phase equilibrium is given. A new multi-component property system based on equations of state has been implemented into the hazard assessment package PHAST and the risk-analysis package SAFETI. Both discharge and dispersion models have been extended to include more advanced multi-component calculations:

-   For dispersion modelling, the occurrence of more than one aerosol must be taken into account.
-   The new multi-component calculations may significantly affect the vapour/liquid composition in the released multi-component pollutant, and also the predicted vapour/ liquid composition, temperature and concentrations of the dispersing cloud. The results may be considerably more accurate than the simplistic pseudo-component approach, where component properties are set using simple averaging.

As part of further work, the property system could be further extended to include activity coefficient models and equations of state with more advanced mixing rules e.g. Excess Gibbs Free Energy rules. These will allow modelling of polar mixtures at low to moderate pressures, and to multi-component extension of other consequence models, e.g. multi-component pool modelling. Also experimental work would be useful to enable the validation of the multi-component models.

Nomenclature

A   cross-section area, m^2
h   specific enthalpy, J/kg
P   pressure, N/m^2
s   specific entropy, J/kg/K
T   temperature, K
u   velocity, m/s
y   mole fraction, -

Greek letters

η   mass fraction, -
ρ   density, kg/m^3
Ψ   vapour mole fraction in mixture, -

Subscripts

a	ambient (atmospheric)
f	final (after atmospheric expansion)
i	component index
L	liquid
m	mixture
o	orifice (immediately downstream of orifice, prior to atmospheric expansion)
pol	released (multi-component) pollutant
st	stagnation (before expansion from storage data to orifice data)
v	vapour

References

Britter, R.E., 1994, Dispersion of two-phase flashing releases - FLADIS field experiments; the modelling of pseudo-source for complex releases, Report FM89/2 by CERC for EEC Commission DGXII.

Britter, R.E., 1995, Dispersion of two-phase flashing releases - FLADIS field experiments; a further note on modelling flashing releases, Report FM89/3 by CERC for EEC Commission DGXII.

Harper, M., Topalis, P., Wilkinson, S. and Witlox, H.W.M., 2005, Multi-component property system XPRP – Theory Manual, DNV Software, London.

Peng, D.Y. and Robinson, D.B., 1976, A new two-constant equation of state, *Ind. Eng. Chem. Fundam.*, 15:59-64.

Perry, R.H, Green, D.W. and Maloney, J.D., (eds.), 1999, *Perry Chemicals Engineering Handbook*, 7th Edition, McGrawhill (1999), Section 26 "Process safety".

Poling B.E., Prausnitz J.M., and O'Connell J.P., 2000, *The properties of gases and liquids*, McGraw-Hill, 5th Edition.

Redlich, O. and Kwong, J.N.S., 1949, On the thermodynamics of solutions, *V. Chem. Rev.*, 44:233-244.

Renon, H. and Prausnitz, J.M., 1968, Local compositions in excess thermodynamic functions for liquid mixtures, *AIChE J.*, 14:135-144.

Soave, G., 1972, Equilibrium constants from a modified Redlich Kwong equation of state. *Chem. Eng. Sci.*, 27:1197-1203.

Topalis, P., 1999, Multi-component thermodynamics in consequence analysis – Phase 1, *HSE Contract Research Report* 207/1999.

Wilson, G.M., 1964, Vapor-liquid equilibrium. XI. A new expression for the excess Gibbs energy of mixing". *J. Am. Chem. Soc.*, 86:127-130.

Witlox, H.W.M, 1993a, Two-phase thermodynamics model for mixing of a non-reactive multi-compound pollutant with moist air, Report TNER.93.022, Thornton Research Centre, Shell Research, Chester, England.

Witlox, H.W.M., 1993b, Thermodynamics model for mixing of moist air with pollutant consisting of HF, ideal gas and water, Report TNER.93.021, Thornton Research Centre, Shell Research, Chester, England.

Witlox, H.W.M., and Holt, A., 1999, A unified model for jet, heavy and passive dispersion including droplet rainout and re-evaporation, *International Conference and Workshop on Modelling the Consequences of Accidental Releases of Hazardous Materials*, CCPS, San Francisco, California, September 28 – October 1, pp. 315-344

Witlox, H.W.M. and Bowen, P., 2002, Flashing liquid jets and two-phase dispersion - A review, Contract 41003600 for HSE, Exxon-Mobil and ICI Eutech, *HSE Contract Research Report* 403/2002.

Witlox, H.W.M., Harper, M., Bowen, P.J., and Cleary, V.M, 2005, Flashing liquid jets and two-phase droplet dispersion, I. Overview (literature survey, experiments and model implementation/validation), *Mary Kay O'Connor Symposium*, Houston, October 2005.