



THEORY

# POOL VAPORISATION

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This document describes the theory of the pool spreading and vaporization model. The model predicts the spreading and vapour flow rate from a pool formed by a spill of liquid onto either land or water.

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





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## ABSTRACT

This report describes the source term model PVAP which calculates the spreading and vapour flow rate from a pool formed by a spill of liquid onto either land or water. The pool may either boil or evaporate while simultaneously spreading, with different models used for spills on land and on water. Detailed mass and heat balances are kept, permitting variations in the temperature of the pool. For spills on water, solution of the spilled liquid is calculated, and also the reaction with water for ammonia. The model has been validated against experimental data.

The model is currently linked with the Unified Dispersion Model UDM in the DNV Phast/Safeti software packages. In case of an elevated two-phase jet release, it calculates the pool spreading/evaporation following rainout.

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## 1 INTRODUCTION

In modelling the consequences of releases of hazardous materials, one of the most important aspects is in determining a realistic source term to provide input into an atmospheric dispersion model. One source term is a pool which has been formed by liquid escaping from containment. The quantities of interest for input into a dispersion model are then the rate at which vapour is produced from the pool, the size of the pool (which determines the initial dimensions of the dispersing cloud), and the temperature of the vapour.

In this report we describe the integrated model PVAP which can describe the spreading and vaporisation of pools of liquid spilled either on land or water. The overall model is composed of a number of sub-models, many of which have been presented in the literature in the past and have become standard models in their own right. However, this is the first time they have been assembled together in a single comprehensive model for liquid spills which is directly integrated with atmospheric dispersion programs. This is particularly true for the models dealing with spills on water.

The original PVAP model was developed by Cook and Woodward<sup>i</sup>. The model was subsequently generalised by Fernandez et al.<sup>ii</sup> to allow for more rigorous modelling of multi-component effects.

The pool model PVAP is currently linked with the Unified Dispersion Model UDM in the DNV software packages Phast and Safeti. In case of an elevated two-phase jet release, the liquid rate or the total liquid mass removed from the cloud (rainout) is used as input to the pool model, and then establishing a vaporisation rate, or set of rates, to simulate a time-varying vaporisation rate.<sup>1</sup>

The plan of this report is as follows. In Section 2 the pool geometry is described, and the mechanisms for change of pool mass are introduced (spillage, evaporation, dissolution). In Sections 3 and 4 the calculation of the pool spreading and the change of pool mass due to pool evaporation and/or dissolution into water is discussed. Section 5 describes the coupling of the pool vaporisation and cloud dispersion. Section 6 describes the extension of the PVAP model to include multi-component effects. Section 6.5 describes the algorithm for solving the pool model equations. Section 7 contains recommendations for further developments. See the accompanying PVAP verification manual and PVAP validation manual for details on verification and validation of the PVAP model.

## 2 POOL GEOMETRY AND MASS CONSERVATION

The shape of the pool is idealised to be a circular cylinder of radius  $r(t)$  and uniform thickness  $h(t)$ , with a point source located at its centre.

The mass of the pool is given by

$$M_{pool}(t) = \pi r^2(t) h(t) \rho_L \quad (2.1)$$

with  $\rho_L$  the liquid density. The pool is formed due to the spillage of liquid at the point source. The spillage could be the result of rainout or a spillage directly at the source. The pool mass reduces as a result of pool evaporation. In the case of a pool on water, it will also reduce due to dissolution on water. Thus conservation of mass requires

$$\frac{dM_{pool}}{dt} = S(t) - E_{vap}(t) - E_{sol}(t) \quad (2.2)$$

where  $S(t)$  is the spill rate (kg/s),  $E_{vap}(t)$  the evaporation rate (kg/s) and  $E_{sol}(t)$  the rate of dissolution on water (kg/s) [ $E_{sol}(t) = 0$  for pool on land].

The above equation describes the case for a general time-dependent release.

When having instantaneous rainout, the initial pool mass  $M_{pool}(0)$  will be the instantaneously released liquid, and the spill rate  $S(t)=0$  for  $t>0$ .

For a time-varying rainout case, the spill rate  $S(t)$  is a function of time. It is constructed by linearly interpolating between rainout events of the cloud. See UDM Theory manual for further details.

For a continuous rainout scenario, the spill rate  $S(t) = S$  is constant. For sufficiently large time, steady-state will be achieved and the above equation reduces to  $dM_{pool}/dt = 0 = S - E_{vap} - E_{sol}$  (with  $E_{vap}$ ,  $E_{sol}$ , pool radius and pool height not further changing).

### 3 POOL SPREADING

This section describes the modelling of the spreading of the pool to give the surface area, which is an important variable in the vapourisation-rate calculations. Different equations are used to calculate the pool radius depending upon whether the spill is on land or water, and whether it is an instantaneous, a continuous or a time-varying release.

#### 3.1 Pool on land

The radius of a pool spreading on land is found by numerically integrating the spreading rate equation given by Opschoor (1979)iii, 2:

$$\frac{dr}{dt} = \sqrt{2g(h - h_{\min})} \quad (3.1)$$

where	r	is the pool radius	(m)
	t	is the time from the start of the release	(s)
	g	is the acceleration due to gravity	(m/s <sup>2</sup> )
	h	is the pool thickness	(m)
	h <sub>min</sub>	is a minimum pool thickness	(m)

This assumes that the driving force for the spread is formed by the hydrostatic difference between the thickness of the current liquid layer and a minimum pool thickness characteristic for the substrate. This results in the rate of spreading decreasing as the pool approaches the minimum thickness.

#### 3.2 Pools on water

Following Dodge et al (1983)<sup>iv</sup>, a three-regime model has been adopted to describe the spreading of liquids on water. Each regime is dominated by the balance of two main forces, the regimes occurring sequentially.

The first regime to occur is the “gravity-inertia” regime when the gravity spreading and inertial forces are approximately equal. This is followed by the “gravity-viscous” regime when the gravity spreading and viscous drag forces are approximately equal. For non-volatile liquids which may spread to form thin slicks there may then be a third regime, the “viscous-surface tension” regime, where the viscous drag and surface tension forces are approximately equal. In practice, with the minimum thickness criterion implemented in the model the viscous-surface tension regime is rarely encountered.

The four forces considered in the three regimes are:

- Gravity spreading force

$$F_G = M_{pool} \left( \frac{gh\Delta}{r} \right) \quad (3.2)$$

- Inertial force

$$F_I = -M_{pool} \frac{d^2 r}{dt^2} \cong M_{pool} \frac{r}{2t^2} \quad (3.3)$$

- Viscous drag force

$$F_D = \pi r^2 \mu_w \left( \frac{r}{t} \right) \left( \frac{\rho_w}{\mu_w t} \right)^{1/2} \quad (3.4)$$

- Surface tension force

$$F_S = 2\pi r \sigma \quad (3.5)$$

<sup>2</sup> JUSTIFY - Code uses  $[2g(h-0.9h_{\min})]^{1/2}$ . This is likely to avoid unforeseen numerical difficulties that may arise when  $h = h_{\min}$ .  
Theory | Pool Vaporisation |

In the equations above  $\Delta = (\rho_w - \rho_L) / \rho_w$  is a relative density factor, with  $\rho_L$ ,  $\rho_w$  being the liquid and water densities ( $\text{kg/m}^3$ ). Furthermore  $\mu_w$  is the dynamic viscosity of the water ( $\text{kg/m/s}$ , and  $\sigma = \sigma_{wa} - \sigma_{La} - \sigma_{Lw}$  is the net surface tension ( $\text{N/m}$ ), with  $\sigma_{wa}$ ,  $\sigma_{La}$ ,  $\sigma_{Lw}$  being the surface tension of water-air, liquid-air, liquid, water, respectively.

### 3.2.1 Instantaneous spills

The radius is given as follows.

- in the gravity-inertia regime when  $0 < t < t_1$  by:
- 

$$r(t) = K_{10} \left( \frac{g\Delta}{\rho_L} \right)^{1/4} M_{pool}^{1/4}(0) t^{1/2} \quad (3.6)$$

- in the gravity-viscous regime when  $t_1 < t < t_2$  by:
- 

$$r(t) = K_{20} \left( \frac{g\Delta}{\rho_L^2 (\mu_w / \rho_w)^{1/2}} \right)^{1/6} M_{pool}^{1/3}(0) t^{1/4} \quad (3.7)$$

- in the viscous-surface tension regime when  $t > t_2$  by:
- 

$$r(t) = \left( \frac{4\sigma^2}{\rho_w \mu_w} \right)^{1/4} t^{3/4} \quad (3.8)$$

The transition from the gravity-inertia to the gravity-viscous regime occurs at the time:

$$t_1 = \left( \frac{K_{20}}{K_{10}} \right)^4 \left( \frac{\rho_w M_{pool}(0)}{\rho_L g \mu_w \Delta} \right)^{1/3} \quad (3.9)$$

and from the gravity-viscous to the viscous-surface tension regime at the time:

$$t_2 = (K_{20})^2 \left( \frac{M_{pool}^2(0) g \mu_w \Delta}{\rho_w \rho_L^2} \right)^{1/3} \left( \frac{\rho_w}{2\sigma} \right) \quad (3.10)$$

### 3.2.2 Continuous spills

The case of a constant spillage  $S(t) = S$  is considered. The radius is given as follows.

- in the gravity-inertia regime when  $0 < t < t_3$  by:

$$r(t) = K_{11} \left( \frac{g\Delta}{\rho_L} \right)^{1/4} S^{1/4} t^{3/4} \quad (3.11)$$

- in the gravity-viscous regime when  $t > t_3$  by:

$$r(t) = K_{21} \left( \frac{g\Delta}{(\mu_w / \rho_w)^{1/2} \rho_L^2} \right)^{1/6} S^{1/3} t^{7/12} \quad (3.12)$$

The transition between these regimes occurs at the time:



$$t_3 = \left( \frac{K_{21}}{K_{11}} \right)^6 \left( \frac{\rho_w}{\rho_L g \Delta \mu_w} S \right)^{1/2} \quad (3.13)$$

For a continuous spill the “viscous-surface tension phase” occurs simultaneously with the gravity-viscous phase rather than following it in time, with the part of the slick that is spreading in the gravity-viscous phase (i.e., the thick slick) supplying the mass for that part in the viscous-surface tension phase (i.e., the thin slick). No transition to the “viscous-surface tension” phase is made for continuous spills.

In the above equations  $K_{10}$ ,  $K_{11}$ ,  $K_{20}$ ,  $K_{21}$  are dimensionless constants. Dodge et al (1983)<sup>iv</sup> conducted experiments specifically designed to test the validity of the above pool spread models<sup>3</sup> and to determine the values for the constants  $K_{10}$ ,  $K_{20}$ ,  $K_{11}$  and  $K_{21}$ . Their recommended values which have been implemented here are shown in Table 1.

**Table 1. Constants in pool-spreading models**

constant	Value
$K_{10}$	1.53
$K_{20}$	1.21
$K_{11}$	1.24
$K_{21}$	1.09

### 3.2.3 Time-varying spills

The case of a time-varying and (possibly) finite-duration release is considered.

Equations ( 3.6 ) - (3.13 ) fail to account for pool spreading behaviour following the end of the spillage (at time  $t = t_{dur}$ )<sup>4</sup>. At any time  $t$  (before and after the end of spillage), the total mass of fluid released,  $M_{pool}(t)$ , is given by:

$$M_{pool}(t) = \int_{\tau=0}^{\tau=\min(t_{dur}, t)} S(\tau) d\tau \quad (3.14)$$

By replacing  $S$  in equations (3.11) - (3.13) with  $M_{pool}(t)/t$  and re-writing in terms of  $M_{pool}(t)$  gives:

- in the gravity-inertia regime when  $0 < t < t_3$ :
- 

$$r(t) = K_{11} \left( \frac{g\Delta}{\rho_L} \right)^{1/4} \left[ M_{pool}(t) \right]^{1/4} t^{1/2} \quad (3.15)$$

- in the gravity-viscous regime when  $t > t_3$  by:
- 

$$r(t) = K_{21} \left( \frac{g\Delta}{\rho_L^2 (\mu_w / \rho_w)^{1/2}} \right)^{1/6} \left[ M_{pool}(t) \right]^{1/3} t^{1/4} \quad (3.16)$$

The transition between these regimes occurs at the time:

$$t_3 = \left( \frac{K_{21}}{K_{11}} \right)^4 \left( \frac{\rho_w M_{pool}(t)}{\rho_L g \mu_w \Delta} \right)^{1/3} \quad (3.17)$$

<sup>3</sup> JUSTIFY - The equations ( 3.6 )-( 3.10 ) for an instantaneous release adopt the spilled mass  $M_{pool}(0)$ , and the equations (3.11)-(3.13) for a continuous release the spill rate  $S(t)$ . They are based on experiments by Dodge et al. (1983) for non-volatile liquids. Therefore the expressions may not be appropriate for volatile liquids, and it may be more appropriate to use the current pool mass  $M_{pool}(t)$ , respectively  $dM_{pool}/dt$  rather than  $M_{pool}(0)$  and  $S(t)$ . This needs comparison against experimental data for volatile liquids.

<sup>4</sup> Dodge et al. (1983) appear to have only considered continuous and instantaneous releases in their studies. As such, there is a need to extend their model to simulate finite duration releases.

Equations (3.15) to (3.17) are assumed to govern pool spreading behaviour for spillages with either a constant or time-dependent spill rate and are employed instead of equations (3.11) to (3.13) for pool spreading calculations resulting from continuous releases<sup>5</sup>. The structure of equations (3.15) to (3.17) is consistent with the equations derived by Dodge et al. (1983) for instantaneous releases (i.e. equations (3.6), (3.7) and (3.9)), and would extrapolate to the limits of infinite duration continuous releases (i.e. equations (3.11) to (3.13)). In addition, the above equations, for all values of  $t_{dur}$ , would provide a smooth and physically representative transition in the variation of pool radii with time for time-varying and continuous releases.

### 3.3 Constraints on spreading

The spreading pool is assumed to grow concentrically until it reaches an obstruction, e.g. a bund (secondary containment area, also referred to as dyke), or it attains a minimum thickness. When the pool has reached a bund the pool radius is constrained to be equal to the radius of the bund. Where the pool has spread and vaporised to produce a pool of depth equal to the minimum thickness, the spreading is constrained to be consistent with this thickness. Thereafter the radius will no longer be a simple function of time.

For an instantaneous release, once the minimum thickness has been reached the pool will start to shrink, keeping this thickness<sup>6</sup>. For continuous and time-varying spills the rate of spread will be constrained once the minimum thickness has been reached but in most cases the pool will continue to grow slowly. Once the release finishes the pool will normally contract as for the instantaneous case.

The minimum thickness depends on the type of surface and is shown in Table 2.

**Table 2. Minimum pool thickness<sup>v,vi</sup>**

	Surface	Minimum thickness (m)
1	Wet soil	0.01
2	Dry soil	0.02 <sup>7</sup>
3	Concrete	0.005
4	Insulating concrete	0.005
5-8	Water	0.001 <sup>8</sup>

<sup>5</sup> Equations (3.15) to (3.17), though equivalent to equations (3.11) to (3.13), are better structured to handle flows with multiple and widely varying discharge rates as they eliminate artificial discontinuities.

<sup>6</sup> JUSTIFY - More realistic would be to assume break up of pool into separate blobs.

<sup>7</sup> IMPROVE- Value obtained from Purple Book. Napier and Roopchard (1986) and Purple book also present a minimum pool thickness value for "very rough soil" (0.025m). This substrate type is currently not included in the available substrate types in PVAP.

<sup>8</sup> This value differs from the value for calm water of 0.0018m as recommended by the Purple Book or Napier and Roopchard (1986). However, its use, when compared with the use of the Purple Book or Napier and Roopchard (1986) recommended value, is observed to yield simulated results which show better agreement with field data (see the PVAP validation manual for details).

## 4 POOL VAPORISATION

The liquid spill model can describe the spreading and vaporisation of pools of liquid spilled either on land or water. For spills on land the model takes into account heat conduction from the ground, ambient convection from the air, radiation and vapour diffusion. These are usually the main mechanisms for boiling and evaporation. Solution and possible reaction of the liquid in water are also included for spills on water, these being important for some chemicals. These effects are modelled numerically, maintaining mass and heat balances for both boiling and evaporating pools. This allows the pool temperature to vary as heat is either absorbed by the liquid or lost during evaporation.

At each time step in the numerical calculations the heat balance on the pool is evaluated and from this the vaporisation mechanism (i.e., boiling or evaporating), vaporisation rate and pool temperature are determined.

Initially, the temperature  $T_{pool}$  of the pool is assumed to be equal to the temperature  $T_{spill}$  of the spilled liquid.

The net rate of heat flow into the pool is calculated from

$$Q_{net} = Q_{cond} + Q_{conv} + Q_{rad} + Q_{sol} + Q_{spill} - Q_{evap} \quad (4.1)$$

where	$Q_{cond}$	is the heat flow rate from conduction	(W)
	$Q_{conv}$	is the heat flow rate from convection	(W)
	$Q_{rad}$	is the heat flow rate from solar radiation	(W)
	$Q_{sol}$	is the heat flow rate from dissolution	(W)
	$Q_{spill}$	is the heat flow rate from spilled liquid	(W)
	$Q_{evap}$	is the heat flow rate from evaporation	(W)

The calculation of each of these terms is described in the sections that follow.

For spills on land, the heat flow rate  $Q_{sol}$  from dissolution (and possibly reaction) is obviously zero.

For continuous and time-varying releases,  $Q_{spill}$  is calculated from the following equation up to the end of the release<sup>9,10</sup>:

$$Q_{spill} = S(t) c_{pL}(T_{spill}(t)) [T_{spill}(t) - T_{pool}] \quad (4.2)$$

where  $C_{pL}(T_{spill})$  is the heat capacity of the liquid (J/kg/K) at the spill temperature. Once the release has ended  $Q_{spill}$  becomes zero.  $Q_{spill}$  is also zero for instantaneous releases.

The rate of change of pool temperature may be calculated from the net rate of heat flow into the pool:

$$\frac{dT_{pool}}{dt} = \frac{Q_{net}}{M_{pool} C_{pL}(T_{pool})} \quad (4.3)$$

where  $M_{pool}$  is the mass of liquid in the pool at that time. This equation is integrated to obtain the pool temperature as a function of time, with the constraint that it cannot exceed the boiling point of the liquid.

If the pool temperature is equal to the boiling point of the liquid then the pool is assumed to be boiling with a rate of heat input given by:

$$Q_{boil} = Q_{cond} + Q_{conv} + Q_{rad} + Q_{sol} + Q_{spill} \quad (4.4)$$

resulting in a vaporisation rate of:

$$E_{vap}(t) = \frac{\max\{Q_{boil}, 0\}}{\Delta H_V(T_{pool})} \quad (4.5)$$

Where,  $\Delta H_V$  is the heat of vaporisation (J/kg).

<sup>9</sup> In the linked model in Phast version 7 and in Phast version 6.7 and previous  $Q_{spill}$  was calculated by:

$Q_{spill} = S(t) \{ C_{pL}(T_{spill}) [T_{spill} - T_K] - C_{pL}(T_{pool}) [T_{pool} - T_K] \}$  where  $T_K = 273.15K$ . This formulation has been replaced by the simplified expression shown on (4.2), by assuming that the specific heat capacity of liquids at constant pressure does not vary greatly with temperature

<sup>10</sup> For time-varying releases the temperature of the spill is time dependent

Otherwise, if the pool temperature is below the boiling point then the pool is assumed to be evaporating at that temperature at a rate of:

$$E_{vap}(t) = \frac{Q_{evap}}{\Delta H_V(T_{pool})} \quad (4.6)$$

## 4.1 Boiling on land

Heat conduction from the ground is modelled assuming a uniform semi-infinite medium on which the pool spreads (Shaw and Briscoe, 1978)<sup>vi</sup>. For a circular spreading pool the heat flow rate  $Q_{cond}$  ( $W=J/s$ ) is given by<sup>11</sup>:

$$Q_{cond} = 2\pi\theta \int_0^{r(t)} \frac{r' dr'}{(t-t')^{1/2}} \quad (4.7)$$

and for a pool which has reached a fixed radius, either by hitting a dike wall or by reaching a minimum thickness, is given by:

$$Q_{cond} = 2\pi\theta \int_0^{r_m} \frac{r' dr'}{(t-t')^{1/2}} \quad (4.8)$$

where  $r_m$  is the fixed radius. Here  $r'$  is the pool radius at time  $t'$ , and:

$$\theta = \frac{\chi_s k_s (T_{surf} - T_{pool})}{(\pi \alpha_s)^{1/2}} \quad (4.9)$$

where	$\chi_s$	is a factor to account for surface roughness	(dimensionless)
	$k_s$	is the thermal conductivity of the surface	(W/m K)
	$\alpha_s$	is the thermal diffusivity of the surface	(m <sup>2</sup> /s)
	$T_{surf}$	is the surface initial temperature	(K)
	$T_{pool}$	is the pool temperature	(K)

The surface parameters are listed in Table 3 for a number of surfaces.

**Table 3. Vaporisation data for surface types<sup>12</sup>**

	Surface	Roughness factor $\chi_s$	Thermal conductivity $k_s$ (W $m^{-1} K^{-1}$ )	Thermal diffusivity $\alpha_s$ (m <sup>2</sup> s <sup>-1</sup> )
1	Wet soil	2.63	2.21	$9.48 \times 10^{-7}$
2	Dry soil	2.63	0.32	$2.44 \times 10^{-7}$
3	Concrete	1.00	1.21	$5.72 \times 10^{-7}$
4	Insulating concrete	1.00	0.22	$8.27 \times 10^{-7}$

Reid and Wang (1978)<sup>viii</sup> in their publication on LNG vaporisation on different type of surfaces present thermal properties values for soil taken from three references. These values have been compared to the default PVAP values for wet and dry soil in the following table.

**Table 4 Comparison of the thermal properties of different soils reported by Reid and Wang (1978) and PVAP**

Reference	$k_s$ (W m <sup>-1</sup> K <sup>-1</sup> )	F (kg m <sup>-2</sup> s <sup>-0.5</sup> )
Reid and Wang (1978) <sup>viii</sup>	~6	0.5 (up to 8% water content)
Gaz de France (1972) <sup>ix</sup>	---	1.1(dry soil) - 1.5 (wet soil)
Drake and Reid (1975) <sup>x</sup>	---	0.3 - 0.5
PVAP wet soil	2.2	1.1 - 1.2
PVAP dry soil	0.32	0.32 - 0.35

<sup>11</sup> Improve: this equation requires revisiting. In the PVAP Verification document David Webber (2003) indicates this formula is derived from a heuristic approximation, and presents an improved formula taken from his paper (Webber, 1987). Furthermore, the term  $1/(t-t')^{0.5}$  increases very rapidly as  $t' \rightarrow t$  (at the limit when  $t = t'$  this term is infinite) making the calculation of the heat of conduction very sensitive to the choice of time and radius discretization  $t'$  and  $r'$ .

Where  $k_s$  is the thermal conductivity and  $F$  is given as: 
$$F = \frac{\chi_s \cdot k_s \cdot (T_{surf} - BPT)}{\pi^{0.5} \cdot \alpha_s^{0.5} \cdot \Delta H_{vap}}$$

$T_{surf}$  is the initial temperature of the surface and BPT is the normal boiling point of the chemical, and the rest of the symbols are as previously defined.

The parameter  $F$  can be obtained from the slope of the curve of the total mass vaporized against the square root of time for a boiling pool of constant radius (Reid and Wang, 1978)<sup>viii</sup>.

Comparing the values listed in Table 3 with those listed in Table 4, it can be seen that PVAP soil properties have been taken from Gaz de France (1972)<sup>ix</sup> and Drake and Reid (1975)<sup>x</sup> studies on soils. The differences found in the values reported in the literature convey the difficulty of establishing standard properties for soil.

## 4.2 Evaporation on land

The vapour diffusion model is based on the formulation by MacKay and Matsugu (1973). Thus the rate of heat loss from the pool in  $W$  caused by material evaporating from its surface is given by<sup>13</sup>

$$Q_{evap} = 0.004786 \pi [u_a (z = 10 \text{ m})]^{0.78} r^{1.89} Sc^{-0.67} \Delta H_v (T_{pool}) \frac{M_c P_v (T_{pool})}{RT_{pool}} \quad (4.10)$$

where	$Sc$	is the Schmidt number for air = $\mu_a / (\rho_a D_{ac})$	(dimensionless)
	$\mu_a$	is the dynamic viscosity of air	(kg/m/s)
	$\rho_a$	is the atmospheric density	(kg/m <sup>3</sup> )
	$D_{ac}$	is the diffusion coefficient of air and gas	(m <sup>2</sup> /s)
	$u_a(z=10m)$	is the ambient wind speed at 10 m height	(m/s)
	$\Delta H_v$	is the heat of vaporisation	(J/kg)
	$M_c$	is the molecular weight of the spilled liquid	(kg/kmol)
	$P_a$	is the atmospheric pressure	(N/m <sup>2</sup> )
	$P_v^c$	is the saturated vapour pressure of spilled liquid	(N/m <sup>2</sup> )
	$R$	is the universal gas constant = 8314 J/K/kmol	

## 4.3 Convection on land or water

The method of Fleischer (1980)<sup>xi</sup> is used to calculate the rate at which heat is convected from the air into the pool. The same method is used whether the pool is on land or water. This transport process is modelled as if it took place over a flat plate of length  $L$  in the downwind direction. Two types of boundary layer may occur in these conditions: laminar and turbulent. Both are accounted for in this model.

Heat is assumed to be convected from the air into the pool at a rate in  $W$  given by<sup>14</sup>:

$$Q_{conv} = \lambda_a Nu \frac{\pi r^2}{L} (T_a - T_{pool}) \quad (4.11)$$

where	$\lambda_a$	is the thermal conductivity of air	(W/m/K)
	$Nu$	is the Nusselt number	(dimensionless)
	$L$	is the pool diameter	(m)
	$T_a$	is the atmospheric temperature	(K)

The boundary layer is assumed to be laminar for a Reynolds number less than 320,000, and turbulent for higher values. The Nusselt number is then given by:

<sup>13</sup> IMPROVED. The formula for the evaporation rate of pools on land has been reverted to the one found in the literature for McKay and Matsugu (1973). Validation against experimental data from Reijnhart and Rose (1980) wind tunnel experiments and Kawamura and MacKay (1987) outdoor tests have shown improved agreement with the literature formulation. Further detail can be found in PVAP Validation Document.)

<sup>14</sup> CODE CORRECTED - In code  $L=1.25r$  is taken as the pool diameter. Code change seems to be applied following paper by Cook and Woodward<sup>i</sup>, to get better pool-evaporation predictions for specific client but this has shown to lead to worse results for other cases. Not scientifically based, and original Fleischer formula should be retained. Thus code has been reverted in Phast 7.0 to this original Fleischer formula with  $L = 2r$ .

$$Nu = \begin{cases} 0.664 Pr^{1/3} Re^{1/2} & Re < 320,000 \\ 0.037 Pr^{1/3} [Re^{0.8} - 15200] & Re > 320,000 \end{cases} \quad (4.12)$$

where	Pr	is the Prandtl number = $C_{pa}\mu_a/\lambda_a$	(dimensionless)
	Re	is the Reynolds number = $u_a(z=10m) \rho_a(2r) / \mu_a$	(dimensionless) <sup>15</sup>
	$C_{pa}$	is the atmospheric specific heat capacity	(J/kg/K)
	$\mu_a$	is the atmospheric dynamic viscosity	(kg/m/s)

## 4.4 Radiation

During the day time the pool may gain heat from solar radiation and long wave radiation may also make a small contribution. At night time when there is no solar radiation and the temperature of the air may be cooler than that of the pool, heat may be lost from the pool by long wave radiation.

The rate of heat input in W from solar radiation for a pool of radius r is calculated as:

$$Q_{solar} = \pi r^2 S \quad (4.13)$$

where S is the solar flux in W/m<sup>2</sup>.

The rate of heat input/loss in  $Q_{long}$  (W) from long-wave radiation is calculated as:

$$Q_{long} = \varepsilon \sigma (T_a^4 - T_{pool}^4) \pi r^2 \quad (4.14)$$

where  $\varepsilon$  is the emissivity of the pool (0.95) and  $\sigma$  the Stefan-Boltzmann constant (W/m<sup>2</sup>/K<sup>4</sup>).

The total rate of heat input from radiation is then

$$Q_{rad} = Q_{solar} + Q_{long} \quad (4.15)$$

## 4.5 Boiling on water

The boiling of cryogen on water may or may not result in the formation of a layer of ice on the surface of the water. In general, spills on a large expanse of water do not form an ice layer since there is a steady convection of heat from the water into the pool. Spills of liquids with a boiling point below that of water into small volumes of water may however result in the formation of an ice layer. The model here assumes that if the water is shallow the convection of heat within the water to the pool is inhibited and a layer of ice is formed.

- No ice formation

A steady rate of heat transfer from the water to the pool is assumed:

$$Q_{cond} = h_s \pi r^2 (T_{surf} - T_{pool}) \quad (4.16)$$

where  $h_s$  is the heat transfer coefficient in W/m<sup>2</sup> K and is stored for each material in the physical properties database.

- Ice formation

The method of Reid and Smith (1978a and 1978b)<sup>xii,xiii</sup> is used to calculate the heat flow rate into the pool when a layer of ice forms on the surface of the water. The thickness of the ice layer is assumed to increase with time as the cryogen cools water at increasing depths. The rate in W at which heat is conducted into the pool is found to be:

<sup>15</sup> JUSTIFY - Note that in original Singapore paper was assumed  $Re = u_a(z=10m) \rho_a/\mu_a$  ! An early sensitivity analysis shows that there is little impact on the pool vaporization results using the formula of the Reynolds number based on the radius or the diameter of the pool. The formula with the pool diameter (which is currently used in PVAP) predicts slightly higher heats of convection and is conservative when heat from the air is being transferred to the pool. However, it is recommended to revert to the original Fleischer formula as the justification for changing this is missing from the present model documentation.

$$Q_{cond} = \frac{\pi r^2 \varepsilon}{t^{1/2}} \quad (4.17)$$

with:

$$\varepsilon = \frac{k_I (T_{frz} - T_{pool})}{(\pi \alpha_I)^{1/2} \operatorname{erf} \left[ \frac{\kappa \beta}{2\sqrt{\alpha_I}} \right]} \quad (4.18)$$

The parameter  $\kappa$  in  $\text{m/s}^{1/2}$  is calculated from:

$$\frac{(T_{frz} - T_{bp}) k_I \exp\left(-\frac{\beta^2 \kappa^2}{4\alpha_I}\right)}{(\pi \alpha_I)^{1/2} \operatorname{erf}\left(\frac{\beta \kappa}{2\sqrt{\alpha_I}}\right)} - \frac{(T_{surf} - T_{frz}) k_w \exp\left(-\frac{\kappa^2}{4\alpha_w}\right)}{(\pi \alpha_w)^{1/2} \left\{1 - \operatorname{erf}\left(\frac{\kappa}{2\sqrt{\alpha_w}}\right)\right\}} = \frac{1}{2} F_w \rho_I^{\beta \kappa} \quad (4.19)$$

The symbols in these equations have the following meanings:

$T_{frz}$	freezing point of water = 273.15 K	(K)
$T_{bp}$	boiling point of liquid	(K)
$k_I$	thermal conductivity of ice at temperature $(T_{frz} + T_{bp})/2$	(W/m K)
$k_w$	thermal conductivity of water at $T_{surf}$	(W/m K)
$\alpha_I$	thermal diffusivity of ice at temperature $(T_{frz} + T_{bp})/2$	( $\text{m}^2/\text{s}$ )
$\alpha_w$	thermal diffusivity of water at temperature $T_{surf}$	( $\text{m}^2/\text{s}$ )
$\beta$	volume expansion for water to ice = 1.0907	(dimensionless)
$F_w$	latent heat of fusion of water = $3.336 \times 10^5$ J/kg	(J/kg)
$\rho_I$	density of ice	( $\text{kg}/\text{m}^3$ )
$t$	time since start of spillage	(s)

## 4.6 Evaporation on water

The model for evaporation of pools on water is based on that described by Dodge et al (1983)<sup>iv</sup>. This model takes into account the roughness of the water and the height of waves on the water, both of which depend upon the wind speed.

The friction velocity for air  $U_a^*$  is calculated from the wind speed  $u_a(z=10\text{m})$  at 10 m height, and a friction factor  $C_f$ :

$$U_a^* = u_a(z=10\text{m}) \left( \frac{1}{2} C_f \right)^{1/2} \quad (4.20)$$

$$\frac{1}{2} C_f = \begin{cases} 1.98 \times 10^{-3} & u_a(z=10\text{m}) < 0.1\text{m/s} \\ 1.25 \times 10^{-3} [u_a(z=10\text{m})]^{-0.2} & 0.1 < u_a(z=10\text{m}) < 3.06\text{m/s} \\ [0.8 + 0.065 u_a(z=10\text{m})] \times 10^{-3} & 3.06 < u_a(z=10\text{m}) < 22.3\text{m/s} \\ 2.25 \times 10^{-3} & 22.3\text{m/s} < u_a(z=10\text{m}) \end{cases} \quad (4.21)$$

From these a dimensionless wave height is calculated<sup>16</sup>:

<sup>16</sup> JUSTIFY - Note constant 0.01384 must have unit  $\text{s}^{-1}$ ! Use of 0.014 rather than 0.01384 more appropriate  
Theory | Pool Vaporisation |

$$h_w = 0.01384 \frac{u_a(z=10m) U_a^* \rho_a}{\mu(T_a)} \quad (4.22)$$

The boundary layer Dalton number is calculated from:

$$Da^* = \frac{1}{\frac{Sc_t \ln(\delta_+)}{k_v} + \beta + 2.35} \quad (4.23)$$

where:

$$\beta = \begin{cases} 12.5 Sc^{2/3} + \frac{Sc_t \ln(Sc)}{k_v} - 5.3 & u_a(z=10m) < 5m/s \\ 0.55 h_w^{1/2} (Sc^{2/3} - 0.2) - \frac{Sc_t \ln(h_w)}{k_v} + 11.2 Sc_t & u_a(z=10m) > 5m/s \end{cases} \quad (4.24)$$

and the dimensionless boundary layer thickness is given by:

$$\delta_+ = \frac{10 U_a^* \rho_a}{\mu_a(T_a)} \quad (4.25)$$

Furthermore  $Sc = \mu_a(T_a) / [\rho_a D_{ac}]$  is the Schmidt number for air, with  $D_{ac}$  the diffusion coefficient for air ( $m^2/s$ ) and the component vapour. The Von Karman number  $k_v$  is set to 0.4 and the turbulent Schmidt number  $Sc_t$  to 0.85. This then gives a heat loss rate from evaporation of:

$$Q_{evap} = \pi r^2 U_a^* Da^* \Delta H_v(T_{pool}) \frac{M_c P_a}{RT_{pool}} \ln\left(\frac{P_a}{P_a - P_v^c(T_{pool})}\right) \quad (4.26)$$

## 4.7 Dissolution on water

The theory for dissolution in water has been developed by analogy with that for evaporation of pools on liquid and is also based upon Dodge et al (1983)<sup>iv</sup>.

For spills on open water the friction coefficient  $C_f$  is calculated as for evaporation [see Equation ( 4.21)], whereas for spills on channel/river water the value used is given by:

$$\frac{1}{2} C_f = 1.61 \times 10^{-3} \quad (4.27)$$

The friction velocity for air is calculated as for evaporation [see Equation ( 4.20)]. In addition a dimensionless wave height  $h_w$  and a friction velocity  $U_w^*$  for water are calculated<sup>17,16</sup>:

$$h_w = \frac{0.01384 u_a(z=10m) U_w^* \rho_w}{\mu_w} \quad (4.28)$$

<sup>17</sup> JUSTIFY - Factor 0.1 added to Eq. for  $\delta_+$  and factor 10 for  $E_{so}(t)$ . Factor 0.1 seems to have been obtained by 'tuning'. It's not clear how equations have been derived from Dodge (lost notes by John). A thorough comparison against original references is essential. In the report by Dodge et al. (1983) there is mention to the height of the boundary layer  $\delta_+$ , assumed to be approximately 1 m, which may be the reason for the factor of 0.1 added to equation (4.31). However this is not enough basis to justify the constants in (4.31) and (4.32)



$$U_w^* = U_a^* \left( \frac{\rho_a}{\rho_w} \right)^{1/2} \quad (4.29)$$

The same equation is used for the Dalton number, although  $\beta$  is based upon a Schmidt number for water:

$$Sc = \frac{\mu_w}{\rho_w D_{wc}} \quad (4.30)$$

where  $D_{wc}$  is the diffusion coefficient of the liquid and water. The dimensionless boundary layer thickness is given by<sup>17</sup>:

$$\delta_+ = \frac{0.1 U_w^* \rho_w}{\mu_w (T_{gnd})} \quad (4.31)$$

Assuming a logarithmic driving force with local molar solubility  $w_s$  and solubility at infinity of  $w_{infinity}$  (assumed zero), the rate at which material dissolves in a pool of radius  $r$  is given by<sup>17</sup>:

$$E_{sol}(t) = 10\pi r^2 U_w^* \rho_w Da^* \ln \left( \frac{1 - w_{infinity}}{1 - w_s} \right) \quad (4.32)$$

The mass solubility  $f_s$  in kg/kg is stored as a constant in the properties database and converted into a molar solubility using:

$$w_s = \frac{f_s}{1 + f_s} \quad (4.33)$$

The solution of material in the water may then generate heat at the rate:

$$Q_{sol} = \Delta H_{sol} E_{sol}(t) \quad (4.34)$$

where  $\Delta H_{sol}$  is the heat of solution in J/kg and is held for each material as a constant in the physical properties database.

## 4.8 Reaction of ammonia pool with water

Alternative methods to that described in the previous section may be required if there is a reaction between the spilled liquid fluid and the water. A model based upon the one developed by Raj and Reid (1978)<sup>xiv</sup> to describe the solution and heat produced when ammonia dissolves in water has been implemented. This model may not, however, be appropriate for other materials which react with water.<sup>18</sup>

The model determines the maximum amount of spilled liquid fluid that would dissolve in the water by making use of the variation of the enthalpy of the water-liquid mixture as a function of the mole fraction of the liquid in the water-liquid mixture. The fraction of dissolved to spilled liquid at which no further dissolution in water is observed to occur is defined as the partition coefficient ( $P_{coef}$ ) [-] of the liquid. This value provides an estimate of the minimum amount of spilled liquid that is expected to vaporise.

The Raj and Reid model assumes water to be added incrementally to the spilled liquid and the resulting change in solution enthalpy to provide the energy required for vapour evolution per increment. The rate of solution of liquid into the water ( $E_{sol}(t)$ ) is calculated as above, while the rate of water entrainment into the liquid pool ( $E_{water}(t)$ ) is related to  $E_{sol}(t)$  by the following expression<sup>19</sup>:

$$E_{water}(t) = \frac{M_{water} E_{sol}(t) (1 - x_{pcoef})}{M_{sol} x_{pcoef}} \quad (4.35)$$

<sup>18</sup> The property system code currently not allows application of this model to non-ammonia pools which are considered to be reactive to water (as set by DIPPR properties). It will ignore any liquid-water solution enthalpy coefficients specified by the product. In the future this may be considered to be further generalized in line with the Raj and Reid paper.

<sup>19</sup> Equation (4.35) assumes a linear relationship between the rate of entrainment of water into the spilled fluid and the rate of reaction of the spilled fluid with the entrained water. This approach is judged to be better than the previous approach, which assumed the two rate processes to be equal in value. The adopted approach makes use of the partition fraction to correlate the entrainment and dissolution rates over time.

Here  $M_{water}$  and  $M_{sol}$  [kg/kmol] are the molecular weights of water and the spilled fluid, while  $x_{pcoef}$  [mol/mol] is the mole fraction of the dissolved fluid in the liquid-water mixture at the partition coefficient. The mass and hence the mole fraction ( $x$ ) of dissolved plus un-dissolved liquid in the pool may then be calculated at each time step, knowing the total masses spilt, vaporised and dissolved.

The following equation, presented by Raj and Reid<sup>xiv</sup>, is employed in determining the amount of vapour produced per infinitesimal increment:

$$\frac{dN_N^V}{dN_W^L} = \frac{H_W - H_{W'}(x)}{H_V - H_{L'}(x)} \quad (4.36)$$

Where:

$H_{L'}(x)$	is the modified partial liquid enthalpy of the material <sup>xiv</sup> at a specified liquid mole fraction $x$ [i.e. $x = \text{moles of liquid} / (\text{moles of liquid} + \text{water})$ ]	(J/kmol)
$H_{W'}(x)$	is the modified partial liquid enthalpy of water <sup>xiv</sup> at a specified mole fraction ( $x$ )	(J/kmol)
$H_W$	is the liquid enthalpy of water at its prevailing temperature	(J/kmol)
$H_V$	is the vapour enthalpy of the material	(J/kmol)
$N_N^V$	Moles of gas produced from dissolution of added water into liquid	(kmol)
$N_W^L$	Moles of added water	(kmol)

Values of  $H_{W'}(x)$  and  $H_{L'}(x)$  can be obtained from empirically determined curve fits (e.g. polynomial equations), which express the fluid-water solution enthalpy as a function of the fluid's composition ( $x$ )<sup>20</sup>.

$x_{pcoef}$  is determined from the solution of the following equation<sup>xiv</sup>:

$$H_W - H_{W'}(x) = 0 \quad (4.37)$$

The molar rate of liquid vaporised due to dissolution only ( $dN_N^V / dt$ ) can be determined from:

$$\frac{dN_N^V}{dt} = \frac{dN_N^V}{dN_W^L} \frac{dN_W^L}{dt} \quad (4.38)$$

So that ( $dN_N^V / dN_W^L$ ) is calculated from equation (4.36) and ( $dN_W^L / dt$ ) is the molar rate of entrained water given by:

$$\frac{dN_W^L}{dt} = \frac{E_{water}(t)}{M_{water}} \quad (4.39)$$

The rate of mass of liquid vaporised due to reactive dissolution only is calculated from:

$$E_{vap}^{by sol} = \frac{M_{sol}}{x} \frac{dN_N^V}{dt} \quad (4.40)$$

Thus, the rate of heat production due to dissolution ( $Q_{sol}$ )<sup>21</sup> can be expressed as<sup>22</sup>:

$$Q_{sol} = \Delta H_V E_{vap}^{by sol} \quad (4.41)$$

<sup>20</sup> These equations are stored as cubic equations in the MDE fluid property system.

<sup>21</sup> The vaporisation rate due to dissolution has an indirect effect on the vaporisation rate from the pool, as it defines the rate of heat generated from the ammonia reactive dissolution

<sup>22</sup>

## 5 COUPLING OF POOL VAPORISATION AND CLOUD DISPERSION

The model described here has been implemented both as a standalone program and as a module in the Unified Dispersion Model. For a typical two-phase release modelled by UDM there will be an initial period when the dispersing cloud contains both liquid and vapour. A fraction of the liquid drops may rain-out onto the ground to form a liquid pool which spreads and vaporises. This vaporisation is added to the vapour which is already present in the cloud.

In the case of an instantaneous release the vapour produced by the spilt liquid is added back into the cloud, so long as the cloud still covers the point at which rain-out occurred. If the spilt liquid all evaporates while covered by the cloud then all that is produced is an instantaneous, circular cloud. If the liquid has not all evaporated then once the upwind edge of the cloud has moved past the spill point any remaining liquid forms a continuous source of vapour until all the pool has vaporised.

For a continuous release, the rate of generation of vapour from the liquid pool is added to the vapour already in the cloud to give a total flow rate for the combined source. When the two-phase or liquid discharge stops there may then be a period when vapour is generated from the liquid pool alone.

In addition, the UDM can also be initiated in Phast/Safeti from a pool source, either by creating a source from a standalone pool or by defining a pool discharge from the user-defined source.

The reader is referred to the documentation of the UDM model for further details.

## 6 MULTI-COMPONENT POOL MODEL

### 6.1 Introduction and overview

The pool model described in the previous sections of this theory document is here extended to handle multi-component releases.

In order to account for real mixture behaviour, the model keeps track of the pool inventory at all times and employs established mixing rules to estimate overall pool properties. As in the single-component model two limiting cases in pool vaporisation are distinguished: boiling and evaporation. The multi-component pool model is able to predict the evaporation rate and phase composition from both types of pool vaporisation. Additionally, the model makes continuous checks for transitions between boiling and evaporation regimes, by performing a bubble point calculation at each step.

The PVAP multi-component model assumes ideal mixing of the components within the liquid pool components. This is based on Raoult's law in line with the methodology proposed by Cavanaugh et al. (1994)<sup>xv</sup>. Thus the multi-component pool model is not recommended for highly non-ideal solutions (e.g. aqueous ammonia) as interaction parameters are not incorporated into the properties estimation.

The multi-component pool model is formulated from the following equations:

- Spreading law:

$$\text{For pools on land: } \frac{dr}{dt} = \sqrt{2g(h - h_{\min})} \quad (6.1)$$

$$\text{For pools on water: } r = f(M_{\text{spill}}(0), S(t), t) \text{ (equations (3.6) to (3.17))} \quad (6.2)$$

- Mass balance per component  $i$  ( $i = 1, \dots, n$ ; where  $n$  is the number of components):

$$\frac{dM_{\text{pool}}^i}{dt} = S_i(t) - E_{\text{vap}}^i(t) - E_{\text{sol}}^i(t) \quad (6.3)$$

- Cumulative mass vaporised per component  $i$  ( $i = 1, \dots, n$ ):

$$\frac{dM_{\text{vap}}^i}{dt} = E_{\text{vap}}^i(t) \quad (6.4)$$

- Cumulative mass dissolved per component  $i$  ( $i = 1, \dots, n$ ) (only for pools on water):

$$\frac{dM_{\text{sol}}^i}{dt} = E_{\text{sol}}^i(t) \quad (6.5)$$

- Energy balance:

$$\frac{dT_{\text{pool}}}{dt} = \frac{\left\{ Q_{\text{in}} + S(t)c_{pL}^{\text{spill}}(T_{\text{spill}})[T_{\text{spill}} - T_{\text{pool}}] - E_{\text{vap}}(t) \sum_{i=1}^n Y_{\text{vap}}^i \Delta H_{\text{vap}}^i(T_{\text{pool}}) - E_{\text{sol}}(t) \sum_{i=1}^n X_{\text{sol}}^i \Delta H_{\text{sol}}^i(T_{\text{pool}}) \right\}}{c_{pL}^{\text{pool}}(T_{\text{pool}})M_{\text{pool}}} \quad (6.6)$$

Where,

$M_{\text{pool}}^i$  is the mass in the pool of component  $i$  (kg)

$S_i(t)$	is the mass spill rate of component i which is equal to 0 for instantaneous spills	(kg/s)
$E_{vap}^i(t)$	is the vaporisation rate of component i	(kg/s)
$E_{sol}^i(t)$	is the dissolution rate of component i only applicable for pools on water	(kg/s)
$Q_{in}$	sum of the heat inputs to the pool = sum of heat of conduction $Q_{cond}$ , convection $Q_{conv}$ and radiation $Q_{rad}$	(J)
$c_{pL}^{spill}(T_{spill})$	is the specific liquid heat capacity at the temperature and composition of the spill	(J/kg/K)
$c_{pL}^{pool}(T_{pool})$	is the specific liquid heat capacity at the temperature and composition of the pool	(J/kg/K)
$\Delta H_{vap}^i(T_{pool})$	is the heat of vaporisation of component i at the temperature of the pool	(J/kg)
$\Delta H_{sol}^i(T_{pool})$	is the heat of dissolution of component i at the temperature of the pool only applicable for pools on water	(J/kg)
$Y_{vap}^i$	is the mass fraction of component i in the vaporisation rate	(fraction)
$X_{sol}^i$	is the mass fraction of component i in the solution rate	(fraction)

To identify molar and mass fractions, the convention used in this document is lower case for mole and upper case for mass fractions.

For the derivation of the energy balance (6.6) for in multi-component pools the reader is referred to Appendix A.

The details of the multi-component pool model will be given in the following sections. These will be divided into: pool spreading, pool vaporisation and heat transfer.

## 6.2 Pool spreading

The spreading equations for single-component pools on water and land as described in Section 3 can be applied to multi-component pools using appropriate mixing rules to determine the pool properties.

The height of the pool is determined by considering a cylindrical geometry as in the single-component case:

$$h = \frac{M_{pool}}{(\pi r^2) \rho_{pool}} \quad (6.7)$$

## 6.3 Pool vaporisation

The main mechanisms for pool vaporisation are boiling and evaporation. In the multi-component pool model they are treated in the following way.

### 6.3.1 Boiling pool

The pool will boil when the pool temperature  $T_{pool}$  equals the bubble-point temperature of the mixture,  $T_{bubble}$ . Here the bubble-point temperature is determined by solving the equation below:

$$\sum_{i=1}^n \left( \frac{P_{vap}^i(T_{bubble})}{P_{atm}} x_{pool}^i \right) - 1 = 0 \quad (6.8)$$

Where (i=1,...n),

$$P_{vap}^i(T_{bubble}) \quad \text{is the saturated vapour pressure of component i at } T_{bubble} \quad (\text{Pa})$$

$x_{pool}^i$	is the mole fraction of component $i$ in the liquid pool	(mol/mol)
$P_{atm}$	is the atmospheric pressure	(Pa)

This is based on Raoult's law of ideal mixing of liquids, and is fully consistent with logic in the UDM thermodynamics sub-model THRM (presuming one single aerosol).

The mole fraction  $y_{vap}^i$  ( $i = 1, \dots, n$ ) of component  $i$  in evaporation rate is given by:

$$y_{vap}^i = \frac{P_{vap}^i(T_{bubble})}{P_{atm}} x_{pool}^i \quad (6.9)$$

The rate of heat added to the boiling pool,  $Q_{bubble}$  (W), also known as 'sensible heat', is calculated from (Cavanaugh et al. (1994)<sup>xv</sup>):

$$Q_{bubble} = M_{pool} c_{pL}^{pool}(T_{bubble}) \left( \frac{dT_{bubble}}{dt} \right) \quad (6.10)$$

And the derivative of  $T_{bubble}$  is evaluated from the derivative of Equation (6.8):

$$\frac{dT_{bubble}}{dt} = - \frac{\sum_{i=1}^n \left( P_{vap}^i \frac{dx_{pool}^i}{dt} \right)}{\sum_{i=1}^n \left( x_{pool}^i \frac{dP_{vap}^i}{dT_{bubble}} \right)} \quad (6.11)$$

As the total heat entering the pool is used in both the vaporisation of the liquid and in maintaining the pool at the bubble point ( $Q_{bubble}$ ), the overall vaporisation rate from a boiling pool is determined by insertion of Equation (6.10) into the energy balance (6.6) as:

$$E_{vap}(t) = \frac{Q_{in} + S(t)c_p^{spill}(T_{spill})[T_{spill} - T_{bubble}] - E_{sol}(t) \sum_{i=1}^n X_{sol}^i \Delta H_{sol}^i(T_{bubble}) - Q_{bubble}}{\sum_{i=1}^n Y_{vap}^i \Delta H_{vap}^i(T_{bubble})}, \text{boiling pool} \quad (6.12)$$

Where,

$\Delta H_{vap}^i(T_{bubble})$	is the heat of vaporisation of each component $i$ at the bubble point, $T_{bubble}$ .	(J/kg)
$\Delta H_{sol}^i(T_{bubble})$	is the heat of dissolution of each component $i$ at the bubble point, $T_{bubble}$ .	(J/kg)

The boiling rate for each component ( $i = 1, \dots, n$ ) is calculated as:

$$E_{vap}^i(t) = Y_{vap}^i E_{vap}(t) \quad (6.13)$$

### 6.3.2 Non-boiling pool

The pool temperature will drop below the rising bubble-point temperature when not enough heat is provided by the surroundings to compensate the heat losses by evaporation and dissolution.

The temperature of the non-boiling pool,  $T_{pool}$  (K) is determined from the energy-balance equation (6.6). Analogous to single-component pools the evaporation rate for each component ( $i = 1, \dots, n$ ) in a non-boiling pool is calculated by:

$$E_{vap}^i(t) = \frac{Q_{evap}^i}{\Delta H_{vap}^i(T_{pool})}, \quad \text{non-boiling pool} \quad (6.14)$$

Here  $Q_{evap}^i$  is calculated as for the single-component pools from the MackKay and Matsugu equation (4.10) for pools on land, and from Dodge et al. equation (4.26) for pools on water.

The overall evaporation rate,  $E_{vap}(t)$ , is calculated from the sum of the evaporation rates:

$$E_{vap}(t) = \sum_{i=1}^n E_{vap}^i(t) \quad (6.15)$$

### 6.3.3 Transition between boiling and non-boiling pools

#### Transition from boiling to non-boiling pools

A transition from boiling to non-boiling will be made when the heat flux gained from the surrounding (spillage, conduction, convection, radiation) is less than the heat flux lost because of increase in bubble point temperature,  $Q_{bubble}$ , pool evaporation and dissolution:

$$Q_{evap} > Q_{in} + Q_{spill} - E_{sol}(t)\Delta H_{sol}(T_{bubble}) - Q_{bubble} \quad (6.16)$$

#### Transition from non-boiling to boiling pools

The pool will start boiling when both of the following conditions are met:

- Enough heat is being provided by the surroundings to compensate the rise in the bubble point temperature and the heat losses by evaporation and dissolution:

$$Q_{evap} < Q_{in} + Q_{spill} - E_{sol}(t)\Delta H_{sol}(T_{bubble}) - Q_{bubble} \quad (6.17)$$

- The temperature of the pool is greater or equal to the bubble point temperature:

$$T_{pool} \geq T_{bubble} \quad (6.18)$$

## 6.4 Heat transfer

The heat transfer mechanisms between the multi-component pool and the surroundings follow the same equations of the single-component pool, with the exception of the following:

- Heat from the spill
- Evaporation on land
- Evaporation on water
- Dissolution on water

These heat terms are reformulated for multi-component pools as described below.

### 6.4.1 Heat from the spill

For continuous or time-varying multi-component spills the heat entering the pool depends on both the temperature of the spill and the composition. The composition of the spill can be variable or constant throughout the release.<sup>23</sup>

$$Q_{spill} = S(t) c_{pL}^{spill}(T_{spill}) [T_{spill} - T_{pool}] \quad (6.19)$$

Where  $c_p^{spill}$  is the specific heat of the multi-component material at the spill conditions (J/kg/K).

### 6.4.2 Evaporation on land

To estimate the heat losses from evaporation on land, the heat losses for each component ( $i = 1, \dots, n$ ) in the pool are estimated using the equation for evaporation of single-component pools on land (equation (4.10)) extended to components in a mixtures:

$$Q_{evap}^i(t) = 0.004786 u_a(z = 10m)^{0.78} \pi r^{1.89} Sc_i^{-0.67} \Delta H_{vap}^i \frac{M_c^i x_{pool}^i P_{vap}^i}{RT_{pool}} \quad (6.20)$$

Where,

$Sc_i$  Is the Schmidt number for each component  $i = 1, \dots, n$  (-)

For the derivation of the above equation for heat of evaporation on land for components in a mixture (equation 6.14), refer to Appendix A.

The overall heat of evaporation is calculated as the sum of the heats of the individual components:

$$Q_{evap} = \sum_{i=1}^n Q_{evap}^i \quad (6.21)$$

<sup>23</sup> This logic for the heat from the spill can be further improved and made more rigorous using  $Q_{spill} = S(t)[h_L^{spill}(T_{spill}) - h_L^{spill}(T_{pool})]$  where  $h_L^{spill}(T_{spill})$  and  $h_L^{spill}(T_{pool})$  is the specific liquid enthalpy at the liquid spill composition



### 6.4.3 Evaporation on water

Analogous to evaporating pools on land, the heat lost by evaporation of the individual components on water surfaces is determined from the single-component equation extended to individual components in a multi-component pool:

$$Q_{evap}^i(t) = (\pi r^2) U_a^* Da_i^* \Delta H_{vap}^i \frac{M_c^i P_a}{RT_{pool}} \left( \frac{x_{pool}^i P_{vap}^i(T_{pool})}{\sum_{i=1}^n x_{pool}^i P_{vap}^i(T_{pool})} \right) Ln \left( \frac{P_a}{P_{atm} - \sum_{i=1}^n x_{pool}^i P_{vap}^i(T_{pool})} \right) \quad (6.22)$$

Where,  $Da_i^*$  is Dalton number for each component  $i$  ( $i=1, \dots, n$ ).

The formulation of Dalton number for each component in a multi-component pool is analogous to the one given in equations ( 4.20) to ( 4.25), as the diffusivity of the component in the vapour mixture is taken equal to the diffusivity of the component in pure air. In other words, it is assumed there is no build-up of concentration in the vapour above the pool.

For the derivation of the evaporation on water equation for components in a mixture refer to Appendix A.

### 6.4.4 Dissolution on water

The heat losses from dissolution are calculated from equation ( 4.32) extended to components ( $i=1, \dots, n$ ) in the mixture:

$$Q_{sol}^i(t) = 10\pi r^2 U_W^* \rho_W Da_i^* \Delta H_{sol}^i(T_{pool}) Ln \left( \frac{1 - w_{infinity}^i}{1 - x_{pool}^i w_s^i} \right) \quad (6.23)$$

$$w_s^i = \frac{f_s^i}{1 + f_s^i} \quad (6.24)$$

Dalton's number for the individual components in a multi-component pool dissolving in water ( $Da_i^*$ ) is calculated from equations ( 4.27) to ( 4.31).  $w_{infinity}^i$  is assumed to be zero as for the single-component case.

The overall heat losses from dissolution are calculated by summing the heats losses of the individual components:

$$Q_{sol} = \sum_{i=1}^n Q_{sol}^i \quad (6.25)$$

The dissolution rate for each component ( $i = 1, \dots, n$ ) is calculated as:

$$E_{sol}^i(t) = 10\pi r^2 U_W^* \rho_W x_{sol}^i Da_i^* Ln \left( \frac{1 - w_{infinity}^i}{1 - x_{pool}^i w_s^i} \right) \quad (6.26)$$

And the total dissolution rate, as:

$$E_{sol}(t) = \sum_{i=1}^n E_{sol}^i \quad (6.27)$$

## 6.5 Numerical solution algorithm

The following section details the pool model equations formulated as a series of ordinary differential equations and gives the calculation procedure followed to obtain the pool results.

### 6.5.1 Model equations

Thus following the above, the pool model comprises a system of ordinary differential equations (ODEs) of the form:

$$\frac{\partial \bar{Y}}{\partial t} = G(\bar{Y}, t) \quad (6.28)$$

where,

$$\bar{Y} = \begin{pmatrix} r \\ T_{pool} \\ M_{pool}^i \\ M_{vap}^i \\ M_{sol}^i \end{pmatrix} \quad (6.29)$$

$$G = \begin{pmatrix} \left. \begin{array}{l} \text{Pools on land} = \left[ 2g \left( \frac{\sum_{i=1}^n M_{pool}^i}{\pi r^2 \rho_{pool}(T_{pool})} - h_{min} \right) \right]^{0.5} \\ \text{Pools on water} = 0 \end{array} \right\} \\ \frac{\sum_{i=1}^n S_i(t) c_{pL}^{spill}(T_{spill}) [T_{spill} - T_{pool}] + Q_{in} - \sum_{i=1}^n E_{vap}^i(t) \Delta H_{vap}^i(T_{pool}) - \sum_{i=1}^n E_{sol}^i(t) \Delta H_{sol}^i(T_{pool})}{M_{pool} c_{pL}^{pool}(T_{pool})} \\ S^i(t) - E_{vap}^i(t) - E_{sol}^i(t) \\ E_{vap}^i(t) \\ E_{sol}^i(t) \end{pmatrix} \quad (6.30)$$

Here  $M_{vap}^i$  and  $M_{sol}^i$ ,  $M_{vap}^i$  and  $M_{sol}^i$  are respectively the cumulative mass vaporised and dissolved (kg). The above equations are: the pool-spreading law, conservation of mass and energy, and equations for the cumulative evaporated and dissolved mass of component i.

The model equations are solved using a public domain numerical solver for ODEs, from Lawrence Livermore National Laboratory (Hindmarsh, 1983)<sup>xi</sup>. For stiff problems, the ODE solver uses the Backward Differentiation Formula (BDF). This method is a linear multi-step predictor-corrector method. The predictor-corrector process for advancing the solution consists of first generating a predicted value. This value is corrected by iterating over the corrector step until convergence is achieved.

### 6.5.2 Calculation procedure

At any point of the calculation the pool may be in different evaporation regimes (either boiling or non-boiling) or spreading regimes (spreading normally, hitting the bund or at the minimum thickness). In addition either the multi-component model (MC) could be applicable or the one-component or pseudo-component model (PC).

The calculation procedure for the different pool conditions is as follows. First, the pool primary variables for each pool scenario (see tables 4 and 5 for indication of primary variables per scenario and initial values given) are initialised and a first estimate for the time step is given. Then the following procedure is repeated iteratively:

1. Call the solver. The solver returns the pool primary variables from the model according to the scenario:
  - 1.1. Pool radius [only for pools on land spreading normally: equation (6.1)]
  - 1.2. Pool temperature [equation (6.6) for MC; equation (4.3) for PC]
  - 1.3. Mass remaining in the pool per component  $i$  [equation (6.3)]<sup>24</sup>
  - 1.4. Cumulative mass vaporised per component  $i$  [equation (6.4)]<sup>24</sup>
  - 1.5. Cumulative mass dissolved per component  $i$  [equation (6.5)]<sup>24</sup>
  - 1.6. Cumulative mass of water entrained for reactive ammonia dissolution [equation (4.35)]
2. Calculate the heat terms, vaporisation and dissolution rates (when applicable), the pool height and the bubble point temperature
3. Determine other secondary variables of the pool, i.e. those properties that are not primary variables in a particular pool scenario (see table of primary variables below)
4. Check for a transition at the current time step:
  - 4.1. Check conditions for transitions and sets a flag to indicate a transition has taken place or not at the current time step
  - 4.2. If transition has taken place:
    - 4.2.1. Interpolate between the start and the end of the time step to find the exact time at which the condition for the transition was met
    - 4.2.2. Recalls the solver from the start of the time step up to the time of the transition and recalculates the secondary properties
    - 4.2.3. Update pool scenario flags after transition has happened and reset the time step estimate to its initial value
    - 4.2.4. Repeat the procedure from step 1
  - 4.3. If transition has not taken place repeat from step 1 for the same pool scenario

<sup>24</sup> The index  $i$  indicates variable per component  $i$  in the mixture, where  $i$  ranges from 1 to the total number of components  $n$ . For a Pseudo-Component (PC) pool  $i = 1$  always

**Table 5. Primary variables MC and PC pool model**

Primary variable	POOL SCENARIOS					
	Boiling			Non-Boiling		
	Normal spreading	Bund hit	$h_{min}$	Normal spreading	Bund hit	$h_{min}$
$R_{pool}$	on land	-----	-----	on land	-----	-----
$M_{pool}^{i24}$	on all surfaces	on all surfaces	on all surfaces	on all surfaces	on all surfaces	on all surfaces
$M_{vap}^{i24}$	on all surfaces	on all surfaces	on all surfaces	on all surfaces	on all surfaces	on all surfaces
$M_{sol}^{i24}$	on water	on water	on water	on water	on water	on water
$T_{pool}$	-----	-----	-----	on all surfaces	on all surfaces	on all surfaces
$M_{water}$	ammonia on water	ammonia on water	ammonia on water	ammonia on water	ammonia on water	ammonia on water

**Table 6. Initial values for primary variables and pool scenarios**

Primary variable	Description	Release	
		Instantaneous	Continuous
$R_{pool}$	Pool radius	0	0
$M_{pool}^{i24}$	Pool mass	$M_{spill}^i$	0
$M_{vap}^{i24}$	Cumulative mass vaporised	0	0
$M_{sol}^{i24}$	Cumulative mass dissolved	0	0
$T_{pool}$	Pool temperature	$T_{spill}$	$T_{spill}$
$M_{water}$	Mass of water entrained for reactive ammonia dissolution	0	0
	Spreading scenario	Normal spreading	Normal spreading
	Vaporisation scenario	Non-boiling	Non-boiling

$M_{spill}^i$  is the total mass spilled for each component  $i=1, \dots, n$

5. The pool calculations will terminate once the duration of interest has been reached (by default this duration is set to one hour). The run can be terminated at an earlier time in the case of :
  - 5.1. A continuous or time-varying spill, if the spill has stopped and the pool vaporisation rate has dropped below the cut-off vaporisation rate
  - 5.2. An instantaneous spill, if the pool vaporisation rate has dropped below the cut-off vaporisation rate
 The cut-off vaporisation rate is a parameter that can be modified by the user and it varies whether the material is toxic or flammable.

## 7 FUTURE DEVELOPMENTS

The following future developments are proposed.

1. The value for the minimum pool thickness  $H_{\min}$  is currently found from Table 2 for a range of surfaces. In reality, the value for  $H_{\min}$  is related to physical properties of the liquid such as surface tension  $\sigma_L$ , viscosity  $\nu_L$  and liquid density  $\rho_L$ . A lower bound for the minimum thickness equals the capillary depth  $h_c = (\sigma_L/g\rho_L)^{1/2}$ . However this value may be too low, and thus leads to pools with a too short spill duration and extension to a too large distance. Following the steady-state model of Webber (1990)<sup>xvii</sup>, (1991)<sup>xviii</sup>, one could suggest for slowly-varying release rates to take  $H_{\min}$  variable as function of the time  $t$ , i.e. to take  $H_{\min} = H_{\min}(t) = \max[h_c, (6\nu_L S(t)/\pi g)^{1/4}]$ , where  $S(t)$  is the spill rate at the present time  $t$ . For a detailed discussion see Appendix 4.A of the HGSYSTEM Technical Documentation<sup>xix</sup>.

The current model now assumes that the pool radius reduces after it has reached the minimum height. In reality however, the pool will break up into a number of separate blobs.

Thus following a further literature survey it is recommended to improve the formulation for the minimum pool thickness.

2. An overview of pool models has been given in Chapter 6 of Torstein Fannelop (1994)<sup>xx</sup>. Following a review of this, further improvements of DNV's pool model may be identified for future implementation into the model.
3. Conduction on land:

The general equation used to determine the heat transferred to the pool from a land surface is based on the following assumptions:

- (a) The ground is *not* an infinite heat sink; i.e., the ground will cool down as a cryogenic liquid spreads over it.
- (b) Heat transfer occurs in one direction only, perpendicular to the surface plane.
- (c) Perfect thermal contact exists between pool and ground surface.

The differential equation to be solved is:

$$\frac{\partial T_{pool}}{\partial t} = \alpha_s \frac{\partial^2 T_{pool}}{\partial t^2} \quad (7.1)$$

Here  $T_{pool}$  (K) is the temperature at the ground surface [made equal to the pool temperature by above assumption (c)],  $\alpha_s$  (m<sup>2</sup>/s) is the ground's thermal diffusivity, and  $t$  (s) is time since the release.

Boundary conditions are needed for the solution of this equation. The PVAP model described in Section 4.1 is based on a formulation by Shaw and Briscoe (1978)<sup>xi</sup>, which assumes a constant temperature at the interface pool-ground surface. This assumption is valid throughout the simulation of pure-component boiling pools, when the pool area doesn't change with time. Otherwise, it is valid if sufficiently small steps are taken in order to guarantee that the pool area and temperature remain constant per step; this assumption can approximate the real behaviour.

Other authors (Webber, 1987)<sup>xxiv</sup> (Leonelli et al., 1994)<sup>xxvii</sup> propose a time-dependent temperature as the boundary condition, and develop a slightly more complicated integral equation. This expression can be valid for pools boiling or evaporating, and with constant or changing area, without restricting the time step.

4. Conduction on water:

The PVAP model distinguishes between two cases for conduction from a water surface, with ice formation or not. When there is no ice formation, the water surface is treated as an infinite heat source, and steady state conditions apply. The method of Reid and Smith (1978) is used in the cases ice can be formed (i.e. shallow open water or shallow river).

Ice formation under cryogenic pools is a much discussed topic in the literature. For example, Ivings et al. (2007)<sup>xxi</sup> argues there is no evidence of ice formation under pools except in very small scale experiments. Verfondern and Dienhart (1997)<sup>xxii</sup> carried out experiments involving liquid hydrogen pools spreading on a water tank of 3.5 m diameter and 1m height, where evidence of ice formation was found.

To determine whether ice formation is possible on shallow water, the PVAP model considers the worst-case scenario of the water surface temperature dropping instantaneously to the liquid's boiling point. If the liquid's boiling point is below the water's freezing temperature, ice is formed, otherwise it is not. For shallow or confined water surfaces, when *no* ice is formed, the assumption of the constant water surface temperature doesn't seem to be consistent with the worst case scenario mentioned above.

Vesovic (2007)<sup>xxiii</sup> studies two limiting cases for the boiling of LNG over water surfaces. The first case considers boiling on deep unconfined surfaces, where heat transfer reduces to a steady state solution. The second one considers transient heat transfer by conduction only. Ice formation is included under the second limiting case, when the decreasing water surface temperature reaches the freezing point. This shows a consistent treatment of shallow or confined water surfaces with and without ice formation.

Accompanying reports contain the results of a review by David Webber of the PVAP model, and the results of a verification of PVAP against the AEA model GASP by Webber<sup>xvii</sup>. The recommendations of his review and PVAP/GASP comparison can be summarised as follows:

#### Pool spreading

1. The PVAP pool-spreading model (based on Opschoor<sup>iii</sup>) may give the right qualitative behaviour in case of an appropriate choice for the minimum pool thickness  $h_{min}$ . Thus an improved formula may be considered, e.g. in terms of liquid viscosity etc. The PVAP spread rate is completely sensitive to the choice of  $h_{min}$ . PVAP does not allow a zero minimum depth, while GASP recommends a zero minimum depth unless puddles are expected to form.

For the Opschoor pool-spreading law in PVAP the radius  $r(t) \sim t^{1/2}$ , which is wrong. In GASP<sup>xxiv</sup>, the spread is larger in the initial gravity-inertia regime [ $r(t) \sim t$ ], and smaller in the subsequent gravity-resistant regimes [turbulent  $r(t) \sim t^{2/7}$  and laminar  $r(t) \sim t^{1/8}$ ].

2. The 'tuned' model of Dodge<sup>iv</sup> adopted for spreading on water may not scale properly, particularly because an inappropriate force balance is used.
3. In the long term both above models could be considered to be replaced by logic in the model of Webber<sup>xvii</sup>, involving solution of two first-order differential equations (spread rate, force balance) instead of one (spread rate).

#### Pool vaporisation

1. Unlike GASP, the DNV model applies a non-unified treatment for evaporation and boiling. This may result in less smooth results.
2. For a boiling pool on land, the formula by Shaw and Briscoe<sup>vii</sup> for heat flow for conduction  $Q_{cond}$  is heuristic, and could be considered to be replaced by an improved correlation introduced by Webber and Jones (1987)<sup>xxiv</sup>. However the conduction models are very similar.
3. For an evaporating pool on land, the formula by McKay and Matsugu<sup>xv</sup> for heat flow from evaporation  $Q_{evap}$  is dimensionally not sound, and could be considered to be replaced by a more sound and well-validated GASP correlation by Brighton (1985)<sup>xxvi</sup>. The GASP correlation leads to significantly less evaporation on land.<sup>25</sup>
4. For an evaporating pool on water, the formula by Dodge<sup>iv</sup> seems to be plausible for including the wind-speed dependent aerodynamic roughness length of the surface but it uses the dimensionally unsound correlation on land. It could be further compared with formulation by Brighton (1985)<sup>xxvi</sup>. Note however that the PVAP evaporation rate is usually less than the dissolution rate.
5. No problems have been found for the following existing models:
  - 5.1. Boiling on water, although ice formation may be discounted and model for ice formation is complicated
  - 5.2. The formula by Fleischer<sup>xi</sup> for heat convection on land or water (also adopted in the original version of HGSYSTEM)
  - 5.3. The formula for radiation
  - 5.4. Dissolution on water, although it may be more complicated than necessary
  - 5.5. Reaction of ammonia pool with water

<sup>25</sup> This recommendation from David Webber was based on comparisons of GASP and the equation for evaporation on land in Phast 6.7 and previous versions. The default equation for land evaporation in Phast 7.0 leads to significant less evaporation when compared against 6.7. Comparison between GASP and the new default equation in Phast 7 is part of the future work on the pool vaporization model.

## APPENDICES

### Appendix A. Derivation of the multi-component pool equations

#### A.1 Energy balance

The variation of enthalpy over time in a multi-component pool can be expressed as:

$$\frac{d(M_{pool} h_{L pool})}{dt} = Q_{in} + S(t) h_{L spill} - E_{vap}(t) \sum_{i=1}^n Y_{vap}^i h_V^i(T_{pool}) - E_{sol}(t) \sum_{i=1}^n X_{sol}^i h_{sol}^i(T_{pool}) \quad (\text{A.1})$$

Where,

$h_{L pool}$	is the liquid enthalpy at the temperature and composition of the pool	(J/kg)
$h_{L spill}$	is the liquid enthalpy at the temperature and composition of the spill rate	(J/kg)
$Y_{vap}^i$	is the vapour mass fraction of component i in the evaporation rate	(kg/kg)
$h_V^i$	vapour enthalpy of component i	(J/kg)
$X_{sol}^i$	is the mass fraction of component i in the dissolution rate	(kg/kg)
$h_{sol}^i$	enthalpy of dissolved component i	(J/kg)
$n$	total number of components	

Focusing first on the left hand side of equation (A.1) the derivative can be solved applying chain rule:

$$\frac{d(M_{pool} h_{L pool})}{dt} = h_{L pool} \frac{dM_{pool}}{dt} + M_{pool} \frac{dh_{L pool}}{dt} \quad (\text{A.2})$$

Remembering the overall mass balance in the pool is given by the following expression:

$$\frac{dM_{pool}}{dt} = S(t) - E_{vap}(t) - E_{sol}(t) \quad (\text{A.3})$$

The term  $dM_{pool} / dt$  can be replaced in equation (A.3):

$$\frac{d(M_{pool} h_{L pool})}{dt} = h_{L pool} (S(t) - E_{vap}(t) - E_{sol}(t)) + M_{pool} \frac{dh_{L pool}}{dt} \quad (\text{A.4})$$

Equation (A.4), which is equal to the left hand side of equation (A.1), is substituted back into equation (A.1) to give:

$$M_{pool} \frac{dh_{L pool}}{dt} = Q_{in} + S(t) h_{L spill} - E_{vap}(t) \sum_{i=1}^n [Y_{vap}^i h_V^i(T_{pool})] - E_{sol}(t) \sum_{i=1}^n [X_{sol}^i h_{sol}^i(T_{pool})] - h_{L pool} (S(t) - E_{vap}(t) - E_{sol}(t)) \quad (\text{A.5})$$

Equation (A.5) is an implicit equation with respect to the temperature of the pool, however it can be further manipulated to explicitly express the pool temperature as a function of time, analogous to the case of a single-component pool.

Substituting the definition for the pool enthalpy ( $h_{L, pool} = \sum_{i=1}^n X_{pool}^i c_p^i (T_{pool} - T_{ref})$ ) the left hand side of equation

(A.5) is transformed to:

$$\begin{aligned} M_{pool} \frac{dh_{L, pool}}{dt} &= M_{pool} \left[ \frac{\partial h_{L, pool}}{\partial T_{pool}} \frac{dT_{pool}}{dt} + \sum_{i=1}^n \left\{ \frac{\partial h_{L, pool}}{\partial x_{pool}^i} \frac{dx_{pool}^i}{dt} \right\} \right] = \\ &= M_{pool} c_{pL}^{pool} \frac{dT_{pool}}{dt} + (T_{pool} - T_{ref}) \sum_{i=1}^n \left\{ c_p^i M_{pool} \frac{dx_{pool}^i}{dt} \right\} \end{aligned} \quad (\text{A.6})$$

Where,

$T_{ref}$  is the reference temperature (= 298.15K) (K)

$c_p^i$  is the liquid specific heat capacity of each component i (J/kg.K)

The last term in equation (A.6)  $\left\{ M_{pool} \left( dx_{pool}^i / dt \right) \right\}$  can be further expanded using the pool mass balance per component  $i = 1, \dots, n$  and the overall mass balance, which yields:

$$M_{pool} \frac{dx_{pool}^i}{dt} = (X_{spill}^i - X_{pool}^i) S(t) - (Y_{vap}^i - X_{pool}^i) E_{vap}(t) - (X_{sol}^i - X_{pool}^i) E_{sol}(t) \quad (\text{A.7})$$

Substituting equation (A.7) into equation (A.6) results in:

$$\begin{aligned} M_{pool} \frac{dh_{L, pool}}{dt} &= M_{pool} c_{pL}^{pool} (T_{pool}) \frac{dT_{pool}}{dt} + (T_{pool} - T_{ref}) \cdot \\ &\sum_{i=1}^n \left\{ c_p^i \left[ (X_{spill}^i - X_{pool}^i) S(t) - (Y_{vap}^i - X_{pool}^i) E_{vap}(t) - (X_{sol}^i - X_{pool}^i) E_{sol}(t) \right] \right\} \end{aligned} \quad (\text{A.8})$$

From the definition of the enthalpy of the pool, equation (A.8) can be expressed as:

$$\begin{aligned} M_{pool} \frac{dh_{L, pool}}{dt} &= M_{pool} c_{pL}^{pool} (T_{pool}) \frac{dT_{pool}}{dt} + \sum_{i=1}^n \left[ X_{spill}^i c_p^i (T_{pool} - T_{ref}) \right] S(t) - \\ &- \sum_{i=1}^n \left[ Y_{vap}^i c_p^i (T_{pool} - T_{ref}) \right] E_{vap}(t) - \sum_{i=1}^n \left[ X_{sol}^i c_p^i (T_{pool} - T_{ref}) \right] E_{sol}(t) \\ &- h_{L, pool} (S(t) - E_{vap}(t) - E_{sol}(t)) \end{aligned} \quad (\text{A.9})$$

By equating equations (A.6) and (A.9) the term  $\left\{ -h_{L, pool} (S(t) - E_{vap}(t) - E_{sol}(t)) \right\}$  which appears on both sides of the equation cancels out, and inserting the definition for the enthalpy of the pool and the enthalpy of the spill

( $h_{L, spill} = \sum_{i=1}^n X_{spill}^i c_p^i (T_{spill}) [T_{spill} - T_{ref}]$ ) we obtain:

$$\begin{aligned} M_{pool} c_{pL} \frac{dT_{pool}}{dt} &= Q_{in} + S(t) \sum_{i=1}^n \left[ X_{spill}^i c_p^i (T_{spill}) [T_{spill} - T_{pool}] \right] \\ &- E_{vap}(t) \sum_{i=1}^n Y_{vap}^i \left( h_v^i (T_{pool}) - c_p^i (T_{pool}) [T_{pool} - T_{ref}] \right) - E_{sol}(t) \sum_{i=1}^n X_{sol}^i \left( h_{sol}^i (T_{pool}) - c_p^i (T_{pool}) [T_{pool} - T_{ref}] \right) \end{aligned}$$



(A.10)

The enthalpy of vaporisation and dissolution of the pool is respectively defined as:

$$\Delta H_{v\ pool} = \sum_{i=1}^n Y_{vap}^i \left( h_v^i(T_{pool}) - c_p^i(T_{pool}) [T_{pool} - T_{ref}] \right) = \sum_{i=1}^n Y_{vap}^i \Delta H_{vap}^i \quad (\text{A.11})$$

$$\Delta H_{sol\ pool} = \sum_{i=1}^n X_{sol}^i \left( h_{sol}^i(T_{pool}) - c_p^i(T_{pool}) [T_{pool} - T_{ref}] \right) = \sum_{i=1}^n X_{sol}^i \Delta H_{sol}^i \quad (\text{A.12})$$

Rewriting equation (A.10) by using the above definitions results in the equation for the variation of the pool temperature with time:

$$\frac{dT_{pool}}{dt} = \frac{Q_{in} + S(t) \sum_{i=1}^n [X_{spill}^i c_p^i(T_{spill}) [T_{spill} - T_{pool}]] - E_{vap}(t) \Delta H_{v\ pool} - E_{sol}(t) \Delta H_{sol\ pool}}{M_{pool} c_p^{pool}(T_{pool})} \quad (\text{A.13})$$

## A.2 Evaporation on land and water

To extend the single-component evaporation equation to multi-component pools is easier to express it in a general form as a product of the mass transfer coefficient ( $k$ ), the concentration at the pool surface ( $C_s$ ):

$$E_{vap}(t) = k C_s \quad (\text{A.14})$$

Where,

- Mass transfer coefficient ( $m^3/s$ ):  
Pools on land:  $k = 0.004786\pi u_{a(z=10m)}^{0.78} r^{1.89} Sc^{-0.67}$  (A.15a)

Pools on water:  $k = (\pi r^2) U_a^* Da^*$  (A.15b)

- Concentration ( $kg/m^3$ ):  $C_s = \frac{M_c P_v^c}{RT_{pool}}$  (B.16)

Equation (A.15a) is independent of the pool properties and remains unchanged in the expression for multi-component pools (see equation (6.20)). Equation (A.15b) although is dependent on the diffusion coefficient of the vapour on air, keeps the formulation for single-component pools to calculate the mass transfer coefficient of a component in the mixture.

Equations (A.16) and (A.17) are extended to multi-component cases using Raoult's Ideal Law ( $P_v^c = x_{pool}^i P_{vap}^i$  for each  $i = 1, \dots, n$ ) and Leonelli et al. (1994)<sup>xxvii</sup> definition for the multi-component correction factor:

- Concentration of component  $i = 1, \dots, n$ :  $C_{s\ i} = \frac{M_c x_{pool}^i P_{vap}^i}{RT_{pool}}$  (A.18)

Where,

$x_{pool\ i}$  is the molar fraction of component  $i$  ( $i = 1, \dots, n$ ) in the pool (fraction)

The evaporation rate on land for a component in a multi-component pool is given by:

$$E_{vap\ i}(t) = 0.004786\pi u_{a(z=10m)}^{0.78} r^{1.89} Sc^{-0.67} \frac{M_c^i x_{pool}^i P_{vap}^i}{RT_{pool}} \quad (\text{A.19})$$

And on water is given by:

$$E_{vap\ i}(t) = (\pi r^2) U_a^* D a_i^* \frac{M_c^i P_{atm}}{RT_{pool}} \left( \frac{x_{pool}^i P_{vap}^i}{\sum_{i=1}^n x_{pool}^i P_{vap}^i} \right) \text{Ln} \left( \frac{P_{atm}}{P_{atm} - \sum_{i=1}^n x_{pool}^i P_{vap}^i} \right) \quad (\text{A.20})$$

## Appendix B. Guidance on inputs and outputs for PVAP

This guidance is applicable only to Phast 7 standalone pool vaporisation model only.

### B.1 Input data

A list of the input data for the pool vaporisation model PVAP is given in Figure 2 and Figure 3. The data is split in two categories, inputs to be entered by the user and parameters to be manipulated only by expert users:

#### I. Inputs (to be entered by the user)

##### 1. Release data

*Number of components:* PVAP can generate a mixture of up to five components entered by the user. It can also handle a mixture of up to 20 components as stored in a property file. For a pure stream specify 1 component.

*Mole (=1) mass (=0) base composition:* flag to specify whether the spill composition entered by the user is in mole or mass fraction. 1 = user entered mole fractions. 0 = user entered mass fractions. The user needs to ensure that the sum of the specified mass or mole component fractions equals 1. If not, the model will recalculate the component fractions to ensure their sum is equal to 1.

*Component name 1 or stream name* (as stored in the property file): all properties of the material are subsequently derived from the property file.

*Component name* (2 to 5): the user should specify the additional components for PVAP to generate the mixture stream.

*Spill fraction:* mass or mole fraction of the corresponding component in the spill, as per flag.

*Name of component of interest:* the user can select an individual component for which pool results will be reported.

*Release type* (1 = instantaneous; 2 = continuous; 3 = time-varying): the user specifies a flag which takes the value of 1 if the spill is instantaneous, meaning all the mass is released in the first instant, 2 if the release is continuous with a constant spill rate of given duration, or 3 if the release is time-varying with a time-dependent spill rate.

*Release rate segment* (not in use)

*Number of release rates – time-varying only:* is the total number of data points for the time-varying spill rate.

Data applicable for instantaneous spill only:

- *Instantaneous spill mass (kg):* total mass released instantaneously.
- *Duration of instantaneous spill (s):* set to a very small value by default, should not be modified by the user.
- *Temperature of instantaneous spill (K):* temperature of the released material for instantaneous spills.

Data applicable for continuous or time-varying spill only:

- *Array of spill rates (kg/s):* mass release rate
- *Array of spill times (s):* for continuous spills is the duration of the spill; for time-varying spills is the time since the beginning of the spill
- *Array of spill temperatures (K):* temperature of the released material

For continuous spills a single value is entered for the spill rate, time and temperature; for time-varying spills the user must enter an array of values of size equal to the *Number of release rates*

##### 2. Ambient data

*Pasquill stability class:* the Pasquill stability class gives a measure of the amount of atmospheric turbulence which is generated by the vertical temperature gradient in the lower atmosphere. In PVAP it is used in the determination of the friction velocity required for pool evaporation and dissolution calculations. The following table shows a reference for selecting the Pasquill stability class according to the prevailing ambient conditions.

Description	Time and Weather	Wind Speed $u$	Monin-Obukhov Length $L$	Pasquill-Gifford Stability Class
Very Stable	Clear night	<3 m/s	10 m	F
Stable	↓	2 to 4 m/s	50 m	E
Neutral	Cloudy or Windy	any	>100 m	D
Unstable	↓	2 to 6 m/s	-50 m	B or C
Very Unstable	Sunny	<3 m/s	-10 m	A

**Table 7. Reference for choosing Pasquill stability class (CCPS)**

*Solar radiation flux ( $W/m^2$ ):* long-wave solar radiation heat flux. For day time  $500 W/m^2$  is the default value. For night time a lower value applies.

*Atmospheric temperature ( $K$ ):* the prevailing ambient temperature at ground level

*Atmospheric pressure ( $Pa$ ):* atmospheric pressure at ground level

*Atmospheric humidity (fraction):* used to determine the mass fraction of water in the moist air; a value of 1 indicates saturated conditions (100% humidity).

*Atmospheric molecular weight ( $kg/kmol$ ) and specific heat capacity ( $J/kg.K$ ):* molecular weight and heat capacity at constant pressure of air at the ambient temperature.

*Wind speed profile flag (1 – constant, 2 – power-law fit):* a power-law fit of the logarithmic wind-speed profile is recommended; see the UDM theory manual for further details<sup>26</sup>

*Wind speed at a reference height ( $m/s$ ):* the wind speed at the reference height specified by the user

*Reference height for windspeed ( $m$ ):* commonly the wind speed is measured at 10 m above ground level

*Cut-off height for wind speed ( $m$ ):* it is the height measured from the pool surface where the wind profile is assumed to be flat. It is set as 0.1 m as default and is not recommended to be changed by the user

### 3. Substrate data

*Surface roughness length ( $m$ ):* surface roughness length upwind from the pool, used in the calculation of the friction velocity. It is also referred as aero-dynamical roughness length and depends on the type of terrain and the presence or absence of obstacles. The following table can be used as reference for choosing the surface roughness length.

<sup>26</sup> FUTURE- The spreadsheet is pending some restructuring and the wind-speed profile flag, atmospheric mole weight, specific heat capacity and cut-off height for wind-speed should be moved to the parameters section to be changed by expert users only

Class	Short terrain description	$z_o$ (m)
1	Open water, fetch <sup>1)</sup> at least 5 km	0.0002
2	Mud flats, snow; no vegetation, no obstacles	0.005
3	Open flat terrain; grass, few isolated obstacles	0.03
4	Low crops; occasional large obstacles, $x/h > 20^2)$	0.10
5	High crops; scattered obstacles, $15 < x/h < 20^2)$	0.25
6	Parkland, bushes; numerous obstacles, $x/h < 15^2)$	0.5
7	Regular large obstacle coverage (suburb, forest)	(1.0) <sup>3)</sup>
8	City center with high- and low-rise buildings	(3) <sup>3)</sup>

- 1) The upwind length over water should be at least 5 km.  
 2) Here  $x$  is a typical upwind obstacle distance and  $h$  the height of the corresponding major obstacles.  
 3) These values are rough indications.

**Table 8. Reference for choosing upwind surface roughness length depending on the terrain type (TNO Yellow Book, p. 4.61)**

*Bund diameter (m) and Bund height (m):* dike or bund dimensions; the bund diameter is the maximum value of the pool diameter

*Surface temperature (K):* initial temperature of the surface.

*Surface type:* eight types of surfaces are predefined in PVAP: 1-Dry soil; 2-Wet soil; 3-Concrete; 4-Insulated concrete; 5-Deep open water; 6-Shallow open water; 7-Deep river or channel; 8-Shallow river or channel. Roughness factor and thermal conductivity and diffusivity values are given for each one, they can be found in table 3 in section 4.1 of this document. The value of the minimum thickness given for predefined each surface can be found in table 2 in section 3.3. It is strongly recommended to use the predefined surfaces in PVAP, but if the type of surface required to be modeled is not included in the above list the user may select to input the surface data selecting option 9-User defined.

*User-defined roughness factor:* this factor is used to account for enhanced heat transfer between the surface and the pool when the surface is rough. If the surface is rough an effectively larger surface area is in contact with the pool. A factor of 1 indicates the surface is smooth.

*User-defined thermal conductivity (W/m.K) and diffusivity (m<sup>2</sup>/s):* Table 9 provides some reference as to which values to use for different surfaces.

Material	$\lambda_s$ (J/(s·m·K))	$\rho_s$ (kg/m <sup>3</sup> )	$C_{p,s}$ (J/(kg·K))	$a_s \times 10^{-7}$ (m <sup>2</sup> /s)
Isolation concrete	0.207	900	920	2.5
Light concrete	0.418	1800	920	2.5
Heavy concrete	1.3	2400	920	5.9
Clinkers	0.7	2000	836	4.2
Average subsoil 8 wt% moist	0.9	2500	836	4.3
Dry sandy subsoil	0.3	1600	799	2.0
Wet sand 8 wt% moist / clay	0.6	1940	937	3.3
Wood	0.2	550	2300	1.6
Gravel	2.5	2000	1140	11
Carbon steel	46	7840	460	128

**Table 9. Thermal conductivity ( $\lambda_s$ ), density ( $\rho_s$ ), specific heat capacity ( $C_{p,s}$ ) and thermal diffusivity ( $a_s$ ) for various materials (TNO Yellow Book, p. 3.76)**

*User-defined minimum thickness (m):* The pool minimum thickness is taken as the average roughness length of the surface.

Table 10 provides values as reference for various types of surfaces. Additional information can also be found in the footnote section of table 2 in section 3.3 of this document.

Soil	Average roughness length (m)
flat sandy soil, concrete, stones, industrial site	0.005
normal sandy soil, gravel, railroad yard	0.010
rough sandy soil, farmland, grassland	0.020
very rough, sandy soil grown over and with potholes	0.025

(a)

Minimum thickness for pool spread

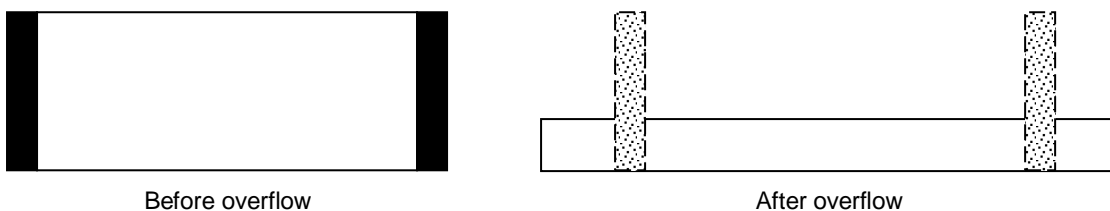
Surface	Minimum pool thickness (mm)
Rough, sandy soil	25
Farmland, pasture	20
Smooth sand, gravel	10
Concrete, stone	5
Calm water	1.8

(b)

**Table 10. Reference for choosing minimum thickness depending on the surface type. (a) taken from TNO Purple Book p. 4.7 (b) taken from Napier and Roopchand (1986) p. 256**

#### 4. Model parameters

*Bund overspill switch:* enables (=1) or disables (=0) the option for the pool to spill over the bund when the pool height exceeds the bund height. If the pool overflows the bund (i.e. pool height exceeds the bund height), the model assumes the pool spreading calculations to continue as if the bund was not present.



**Figure 1. Pool behaviour before and after if the bund overspill option is on**

*Cut-off rate for pool evaporation (kg/s):* pool calculations will terminate when the evaporation rate falls below this value and results will be printed up to that point.

*Minimum temperature (K):* indicates the lowest temperature the pool is allowed to be at; this parameter is given a default value of 9.99 and is not recommended to be modified by the user

*Maximum duration (s):* is the maximum simulated time and results will be printed up to that point in the case another termination condition (see cut-off rate for pool evaporation) has not been met.

*Concentration power for toxic load calculation:* This parameter is used to divide the time-varying pool behaviour into ten segments of different constant rates. Each segment produces the same quantity of vapour if this parameter is set to 1, or the same (toxic) "load" if different from 1.

*Maximum number of pool evaporation rates:* maximum number of time segments into which the time-varying pool evaporation rate is divided.

## II. Parameters (to be changed by expert users only)

*Time-varying rainout curve fit [1 = linear; 2 = spline (not in use)]:* only linear interpolation is used at the moment

*Record length of results file and Index of next results file record to write to (not in use)*

*Solver flag:* three solvers are available for PVAP Phast 7, a Runge-Kutta method and two open source methods from the ODEPACK family of solvers. The Runge-Kutta method is not recommended as it requires more CPU time. The ODEPACK solvers are more efficient. One is an adaptive solver which switches between stiff and non-stiff methods depending on the problem and is the default recommended option. The other ODEPACK solver is only applicable to non-stiff problems and is generally less robust than the adaptive solver.

*Solver tolerance:* controls the accuracy of the numerical integration carried out by the numerical solver. The default value for the relative tolerance is  $10^{-3}$ . The tolerance can be increased by the user where there are problems of non-convergence. Otherwise, it is not advisable to change the default solver tolerance. Increasing the solver tolerance leads to higher resolution at the cost of increasing CPU time.

*Evaporation on land flag:* this allows selecting the evaporation on land equation to be used in the pool calculations. For checking purposes against older Phast versions the Phast 6.7 option should be selected. The default option is MacKay and Matsugu as it has been found to be more accurate than Phast 6.7 and is conservative with respect to the available experimental data. Further information can be found in section 4.1.2 in the PVAP validation manual.

*Pseudo/Multi-component flag:* PVAP allows MC and PC calculations. In PC mode average mixtures properties are used in the calculations and the vapour-liquid equilibrium is not given a detailed treatment. For pure components, PC and MC results are identical; for mixtures, the MC flag is recommended to be always selected and PC-flag should only be used for checking purposes against older Phast versions.

*Maximum array size for variable output arrays:* maximum size of the results arrays. The default value is 6000. This value may be increased if the warning message "Size of result arrays exceeds the maximum, printing result arrays up to the maximum size" appears. Otherwise, it is not advisable to modify this parameter.

Description	Units	Limits		Cont	Inst
		Lower	Upper		
<b>RELEASE DATA</b>					
Number of components		1	5	2	
Mole (=1) or Mass (=0) based composition		0	1	0	
Component name 1 or stream name	-			methane	
Spill fraction	kg/kg	0	1	0.85	
Component name 2	-			ethane	
Spill fraction	kg/kg	0	1	0.15	
Component name 3	-			propane	
Spill fraction	kg/kg	0	1	0	
Component name 4	-			butane	
Spill fraction	kg/kg	0	1	0	
Component name 5	-			pentane	
Spill fraction	kg/kg	0	1	0	
Name of component of interest in the stream				methane	
Instantaneous/continuous flag	-	1	2	2	1
Release rate segment	-	1	11	1	
Number of release rates	-	1	11	1	
<b>Instantaneous</b>					
Instantaneous spill mass	kg	0	1.00E+07	1000	1000
Duration of instantaneous spill	s			0.001	0.001
Temperature of instantaneous spill	K	10	10000	112	112
<b>Continuous</b>					
Array of spill rates	kg/s	0	1.00E+07	5	
Array of spill durations	s	0		600	
Array of spill temperatures	K	10	10000	112	
<b>AMBIENT DATA</b>					
Pasquill stability class (1-A, 2-AB, ..., 7-D, 8-E, 9-F, 10-G)	-	1	10	7	
Solar Radiation Flux	W/m2	0	1200	500	
Atmospheric temperature	K	200	350	298	
Atmospheric Pressure	N/m2	50000	120000	101325	
Atmospheric humidity	-	0	1	0.7	
Atmospheric Molecular weight	-	10	100	28.966	
Atmospheric heat capacity at constant pressure	J/kg K	800	1200	1004	
Wind speed profile flag (1-Constant, 2-Linear)	-	1	2	2	
Wind speed at reference height	m/s	0.1	50	5	
Reference height for windspeed	m	0	100	10	
Cut-off height for windspeed	m	0.1	1	0.1	
<b>SUBSTRATE DATA</b>					
Surface roughness length	m	0.001	3	0.1	
Bund diameter	m	0		0	
Bund height	m	0		0	
Surface temperature	K	10	10000	298	
Surface type (1-dry soil, 2-wet soil, 3 - concrete, 4 - insulated concrete, 5 - deep open water, 6 - shallow open water, 7 - deep river or channel, 8 - shallow river or channel, 9 - user-defined type)	-	1	9	9	3
User-Defined surface roughness factor	-	1	5	2.634	
User-Defined thermal conductivity	W/mK	0.1	5	2.21	
User-Defined thermal diffusivity	m2/s	1.00E-08	1.00E-06	9.48E-07	
User-Defined minimum thickness	m	0.001	0.3	0.005	
<b>MODEL PARAMETERS</b>					
Bund overspill switch (0-Off, 1-On)	-	0	1	0	
Cut-off rate for pool evaporation	kg/s	0	100	0.1	
Minimum temperature	K	0	300	9.99	
Maximum duration	s	0	1.00E+08	3600	
Concentration power for toxic load calculation	-	0		1	
Maximum number of pool evaporation rates	-	1	10	10	

Figure 2. List of inputs to pool vaporization model PVAP to be entered by the user<sup>26</sup>

<b>Parameters to be changed by Expert Users Only</b>					
Pool model debug flag					0
Record length of results file					50
Index of next results file record to write to					1
Solver flag (1= RK4, 2= non-stiff, 3= adaptive)	-	0	3	3	
Solver tolerance		1.00E-06	1.00E-01	1.00E-03	
Evaporation on land flag (1=MacKay&Matsugu 2=Phast 6.7 3=Opschoor)		1	3	2	
Pseudo-component / Multi-component flag (0 = PC; 1 = MC)	-	0	1	1	
<b>OUTPUT LIMIT-To be changed by Expert Users Only</b>					
Maximum array size for variable output arrays	-	100	8000	6000	

Figure 3. List of input parameters to PVAP only to be manipulated by expert users only

Above input data are derived from the PVAP generic spreadsheet. The first part of the input data shown in Figure 2 should always be specified by the user (release data, ambient data, substrate data and model parameters). For each input parameter a brief description of the meaning of the parameter is given, its unit, and its lower and upper limits. The next





column contains a complete list of input data corresponding to the base case. Subsequent columns need to include only those values that need to be changed to invoke other runs.

The second part of the input data shown in Figure 3 corresponds to the input parameters and should only be changed by expert users only.

## B.2 Model run and output data

Following the data initialisation the pool model is run as detailed in section 7. A list of the outputs can be seen in Figure 4. The results for the overall stream are reported under pool spread and vapourisation data, the results of the component of interest selected by the user are also printed out.

Output Index	Description	Units				
	<b>ERROR STATUS</b>					<b>OK OK</b>
	1 Array of output integers	-				
	2 Array of output doubles	-				
A	Bund overspill flag (0-Bund did not overspill,1-Bund overspilled)	-			0	0
A	Bund hit flag (1-Bund hit,2-Bund not hit or Undefined)	-			2.00E+00	2
A	Maximum pool radius	m			4.661559324	9.69E+00
A	Pool temperature at maximum pool radius	K			147.0411108	216.2783952
A	Remaining mass in the pool	kg			7.902629477	34.94337225
	<b>Pool segment data</b>					
3	Number of rates	-			3	3
4	Array of pool radius	m				
5	Array of pool rates	kg/s				
6	Array of pool times	s				
7	Array of pool temperatures	K				
	<b>POOL SPREAD AND VAPOURISATION DATA</b>					
8	Number of output step sizes	-			427	302
9	Step number	-				
10	Time since release	s				
11	Total mass spilt	kg				
12	Total mass vapourised	kg				
13	Total mass of fluid vaporised, due to dissolution only,	kg				
14	Total mass dissolved	kg				
15	Total mass of entrained water during dissolution	kg				
16	Remaining mass	kg				
17	Vapourisation rate	kg/s				
18	Solution rate	kg/s				
19	Water entrainment rate	kg/s				
20	Pool radius	m				
21	Pool depth	m				
22	Pool Temperature	K				
23	Bubble point temperature	K				
24	Net heat transfer rate	W				
25	Conductive heat transfer rate	W				
26	Convective heat transfer rate	W				
27	Radiative heat transfer rate	W				
28	Heat of solution	W				
29	Heat added from spill	W				
30	Heat of evaporation	W				
31	Sensible heat rate	W				
32	Model Flag (1-Boiling, 2-Evaporating)	W				
33	Spreading flag (1-Normal spreading, 2-Bund hit, 3-Minimum depth)	-				
	<b>RESULTS FOR COMPONENT OF INTEREST</b>					
34	Vaporisation rate of component of interest	kg/s				
35	Remaining mass of component of interest	kg				
36	Solution rate of component of interest	kg/s				
37	Total mass vaporised of component of interest	kg				
38	Total mass dissolved of component of interest	kg				

Figure 4. List of outputs from PVAP

The above figure shows the output from the PVAP spreadsheet corresponding to the inputs shown in Figure 2 and Figure 3. Only the scalar results are shown.

### **B.3 Errors and warning messages**

For which additional information can be given on how to resolve problems.

#### Errors

##### **38: "Pool depth falls below minimum thickness after first iteration"**

The pool cannot handle depths less than the minimum thickness initially, as this would result in the pool depth remaining constant through the simulation. This result may be triggered in some continuous cases when the spill temperature input by the user has had to be reset to the normal boiling point, causing the density and the pool dimensions to change in the initial step. Slightly reducing the spill temperature or making the solver take smaller steps by reducing the tolerance may overcome this.

#### Warnings

## NOMENCLATURE

$C_{pa}$	specific heat of air (J/kg/K)
$C_{pL}$	specific heat of liquid in pool (J/kg/K)
$D_{ac}$	diffusion coefficient of air and gas, $m^2/s$
$D_{wc}$	diffusion coefficient of water and gas, $m^2/s$
$Da^*$	boundary layer Dalton number, -
$E_{sol}$	rate of dissolution of material of liquid pool into water, kg/s
$E_{vap}(t)$	pool evaporation rate, kg/s
$g$	gravitational acceleration, $m/s^2$
$h$	pool thickness, m
$h_{min}$	minimum pool thickness, m
$h_s$	heat transfer coefficient, $W/m^2/K$
$H_L$	modified partial liquid enthalpy of the material, J/kg
$H_V$	vapour enthalpy of the material, J/kg
$H_w$	liquid enthalpy of water, J/kg
$H_w'$	modified partial liquid enthalpy of water, J/kg
$k_l$	thermal conductivity of ice, $W/m/K$
$k_s$	thermal conductivity of surface, $W/m/K$
$M_{pool}$	mass of pool material, kg
$M_c$	molecular weight of spilled liquid, kg/kmol
$P_a$	atmospheric temperature, Pa
$P_v^c$	saturated vapour pressure of spilled liquid, Pa
$Pr$	Prandtl number = $C_{pa}\mu_a\lambda_a$ , -
$Q_{cond}$	heat flow rate from conduction, W
$Q_{conv}$	heat flow rate from convection, W
$Q_{evap}$	heat flow rate from evaporation, W
$Q_{rad}$	heat flow rate from solar radiation, W
$Q_{sol}$	heat flow rate from dissolution, W
$Q_{spill}$	heat flow rate from spilled (leaking) liquid, W
$r$	pool radius, m
$R$	universal gas constant, J/kg/kmol
$Re$	Reynolds number = $2U_a\rho_a L/\mu_a$ , -
$S$	solar flux, $W/m^2$
$Sc$	Schmidt number for air = $\mu_a/(\rho_a D_{ac})$ , -
$t$	time, s
$t_{dur}$	spill duration, s
$T_a$	air temperature, K
$T_{frz}$	freezing point of water, K
$T_{spill}$	temperature of liquid spilled (leaked) into pool, K
$T_{surf}$	surface temperature, K
$T_{pool}$	pool temperature, K
$u_a(z)$	wind speed as function of the height $z$ above the substrate, m/s
$w_s$	molar solubility, -

### Greek letters

$\alpha_l$	thermal diffusivity of ice, $m^2/s$
$\alpha_s$	thermal diffusivity of surface, $m^2/s$
$\alpha_w$	thermal diffusivity of water, $m^2/s$
$\beta$	volume expansion from water to ice, -
$\Delta$	relative density factor $(\rho_w - \rho_L)/\rho_w$ , -
$\Delta H_{sol}$	heat of solution, J/kg
$\Delta H_V$	heat of vaporisation, J/kg
$\varepsilon$	emissivity of the pool, -
$\lambda_a$	thermal conductivity of air, $W/m/K$
$\mu_a$	dynamic viscosity of air, kg/m/s
$\mu_w$	dynamic viscosity of water, kg/m/s
$\rho_a$	air density, $kg/m^3$
$\rho_l$	ice density, $kg/m^3$
$\rho_L$	density of liquid in the pool, $kg/m^3$
$\rho_w$	water density, $kg/m^3$
$\sigma$	net surface tension (N/m)
$\sigma$	Stefan-Boltzmann constant, $W/m^2/K^4$
$\chi_s$	factor to account for surface roughness



## About DNV

We are the independent expert in risk management and quality assurance. Driven by our purpose, to safeguard life, property and the environment, we empower our customers and their stakeholders with facts and reliable insights so that critical decisions can be made with confidence. As a trusted voice for many of the world's most successful organizations, we use our knowledge to advance safety and performance, set industry benchmarks, and inspire and invent solutions to tackle global transformations.

## Digital Solutions

DNV is a world-leading provider of digital solutions and software applications with focus on the energy, maritime and healthcare markets. Our solutions are used worldwide to manage risk and performance for wind turbines, electric grids, pipelines, processing plants, offshore structures, ships, and more. Supported by our domain knowledge and Veracity assurance platform, we enable companies to digitize and manage business critical activities in a sustainable, cost-efficient, safe and secure way.

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