

# Complex Hazardous Air Release Model (CHARM®)

## Technical Reference Manual

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## 1.0 INTRODUCTION

This document describes the algorithms used in the Complex Hazardous Air Release Model (CHARM®) software program. CHARM is a modeling program that calculates and predicts the dispersion and concentration of airborne vapor and particle plumes from released chemicals. CHARM also predicts the footprints of thermal radiation, overpressures, and particle deposition. CHARM is especially useful for evaluating the impact of accidental releases, designing emergency response plans, and implementing training programs.

The CHARM program provides a chemical database containing data on the physical, chemical, and toxic properties of over 100 chemical compounds. CHARM requires the user to select the chemical released, describe the release, select a terrain grid, and specify the meteorological conditions at the release site. A release can be described as instantaneous or continuous, contained or uncontained, liquid, gas, or particles. The release may be a liquid pool fire, Boiling Liquid Expanding Vapor Explosion (BLEVE), or jet fire. Overpressures for a flammable vapor cloud or mechanical failure of a pressurized vessel can also be predicted. Meteorological data for input to CHARM can be obtained from instruments brought to the site, from a nearby meteorological station, or from estimates prepared by a remote weather center. The user input combined with the chemical data enables CHARM to simulate the release.

CHARM is a puff model that considers any release to be a series of puffs, each of which can be described somewhat independently. The model treats temporal variations in the emission rate by approximating continuous emissions with a series of discrete puffs. Each puff is considered a symmetrical cloud of contaminant, with advection due to prevailing winds and dispersion by atmospheric mixing. The model uses a Gaussian distribution to describe the concentration within a puff.

Section 2 of this document explains the formulations used in the source term calculations. CHARM's Source Term module calculates the state of the release (e.g emission rate, temperature, partitioning of liquid and vapor, densities, etc.). This information is then provided to the Transport/Dispersion module.

Section 3 of this document explains the transport and advection calculations. CHARM models releases that are heavier than air, neutrally buoyant, or positively buoyant. The model automatically switches between these cases as needed. The Eidsvik, Sheih, and Ooms/Emerson algorithms are used to describe aloft puffs, heavier-than-air puffs, and jets. The resulting graphic displays simulate the release according to the specified input and the calculations.

Section 4 describes the liquid pool fire module, which involves large spills of volatile organic chemicals that evaporate quickly and can form a combustible mixture with the air above the pool.

Section 5 provides the fireball/BLEVE (Boiling Liquid Expansion Vapor Explosion) calculations used in CHARM.

Section 6 describes CHARM's method for calculating jet fire radiation.

Section 7 explains the algorithms used by CHARM to calculate two types of explosion overpressures: sphere bursts and vapor cloud explosions.

This document provides all the major equations used in CHARM; however, it is not intended to repeat the detailed derivations of the equations when these derivations are given in cited references. This document deals with the physical models used in CHARM and does not discuss the computer code used to create graphics or to control the user interface. For information on how to operate the modeling software to produce useful output, refer to the *CHARM User's Manual*.

## 2.0 SOURCE TERM ALGORITHM

The user initially provides input describing the release and the meteorological conditions at the release site. The Source Term calculation takes the user input and determines the characteristics of the release (phases, emission rate, temperature, etc.).

The required calculations depend on the thermodynamic properties of the species released, the mechanism of the release, and the meteorological conditions. CHARM retrieves the thermodynamic properties of the release species from the CHARMED chemical database. CHARM comes with a number of chemicals in the database. Other chemicals can be added through use of CHARMED.

After the user selects a release type, CHARM prompts the user for the appropriate input. Depending on the species and release type, CHARM will allow the calculation of impacts of concentrations, thermal radiation from BLEVEs, jet fires, pool fires, or overpressures from mechanical failure or vapor cloud explosions.

The puff description, which is calculated by the Source Term module, is prerequisite information for the Transport/Dispersion module. The calculated puff description data includes the following:

- X, Y, Z position;
- Chemical mass rate (vapor and liquid phases);
- Temperature;
- Mass of air;
- Mass of water vapor;
- Direction and speed of exit velocity;
- Dimensions; and
- Latent energy.

The release type determines the calculations used in the Source Term module. CHARM models the following types of releases:

- Container/surface description;
- Evaporating pool/lagoon; and
- User-specified;

Sections 2.1 through 2.3 describe the calculations used in the Source Term module. The algorithms used in the calculation come from EPA (1993), Crowl and Louvar (1990), and Fauske and Epstein (1987). The user-defined grid of concentrations requires no source term calculation.

## **2.1 Container/Surface Description Release**

If a liquid is present during the release the emission into the atmosphere may be from two sources. Assuming that liquid is in the container, the emission directly from the container may consist of flashed vapor and droplets. The second source could be from a pool that would form from any liquid that did not flash or become droplets. The release is divided into these two major divisions. The pool evaporation calculation is given in Section 2.2.

The calculations given in this section are performed for a point in time. The changes in the source are then accounted for (e.g. some mass is gone or the pressure may fall) over an internally calculated time step. The calculation is then repeated with the new source characteristics. This is repeated until the end condition of a calculation is reached.

### **2.1.1 Release From Container**

A release from a container can consist of up to four steps or phases. Figure 2-1 is a schematic of these four phases. The phases are:

- Liquid release;
- Depressurization to liquid/vapor equilibrium pressure;
- Boiling; and
- Depressurization to atmospheric pressure.

If there is no liquid in the container the first three phases do not occur. If a liquid is stored at a pressure in equilibrium with its storage temperature the second phase will not occur. This section describes the calculations performed to define the release from a container. The depressurization phases use the same calculation method. The two phases vary only by the pressure at which the depressurization is assumed to stop.

As the liquid is released some may form a pool that then evaporates. An example of what the emission rate versus time looks like for the four phases of the container release and the evaporating pool is given in Figure 2-2. The relationships between the container release rates and the emission from the pool will vary depending on chemical spilled, hole size, surface description, etc.

#### **Liquid Release**

Figure 2-3 is a blowup view of the liquid release phase in Figure 2-1. Depending on the storage conditions of a liquid there are three fates for the liquid:

- Flash to vapor in atmosphere;
- Become suspended droplets; or
- Form a pool and evaporate.

The liquid in the container in Figure 2-3 will continue to come out until the depth of the liquid in the container reaches the bottom of the hole in the container. The characteristics of the emission depend on the storage conditions, the species, and the meteorology. The amount of liquid mass that goes into suspended droplets is not well defined. In CHARM the model can be made to assume that the same amount of mass that flashes will also go into forming droplets. The user can also override this assumption and force the amount of mass going into droplets to be a fraction between 0 and 1 of the amount of liquid that does not flash.

The first calculation performed is for the fraction of species that flashes (F).

$$F = \frac{C_{pL}(T_c) - C_{pL}(T_b)}{H_v} \quad (2-1)$$

where  $C_{pL}(T)$  = heat capacity of liquid at constant pressure and temperature T;  
 $T_c$  = temperature in the container;  
 $T_b$  = boiling point of chemical at ambient pressure; and  
 $H_v$  = latent heat of evaporation at normal boiling point.

The flash fraction is restricted to be between zero and one, inclusive.

#### Flash Fraction is Zero

If the flash fraction is zero it is treated as a pure liquid release. The emission rate is determined by first calculating the exit velocity (u). From Crowl and Louvar (1990) the exit velocity is given by:

$$u = C_d \sqrt{\frac{P_c - P_a + g(z_L - z_H)}{\rho_L \left( \frac{1}{2} + \frac{2fL}{d} \right)}} \quad (2-2)$$

where  $C_d$  = discharge coefficient (0.65);  
 $P_c$  = pressure in container;  
 $P_a$  = ambient pressure;  
 $\rho_L$  = liquid density;  
 $g$  = gravitational acceleration;  
 $z_L$  = height of liquid;  
 $z_H$  = height of hole;  
 $f$  = Fanning friction factor;  
 $L$  = connecting pipe equivalent length (see Section 2.1.2); and  
 $d$  = connecting pipe diameter.



The value of  $f$  is calculated from:

$$\frac{1}{\sqrt{f}} = -4 \log \left( \frac{1}{3.7} \frac{\varepsilon}{d} + \frac{1.255}{Re_e \sqrt{f}} \right) \quad (2-3)$$

where  $\varepsilon$  = roughness length for clean pipes;  
 $Re$  = Reynolds number ( $= \frac{d u \rho_L}{\nu}$ ); and  
 $\nu$  = liquid viscosity at normal boiling point.

Once the exit velocity is calculated the emission rate ( $\dot{m}$ ) can be calculated from:

$$\dot{m} = \rho_L u A \quad (2-4)$$

where  $A$  = area of hole.

For the release of a pure liquid with no flashing the release temperature is assumed to be the storage temperature.

#### Flash Fraction is Not Zero

For this case the release temperature is assumed to be the atmospheric boiling point of the chemical.

If the storage pressure is greater than 1.05 times the vapor pressure in equilibrium with the storage temperature and the equilibrium vapor pressure is greater than the ambient pressure the release is treated as that of a sub-cooled liquid. In a sub-cooled liquid release it is assumed that the flashing that takes place occurs after the liquid has been released. In this case the release rate is calculated in the same manner as for the flash fraction being zero with one exception. The exception is that if a pipe exists the ambient pressure (Pa) used in the zero flash case is replaced with the maximum of the ambient pressure and the vapor pressure of the chemical in equilibrium with the ambient temperature. If a pipe is present it is assumed that it is at ambient temperature.

If the release is not treated as that of a sub-cooled liquid it is assumed that the release is that of a pressurized liquid in thermal equilibrium. The release rate for this case consists of a basic formula that then gets modified depending on the existence of a connecting pipe. The basic formula for the emission rate ( $Q$ ) is from Fauske and Epstein (1987):

$$Q = \frac{H_v A}{v_{lg} \sqrt{T_c C_{pL}}} \quad (2-5)$$

where  $v_{lg}$  = specific volume ( $= 1/\rho_v + 1/\rho_L$ ) at container conditions; and  
 $\rho_v$  = vapor density.

The parameter to determine how to alter Q is  $L/L_e$  where  $L_e$  is the pipe length required to establish equilibrium flow conditions. The value of  $L_e$  is assumed to be 0.1 meters. If  $L/L_e < 1$  then the emission rate is given by:

$$\dot{m} = \frac{Q}{N} \quad (2-6)$$

where N = the correction factor given as:

$$N = \sqrt{\frac{H_v^2}{2(P_c - P_a)\rho_L C_D^2 V_{lg}^2 T_c C_{pL}} + \frac{L}{L_e}} \quad (2-7)$$

Otherwise the emission rate is given by:

$$\dot{m} = Q F \quad (2-8)$$

where F = the correction factor for friction in the pipe and is given as:

$$F = \sqrt{\frac{1}{1 + \frac{0.006L}{d}}} \quad (2-9)$$

### **Depressurization Release**

The depressurization release continues until the pressure in the container reaches a specific value. For the first depressurization phase this pressure is the one reached when the liquid and vapor are in equilibrium in the container. After this first depressurization it is assumed that boiling occurs and the container's pressure is held constant until all liquid is gone. Then the second depressurization occurs. The stopping pressure of the second depressurization is the atmospheric pressure.

The depressurization release calculation's first subdivision is if the release is occurring through a pipe or not. The calculation is then further subdivided into choked/unchoked flow and whether condensation occurs (two-phase release).

#### No Connecting Pipe

The first calculation is to determine whether the vapor flow is choked or not. This is done through:

$$P_* = P_c \left( \frac{2}{\gamma + 1} \right)^{\frac{\gamma}{\gamma - 1}} \quad (2-10)$$

where  $\gamma$  = ratio of heat capacities ( $C_{pv}/C_{vv}$ ) for the vapor phase  
 $C_{pv}$  = heat capacity of vapor at constant pressure  
 $C_{vv}$  = heat capacity of vapor at content volume.

If  $P_*$  is greater than the ambient pressure, the flow is choked.

**Choked Flow** - If the flow is choked, the formation of liquid droplets at choked conditions needs to be investigated. The temperature at choked conditions ( $T_*$ ) can be estimated from:

$$T_* = T_c \left( \frac{2}{\gamma + 1} \right) \quad (2-11)$$

This temperature can be used to determine if condensation occurs. If condensation does occur the value of  $T_*$  is invalid. If  $T_*$  is greater than the critical temperature of the chemical, no condensation occurs. If  $T_*$  is less than the critical temperature, the vapor pressure at  $T_*$  needs to be compared to  $P_*$ . If the vapor pressure is greater than  $P_*$  then condensation does not occur.

Choked Flow (No Condensation) - The emission rate for choked flow with no condensation is given by:

$$\dot{m} = C_d A \sqrt{P_c \rho_c \gamma \left( \frac{2}{\gamma + 1} \right)^{\frac{\gamma + 1}{\gamma - 1}}} \quad (2-12)$$

where  $\rho_c$ , = density of vapor in container.

The release temperature ( $T_{rel}$ ) is given by:

$$T_{rel} = T_c \left[ 1 - 0.85 \left( \frac{\gamma - 1}{\gamma + 1} \right) \right] \quad (2-13)$$

Choked Flow (Condensation) - For this case a more detailed calculation at the choked conditions is needed. First, the value of  $T_*$  is needed. In this case  $T_*$  is the equilibrium temperature at the pressure  $P_*$ . The vapor fraction at choked flow conditions ( $x_e$ ) is required. It is calculated from:

$$x_* = 1 + \frac{T_*}{MH_v} \left[ MC_{pv} \ln\left(\frac{T_c}{T_*}\right) - R \ln\left(\frac{P_c}{P_*}\right) \right] \quad (2-14)$$

where M = molecular weight of chemical; and  
R = gas constant.

Given  $T_*$  and  $x_*$  allows an estimate of enthalpy change ( $\Delta H$ ) and density ( $\rho_*$ ) to be made.

The estimates are given by:

$$\Delta H = C_{pv}(T_c - T_*) + H_v(1 - x_*) \quad (2-15)$$

and

$$\rho_* = \left[ \frac{x_*}{\rho_v} + \left( \frac{1 - x_*}{\rho_L} \right) \right]^{-1} \quad (2-16)$$

The emission rate is then given by:

$$\dot{m} = A \rho_* \sqrt{1.70 \Delta H} \quad (2-17)$$

The release temperature is assumed to be that in equilibrium with the ambient pressure (i.e. normal boiling point if the release is at sea level). With this assumption a vapor fraction at release ( $x_{rel}$ ) can be estimated by:

$$x_{rel} = x_* - \frac{C_{pv}(T_* - T_{rel})}{H_v} \quad (2-18)$$

If  $x_{rel}$  is between 0 and 1 the estimate of  $T_{rel}$  is valid. Otherwise the value of  $x_{rel}$  is set to one and the release temperature is calculated from:

$$T_{rel} = T_* + \frac{H_v(1 - x_*)}{C_{pv}} \quad (2-19)$$

**Unchoked Flow** - If the flow is not choked, the formation of liquid droplets still needs to be investigated. The method is to assume that the release has no condensation. The temperature at released conditions ( $T_{rel}$ ) can then be estimated. A check can be performed to determine if the release has condensation occurring.

Unchoked Flow (No Condensation) - The emission rate for unchoked flow with no condensation is given by:

$$\dot{m} = C_d A \sqrt{P_c \rho_c \left( \frac{2\gamma}{\gamma+1} \right) \left( \left( \frac{P_a}{P_c} \right)^{\frac{2}{\gamma}} - \left( \frac{P_a}{P_c} \right)^{\frac{\gamma+1}{\gamma}} \right)} \quad (2-20)$$

The release temperature ( $T_{rel}$ ) is given by:

$$T_{rel} = 2 \left[ \frac{T_c}{1 + \sqrt{1 + 4aT_c}} \right] \quad (2-21)$$

where

$$a = \frac{1}{2C_{pv}} \left( \frac{\dot{m}R}{P_a MA} \right)^2 \quad (2-22)$$

This temperature can be used to determine if condensation occurs. If condensation does occur the value of  $T_{rel}$  is invalid. If  $T_{rel}$  is greater than the critical temperature of the chemical, no condensation occurs. If  $T_{rel}$  is less than the critical temperature, the vapor pressure at  $T_{rel}$  needs to be compared to  $P_a$ . If the vapor pressure is greater than  $P_a$  then condensation does not occur. If condensation does occur the unchoked flow with condensation calculation needs to be done.

Unchoked Flow (Condensation) - First, the value of  $T_{rel}$  is needed. In this case  $T_{rel}$  is the equilibrium temperature at the pressure  $P_a$ . The vapor fraction at release ( $x_{rel}$ ) is required. It is calculated from:

$$x_{rel} = 1 + \frac{T_{rel}}{MH_v} \left[ MC_{pv} \ln \left( \frac{T_c}{T_{rel}} \right) - R \ln \left( \frac{P_c}{P_a} \right) \right] \quad (2-23)$$

Given  $T_{rel}$  and  $x_{rel}$  allows an estimate of enthalpy change ( $\Delta H$ ) and density  $\rho_{rel}$  to be made. The estimates are given by:

$$\Delta H = C_{pv}(T_c - T_{rel}) + H_v(1 - x_{rel}) \quad (2-24)$$

and

$$\rho_{rel} = \left[ \frac{x_{rel}}{\rho_v} + \left( \frac{1 - x_{rel}}{\rho_L} \right) \right]^{-1} \quad (2-25)$$

The emission rate is then given by:

$$\dot{m} = A \rho_{rel} \sqrt{1.70 \Delta H} \quad (2-26)$$

### Connecting Pipe

As in the No Connecting Pipe case the first determination is whether the flow is choked or not. This is done in the following manner.

By assuming that the Reynolds number is very large (i.e. the flow is turbulent) the Fanning friction factor can be estimated from:

$$\frac{1}{\sqrt{f}} = 4 \log \left( 3.7 \frac{d}{\varepsilon} \right) \quad (2-27)$$

The Mach velocity in the pipe ( $Ma_1$ ) can be calculated, with an iterative method, from:

$$\frac{\gamma+1}{2} \ln \left( \frac{2Y_1}{(\lambda+1)Ma_1^2} \right) - \left( \frac{1}{Ma_1^2} - 1 \right) + \frac{4\gamma f L}{d} = 0 \quad (2-28)$$

where

$$Y_1 = 1 + \frac{\gamma-1}{2} Ma_1^2 \quad (2-29)$$

The value of  $P_*$  can then be calculated from:

$$P_* = P_c Ma_1 \sqrt{\frac{2Y_1}{\gamma+1}} \quad (2-30)$$

If  $P_*$  is less than  $P_a$  or if it is less than  $P_c$  the flow is unchoked. Otherwise the flow is choked.

**Choked Flow** - If the flow is choked, the formation of liquid droplets needs to be investigated. The temperature at choked conditions ( $T_*$ ) can be estimated from:

$$T_* = T_c \left( \frac{2Y_1}{\gamma+1} \right) \quad (2-31)$$

This temperature can be used to determine if condensation occurs. If condensation does occur the value of  $T_*$  is invalid. If  $T_*$  is greater than the critical temperature of the chemical, no condensation occurs. If  $T_*$  is less than the critical temperature, the vapor pressure at  $T_*$  needs to be compared to  $P_*$ . If the vapor pressure is greater than  $P_*$  then condensation does not occur.

Choked Flow (No Condensation) - The emission rate for choked flow with no condensation is given by:

$$\dot{m} = P_* C_d A \sqrt{\frac{\gamma M}{R T_*}} \quad (2-32)$$

The release temperature ( $T_{rel}$ ) is equal to  $T_*$

Choked Flow (Condensation) - For this case the calculation is identical to the case for No Connecting Pipe except that the emission rate calculation formula is:

$$\dot{m} = A \rho_* \sqrt{1.70 \frac{\Delta H}{1 + \frac{4fL}{d}}} \quad (2-33)$$

**Unchoked Flow** - If the flow is not choked, the formation of liquid droplets still needs to be investigated. The method is to assume that the release has no condensation. The temperature at released conditions ( $T_{rel}$ ) can then be estimated. A check can be performed to determine if the release has condensation occurring.

Unchoked Flow (No Condensation) - The emission rate for unchoked flow with no condensation is solved for by first determining the emission temperature ( $T_{rel}$ ) from the formula (solved iteratively):

$$\frac{\gamma + 1}{\gamma} \ln\left(\frac{P_c T_{rel}}{P_a T_c}\right) - \frac{\gamma - 1}{2\gamma} \left(\frac{P_c^2 T_{rel}^2 - P_a^2 T_c^2}{T_{rel} - T_c}\right) \left(\frac{1}{P_c^2 T_{rel}} - \frac{1}{P_a^2 T_c}\right) + \frac{4fL}{d} = 0 \quad (2-34)$$

The emission rate is then given by:

$$\dot{m} = C_d A \sqrt{\frac{2M}{R} \frac{\gamma}{\gamma - 1} \frac{T_{rel} - T_c}{\left(\frac{T_c}{P_c}\right)^2 - \left(\frac{T_{rel}}{P_a}\right)^2}} \quad (2-35)$$

The release temperature can be used to determine if condensation occurs. If condensation does occur the value of  $T_{rel}$  is invalid. If  $T_{rel}$  is greater than the critical temperature of the chemical, no condensation occurs. If  $T_{rel}$  is less than the critical temperature, the vapor pressure at  $T_{rel}$  needs to be compared to  $P_a$ . If the vapor pressure is greater than  $P_a$  then condensation does not occur. If condensation does occur the unchoked flow with condensation calculation needs to be done.

Unchoked Flow (Condensation) - For this case the calculation is identical to the case for No Connecting Pipe except that the emission rate calculation formula is:

$$\dot{m} = A \rho_* \sqrt{1.70 \frac{\Delta H}{1 + \frac{4fL}{d}}} \quad (2-36)$$

## Boiling Release

The emission rate from this portion of the release is calculated the same as for the depressurization portion of the release except that the emission rate is held constant until all liquid remaining in the container below the hole level has been emitted. The temperature assumed is the given storage temperature and the pressure assumed is that in equilibrium with the storage temperature. Whether the emission is choked/unchoked with or without condensation is the same as described for the depressurization.

### 2.1.2 Connecting Pipe Description

The connecting pipe specified by the user is allowed to have characteristics such as valves, elbows, tees, and connections. The number and types of these characteristics are used to calculate an equivalent pipe length. These valves etc. have the effect of lengthening the pipe. In all calculations where the pipe length  $L$  is used it is assumed that the equivalent pipe length is actually being used. Each valve, elbow, etc. increases the apparent length of the pipe by some factor that is to be multiplied by the diameter of the pipe and added to the actual pipe length. Table 2-1 lists these factors for the pipe characteristics used in CHARM. Another input to describe the connecting pipe that affects the frictional losses of flow is the Relative Roughness Factor. Some representative roughness lengths are given in Table 2-2.

### 2.1.3 Pool Evaporation Release

The evaporation emission from the pool is described in Section 2.2. The pool is allowed to grow in size with time as the liquid emission continues or the chemical spreads.

## 2.2 Pool Dynamics for Container/Surface and Pool/Lagoon Release Descriptions

This section describes the algorithms used to simulate the source term from an evaporating pool. In CHARM a pool may form in a Container/Surface Description release or a pool may be defined with the Pool/Lagoon Description release. In the Container/Surface Description release the pool is allowed to grow in diameter and depth as mass is added to it. In a Pool/Lagoon Description release CHARM assumes that the pool is of a constant diameter with no mass being added as the evaporation occurs. In other words, the Pool/Lagoon Description release assumes that there is no container or mass source for the pool. This also means that no flash calculation (Eq. 2-1) or droplet



suspension is assumed in the Pool/Lagoon Description release. Since the Pool/Lagoon Description assumes there is no flash, it should only be used for releases where no flash occurs, such as for low volatility liquids. Use the Pool/Lagoon Description release with care for high volatility liquids since flashing may actually occur.

### 2.2.1 Pool Growth

A constraint on the pool spreading is a minimum depth that the pool is allowed to be. The theoretical minimum that a pool should form at is the capillary depth ( $h_{cap}$ ). The capillary depth is given by:

$$h_{cap} = \sqrt{\frac{\sigma_L}{g \rho_L}} \quad (2-37)$$

where  $\sigma_L$  = surface tension of the liquid.

For a spreading pool that is being fed by a mass rate ( $\dot{m}_L$ ), the minimum depth ( $h_{fed}$ ) is given by (Webber, 1990, 1991):

$$h_{fed} = \left( \frac{6 v_L \dot{m}_L}{\pi g} \right)^{\frac{1}{4}} \quad (2-38)$$

CHARM uses the maximum of  $h_{cap}$  and  $h_{fed}$  to determine a minimum depth ( $h_{min}$ ). If the pool becomes lower than  $h_{min}$  no pool diameter growth occurs. The rate of pool radius (R) growth is given by:

$$\frac{dR}{dt} = \sqrt{2g \max(0, h - h_{min})} \quad (2-39)$$

where  $h$  = present depth of pool.

For any time step ( $\Delta t$ ) the value of  $h$  is given by:

$$h = h_{old} + \frac{dh}{dt} \Delta t \quad (2-40)$$

where

$$\frac{dh}{dt} = \frac{\dot{m}_L}{A_{pool}} \quad (2-41)$$

where  $A_{pool}$  = pool area.

If the pool gets to the maximum diameter allowed then the rate of change of the pool radius is forced to be zero. This maximum diameter is explicitly defined by the user in the Container/Surface Description release option. In the Pool/Lagoon Description release the maximum diameter is assumed to be the initial diameter and  $\dot{m}_L$  is zero. Therefore in the Pool/Lagoon Description release no pool growth is assumed.

## 2.2.2 Pool Evaporation

There are three processes allowed for adding energy to the pool to allow it to evaporate. These are heat transfer ( $Q_{HT}$ ), mass transfer ( $Q_{MT}$ ), and solar radiation ( $Q_S$ ). The heat transfer is subdivided into heat transfer from conduction with the surface and from convection in the air. As suggested in the SPILLS model (Fleischer, 1980) only the maximum of heat transfer and mass transfer is used to determine the evaporation rate ( $Q_{EVAP}$ ). So  $Q_{EVAP}$  is given by:

$$Q_{EVAP} = \max(Q_{HT}, Q_{MT}) + Q_S \quad (2-42)$$

In the case of the Container/Surface Description release all flash and droplet suspension calculations are carried out in the Container release portion of the code. For the Pool/Lagoon Description release no flash or droplets are assumed.

### Heat Transfer

The equation for the heat transfer emission rate ( $Q_{HT}$ ) is:

$$Q_{HT} = \frac{D_F k_s A (T_a - T_b)}{p \Delta H_v \sqrt{\pi \alpha_s t}} + \frac{k_a Nu_L A}{\Delta H_v L} (T_a - T_b) \quad (2-43)$$

- where  $D_F$  = freezing factor (see below);  
 $k_s$  = thermal conductivity of the soil;  
 $A$  = area of spill;  
 $T_b$  = normal boiling point;  
 $p$  = percolation factor (see below);  
 $\alpha_s$  = thermal diffusivity of the soil;  
 $t$  = time;  
 $k_a$  = thermal conductivity of air; and  
 $Nu_L$  = Nusselt number =  $h L/k_a$   
 where  $h$  = convective heat transfer coefficient

The first term in the heat transfer equation is the conduction term. The second term is that due to convection.

The expression for the freezing factor ( $D_F$ ) is

$$D_F = \frac{T_b}{T_b - T_a} \frac{1}{\text{erf}(\lambda)} \quad (2-44)$$

where  $\lambda$  is solved from the following equation:

$$\frac{1}{\lambda \exp(\lambda^2) - \lambda \exp(\lambda^2) \text{erfc}(\lambda)} + \frac{E_1}{\lambda \chi \exp^2(\lambda \chi) \text{erfc}(\lambda \chi)} - E_2 = 0 \quad (2-45)$$

where

$$\chi = \sqrt{\frac{\alpha_F}{\alpha_{UF}}}$$

$$E_1 = \frac{T_a (\rho c)_{UF}}{T_b (\rho c)_F}$$

$$E_2 = \frac{F \sqrt{p}}{c_F T_b}$$

$\alpha$  = thermal diffusivity;

$\rho$  = density;

$c$  = specific heat;

$F$  = latent heat of freezing water; and subscripts F and UF refer to frozen and unfrozen, respectively.

The expression for the percolation factor ( $p$ ), is:

$$p = \exp\left(\frac{K^2}{4\alpha_D}\right) \text{erfc}\left(\frac{K}{2\sqrt{\alpha_D}}\right) \quad (2-46)$$

$K$  is solved from the following equation:

$$\left(\frac{C_1}{\eta^2} - C_2\right) \eta \exp(\eta^2) (1 - \text{erf}(\eta)) - 1 = 0 \quad (2-47)$$

where

$$\eta = \frac{K}{2\sqrt{\alpha_D}}$$

$$C_1 = \frac{\sqrt{\pi} \rho_L \Delta H_v K' \gamma_L}{2(\rho c)_D (T_a - T_b) \mu_L \alpha_D}$$

$$C_2 = \frac{\sqrt{\pi} \Delta H_v \varepsilon}{(\rho c)_D (T_a - T_b)}$$

$K'$  = modified Darcy's constant;  
 $\gamma_L$  = liquid surface tension;  
 $\mu_L$  = dynamic liquid viscosity;  
 $\varepsilon$  = porosity; and  
 subscripts L and D refer to liquid and dry, respectively.

For laminar flow, the Nusselt number ( $Nu_L$ ) is:

$$Nu_L = 0.664 Pr^{\frac{1}{3}} \sqrt{Re} \quad (2-48)$$

where  $Pr$  = Prandtl number =  $v_{air}/D_{air}$

For turbulent flow, the Nusselt number is

$$Nu_L = 0.037 Pr^{\frac{1}{3}} (Re^{0.8} - 15,200) \quad (2-49)$$

### Mass Transfer

The equation used to calculate the mass transfer emission rate ( $Q_{MT}$ ) is:

$$Q_{MT} = D_{c-a} Sh_L \rho_G \left( \frac{A}{L} \right) \quad (2-50)$$

where  $D_{c-a}$  = molecular diffusion coefficient between the chemical and air;  
 and

$Sh_L$  = Sherwood number =  $k_c L / D_{air}$

The SPILLS model has the following assumptions:

$$Nu_L \cong Sh_L \text{ and } Pr \cong Sc = \frac{v_{air}}{D_{air}}$$

This assumption allows the use of equations of the same form as those used for the Nusselt Number. For laminar flow, the Sherwood Number is calculated as follows:

$$Sh_L = 0.664 Sc^{\frac{1}{3}} \sqrt{Re} \quad (2-51)$$

For turbulent flow, the equation for the Sherwood number is:

$$Sh_L = 0.037 Sc^{\frac{1}{3}} (Re^{0.8} - 15,200) \quad (2-52)$$

## Solar Radiation

The equation for the solar radiation transfer emission rate ( $Q_s$ ) is:

$$Q_s = f_s S_{\text{rad}} A \quad (2-53)$$

where  $S_{\text{rad}}$  = solar radiation (from user); and  
 $f_s$  = efficiency that the solar radiation is used in evaporation (from user).

### 2.2.3 Pool and Surface Temperature

The temperature of the surface beneath the pool is calculated using the conduction term of the heat transfer ( $Q_{HT}$ ) calculation. The conduction term determines an energy transfer rate (Joules/m<sup>2</sup> s) when multiplied by the chemical's heat of evaporation,  $\Delta H_v$ . In the conduction calculation, the surface temperature used in the calculation is the initial surface temperature, assumed to be the driving temperature away from the pool, and the current pool temperature.

The rate of change of energy ( $dE/dt$ ) across the liquid/surface interface is given as:

$$\frac{dE}{dt} = Q_{HT-cond} \Delta H_v A \quad (2-54)$$

The rate of change of temperature ( $dT_{\text{liq}}/dt$ ) for the liquid would then be:

$$\frac{dT_{\text{liq}}}{dt} = \frac{dE}{dt} \frac{1}{m_{\text{pool}} C_{p-\text{liq}}} \quad (2-55)$$

where  $m_{\text{pool}}$  = mass in pool; and  
 $C_{p-\text{liq}}$  = heat capacity of the liquid in the pool.

The rate of change of the temperature ( $dT_{\text{surf}}/dt$ ) directly beneath the pool is calculated by equating the energy flow across the interface to the temperature change divided by the thermal diffusivity of each side of the interface. This leads to:

$$\frac{dT_{\text{surf}}}{dt} = \frac{dT_{\text{liq}}}{dt} \frac{\kappa_{\text{surf}}}{\kappa_{\text{liq}}} \quad (2-56)$$

where  $\kappa_{\text{surf}}$  = thermal diffusivity of the surface; and  
 $\kappa_{\text{liq}}$  = thermal diffusivity of the liquid in the pool.

Thermal diffusivity is calculated using:

$$\kappa = \frac{K}{\rho C_p} \quad (2-57)$$

where K = thermal conductivity of the material;  
ρ = density of the material; and  
C<sub>p</sub> = heat capacity of the material.

These values are provided as part of the surface description. The thermal conductivity of the liquid is not provided as part of the database and is estimated using a formulation from Latini and Pacetti (1977):

$$K = \frac{A(1-T_r)^{0.38}}{T_r^{1/6}} \quad (2-58)$$

where K = thermal conductivity of the material (W/m K);  
T<sub>r</sub> = reduced temperature (=T/T<sub>c</sub>);  
T = temperature of liquid (K);  
T<sub>c</sub> = critical temperature of liquid (K); and

$$A = \frac{A^* T_b^\alpha}{M^\beta T_c^\gamma} \quad (2-59)$$

where A\* = 0.00350;  
α = 1.2;  
β = 0.5;  
γ = 0.167;  
T<sub>b</sub> = boiling point of liquid (K); and  
M = molecular weight of liquid (g/mole).

### **2.3 User-Specified Release**

The module for a user-specified release requires the user to supply most of the parameters needed for the Transport/Dispersion model. The required user input for this module includes:

- Exit temperature;
- Source diameter;
- Puff depth (should be calculated by CHARM, leave blank);
- Release direction of movement;
- Horizontal release speed;
- Vertical release speed;

- Droplet mass fraction;
- Molar water vapor fraction; and
- Molar air fraction.

The user must also specify whether the release is continuous or instantaneous. Continuous releases have emission rates that can be described as constant, linearly decreasing, exponentially decreasing, or some user-defined schedule. The module does not modify the input but performs the calculations described in the following paragraphs.

CHARM can calculate one of three other variables for the user: emission rate, molar air fraction, or exit velocity.

The volume of material being emitted per unit time ( $V_T$ ) is calculated by the following equation, which is a restatement of the Perfect Gas Law.

$$V_T = \frac{E R T_e}{M P_a} \quad (2-60)$$

where E = emission rate (mass/time);  
M = molecular weight of the vapor;  
R = universal gas constant;  
 $P_a$  = atmospheric pressure; and  
 $T_e$  = exit temperature.

The value of  $V_T$  can also be stated as

$$V_T = \frac{\pi}{4} D_h^2 v_e FG \quad (2-61)$$

where  $D_h$  = diameter of hole;  
 $v_e$  = exit velocity; and  
FG = molar fraction of emitted material.

The sum of the fractional compounds in a release must be equal to one; the calculation for the molar fraction of emitted material (FG) is expressed as follows.

$$FG = 1 - FW - FA \quad (2-62)$$

where FW = molar fraction of water vapo; and  
FA = molar fraction of air.

Equating the two formulas for  $V_T$  and using the relationships between FG, FW, and FA leads to an equation where, one of  $v_e$ , E, or FA can be calculated, if two of the three variables are known and all other input (such as the hole diameter) is provided. CHARM

considers only turbulent mixing as a source of FA. Therefore, if the user enters an exit velocity of zero, FA is assumed to be zero.

The user-specified release can be defined as continuous or instantaneous. If the release is defined as continuous, the user must enter the length of time in which the emission took place and whether the emission rate is constant, decreasing linearly, decreasing exponentially, or user-defined. CHARM estimates the emissions as a function of time (t).

For constant emissions, CHARM uses the specified rate throughout the release. For linearly decreasing emissions, CHARM calculates the emission rate as follows:

$$E = E_0 \left( 1 - \frac{t}{t_e} \right) \quad (2-63)$$

where E = emission rate (mass/time);  
 $E_0$  = initial emission rate; and  
 $t_e$  = total time of emission.

The amount of mass emitted (GM) between times  $t_1$  and  $t_2$  (where  $t_2 = t_1 + \Delta t$ ) is calculated as follows:

$$GM = E_0 \Delta t \left( 1 - \frac{(t_1 + t_2)}{2t_e} \right) \quad (2-64)$$

For exponentially decreasing emissions, the total emission time is assumed to be the time it takes for the emission rate to reach one percent of its original value. The time it takes for the emission rate to become one-half of its original value ( $t_{1/2}$ ) is calculated as follows:

$$t_{1/2} = \frac{\ln(1/2)}{\ln(0.01)} t_e \quad (2-65)$$

Therefore, the rate for an exponentially decreasing emission has the following form:

$$E = E_0 \exp\left(-\frac{t}{\tau}\right) \quad (2-66)$$

where

$$\tau = \frac{t_{1/2}}{\ln(2)}$$



The amount of mass emitted between times  $t_1$  and  $t_2$  is then calculated with the following equation:

$$GM = E_0 \tau \left( 1 - \exp\left(\frac{\Delta t}{t}\right) \right) \exp\left(\frac{-t_1}{\tau}\right) \quad (2-67)$$

For a user-defined schedule, the emission rate between any two times is assumed to be linear.

The mass of each puff is calculated as the mass emitted during a time  $\Delta t$ . The calculation for the number of puffs and time step  $\Delta t$  are described in Section 2.4.

## **2.4 Final Puff Calculations**

To determine the number of puffs to use and the time step between puffs ( $\Delta t$ ), CHARM makes a series of assumptions. To simulate dispersion with a puff model in the original method, a sufficient number of puffs are required to be able to create a smooth distribution of concentrations. In other words, when the contribution of each puff to the concentration at all the locations on a grid is plotted, individual puffs should not be recognizable. In such a case, a large number of puffs may be required, which calls for more computer storage and calculation time. To alleviate the problem CHARM uses significant puffs and allows a maximum of 10 such significant puffs.

Significant puffs are so named because the assumption is that no major changes occur between any two puffs; if changes are occurring they are monotonic. The puffs actually represent cross sections of a plume at varying locations. To bring back into existence the ignored puffs, all the puff parameters are interpolated to estimate what the intervening puffs looked like. The interpolation mechanism is discussed in Section 3.

CHARM calculates the Pasquill-Gifford horizontal dispersion coefficient ( $\sigma_y$ ) at the distance reached downwind (at the specified wind speed) at the time of the release and over a time interval. The time interval is the emission time or 15 minutes, whichever is less. CHARM assumes  $2.5 \sigma_y$  between each puff at the end of the time period. This value allows enough spacing between puffs to create a smooth distribution from overlapping puffs at the end of the release. CHARM treats the puffs as plume cross-sections. The interpolation performed by the model creates a continuum of puffs, which is necessary because the puff spacing near the beginning of the release alone is insufficient to fully resolve the plume. Since the initial puff sizes are smaller, the puff spacing near the beginning of the release has to be less than the spacing at the end.

The distance between the puffs is divided by the wind speed at release time to determine a time spacing between puffs. This time spacing is then divided into the total time of emission to determine the number of puffs required for the simulation. The model currently supports a maximum of 175 puffs. If more than 175 puffs are required,

CHARM selects 175 puffs equally spaced in time throughout each section of the release (liquid release and depressurizations) and treats them as the significant puffs.

The time spacing between significant puffs cannot be more than five minutes. Beyond that separation, the interpolation mechanism begins to fail. The spacing requirement leads to a maximum source release time for simulation. The maximum release time is fourteen and one half hours (175 puffs separated by five minutes each). If the time spacing is less than thirty seconds, a single puff is assumed. The maximum release time limit of fourteen and one half hours is not as restrictive as it may initially seem; one of the following normally occurs before the limit is reached:

- The release is finished;
- Steady state is reached for a constant release; or
- The major part of the release occurs at the beginning;

Since an interpolation mechanism is used to generate a continuum of released puffs from a small number of puffs, the number of simulated puffs is one more than what it should be. For interpolation to function properly, it must have available anchor points at either end of the period being interpolated. Because of this, CHARM adds an extra puff at the end of the release to provide a final anchor point for interpolation.

Each puff is emitted at the beginning of an interval. The first puff begins emission at time zero, the very beginning of the release. For example, assume there is a 15-minute release and the time interval between each puff is 5 minutes. The first puff begins to be emitted at time 0. The second puff begins emission at time 5 minutes. All puffs between time 0 and 5 minutes can be interpolated because there are anchor points at each end of the interval. The third puff begins emission at time 10 minutes. The second and third puffs provide anchors for the interval 5 to 10 minutes. At minute 15 the release is over and a puff should not begin emission. However, if no puff begins emission at 15 minutes, then all puffs between minutes 10 and 15 will be lost. The extra puff provides a little more exposure time than would be actually seen. The most obvious effect is that a little more mass is reported than was truly emitted.

The horizontal dispersion coefficient ( $\sigma_y$ ) used in determining the puff spacing has another purpose in CHARM. It is assumed that the concentration of each puff follows a Gaussian distribution. Gaussian models seem to under-predict in the far field. CHARM uses  $\sigma_y$  to determine the point beyond which the rate of dispersion decreases. This is discussed further in Section 3.5 under post-processing.

After the number of puffs to be calculated is determined, the parameters required by the Transport/Dispersion portion of the model are derived from the output of the Source Term module. Most output parameters of the source term module are provided in the proper form. The actual masses of air, water vapor, and material droplets must be calculated from the molar fractions returned from the modules.

For all modules, the energy contained in each puff ( $E_p$ ) is calculated with the following formula:

$$E_p = T_p (m_G C_{vG} + m_A C_{vA} + m_W C_{vW}) \quad (2-68)$$

where  $T_p$  = temperature of the puff;  
 $m$  = amount of mass in puff;  
 $C_v$  = heat capacity at constant volume; and  
subscripts G, A, and W, respectively, indicate emitted gas, air, and water.

**Table 2-1. Equivalent Pipe Length Factors (Turbulent Flow, Multiply By Pipe Diameter For Equivalent Length)**

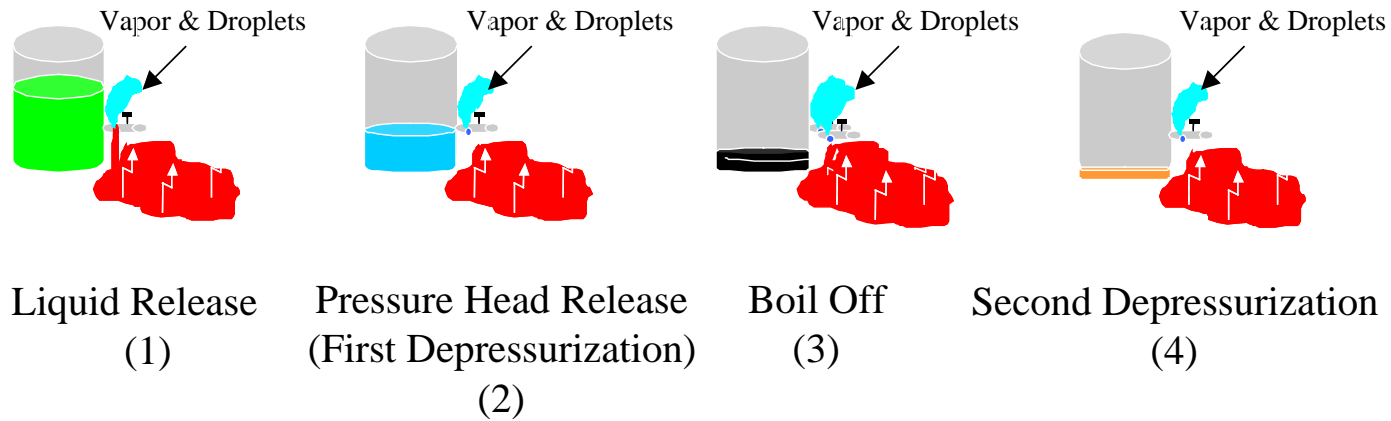
Globe Valves (100% open)	300
Gate Valves (100% open)	7
Gate Valves (75% open)	40
Gate Valves (50% open)	200
Gate Valves (25% open)	900
90° Elbows	30
45° Elbows	15
Tee Elbows-Entering Stem	90
Tee Elbows-Entering Side	60
Tee Straight Throughs	20
Flush Pipe-Vessel Connections	16
Borda Pipe-Vessel Connections	30
Round Pipe-Vessel Connections	0

**Table 2-2. Example Roughness Lengths (mm) For Clean Pipes**

Riveted Steel	0.9-9.1
Concrete	0.3-3
Cast iron	0.26
Galvanized iron	0.15
Commercial steel	0.046
Wrought iron	0.046
Drawn tubing	0.0015
Glass	0
Plastic	0

Source: Perry's Chemical Engineer's Handbook, 7<sup>th</sup> Edition, 1997

# Container/Surface Description Release



**Figure 2-1. Schematic of Release Phases for Container/Release Description.**

# Phases of Emission

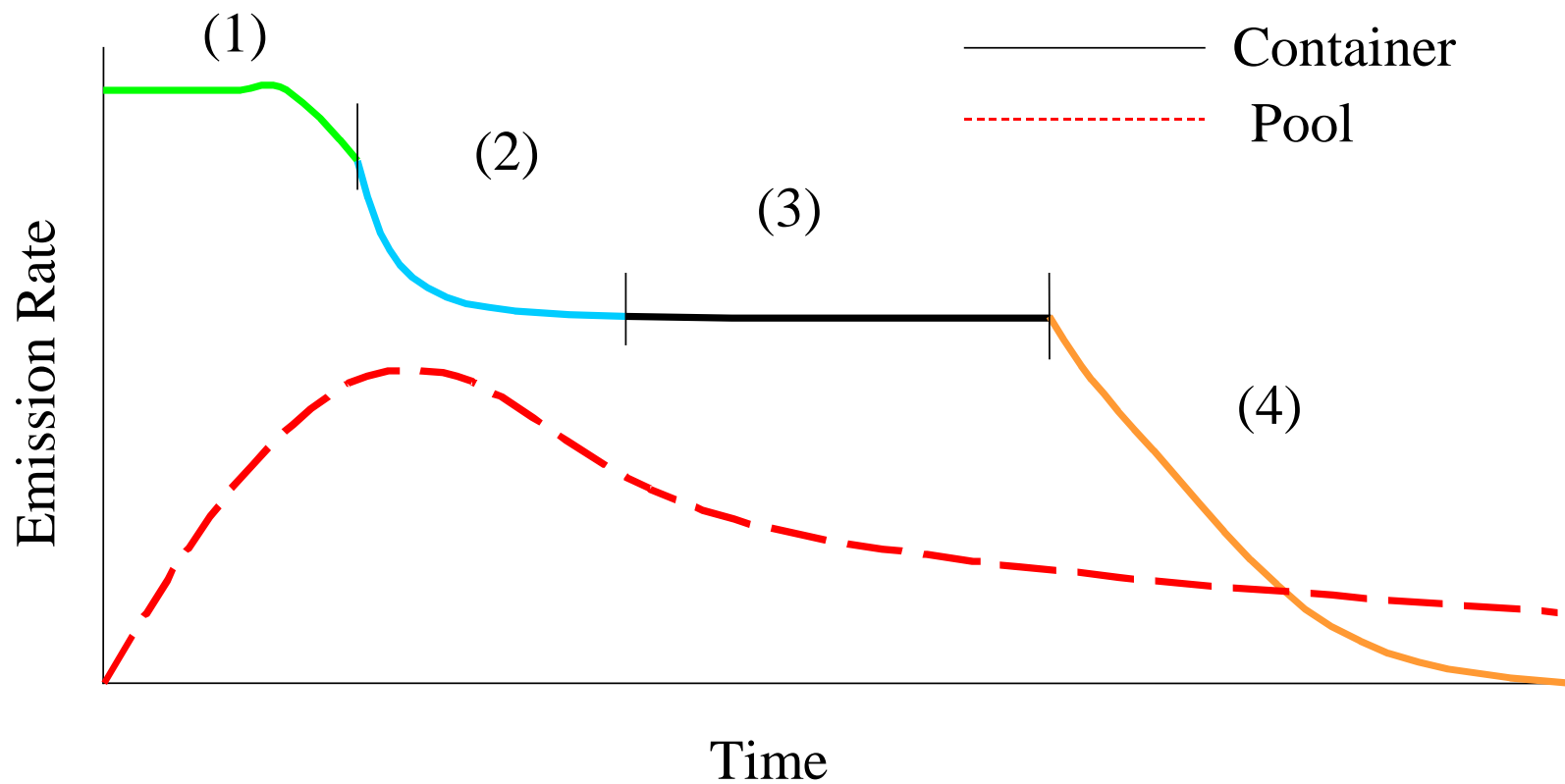


Figure 2-2. Example Emission Rate Over Time For Container Release With Pool Formation.

# Liquid Release Fates

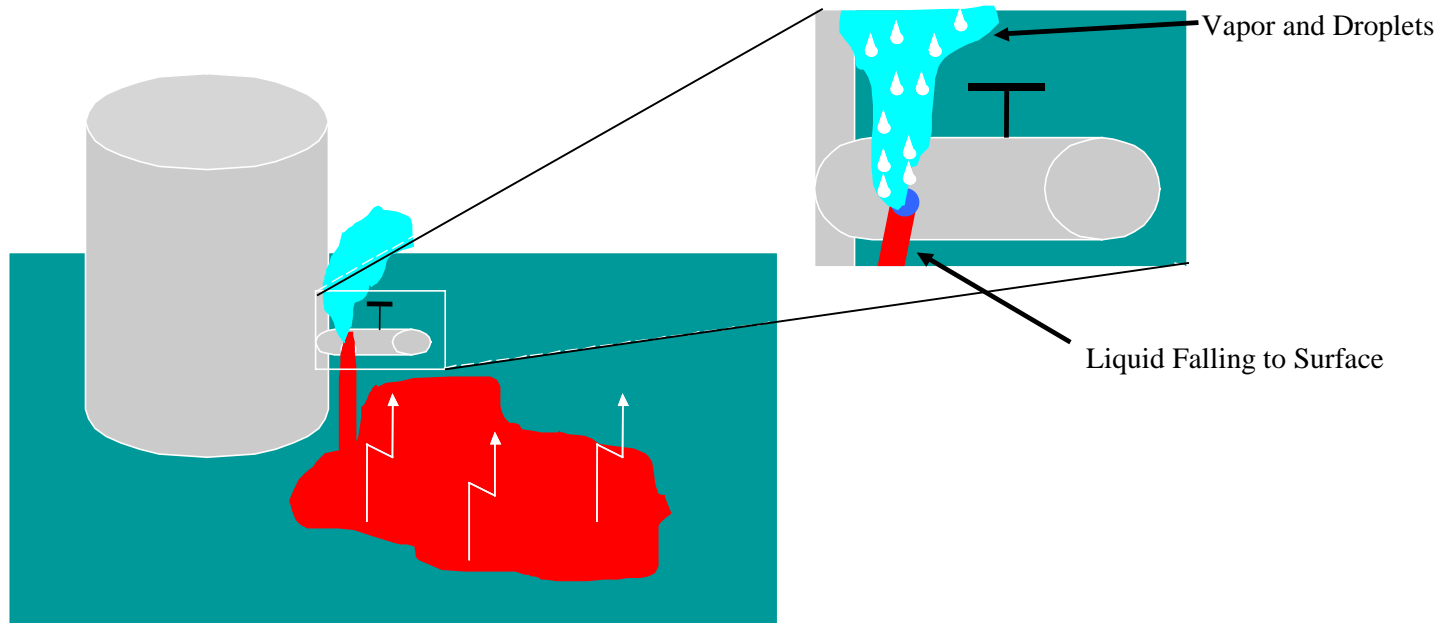


Figure 2-3. Closeup of Liquid Release Phase.



### 3.0 TRANSPORT/DISPERSION ALGORITHMS

The CHARM software models releases that are denser-than-air, neutrally buoyant, or positively buoyant. The model automatically switches between these cases as needed. CHARM uses the puff plume rise model developed by Sheih to describe buoyant puffs and puffs that are denser-than-air but not in contact with the ground. Aloft puffs are assumed to be ellipsoidal in shape. CHARM uses Eidsvik's algorithm to describe puffs that are denser-than-air and in contact with the ground. Denser-than-air puffs and puffs on the ground are assumed to be pancake-shaped. Once any puff contacts the ground with a downward velocity that is greater than or equal to zero, it is assumed that the puff remains in contact with the ground for the rest of the simulation. If the initial part of a release is a jet, CHARM uses the Ooms algorithm (1972), as modified by Emerson (1986). The Sheih, Eidsvik, and Ooms/Emerson algorithms are used in the Transport/Dispersion module of CHARM, which is described in this Section.

The Transport/Dispersion module of CHARM is a combination lookup table and integrator, which calculates up to a user-specified time. If results for the requested time have not been calculated, CHARM performs the Transport/Dispersion calculations and stores them for access by the user interface. If results for the requested time have already been calculated, the module returns to the CHARM user interface. If winds have been added or modified (in the Met Data portion of the input window) since the last calculation, CHARM begins calculations with the values for the last unchanged wind.

When the user requests a plume display and specifies a release time, the Transport/Dispersion calculations numerically integrate the parameters for each puff (from the Source Term calculations) until the specified time is reached or surpassed. Each puff is integrated using its own CHARM-calculated time step. The initial time step is thirty seconds or a characteristic time scale from derivative considerations, whichever is less. A minimum time step of 0.0036 seconds is allowed.

CHARM handles buoyant or neutral releases as well as denser-than-air releases. CHARM has algorithms for three types of puffs that compute the following:

- Time history of aloft puffs and puffs not denser-than-air;
- Time history of a denser-than-air puff in contact with the ground; and
- Jet emissions.

This section describes the basic model, the algorithms for aloft puffs, denser-than-air puffs, and jet emissions. The numerical integration technique used and some of the post-processing information are also provided.

### 3.1 Aloft Puffs and Puffs Not Denser-than-air

A puff is assumed to be denser-than-air if the density of the puff is greater than the density of the ambient air by one percent or more. The shape of an aloft puff is assumed to be ellipsoidal. A set of equations simulates the behavior of a dense or non-dense puff when it is aloft or not denser-than-air but in contact with the ground. The basic concept for this CHARM model is adapted from Sheih (1978). Formulas for various puff properties are derived from thermodynamics, mass, momentum, and energy conservation laws. The following assumptions are made:

- Perfect gas behavior for both the puff and the ambient atmosphere;
- Uniform properties within the puff (temperature, density, etc.);
- Well-mixed gas and air (i.e., the puff or plume does not separate);
- Hydrostatic ambient pressure profile;
- Equal puff pressure and ambient pressure;
- No temperature dependence of heat capacity with latent heat of evaporation/condensation;
- No heat exchange between the puff and the surrounding environment (except by turbulent entrainment);
- Instantaneous mixing throughout the puff;
- Boussinesq approximation (i.e., the effect of density variations on puff inertia are ignored);
- No variation of dew point temperature or humidity with height; and
- Condensed water vapor instantaneously “rained out” of the puff.

#### 3.1.1 Conservation Principles of Gas, Air, and Water

The conservation principles from which the CHARM equations are derived include the conservation of emitted gas in a puff and the conservation of air and water vapor in a puff.

The principle for the conservation of emitted gas in a puff is

$$\frac{dm_G}{dt} = 0 \quad (3-1)$$

where  $m_G$  = mass of emitted gas in puff.

The principle for the conservation of air in a puff is

$$\frac{dm_A}{dt} = M_e(1 - X) \quad (3-2)$$

where  $m_A$  = mass of air in puff;

- $M_e$  = turbulent mass entrainment rate (see Section 3.1.2 for calculation); and  
 $X$  = ambient water vapor mass fraction (see Section 3.1.3 for calculation).

The principle for the conservation of water vapor in a puff is

$$\frac{dm_w}{dt} = M_e X F(T_p - T_{dp}) \quad (3-3)$$

- where  $m_w$  = mass of water vapor in puff;  
 $F(x)$  = Heaviside unit indicator function;  
= 1 if  $x \geq 0$ ; or  
= 0 if  $x < 0$   
 $T_p$  = puff temperature (See Section 3.1.2 for calculation); and  
 $T_{dp}$  = dewpoint temperature, which is solved using the Newton-Raphson interactive technique as follows:  
=  $\frac{P_a F_m}{P_s}$  (see Section 3.1.3 for calculations of  $P_a F_m$ , and  $P_s$ ).

### 3.1.2 Calculation of the Rate of Entrainment of Turbulent Mass

The value for the rate of entrainment of turbulent mass ( $M_e$ ) is calculated as follows:

$$M_e = \rho_a \sqrt{\alpha^2 (\Delta u^2 + \Delta v^2) A_h^2 + \beta^2 \Delta w^2 A_v^2} \quad (3-4)$$

- where  $\rho_a$  = ambient air density;  
=  $\frac{P_a}{R T_a} [(1 - X)m_A + m_w]$

- where  $P_a$  = atmospheric pressure;  
 $R$  = universal gas constant;  
 $T_a$  = ambient temperature; and  
 $X$  = water vapor mass fraction (see calculation below.).

- $\alpha, \beta$  = entrainment coefficients;  
 $\Delta u$  = difference in X-direction speed between puff and ambient air;  
 $\Delta v$  = difference in Y-direction speed between puff and ambient air;  
 $\Delta w$  = difference in Z-direction speed between puff and ambient air;  
 $A_h$  = puff side surface area exposed to ambient air;  
=  $\pi r h_p$  if puff is aloft; or  
=  $2 \pi r h_p$  if puff is on ground.  
 $h_p$  = depth of puff;

$A_v$  = puff top surface area exposed to ambient air;  
 $= \pi r^2$   
 $r$  = radius of puff  
 $= \sqrt{\frac{3V}{4\pi h_p}}$  if puff is aloft; or  
 $= \sqrt{\frac{V}{\pi h_p}}$  if puff is on ground.  
 $V$  = volume of puff  
 $= \frac{R T_p}{P_a} \left( \frac{m_G}{M_G} + \frac{m_A}{M_A} + \frac{m_W}{M_W} \right)$   
 $M$  = molecular weight of material in puff;  
 $m$  = mass of material in puff;  
subscripts G, A, W are gas, air, and water;  
 $T_p$  = temperature of puff;  
 $= \frac{E_p}{C_{vG} m_G + C_{vA} m_A + C_{vW} m_W}$   
 $C_v$  = specific heat at constant volume; and  
 $E_p$  = energy of puff (See Section 2.4).

### 3.1.3 Calculation of the Water Vapor Mass Fraction

The water vapor mass fraction (X) is calculated using a technique based on that of McRae (1980), as shown by the following equation:

$$X = \left( \frac{RH}{100} \right) \left( \frac{P_s}{P_a} \right) \left( \frac{M_W}{M_A} \right) \quad (3-5)$$

where RH = relative humidity;  
 $P_s$  = saturation pressure;  
 $= P_a \exp(13.385t - 1.9760t^2 - 0.6445t^3 - 0.1299t^4)$   
 $t = 1 - \frac{373.15}{T_a}$   
 $P_a$  = atmospheric pressure;  
 $M_W$  = molecular weight of water vapor; and  
 $M_A$  = molecular weight of air.

The term  $\left( \frac{RH}{100} \right) \left( \frac{P_s}{P_a} \right)$  is also called the mass fraction of water vapor ( $F_m$ ). Therefore, the value of X can also be written as follows:

$$X = F_m \left( \frac{M_w}{M_A} \right) \quad (3-6)$$

### 3.1.4 Principle for the Conservation of Vertical Momentum

The principle for the conservation of vertical momentum can be stated as follows:

$$\frac{dm_t w}{dt} = (V \rho_a - m_t)g \quad (3-7)$$

where  $w$  = vertical puff speed;  
 $V$  = volume of puff;  
 $\rho_a$  = density of ambient air;  
 $m_t$  = total mass in puff;  
=  $m_G + m_A + m_W$ ; and  
 $g$  = acceleration due to gravity.

### 3.1.5 Principle for the Conservation of Horizontal Momentum

The principle for the conservation of horizontal momentum can be stated with the following equations:

$$\begin{aligned} \frac{d}{dt} m_t u_p &= M_e u_a \\ \frac{d}{dt} m_t v_p &= M_e v_a \end{aligned} \quad (3-8)$$

where  $m_t$  = total mass in puff;  
=  $m_G + m_A + m_W$ ;  
 $u_p$  = speed of puff in X direction;  
 $u_a$  = speed of ambient air in X direction;  
 $v_p$  = speed of puff in Y direction;  
 $v_a$  = speed of ambient air in Y direction; and  
 $M_e$  = turbulent mass entrainment rate.

### 3.1.6 Rate of Puff Energy Change Over Time

The First Law of Thermodynamics states

$$\frac{dE_p}{dt} = M_e T_a [(1-X) C_{vA} + X C_{vW}] + H_{vW} X M_e F(T_{dp} - T_p) - g w_p \left( \frac{C_{vG}}{C_{pG}} m_G + \frac{C_{vA}}{C_{pA}} m_A + \frac{C_{vW}}{C_{pW}} m_W \right) \quad (3-9)$$

where  $E_p$  = energy of the puff (see Section 2.5 for calculation);  
 $M_e$  = rate of entrainment of turbulent mass;  
 $T_a$  = temperature of ambient air;  
 $X$  = water vapor mass fraction;  
 $C_v$  = specific heat at constant volume;  
 $H_v$  = latent heat of evaporation;  
 $F$  = Heaviside unit indicator function;  
 $T_{dp}$  = dewpoint temperature;  
 $T_p$  = temperature of puff;  
 $g$  = gravitational acceleration;  
 $w_p$  = vertical speed of puff;  
 $C_p$  = heat capacity of puff at constant pressure;  
 $m$  = mass in puff; and  
subscripts G, A, and W are gas, air, and water, respectively.

The first two terms on the right side of the equation represent internal energy entrained from the ambient air as sensible and latent heat, respectively. The third term represents energy losses due to the adiabatic expansion of the puff.

If droplets are present in the puff, the rate of energy change is represented as follows:

$$\frac{dE_p}{dt} = T_a \left[ C_{vA} \frac{dm_A}{dt} + C_{vW} \frac{dm_W}{dt} \right] \quad (3-10)$$

This represents the first term in the previous energy equation. All latent heat entering the puff is used to evaporate the droplets, which in turn releases enough heat to counterbalance the adiabatic expansion term. The temperature of the puff remains at the boiling point and the process continues until all the droplets have evaporated.

### 3.1.7 Calculation of Air Entrainment to Allow Droplet Evaporation

The amount of air that must be entrained to allow total evaporation of the droplets ( $m_{crit}$ ) can be determined by equating the latent heat of evaporation contained in the droplets to the heat that must be entrained. The calculation is

$$M_G F_d H_{vG} = m_{crit} [C_{pA} (T_a - T_p) + H_{vW} X] \quad (3-11)$$

where  $M_G$  = molecular weight of gas;  
 $F_d$  = mass fraction of droplets;  
 $H_{vG}$  = latent heat of evaporation of emitted gas; and  
 $m_{crit}$  = mass required to be entrained.

Therefore, the amount of air that must be entrained to allow total evaporation of the droplets is

$$m_{crit} = \frac{M_G F_d H_{vG}}{C_{pA}(T_a - T_p) + H_{vW} X} \quad (3-12)$$

### 3.1.8 Calculation of Acceleration of Puff

The calculation of the acceleration of the puff results from expanding the vertical momentum equation (Section 3.1.4) and using the conservation of mass calculation:

$$\frac{dw_p}{dt} = \left( \frac{V \rho_a}{m_t} - 1 \right) g - \left( \frac{M_e w_p}{m_t} \right) \quad (3-13)$$

The first term on the right side of the equation represents the buoyant acceleration of the puff. The second term represents deceleration of the puff due to turbulent drag forces. As the density of the puff  $\left( \frac{m_t}{V} \right)$  approaches the density of ambient air ( $\rho_a$ ), the buoyant acceleration of the puff  $\left( \frac{dw_p}{dt} \right)$  approaches zero. As  $w_p$  approaches zero, the equation may lead to an oscillation in the vertical. As the puff moves further downwind, the oscillation dampens.

### 3.1.9 Calculation of Speed of Puff

The speed of the puff can be calculated using the horizontal momentum equation

$$\frac{du_p}{dt} = \frac{M_e}{m_t} (u_a - u_p) \quad (3-14)$$

and the vertical momentum equation

$$\frac{dv_p}{dt} = \frac{M_e}{m_t} (v_a - v_p) \quad (3-15)$$

### 3.1.10 Calculation of Atmospheric Temperature and Pressure

The ambient atmospheric temperature ( $T_a$ ) at the puff location is determined by the following equation:

$$\frac{dT_a}{dt} = \Gamma w_p \quad (3-16)$$

where  $\Gamma$  = temperature lapse rate; and  
 $w_p$  = vertical speed of puff.

The atmospheric pressure ( $P_a$ ) at the puff location is determined by the following calculation.

$$\frac{dP_a}{dt} = -w_p \rho_a g \quad (3-17)$$

where  $\rho_a$  = density of ambient air; and  
 $g$  = gravitational acceleration.

CHARM determines the lapse rate ( $G$ ) from the stability class.

Stability Class	Lapse Rate (K/m)
A	-0.019
B	-0.017
C	-0.015
D	-0.005
E	0.015
F	0.025

### 3.1.11 Calculation of the Puff Location

The calculation of the puff location involves using the following equations for the altitude ( $Z$ ) and horizontal distances ( $X$  and  $Y$ ) of a puff from the source.

$$\frac{dz}{dt} = w_p = \text{vertical speed of puff}; \quad (3-18)$$

$$\frac{dx}{dt} = u_p = \text{speed of puff in X direction; and} \quad (3-19)$$



$$\frac{dy}{dt} = v_p = \text{speed of puff in Y direction.} \quad (3-20)$$

### 3.1.12 Summary Equations

All of the equations in Section 3.1 lead to the following summary equations that CHARM solves by a technique described in Section 3.4.

$$\frac{dx}{dt} = u_p \quad (3-21)$$

$$\frac{dy}{dt} = v_p \quad (3-22)$$

$$\frac{dz}{dt} = w_p \quad (3-23)$$

$$\frac{dm_A}{dt} = M_e (1 - X) \quad (3-24)$$

$$\frac{dm_w}{dt} = M_e X F(T_a - T_{dp}) \quad (3-25)$$

$$\frac{du_p}{dt} = \frac{M_e}{m_t} (u_a - u_p) \quad (3-26)$$

$$\frac{dv_p}{dt} = \frac{M_e}{m_t} (v_a - v_p) \quad (3-27)$$

$$\frac{dw_p}{dt} = \left( \frac{V \rho_a}{m_t} - 1 \right) g - \left( \frac{M_e w_p}{m_t} \right) \quad (3-28)$$

$$\frac{du_a}{dt} = \text{linearly interpolated from the user-supplied wind data;} \quad (3-29)$$

$$\frac{dv_a}{dt} = \text{linearly interpolated from the user-supplied wind data;} \quad (3-30)$$

$$\frac{dT_a}{dt} = \Gamma w_p \quad (3-31)$$

$$\frac{dP_a}{dt} = -w_p \rho_a g \quad (3-32)$$

$$\frac{d(m_A + m_W)}{dt} = M_e \quad (3-33)$$

$$\frac{dE_p}{dt} = M_e T_a [(1-X) C_{vA} + X C_{vW}] + K \left[ H_{vW} X M_e F(T_{dp} - T_p) - g w_p \left( \frac{C_{vG}}{C_{pG}} m_G + \frac{C_{vA}}{C_{pA}} m_A + \frac{C_{vW}}{C_{pW}} m_W \right) \right] \quad (3-34)$$

where  $K = 0$  if  $(m_A + m_W) < m_{crit}$ ; or  
 $K = 1$  if  $(m_A + m_W) \geq m_{crit}$

### 3.1.13 Calculations for the Puff Dimensions

The dimensions of a puff are determined by first calculating the volume of the puff (V), as shown previously in Section 3.1.2.

Next, the height of the puff (hg) is estimated as follows:

$$h_p = 2.14 \sigma_z \quad (3-35)$$

where  $\sigma_z$  = the Pasquill-Gifford vertical dispersion parameter as defined in the Industrial Source Code (ISC) model of EPA (Bowers, et al, 1979).

However,  $\sigma_z$  is not calculated by simply looking up the curves for a specific distance. Rather, the value of  $\sigma_z$  is calculated using its value at the beginning of a time step and

assuming it changes according to  $\frac{1}{\sigma_z} \frac{d\sigma_z}{dx}$ . The Pasquill-Gifford curves are used to

determine the derivative. While the Sheih algorithm is invoked, a virtual distance is used in calculating the  $\sigma_z$  for each puff. The virtual distance is calculated using the  $\sigma_z$  of a puff when the Sheih algorithm is first entered. The Sheih algorithm may not be invoked until after the Eidsvik or Ooms algorithms have already been used. The conditions upon leaving one algorithm are used as the initialization point for the following algorithm.

The value of 2.14 is used because at a distance of  $2.14 \sigma_z$  from a puff, the concentration is 10 percent of the maximum value at the puff's center.

Then the radius of the puff ( $r$ ) is calculated as follows:

$$r = \sqrt{\frac{3V}{4\pi h_p}} \quad (3-36)$$

where  $V$  = volume of puff; and  
 $h_p$  = depth of puff.

### 3.2 Denser-Than-Air Puffs

A puff is assumed to be denser-than-air if its density is more than one percent greater than the ambient air density. A puff in contact with the ground is assumed to be pancake-shaped. The calculations for puffs that are denser-than-air are based on the work of Eidsvik (1980). The dispersion due to gravitation in a denser-than-air puff is not demonstrated until the puff is in contact with the ground. Since the puff is on the ground, there are no vertically varying terms; therefore, fewer equations have to be explicitly solved. Otherwise, the basic principles used are the same as those described previously for an aloft puff.

#### 3.2.1 Calculation of the Rate of Entrainment of Turbulent Mass

The turbulent mass entrainment rate ( $M_e$ ) is calculated as follows:

$$M_e = \rho_a \pi r^2 w_e^* \quad (3-37)$$

where  $\rho_a$  = density of ambient air;  
 $r$  = radius of the puff;  
 $w_e^*$  = vertical entrainment speed  
 $= 2 \frac{h_p}{r} u_e + w_e$   
 $u_e$  = horizontal entrainment speed (see Section 3.2.2 for calculation);  
 and  
 $w_e$  = vertical entrainment speed (see Section 3.2.3 for calculation).

#### 3.2.2 Calculation of the Horizontal Entrainment Speed

The rate of change of the radius of the puff for a frictionless heavy gas flow has the following calculation.

$$\frac{dr}{dt} = U_g = \sqrt{\frac{2 g h_p (\rho_G - \rho_a)}{\rho_G}} \quad (3-38)$$

where  $U_g$  = speed of the leading edge of puff due to gravitational spreading;  
 $g$  = gravitational acceleration;  
 $h_p$  = depth of puff;  
 $\rho_G$  = density of emitted material; and  
 $\rho_a$  = density of ambient air.

Eidsvik relates the horizontal entrainment speed ( $u_e$ ) to the speed of the leading edge of the puff ( $U_g$ ) from experimental data as

$$u_e = \frac{0.8 U_g^2}{U_{g0}} \quad (3-39)$$

where  $U_{g0}$  = the initial value of  $\frac{dr}{dt}$ .

### 3.2.3 Calculation of the Vertical Entrainment Speed

The Zeman-Tennekes entrainment equation is used for the vertical entrainment speed ( $w_e$ ).

$$w_e = \frac{2.5 v_v}{8.333 + Ri} \quad (3-40)$$

where  $v_v$  = vertical turbulence speed; and  
 $Ri$  = Richardson's number

$$= \frac{g h_p \frac{\Delta\rho}{\rho_a}}{v_v^2}$$

$$v_v^2 = (0.7 v_t)^2 + (1.3 v_*^2)$$

$v_t$  = convective turbulence speed;

$$= \left( -(\bar{\theta}_w)_0 \frac{g h_p}{T_p} \right)$$

$(\bar{\theta}_w)_0$  = surface heat flux;

$$= \frac{1}{2} C_F U (T_a - T_p)$$

$v_*$  = mechanical turbulence speed

$$= U \sqrt{\frac{1}{2} C_F}$$

$$\begin{aligned}
C_F &= \text{surface drag coefficient} \\
&= 0.014; \\
U &= \sqrt{\left(\frac{2}{3} U_g\right)^2 + u_a^2 + v_a^2} \\
u_a &= \text{ambient air speed in X direction; and} \\
v_a &= \text{ambient air speed in Y direction.}
\end{aligned}$$

### 3.2.4 Calculation of the Enthalpy of Convective Boundary Layers

The enthalpy equation for convective boundary layers is

$$\frac{dT}{dt} = \frac{1}{h_p} [(\bar{\theta}_w)_0 - (\bar{\theta}_w)_h] \quad (3-41)$$

where  $(\bar{\theta}_w)_h$  = heat flux at height h

$$= \left[ (T_a - T_p) + \frac{H_{vw}}{C_{pA}} X F(T_{dp} - T_a) \right] \left( \frac{\rho_a C_{pA}}{\rho_G C_{pG}} w_e^* \right)$$

If droplets are present in the puff, CHARM assumes that all entrained energy goes into evaporating the droplets rather than warming the puff. Therefore, if the value for the entrained mass is less than the value for the amount of air that must be entrained to allow evaporation of the droplets ( $m_{crit}$ ) shown in Section 3.1.7, then

$$\frac{dT_p}{dt} = 0 \quad (3-42)$$

### 3.2.5 Summary Equations

A system of nine equations can be formed with the experimentally derived and estimated theoretical expressions and considerations presented so far in Section 3.2. These equations are

$$\frac{dx}{dt} = u_p \quad (3-43)$$

$$\frac{dy}{dt} = v_p \quad (3-44)$$

$$\frac{dT}{dt} = \frac{1}{h_p} [(\bar{\theta}_w)_0 - (\bar{\theta}_w)_h] K \quad (3-45)$$

$$\text{where } K = \begin{cases} 0 & \text{if } m_a < m_{\text{crit}} \text{ or} \\ 1 & \text{if } m_a \geq m_{\text{crit}} \end{cases}$$

$$\frac{dm_a}{dt} = \pi r^2 \rho_a w_e^* = M_e \quad (3-46)$$

$$\frac{du_p}{dt} = \frac{M_e}{m_A + m_G} (u_a - u_p) \quad (3-47)$$

$$\frac{dv_p}{dt} = \frac{M_e}{m_A + m_G} (v_a - v_p) \quad (3-48)$$

$$\frac{du_a}{dt} = \text{linearly interpolated from the user-supplied wind data;} \quad (3-49)$$

$$\frac{dv_a}{dt} = \text{linearly interpolated from the user-supplied wind data;} \quad (3-50)$$

$$\frac{dr}{dt} = \sqrt{\frac{2 g h_p (\rho_G - \rho_a)}{\rho_G}} \quad (3-51)$$

Note that water vapor is ignored when the mass of the puff is calculated. This is consistent with the Eidsvik model, which contains many experimentally derived and estimated numerical coefficients to enhance its ability to agree with the data. The inclusion of water vapor mass without altering the coefficients can create an error in the calculations.

### 3.2.6 Calculation of the Puff Dimensions

The volume of the puff is calculated using the same method shown in Section 3.1.2. Since the radius ( $r$ ) is explicitly computed, the height ( $h_p$ ) can be calculated by assuming a pancake-shaped puff.

The height of the puff is calculated as follows:

$$h_p = \frac{V}{\pi r^2} \quad (3-52)$$

The dispersion parameters are calculated as follows:

$$\sigma_z = \frac{h_p}{2.14} \quad (3-53)$$

$$\sigma_y = \frac{r}{2.14} \quad (3-54)$$

### 3.3 Jet Releases

A release is assumed to be a jet if any of the following criteria is met:

- The puff's speed is greater than twice the ambient wind speed;
- The puff's speed exceeds the ambient wind speed by 1 meter per second or more;  
or
- The puff's speed is greater than 1.5 meters per second.

The jet algorithm used in CHARM is based on the model by Ooms(1972) and modified by Emerson (1986). The jet algorithm normally leads to lower downwind concentrations than non-jet specific algorithms. All variables are calculated with respect to the distance down the center of the jet and the radial distance from the center of the jet. This leads to Gaussian distributions for quantities such as speed, concentration, and density.

The velocity (u) inside the jet due to jet and ambient wind velocity is calculated as follows:

$$u = U_a + u_{p0} \exp\left(\frac{-r^2}{b^2}\right) \quad (3-55)$$

- where  $U_a$  = ambient wind velocity;  
 $u_{p0}$  = jet velocity at the jet centerline;  
 $r$  = radial distance from jet centerline; and  
 $b$  =  $\sqrt{2}$  times the standard deviation of the distribution.

The concentration (c) in the jet is calculated as follows:

$$c = c_0 \exp\left(\frac{-r^2}{\lambda^2 b^2}\right) \quad (3-56)$$

- where  $c_0$  = concentration at the jet centerline; and  
 $\lambda$  = constant relating concentration and velocity distributions = 1.1.

The density ( $\rho$ ) in the jet is calculated as follows:

$$\rho = \rho_a + \rho_0 \exp\left(\frac{-r^2}{\lambda^2 b^2}\right) \quad (3-57)$$

where  $\rho_a$  = density in ambient air; and  
 $\rho_0$  = density at jet centerline.

The variables  $u_{p0}$ ,  $b$ ,  $c_0$ , and  $\rho_0$  are functions of distance down the jet centerline ( $s$ ). The quantities are calculated with respect to these distances. Afterward, the quantities are represented in Cartesian coordinates. The problem is two-dimensional for axial symmetry; since centerline velocity is a function of the distance down the centerline of the jet, the solution with respect to  $s$  is related to solutions in time.

### 3.3.1 Velocity Components

As with all vectors in this problem, the velocity is split into two components: vertical and horizontal.

The horizontal component of the velocity ( $u_h$ ) is calculated as follows:

$$u_h = U_a \left[ 1 - \sin^2 \theta \exp\left(\frac{-r^2}{b^2}\right) \right] + u_0 \cos \theta \exp\left(\frac{-r^2}{b^2}\right) \quad (3-58)$$

The vertical component of the velocity ( $u_v$ ) is calculated as follows:

$$u_v = (U_a \cos \theta + u_0) \sin \theta \exp\left(\frac{-r^2}{b^2}\right) \quad (3-59)$$

where  $u_h$  = horizontal speed;  
 $u_v$  = vertical speed;  
 $\theta$  = angle between  $v_0$  and the ambient wind speed;  
 $u_0$  =  $v_0 - U_a \cos \theta$ ; and  
 $v_0$  = total jet centerline velocity, due to jet and ambient wind speed.

### 3.3.2 Mass and Momentum

The horizontal momentum ( $I_x$ ) through the jet is calculated as follows:

$$I_x = \int_A \rho(r) u_c(r) u_h \, dS \quad (3-60)$$



where  $u_c$  = component of  $U_a$  parallel to  $v_0$  + component of  $u_p$  parallel to  $v_0$ ; and  
 $S$  = surface of the area integral (A) represented as a horizontal cylinder.

This integral can be evaluated from the velocity and density definitions for the jet and the result follows:

$$I_{x1} = M_1 U_a + I_{x2} \quad (3-61)$$

where  $I_{x1}$  = the integral after a constant term (due to ambient advection) is subtracted from  $I_x$   
 $M_1 = \pi b^2 (\rho_a + \rho_0 v_1)$ ;  
 $v_1 = \lambda^2 U_a \cos \theta + f_1 u_0$ ;  
 $f_1 = \frac{\lambda^2}{1 + \lambda^2}$ ;  
 $I_{x2} = M_2 (v_0 \cos \theta - U_a)$ ;  
 $M_2 = \pi b^2 (\rho_1 U_a \cos \theta + \rho_2 u_0)$ ;  
 $\rho_1 = \rho_a + f_1 \rho_0$ ;  
 $\rho_2 = \frac{\rho_a}{2} + f_2 \rho_0$ ;  
 $f_2 = \frac{\lambda^2}{1 + 2 \lambda^2}$ ;

The vertical momentum integral is calculated as follows:

$$\begin{aligned} I_z &= \int_A \rho(r) u_c(r) u_v dS \\ &= M_2 v_0 \sin \theta \end{aligned} \quad (3-62)$$

The rates of change of momentum are also required for calculation of the rate of change of  $\theta$ . The rate of change of  $I_z$  is:

$$\frac{dI_z}{dt} = \int_A (\rho_a - \rho(r)) g dS + C_d \pi b \rho_a U_a^2 \sin^2 \theta \cos \theta \quad (3-63)$$

The first term accounts for gravitational forces on the jet and the second term covers drag forces. ( $C_d$  is the drag coefficient.)

The horizontal momentum rate of change is due solely to drag forces, as shown in the following calculation:

$$\frac{dI_{x_2}}{dt} = C_d \pi b \rho_a U_a^2 |\sin^3 \theta| \quad (3-64)$$

By taking the derivatives of the above definitions for  $I_z$  and  $I_{x_2}$  and equating them with the last two equations, CHARM can determine the rate of change of  $\theta$  with respect to  $s$ .

### 3.3.3 Entrained Mass

Because of problems that arise when a jet is directed upwind, Emerson (1986) suggests using  $M_2$  as the entrained air term and ignoring  $M_1$ . The rate of change of  $M_2$  with respect to  $s$  is calculated as follows:

$$\frac{dM_2}{dt} = a_1 \sqrt{r_a M_2 u_0} + 2 \rho b (a_2 U_a |\sin \theta| + a_3 u') \quad (3-65)$$

where  $a_1$  = a constant = 0.141;  
 $a_2$  = a constant = 0.17;  
 $a_3$  = a constant = 1.0;  
 $u'$  = an entrainment velocity due to ambient turbulence;  
=  $U_a (0.35 - 0.05 \text{ istab})$   
 $\text{istab}$  = Pasquill stability class, 1 = A, 2 = B, etc.

Setting the equation for the rate of change of  $M_2$  equal to the derivative of the previous equation for  $M_2$  results in a solution for the rate of change of the  $b$  parameter.

### 3.3.4 Relationship Between Centerline Concentration and Density

Since  $c_0$  and  $p_0$  follow similar distributions, a relationship can be derived between the two variables. In fact, since the initial concentration in a jet is known, a relationship is required to initialize the value of  $p_0$ . This relationship is achieved by equating two like volumes of air and puff.

$$V_T = \frac{(n_g + n_a') R T_p}{P_a} = \frac{n_a R T_a}{P_a} \quad (3-66)$$

where  $V_T$  = a volume;  
 $n_g$  = moles of gas in the volume in puff;  
 $n_a'$  = moles of air in the volume in puff; and  
 $n_a$  = moles of air in the volume outside of the puff.

From this relationship, an expression relating the concentration of the gas to the density of the air can be derived using the expression for the density and concentration inside a jet (given at the beginning of Section 3.3).

$$\frac{\rho_0}{c_0} = 1 - \frac{T_p M_a}{T_a M_g} + \frac{m_a}{m_g} \left( 1 - \frac{T_p}{T_a} \right) \quad (3-67)$$

### 3.3.5 Summary Equations

All of the equations in Section 3.3 lead to the following summary of equations that CHARM solves by a technique described in Section 3.4.

$$\frac{dx}{dt} = u_p \quad (3-68)$$

$$\frac{dy}{dt} = v_p \quad (3-69)$$

$$\frac{dz}{dt} = w_p \quad (3-70)$$

$$\frac{dm_A}{dt} = M_e (1 - X) \quad (3-71)$$

$$\frac{dm_w}{dt} = M_e X F(T_a - T_{dp}) \quad (3-72)$$

$$\frac{du_p}{dt} = \left( \frac{dv_0}{ds} \cos \theta + v_0 \frac{d \cos \theta}{ds} \right) \cos \beta v_0 + \frac{M_2}{M_1} (u_a - u_p) \quad (3-73)$$

$$\frac{dv_p}{dt} = \left( \frac{dv_0}{ds} \cos \theta + v_0 \frac{d \cos \theta}{ds} \right) \sin \beta v_0 + \frac{M_2}{M_1} (v_a - v_p) \quad (3-74)$$

$$\frac{dw_p}{dt} = \left( \frac{dv_0}{ds} \sin \theta + v_0 \frac{d \sin \theta}{ds} \right) v_0 \quad (3-75)$$

$$\frac{du_a}{dt} = \text{linearly interpolated from the user-supplied wind data;} \quad (3-76)$$

$$\frac{dv_a}{dt} = \text{linearly interpolated from the user-supplied wind data;} \quad (3-77)$$

$$\frac{dT_a}{dt} = \Gamma w_p \quad (3-78)$$

$$\frac{dP_a}{dt} = -w_p \rho_a g \quad (3-79)$$

$$\frac{d(m_A + m_W)}{dt} = M_2 \quad (3-80)$$

$$\frac{dE_p}{dt} = M_2 T_a [(1-X) C_{vA} + X C_{vW}] + K H_{vW} X M_2 F(T_{dp} - T_p) \quad (3-81)$$

where  $K = 0$  if  $(m_A + m_W) < m_{crit}$ ; or  
 $= 1$  if  $(m_A + m_W) \geq m_{crit}$

$$\frac{dc_0}{dt} = \frac{c_0}{\rho_0} v_0 \frac{d\rho}{ds} \quad (3-82)$$

$$\frac{db}{dt} = \left( C_1 - R_1 \frac{d\rho}{ds} \right) \frac{v_0}{B_1} \quad (3-83)$$

$$C_1 = \frac{dM_2}{ds} - \pi b^2 \left( \rho_1 U_a \frac{d \cos \theta}{ds} + \rho_2 \frac{du_0}{ds} \right) \quad (3-84)$$

$$R_1 = \pi b^2 (f_1 U_a \cos \theta + f_2 u_0) \quad (3-85)$$

$$B_1 = 2 \pi b (\rho_1 U_a \cos \theta + \rho_2 u_0) \quad (3-86)$$

$$\frac{d\rho}{dt} = \left( \frac{C_1 B_2 - C_2 B_1}{R_1 B_2 - R_2 B_1} \right) v_0 \quad (3-87)$$

$$B_2 = 2 \rho_0 v_1 \quad (3-88)$$

$$R_2 = b v_1 \quad (3-89)$$

$$\frac{d\theta}{dt} = D_1 \cos \theta - D_2 \sin \theta \quad (3-90)$$

$$D_1 = \left( \frac{dI_z}{ds} - v_0 \sin \theta \frac{dM_2}{ds} \right) \frac{1}{M_2} \quad (3-91)$$

$$D_2 = \left( \frac{dI_x}{ds} - (v_0 \cos \theta - U_a) \frac{dM_2}{ds} \right) \frac{1}{M_2} \quad (3-92)$$

### 3.4 Numerical Technique

The systems of equations described in Sections 3.1, 3.2, and 3.3 can be represented as

$$\frac{dy}{dt} = f(y) \quad (3-93)$$

where  $y$  = the vector of primary variables; and;  
 $f$  = the vector function described by the sets of equations listed in Sections 3.1, 3.2, and 3.3.

The solution for the equations is an initial value problem, because  $y$  is known at time zero and the equations must be solved for a future time ( $t$ ). Since the system variables can change rapidly during the initial phase of the simulation, a small integration time step ( $\Delta t$ ) may be required. During later stages when each puff is approaching some equilibrium, the system variables change more slowly and a larger time step can be used.

To maintain reasonable solution accuracy while avoiding excessive computations, CHARM uses a variable step size, fourth-order Runge-Kutta technique. This technique is used in computations for aloft puffs, denser-than-air puffs that are in contact with the ground, and jets.

For a time step of length  $\Delta t$  CHARM performs the following operations (given  $y_t$  which is the estimated current value of  $y$  at time =  $t$ ).

(1) A fourth-order, Runge-Kutta method estimates  $y_{t+\Delta t}$  as follows:

$$\begin{aligned} K_1 &= f(y_t) \Delta t \\ K_2 &= f\left(y_t + \frac{1}{2} K_1\right) \Delta t \\ K_3 &= f\left(y_t + \frac{1}{2} K_2\right) \Delta t \\ K_4 &= f(y_t + K_3) \Delta t \\ y_{t+\Delta t} &= \frac{1}{6} (K_1 + 2 K_2 + 2 K_3 + K_4) \end{aligned} \quad (3-94)$$

For reference purposes, call this first estimate  $y^1$ .

(2) Evaluate the above equation again using a time step of  $t_1 = \Delta t/2$ . Call this second estimate  $y^{11}$ .

(3) Obtain the final estimate of  $y_{t+\Delta t}$  by Richardson extrapolation as follows:

$$y_{t+\Delta t} = y^{11} + \frac{y^{11} - y^1}{2^4 - 1} \quad (3-95)$$

(4) Estimate the relative error accrued in the current step (Björk and Dahlquist, 1974) as follows:

$$\text{RERR} = \frac{1}{2^4 - 1} \sum_{i=1}^N \sqrt{\frac{(y_i^{11} - y_i^1)^2}{\text{YMAX}_i^2}} \quad (3-96)$$

where  $N$  = the length of the vector  $y$ ; and;  
 $\text{YMAX}_i$  is initially set equal to 1, and is subsequently set equal to the largest value of  $y_i$ .

(5) Compare the relative error to a user-defined relative error criteria ( $\epsilon$ , which is currently set to 0.001). If the estimated error is not acceptable, retry the integration step with a new step size as follows:

$$\Delta t_{\text{new}} = \left( 0.8 \frac{\epsilon}{\text{RERR}} \right) \Delta t_{\text{old}} \quad (3-97)$$

The time step is reduced up to 10 times before the integration procedure fails. If the estimated error is acceptable, the integration routine attempts to increase the next time step to  $\Delta t_{\text{new}}$  and integration continues for the next time step.

Steps (1) through (5) are repeated until the end of the integration period is reached.

CHARM selects the initial time step in the integration according to whether the calculation is for an aloft puff, a denser-than-air puff in contact with the ground, or a jet.

For aloft puffs, CHARM selects the minimum value of two time scales. The first time scale is given by the following equation:

$$\Delta t_0 = \frac{0.01 z_p}{w_p} \quad (3-98)$$

which represents 1 percent of the time required for a puff to reach the ground from its height ( $z_p$ ).

The second time scale is calculated as follows:

$$\Delta t_0 = \frac{0.01 m_t}{M_e} \quad (3-99)$$

which represents 1 percent of the time required for the puff to entrain an amount of mass already present in the puff.

For denser-than-air puffs in contact with the ground, CHARM selects the initial time step as the minimum value of

$$\Delta t_0 = \frac{1}{4} \frac{y}{\left| \frac{dy}{dt} \right|} \quad (3-100)$$

where  $y$  represents any of the nine parameters being solved for.

The minimum value allowed in time step calculations for aloft and denser-than-air puffs is 0.0036 seconds. For a jet emission, the initial and minimum time step are set to 0.000036 seconds. There is no scaling for the initial time step in jet calculations.

Once any puff, whether denser-than-air or not, contacts the ground with a downward velocity  $\geq 0$ , it is assumed to remain in contact with the ground for the rest of the simulation. The applicability of methods for determining whether or not a puff will lift off is questionable, and continued contact with the ground is a worst-case assumption.

### **3.5 Post-Processing**

After the new puff parameters are determined, CHARM performs post-processing for numerical information, graphics, and physical constraints. Since each puff is calculated independently of all other puffs, some consideration is given to their possible interactions. In many cases, the initial puff emitted has the largest amount of mass of any of the puffs. Because of its added inertia, the first puff accelerates and moves much more slowly than do the other puffs. If the puff parameters are calculated independently and no corrections are made, less massive puffs can move through more massive puffs and pass them. Since this is an unrealistic situation, CHARM makes a correction. CHARM determines whether any puffs are moving through other puffs. If so, the lighter puff is retarded until there is a distance of one  $\sigma_y$  between the puffs. If a line of puffs is emitted and the wind shifts so that puffs do not interact, CHARM takes no action.

When CHARM determines the isopleths for up to three concentration values, the modeling of individual puffs is a consideration. CHARM assumes that each modeled puff is a cross-section of a plume. To create isopleths, CHARM constructs a line between the first (oldest) puff and the second puff. A second line is constructed perpendicular to the

first line and passing through the first puff point. The distance from the first puff point to a point on the second line where the concentration is equal to one of the three concentration values is then determined. The Gaussian formula for the concentration (C) due to a puff is calculated as follows

$$C = \frac{m_g}{\sqrt{2\pi} \sigma_y \sigma_z} \exp\left(-\frac{r^2}{2\sigma_y^2}\right) \left[ \exp\left(-\frac{(z+h)^2}{2\sigma_z^2}\right) + \exp\left(-\frac{(z-h)^2}{2\sigma_z^2}\right) \right] \quad (3-101)$$

where C = concentration;  
r = radius of puff; and  
h = altitude of puff.

Given C, this equation solves for the radius (r). After the modeled puffs are used to determine isopleth points, the Gaussian formula is used again to determine if a wider portion of the plume (larger r) lies between the modeled puffs. The Gaussian formula determines the derivative of r with respect to downwind distance. A binary search routine is then used to see if the derivative becomes zero at any point between the two modeled puffs. If so, that point is at the widest portion of the plume and is added to the isopleth points.

In the concentration equation, the concentration falls off as the square of  $\sigma_y$ . In Section 2.5, a  $\sigma_y$  was calculated for the downwind distance that a parcel of air travels after some time. That time was the emission time or 15 minutes, whichever was less. A frequent problem with CHARM's implementation of the Gaussian formulation is that the concentration tends to fall off too rapidly at distances far downwind. For convenience, name the  $\sigma_y$  in Section 2.5  $\sigma_{y0}$ . CHARM uses  $\sigma_{y0}$  as a point of inflection. Before the  $\sigma_y$  of the plume reaches that of  $\sigma_{y0}$  the concentration is assumed to fall off as in the above concentration equation. Once the  $\sigma_y$  of the plume exceeds  $\sigma_{y0}$ , CHARM assumes the  $\sigma_y$  term is  $\sigma_y \sigma_{y0}$  rather than  $\sigma_y^2$ . This has the concentration fall-off as inverse  $\sigma_y$  rather than inverse square  $\sigma_y$ .

### 3.6 Interpolation

The two types of interpolation used are temporal and spatial. As CHARM solves the advection and dispersion equations for a release, it saves the description every thirty seconds (or less) of simulation time. When a time is selected for display, CHARM interpolates temporally the modeled puffs to the specified time. The two stored times closest to the specified time are chosen for the interpolation. Each parameter is assumed to vary monotonically in time. Puffs at the requested time are formed from the puffs at surrounding times.

Since CHARM uses the stored results only to determine concentrations, not all parameters require interpolation. A quantity such as energy content from entrainment is not required. The amounts of entrained air or water vapor are not required because some



of that information is contained in the  $\sigma$ s. The only quantities requiring interpolation are those that are used in the concentration equation (shown in the previous section). These quantities are the three-dimensional location of a puff, the mass in a puff, and the  $\sigma$ s in a puff.

When puffs are determined for a specific time, further interpolation is needed to determine if other puffs are between any two modeled-puffs. Each quantity in the concentration equation is assumed to vary monotonically between any two puffs. The values for the parameters of the puffs are used to create spatially varying parameters that can be used in analytical expressions for the various quantities in the concentration equation. For example, the radial distance from plume centerline( $r$ ) can be expressed in terms of the other parameters in the concentration equation. If the other parameters can be expressed as simple functions of distance between puffs, an analytic expression can be derived for the derivative of  $r$  as a function of the distance between two puffs. This derivative may not be analytically soluble, but it can be used in a search function to determine when the derivative goes to zero for the location of a maximum.

The location parameters of a puff are all assumed to vary linearly for both spatial and temporal interpolations. The values for  $\sigma$  vary as follows:

$$\sigma = a x^b \quad (3-102)$$

where  $a$  and  $b$  = the coefficient and exponent of the variation; and  
 $x$  = distance for spatial interpolation and time for temporal interpolation.

The mass between puffs is assumed to vary exponentially in the form:

$$m = a e^{bx} \quad (3-103)$$

### **3.7 Hydrogen Fluoride**

Hydrogen Fluoride exhibits non-ideal dynamics. At high concentrations, the individual molecules can form oligomers (polymers which contain two, three, or four monomers). The dynamic effect is to increase the molecular weight of the release. It may be desirable to have different data sets for a compound such as hydrogen fluoride. One set of parameters could be used for low concentration releases, the other for pure releases. From Bekerdite et al (1983), there is sufficient data to create a table relating the apparent molecular weight of hydrogen fluoride to the temperature and concentration of the hydrogen fluoride gas. Such a table is presented in Table 3-1. As that table shows, in pure concentration (1,000,000 ppm) hydrogen fluoride at 20°C has an apparent molecular weight of 51.6. Above 70°C, however, hydrogen fluoride is present as a monomer at all concentrations giving a molecular weight of 20.

The dispersion of hydrogen fluoride is handled by the algorithms in this section with the molecular weight of the hydrogen fluoride varying according to Table 3-1. CHARM uses the name of the chemical to determine if the table should be used. The chemical name in the database must match exactly “Hydrogen Fluoride” for the table to be invoked.

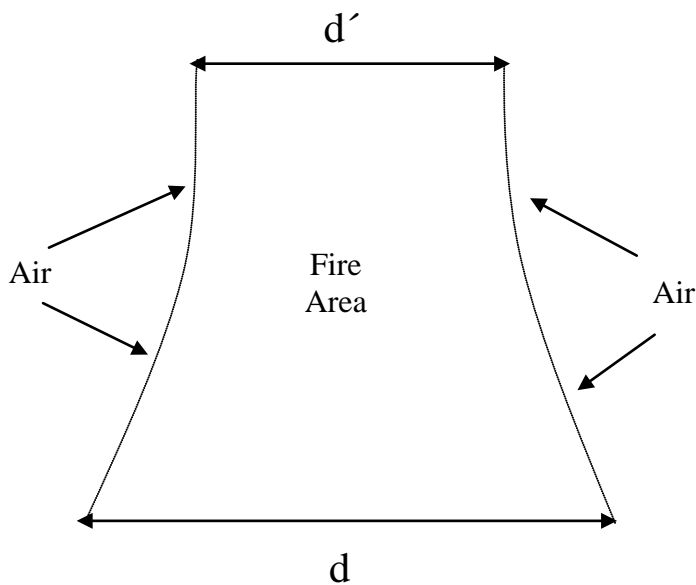
Table 3-1. Hydrogen Fluoride Apparent Molecular Weight As A Function Of Temperature And MolarFraction Concentration.

Temp(°C)/fj	1.0	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1
20	51.59	48.58	43.78	39.53	35.47	31.56	27.03	23.78	21.53	20.32
30	36.22	33.45	30.51	27.20	24.65	22.91	21.65	20.68	20.37	20.03
40	25.26	23.66	22.50	21.51	20.88	20.53	20.36	20.15	20.02	20.01
50	21.06	20.65	20.53	20.32	20.18	20.09	20.02	20.01	20.01	20.01
60	20.17	20.10	20.05	20.01	20.01	20.01	20.01	20.01	20.01	20.01
70	20.01	20.01	20.01	20.01	20.01	20.01	20.01	20.01	20.01	20.01

## 4.0 LIQUID POOL FIRE ALGORITHM

Large spills of volatile organic chemicals evaporate readily and can form a combustible mixture with air above the pool. When ignited, a major fire can result. Experience has shown that flames initially appear at several locations over the pool and spreading begins. In a typical fire, the intensity grows and combustion products reach 1500°F after several minutes. The intensity and speed of growth depend largely on the material involved and its heat of combustion. The algorithms shown in this section were prepared by Shirley (1982).

After a stable flame involving the entire pool has been established, the overall shape of the fire appears to be a truncated cone whose sides are slightly concave (Blackshear, 1974). Figure 4-1 shows the general appearance and configuration.



**Figure 4-1. General Appearance of a Liquid Pool Fire**

The base of the flame area is only slightly smaller than the pool itself. The diameter of the cone top is about  $2/3$  that of the base at a height roughly equal to the diameter of the base. Fuel evaporates from the pool surface, and air is drawn into the cone sides to mix with the fuel. Since air enters from the outside of the cone surface, fuel vapors in the center move up the axis of the cone with flames surrounding them. Near the upper end of the cone, these fuel vapors mix with the combustion products and react with them, as well as with the air being drawn further toward the cone center. As the unburned material is heated, cracking reactions form soot causing the pool fires to be generally very smoky. Mixing conditions at the lower levels of the cone are very poor, but a considerable amount of turbulence appears in the upper levels.

The air supply in such fires is not enough to burn all the vapors of combustible material evaporated. These unburned vapors are entrained in the plume and carried up with it. When the fire occurs in a diked area containing tanks, heating of the tank walls occurs, with rapid evaporation of material in the tanks. This material joins the plume (if the tank vent is not remotely located). The plume is then very rich in the organic chemicals involved. The fire reactions are a complex mixture of oxidation, cracking, reduction, and recombinations. In this technique, gross estimates were used to predict likely quantities of heat released and the reaction products obtained. A kinetic model that accounts for reaction rates and residence times at various temperatures is needed to improve the predictions.

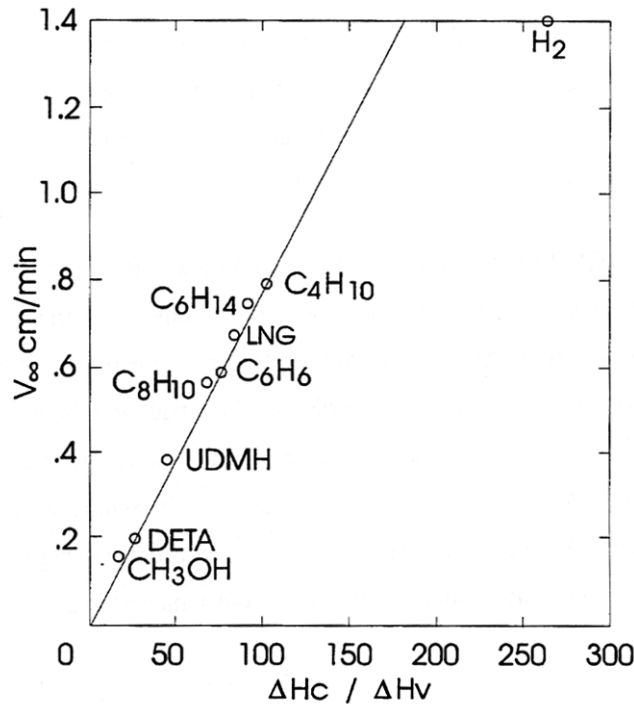
#### **4.1 Heat Release and Product Composition**

Fuel supply to the fire comes from evaporation at the surface of the pool in response to heat from the fire. A study (Zabetakis, 1964) of pool fires using various combustible materials produced an equation for predicting the drop in liquid level during burning. The equation is:

$$V_{\infty} = 0.0076 \frac{H_c}{H_v} \quad (4-1)$$

where  $V_{\infty}$  = maximum decrease in pool level (cm / min);  
 $H_c$  = heat of combustion; and  
 $H_v$  = heat of evaporation.

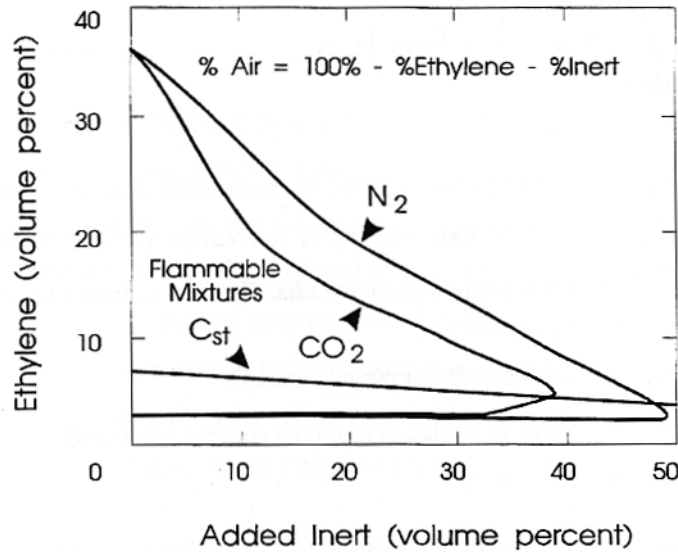
The study included butane, hexane, benzene, xylene, unsymmetrical dimethyl hydrazine, methanol, and diethylene triamine. Figure 4-2 plots these data.



**Figure 4-2. Relationship between liquid-burning rate (large pool diameter) and ratio of net heat of combustion to sensible heat of vaporization.**

This equation for the decrease in pool level is valid for pools in still air that are larger than two meters diameter and for all sizes of pools in windy conditions. No increase in rate is indicated at reasonable wind conditions. Small pools less than one meter in diameter had lower rates of surface level decreases.

Air supply enters the fire area by diffusion and by reduced pressure in the cone caused by the rising of hot gases. Data on the quantity of air that entered were not available. The assumption was made that the burning took place at the upper flammability limit for the organic compound involved. Using the evaporation rate for the pool area ( $V$ ) produced a value for the fuel rate, which was divided by the upper flammability limit value to get the air rate. In the formaldehyde and phenol cases evaluated, both water vapor and the chemical evaporated. The upper flammability limit is affected (Zabetakis, 1964) by an inert diluent, as shown in Figure 4-3.



**Figure 4-3. Limits of flammability of ethylene-carbon dioxide-air and ethylene-nitrogen-air mixtures at atmospheric pressure and 26° C.**

This figure shows the effect of N<sub>2</sub> diluent and CO<sub>2</sub> diluent for ethylene. The upper flammability limits for formaldehyde and phenol were adjusted using the nitrogen example, because the molar heat capacities of nitrogen and water are similar.

The stoichiometric amount of combustible in air is related to its molecular constituents. Given the compound C<sub>N</sub>H<sub>M</sub>O<sub>L</sub>F<sub>K</sub>, where C is carbon, H is hydrogen, O is oxygen and F is a halogen, the equation (Zabetakis, 1964) is:

$$C_{ST} = \frac{100}{1 + 4.733 \left( N + \frac{M - K - 2L}{4} \right)} \quad (4-2)$$

where C<sub>ST</sub> = concentration (volume percent) of combustible in air at stoichiometric ratio.

An estimate for the percent burned is required. The percent burned can be estimated by assuming the burning plume is axially symmetric. The value of C<sub>ST</sub> should lie between the lower and the upper flammable limits. Above the lower flammable limit and below C<sub>ST</sub> all is burned. Above C<sub>ST</sub>, too much organic is present to burn entirely. One hundred percent is assumed to be burned at C<sub>ST</sub>, and zero percent is assumed burned at the upper flammable limit. Between C<sub>ST</sub> and the upper flammable limit, the relationship between the concentration and the percent burned is assumed to be linear. The amount of material burned (m<sub>B</sub>) is:

$$m_B = \int_{r(F_L)}^{r(C_{ST})} c dV + \int_{r(C_{ST})}^{r(F_U)} \left( \frac{F_U - c}{F_U - C_{ST}} \right) c dV \quad (4-3)$$

where  $F_L$  = concentration, vol. %, of combustible in air at lower flammable limit;

$F_U$  = concentration, vol. %, of combustible in air at upper flammable limit;

$c$  = concentration at some radial distance,  $r$ , from plume center;  
 $= c_0 \exp(-a^2 r^2)$ ;

$c_0$  = concentration at plume center;

$a$  = inverse of standard deviation of plume concentration; and

$dV$  =  $2 \pi r dr dz$ .

The total mass,  $m_T$ , in the plume is given as:

$$m_T = \int_0^{\infty} c dV \quad (4-4)$$

The percent burned,  $B_{\%}$ , is then given as:

$$B_{\%} = \frac{100 m_B}{m_T} \quad (4-5)$$

Integrating and using the mass per vertical length  $dz$ , leads to:

$$B_{\%} = \frac{100}{c_0} \left[ \left( \frac{F_U + C_{ST}}{2} \right) - F_L \right] \quad (4-6)$$

The value of  $c_0$  is assumed to be identical to  $F_U$  since that is the first concentration at which a burn will occur.

In a review of the literature on carbon black manufacture, Schwartz et al (1974), Hustvedt et al. (1976), Shreve and Brink (1977), and U.S. EPA (1979)) provide an estimate of heat release and product composition for a combustion reaction involving cracking. The data indicates that at 1500 to 1800°F, an approximate 10 percent yield of carbon could be obtained from heavy aromatic compounds. The ratio of CO to CO<sub>2</sub> in the gas stream would be about 1:1, and 1/2 mole of H<sub>2</sub> would be present for each mole of CO and CO<sub>2</sub> present. Under these conditions, the endothermic reactions reduce the heat of reaction to about 80 percent of the standard net heat of combustion. These conditions were chosen for evaluating liquid pool fires. The heat evolved in these fires is calculated as evaporation rate times the fraction burned times 80 percent of the heat of reaction. If chlorine is present in the material being burned, the model assumes that 10 percent of the CO is being converted to phosgene.

The one-to-one ratio for CO:CO<sub>2</sub> is accurate to ±30% and the 0.5-to-one ratio for H<sub>2</sub> to (CO + CO<sub>2</sub>) is accurate to about ±50%. There will be some CO and some H<sub>2</sub> remaining in the plume after it cools to a temperature that is below the activation temperature. The amount depends on the equilibrium approach in the CO<sub>2</sub>-H<sub>2</sub>O-soot system, which exists at high temperatures for relatively long residence times (two or three seconds) in the fire area. The carbon black production data used for these assumptions were at slightly higher temperatures for very short residence times (< 1/2 second). Lower values for these ratios result in higher temperature plumes with less potential for hazards, while higher values yield lower temperature plumes.

The assumption of 10 percent of CO being converted to phosgene in the presence of chlorine atoms is a gross estimate of unknown accuracy. Most or very few of the chlorine atoms may be converted to phosgene; the only data available indicates that phosgene has been observed in fires with chlorine present. As a case in point, carbon tetrachloride is no longer recommended for fire extinguisher use, with phosgene evolution being the primary cause.

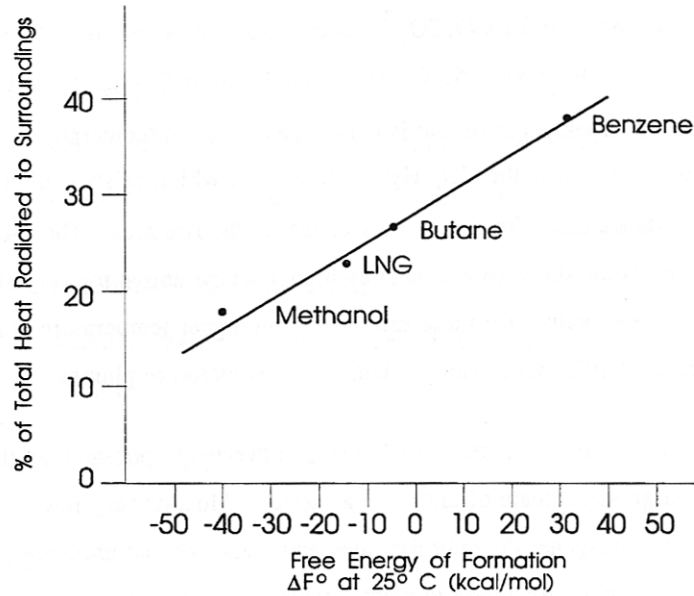
## **4.2 Heat Sumps**

Heat from the fire evaporates the materials from the pool, heats the evaporated material and air to auto-ignition temperature, radiates to the surroundings, and heats the combustion/reaction products in the plume. The considerations for heat include:

- Heat of evaporation, which is the product of quantity of material evaporated times the latent heat of evaporation;
- Quantity of vapor generated multiplied by its heat capacity;
- Temperature difference between boiling point and auto-ignition temperature;
- Quantity of air times its heat capacity; and
- Temperature difference between ambient temperature and auto-ignition temperature.

In the original study (Burgess et al, 1961), which developed the evaporation rate equation, infrared sensors were located around the pool to measure radiation and determine the percent of total heat that radiated to the surroundings from various fires. These data were found to correlate with free energy of formation ( $\Delta F$  at 25°C) for the chemicals burned. This relationship does not apply for hydrogen, but appears usable for hydrocarbons and alcohols. Figure 4-4 shows a plot of the data in this form.





**Figure 4-4. Relationship between percent of total heat radiated to the surroundings and free energy of formation.**

The developed equation is:

$$R = 0.26\Delta F + 27 \quad (4-7)$$

where R = percent of total heat release radiated to surroundings; and  
 $\Delta F$  = free energy of formation (kcal/mole).

The radiant heat is the product of total heat evolved in the fire times R/100.

To obtain a heat available for raising the combustion product temperature, the total heat release is reduced by the latent heat of evaporation, by sensible heats of the air and organic vapors up to auto-ignition temperature, and by the radiant heat to surroundings. To determine this temperature rise, the composition of the combustion products and the quantity of each component is determined by a material balance. Then each component is multiplied by its heat capacity. The summation of these multiplications is the heat capacity of the plume in units of BTU per unit time per °F temperature difference. Dividing the heat available by the heat capacity of the plume gives the increase in temperature of the products above the auto-ignition temperature. The sum of these is the plume temperature. The equations are:

$$E_{\text{plume}} = \sum_{i=1}^n W_i C_{pi} \quad (4-8)$$

where  $E_{\text{plume}}$  = energy addition to plume (BTU °F / second);  
n = number of components  
 $W_i$  = rate each component is added to plume (pounds / second); and

$C_{pn}$  = heat capacity of each component (BTU °F / pound).

$$\Delta T_{\text{plume}} = \frac{Q}{E_{\text{plume}}} \quad (4-9)$$

where  $\Delta T_{\text{plume}}$  = temperature rise of plume; and  
 $Q$  = heat available from combustion.

$$T_{\text{plume}} = T_i + \Delta T_{\text{plume}} \quad (4-10)$$

where  $T_{\text{plume}}$  = final plume temperature; and  
 $T_i$  = auto-ignition temperature.

The material balance provides information on hazardous chemicals remaining in the plume and the total quantities of components in the plume. The total volume at the final temperature is computed to obtain a plume velocity at the top of the cone-shaped fire area.

### 4.3 Tank Involvement in Fire

When a fire surrounds a tank, materials in the tank are heated and vented. National Fire Codes (National Fire Protection Association, 1973-74) specify the size of vents required in terms of the volume rate of release for tanks with fire surrounding them. Table 4-1 shows the required venting rates as free airflow. The table shows the wetted area versus cubic feet free air per hour at 14.7 psia and 60° F.

**Table 4-1. Wetted Area Versus Cubic Feet Free Air\***

Square Feet	Cubic Feet/Hour
20	21,100
30	31,600
40	42,100
50	52,700
60	63,200
70	73,700
80	84,200
90	94,800
100	105,000
120	126,000
140	147,000
160	168,000
180	190,000
200	211,000
250	239,000
300	265,000
350	288,000

400	312,000
500	354,000
600	392,000
700	428,000
800	462,000
900	493,000
1,000	524,000
1,200	557,000
1,400	587,000
1,600	614,000
1,800	639,000
2,000	662,000
2,400	704,000
2,800 and over	742,000

\* Interpolate for intermediate values.

The wetted surface area is the area inside the tank in contact with the liquid. This table was used to determine airflow rate, and a conversion to the equivalent flow of organic chemical was made by using the density of the chemical vapor at its boiling point. This procedure gave a slightly higher venting rate than an alternate procedure that estimates the heat transfer rate shown in the appendix of the National Fire Codes.

The effect of the blending vapors into the plume is the reduction of the plume temperature and the increase of the total component weight of the plume due to the added chemical. The heat capacity of the added chemical vapor times its weight included in the plume heat capacity provided a smaller  $T_{\text{plume}}$  for the mixed system. The heat used to vaporize the material in the tank was assumed to be included in the heat radiated to surroundings.

## 5.0 FIREBALL/BLEVE ALGORITHM

The Fireball/BLEVE (Boiling Liquid Expanding Vapor Explosion) algorithm is one of the simplest in CHARM; only a few equations must be solved. The method comes from Moorhouse and Pritchard (1982) and Roberts (1982). Instead of being derived from fundamental principles, the BLEVE equations are parametric.

### 5.1 Calculation of the Efficiency of Explosion

An efficiency of explosion is either entered by the user or calculated by CHARM. If calculated, the explosion efficiency ( $v$ ) is a function of the vapor pressure of the material and is:

$$v = 0.27P_s^{0.32} \quad (5-1)$$

where  $P_s$  = vapor pressure in Pascals of the chemical at the storage pressure.

The radius ( $R_f$ ) of the ensuing fireball (in meters) is calculated as follows:

$$R_f = 2.665 m_{kg}^{0.327} \quad (5-2)$$

where  $m_{kg}$  = mass of material in kilograms involved in the explosion.

The duration ( $T_f$ ) of the fireball in seconds is given as:

$$T_f = 1.089 m_{kg}^{0.327} \quad (5-3)$$

Finally, the amount of radiation ( $W$ ) being emitted is given as:

$$W = \frac{H_c m_{kg} v 1000}{T_f} \quad (5-4)$$

where  $W$  = energy emission rate in watts; and  
 $H_c$  = heat of combustion of the material in Joules per gram.

## **5.2 Calculation of Fluxes**

Once the energy emission rate ( $W$ ) is calculated, the fluxes can be determined at any distance from the source. The fireball is assumed to be a point source. As such, the flux ( $F$ ) at some distance ( $r$ ) from the fireball can be calculated using the inverse square property of radiation:

$$F = \frac{W}{4\pi r^2} \quad (5-5)$$

Because the fireball is assumed to be a point source, either  $F$  or  $r$  can be specified and the other parameter calculated.

## 6.0 JET FIRES

The jet fire algorithm used is designed around the Multiple Point Source Model (MPSM) described by Crocker and Napier (1988). In this method, the radiation from a jet fire is divided into three components: that which falls on a vertical target perpendicular to the X-axis, that which falls on a vertical target parallel to the X-axis, and that which falls on a horizontal target.

### 6.1 Calculation of the Flame Length

Crocker and Napier present an expression relating the flame length to jet fluid mole fraction in an unreacted stoichiometric mixture, flame temperature, and ratio of reactants to products in the unreacted stoichiometric mixture. These values would change for different releases and may be difficult to discern for any single release. Because of this, CHARM uses another expression for the flame length, which is also given by Crocker and Napier. The flame length calculation is actually for a vertical flame, but it has simpler parameters for its computation, which should result in longer flames.

The length of flame (L) expression is:

$$L = 1.32 \times 10^{-3} Q^{0.52} - a \quad (6-1)$$

where Q = total heat released by combustion (W); and  
a = distance of the base of the flame from the exit (m).

Q is the emission rate times the heat of combustion. The emission rate is calculated from one of the source term algorithms described in Section 2.0. Only those sources with an exit velocity greater than zero are allowed to also have a jet fire analysis performed.

### 6.2 Calculation of the Lift-Off Distance of the Flame

The lift-off distance (a) of the flame from the exit, is:

$$a = 1.6 \pi d_j \frac{U_j}{U_1} \quad (6-2)$$

where  $d_j$  = diameter of the jet;  
 $U_j$  = exit velocity of jet; and  
 $U_1$  = velocity of jet at distance a from the exit, given as 0.2 Mach.

If  $U_j$  is less than  $U_1$ , the value of a is set equal to zero.

### 6.3 Calculation of the Radiation Fields of the Flame

The values of  $a$  and  $L$  are used in placement of the flame. In CHARM, the radiation fields are calculated as if the flame is at the origin of the coordinate system and the centerline is in the direction of the X-axis. The flame may be at an upward angle but the projection of the flame axis into the X-Y plane is assumed to fall on the X-axis. After the calculation is completed, the radiation field is rotated and translated to reflect the actual location of the flame base. This action makes the calculation somewhat simpler by eliminating cross terms in the formulae presented by Crocker and Napier.

#### 6.3.1 Calculation of Radiation Falling on a Horizontal Target

The equation used for the intensity of radiation falling on a horizontal target ( $q_h$ ) is:

$$q_h = \frac{f Q \sqrt{1+m^2}}{2\pi L(b^2 - 4dc)} \left( \frac{B x_L + C}{P_L} - \frac{C}{P_O} \right) \quad (6-3)$$

where  $f$  = fraction of total heat released as radiation

$$= 2.2 \times 10^{-4} \sqrt{H_c M_j}$$

where  $H_c$  = heat of combustion (J/g); and

$M_j$  = molecular weight of jet fluid at exit;

$m$  = slope of flame;

$b$  =  $-2(x-mz)$

$c$  =  $x^2 + y^2 + z^2$ ;

$d$  =  $1+m^2$ ;

$B$  =  $m b + 2dz$ ;

$C$  =  $2 m c + b z$ ;

$$P_L = \sqrt{d x_L^2 + b x_L + c}$$

$$P_O = \sqrt{c}$$

$$x_L = L \cos\left(\frac{\pi}{2} - \Theta\right)$$

$\Theta$  = flame tilt from vertical; and

$x, y, z$  = location of the center of the target relative to the source.

### 6.3.2 Calculation of Radiation Falling on a Vertical Target

The equation for the radiation falling on a vertical target perpendicular to the X-axis ( $q_{v\perp}$ ), outside of the flame and where  $x > x_L$ , is given by:

$$q_{v\perp} = \frac{f Q \sqrt{1+m^2}}{2\pi L(4dc-b^2)} \left( \frac{D x_L + E}{P_L} - \frac{E}{P_O} \right) \quad (6-4)$$

$$\begin{aligned} \text{where } D &= 2x d + b; \text{ and} \\ E &= x b + 2c \end{aligned}$$

Finally, the equation for the radiation falling on a vertical target parallel to the X-axis ( $q_{v=}$ ) is:

$$q_{v=} = \frac{f Q y \sqrt{1+m^2}}{2\pi L(4dc-b^2)} \left( \frac{2d x_L + b}{P_L} - \frac{b}{P_O} \right) \quad (6-5)$$

### 6.3.3 Calculation of the Total Radiation

The intensity of radiation falling on horizontal and vertical targets contributes to the entire radiation being received at the target. The total radiation ( $q$ ) received is calculated as follows:

$$q = \sqrt{q_h^2 + q_{v\perp}^2 + q_{v=}^2} \quad (6-6)$$

The isopleths of radiation flux for the jet fire are determined by performing a binary search in both directions pointed at by the flame. For example, if the flame is pointing from the origin down the X-axis, CHARM first searches down the positive X-axis until the desired radiation flux value is passed, and then it searches down the negative X-axis.

Once the two extremes are found, CHARM arbitrarily divides the distance into twenty segments. For each segment, CHARM performs a binary search left and right of the line on which the flame lays to find the extremes of the desired radiation.



## 7.0 EXPLOSION OVERPRESSURES

CHARM calculates overpressures or shockwave pressures for two scenarios: a sphere bursting due to failure of the vessel and an unconfined vapor cloud explosion. Both of these phenomena are modeled using methods from Baker et al. (1983).

### 7.1 Sphere Burst Overpressure

Although the equations described here are strictly for the mechanical failure of a pressurized sphere, they are used for all cases of pressurized failure. A mechanical failure, such as in an instantaneous gas release, is always assumed to be from a spherical vessel.

Two important factors in a pressurized vessel failure shockwave calculation are the storage pressure and the amount of material stored. Pressure has the units of energy density and describes the amount of energy available for shockwave formation.

The equation for calculating the maximum overpressure of a sphere burst is provided by Liepman and Roshko (1967):

$$\frac{p_1}{p_0} = \frac{p_{s0}}{p_0} \left\{ 1 - \frac{(\gamma_1 - 1) \left( \frac{a_0}{a_1} \right) \left( \frac{p_{s0}}{p_0} - 1 \right)}{\sqrt{2\gamma_0 \left[ 2\gamma_0 + (\gamma_0 + 1) \left( \frac{p_{s0}}{p_0} - 1 \right) \right]}} \right\}^{\left( \frac{-2\gamma_1}{\gamma_1 - 1} \right)} \quad (7-1)$$

- where
- $p_1$  = pressure inside the sphere;
  - $p_0$  = atmospheric pressure;
  - $p_{s0}$  = air shock pressure at the instant of burst;
  - $\gamma_1$  =  $C_p/C_v$  for gas in sphere;
  - $\gamma_0$  =  $C_p/C_v$  for air;
  - $C_p$  = specific heat at constant pressure;
  - $C_v$  = specific heat at constant volume;
  - $a_0$  = speed of sound in air; and
  - $a_1$  = speed of sound in sphere;

The parameter that must be solved for by iteration, is  $p_{s0}/p_0$ .

The value used in CHARM is the overpressure ( $\bar{P}_s$ ), which is defined as follows:

$$\bar{P}_s = \frac{P_s}{P_0} - 1 \quad (7-2)$$

At the sphere surface, the overpressure equation is:

$$\bar{P}_{s0} = \frac{P_{s0}}{P_0} - 1 \quad (7-3)$$

The other parameter required for predicting the overpressure at distances downwind is an energy-scaled radius ( $\bar{R}$ ). At the surface of the sphere, the energy-scaled radius ( $\bar{R}_1$ ) given by Baker is:

$$\bar{R}_1 = \left[ \frac{3(\gamma_1 - 1)}{4\pi \left( \frac{P_1}{P_0} - 1 \right)} \right]^{\frac{1}{3}} = \frac{r_1}{R_0} \quad (7-4)$$

where  $r_1$  = radius of the sphere;

$R_0$  = energy radius

$$= \left( \frac{E}{P_0} \right)^{\frac{1}{3}}$$

$$E = \left( \frac{P_1 - P_0}{\gamma_1 - 1} \right) V_1; \text{ and}$$

$V_1$  = volume of sphere.

Once the values of  $\bar{P}_s$  and  $\bar{R}$  are known at the sphere surface, a curve that agrees with these values can be selected from Figure 7-1. Once a curve is selected, if either value,  $\bar{R}$  or  $\bar{P}_s$ , is known, the other can be calculated. The curves shown in Figure 7-1 have been digitized, and CHARM interpolates the actual curve to use once the conditions at the sphere surface are known. The dimensional pressure and radius can be found by multiplying the dimensionless overpressures and radii by  $p_0$  and  $R_0$ , respectively.

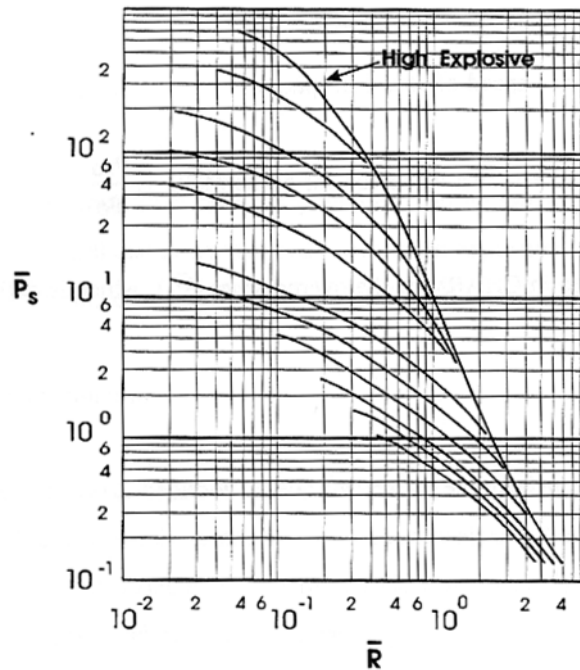


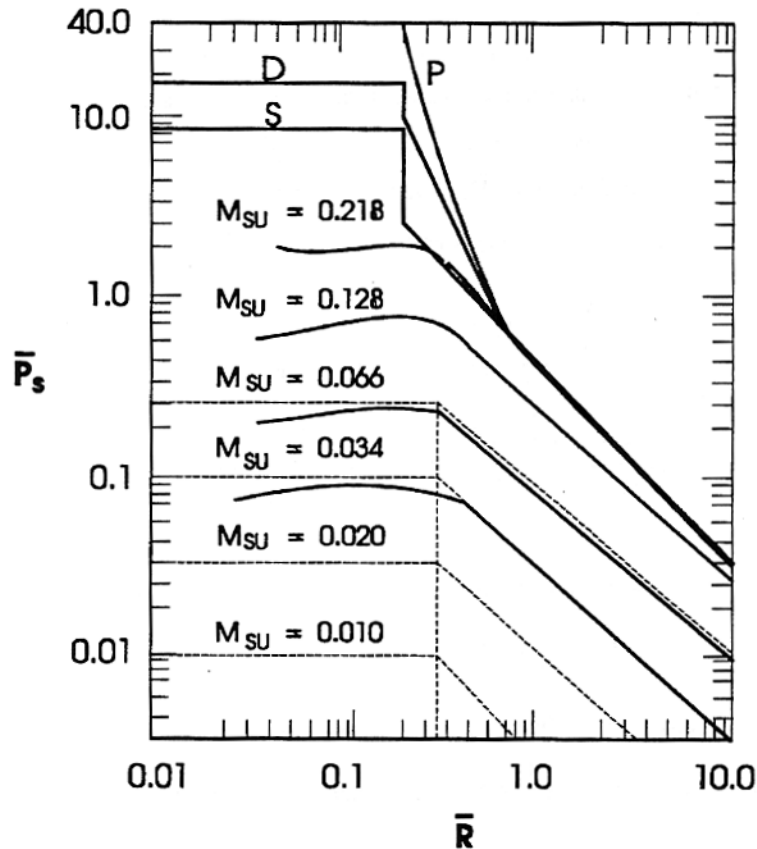
Figure 7-1.  $\bar{P}_s$  Versus  $\bar{R}$  for Sphere Burst Overpressure Calculations.

## 7.2 Unconfined Vapor Cloud Explosion

Vapor cloud explosions are modeled also by determining the  $\bar{P}_s$  and  $\bar{R}$  at some location in the vapor cloud and then using Figure 7-1 to predict the overpressures at any distance. The vapor cloud is subdivided into user-definable cells. These cells are not the ones that CHARM uses to calculate the advection and dispersion of the release. Each cell is exploded individually, and its contribution at a point is individually determined. The maximum overpressure at a point is selected as the maximum overpressure from any of the exploding cells.

The creation of isopleths of overpressure is handled similarly to the jet fire case. The maximum extents of the selected overpressure values upwind and downwind are determined. Once the two extremes are found, CHARM creates a grid containing the impact region.

The amount of mass within an exploding cell is only the amount that is in concentrations greater than the lower explosive limit (LEL). A cloud can either detonate or deflagrate. Detonation is treated as the case limit of deflagration as the flame speed increases. If the flame speed is greater than Mach 1, CHARM treats it as a detonation. Otherwise, CHARM treats it as a deflagration. Figure 7-2 illustrates the hierarchy of mechanisms used. The chosen mechanism is determined by flame speed.



**Figure 7-2. Maximum Wave Overpressure Versus Energy-Scaled Distance for Explosions With an Energy Density  $q = 8$  and Various Normal Burn Velocities.**

Figure 7-2 illustrates the different overpressures that can be expected in the case of a cloud with energy density of 8. The curve labeled P represents Pentolite. All other solid curves were calculated using the CLOUD program. The curve labeled D is for Detonation and S is for a Sphere Burst of the same energy density. The horizontal dashed lines represent the predicted flame overpressures for very low-velocity flames calculated using the theory of Taylor (1946) for piston motion where the piston motion has been transformed to an equivalent normal burning velocity for a flame system. The vertical dashed line in the figure represents the final radius of the cloud based on energy-scaled radius for an energy density of 8 when the energy is added so slowly that there is no pressure rise.

The dashed lines outside this vertical line are predicted overpressures based on the following equation:

$$\bar{P}_s = \frac{1}{\bar{R}} \quad (7-5)$$

The dashed vertical line in the figure represents the final radius of a deflagrating cloud based on an energy-scaled radius when the energy is added so slowly that there is no

pressure rise. This scaled radius is equivalent to the  $\bar{R}_1$  in the sphere burst calculation.  $\bar{R}_1$  is different for a deflagration than a detonation. The value of  $\bar{R}_1$  is:

$$\bar{R}_1 = \begin{cases} \left[ \frac{3(\gamma_1 - 1)}{4\pi q} \right]^{\frac{1}{3}} & \text{detonation} \\ \left[ \left( \frac{q}{\gamma_1} + 1 \right) \frac{3(\gamma_1 - 1)}{4\pi q} \right]^{\frac{1}{3}} & \text{deflagration} \end{cases} \quad (7-6)$$

where  $q$  = energy density  
 $= \frac{H_{\text{ceff}}}{C_{va} T_a}$   
 $H_{\text{ceff}}$  = effective heat of combustion; and  
 $C_{va}$  = specific heat at constant volume of air.

$H_{\text{ceff}}$  is the molar weighted average of the heats of combustion of the released material ( $M_g$ ) and air ( $M_a$ ). Normally, the heat of combustion of air is ignored, so that it can be calculated from:

$$H_{\text{ceff}} = \frac{FG H_c M_g}{FG M_g + (1 - FG)M_a} \quad (7-7)$$

where  $FG$  = molar fraction of the emitted material in the cell

In either deflagration or detonation the value of  $R_0$  is the same:

$$R_0 = \left( \frac{E}{P_0} \right)^{\frac{1}{3}} \quad (7-8)$$

where  $E$  = energy expended from the burn  
 $= m_{\text{lel}} \varepsilon H_c$ ;  
 $m_{\text{lel}}$  = mass above LEL; and  
 $\varepsilon$  = efficiency of explosion.

Given values for  $\bar{R}_1$  and  $R_0$ , a value for  $r_1$  can be calculated. This leaves the computation of the value of  $\bar{P}_s$ . Consider the case of a flame speed of less than Mach 1, which is considered by CHARM to be a deflagration. The value of  $\bar{P}_s$  at  $\bar{R}_1$  is given by Taylor (1946) as:

$$\bar{P}_s = \frac{2\gamma_0 \left(1 - \frac{\rho_2}{\rho_1}\right) \left(\frac{\rho_1}{\rho_2}\right)^2 M_{SU}^2}{1 - \left(1 - \frac{\rho_2}{\rho_1}\right)^{\frac{2}{3}} \left(\frac{\rho_1}{\rho_2}\right)^2 M_{SU}^2} \left(1 - M_{SU} \frac{\rho_1}{\rho_2}\right) \quad (7-9)$$

where  $\rho_1$  = density ahead of the flame;  
 $\rho_2$  = density behind the flame; and  
 $M_{SU}$  = flame speed in Mach.

The ratio of  $\rho_2/\rho_1$  can be taken as the zero pressure rise density change across the flame if the overpressure is assumed to be low, which is valid for many deflagration cases. Using this assumption leads to:

$$\frac{\rho_2}{\rho_1} = \frac{q}{\gamma_1} + 1 \quad (7-10)$$

The Taylor equation breaks down as  $M_{SU}$  gets large. If  $M_{SU}$  gets larger than  $(\rho_2/2) \rho_1$  an extrapolation is made from lower  $M_{SU}$  values. In such a case, the value of  $\bar{P}_s$  is assumed to go as the logarithm of  $M_{SU}$ .

In the detonation case, the sphere burst technique of solution is used after determining an equivalent storage pressure. As shown in Figure 7-2, the detonation and sphere burst curves are similar. In a detonation, there is a choking limit velocity called the Chapman-Jouguet velocity ( $M_{CJ}$ ) that cannot be exceeded.  $M_{CJ}$  is given by:

$$M_{CJ} = \sqrt{\left[\frac{(\gamma_1 + 1)q}{\gamma_1} + 1\right]} + \sqrt{\left[\frac{(\gamma_1 + 1)q}{\gamma_1} + 1\right]^2 - 1} \quad (7-11)$$

The  $\bar{P}_s$  at the speed  $M_{CJ}$  is treated as equivalent to the storage pressure in a bursting sphere and is calculated as:

$$\bar{P}_{CJ} = \frac{1 + \gamma_1 M_{CJ}^2}{\gamma_1 + 1} \quad (7-12)$$

If  $M_{SU}$  is greater than or equal to  $M_{CJ}$ , the problem is treated as a bursting sphere with the internal storage pressure given as  $\bar{P}_{CJ}$ . If  $M_{SU}$  is less than  $M_{CJ}$ , a second  $\bar{P}_s$  is calculated for a bursting sphere at the same value of  $q$  as in the vapor cloud explosion calculation.

The shockwave speed for the bursting sphere ( $M_{bs}$ ) from Liepmann and Roshko (1967) is:

$$M_{bs} = \sqrt{1 + \frac{(\gamma_1 + 1)q}{2\gamma_1}} \quad (7-13)$$

Once again,  $\bar{P}_s$  is assumed to go as the logarithm of  $M_{SU}$ . With the two values of  $\bar{P}_s$  and the two values of  $M$ , an equation can be formulated to estimate the value of  $\bar{P}_s$  for the given flame speed,  $M_{SU}$ .

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