

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 3D Eulerian grid model. The grid determines the region of computation. Beyond the grid all concentrations and impacts are assumed to be zero.

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's calculations consider vapor and particle mass, particle number, energy, and momentum.

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

- X, Y, Z position;
- Chemical mass rate (vapor and liquid phases);
- Temperature;
- Air mass rate;
- Water vapor mass rate;
- Direction and speed of exit velocity; and
- Dimensions.

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;
- User-specified; and
- User-defined grid of concentrations.

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. The concentrations at the grid cells are held constant throughout the release.

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:

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

where C_d = discharge coefficient (0.65);
 P_c = pressure in container;
 P_a = ambient pressure;
 ρ_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 ε = roughness length for clean pipes;
 Re = Reynolds number ($= \frac{d u \rho_L}{\nu}$); and
 ν = 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
 ρ_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:

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

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 γ = 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 ρ_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 (ΔH) and density (ρ_*) 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

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

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:

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

Given T_{rel} and x_{rel} allows an estimate of enthalpy change (ΔH) and density ρ_{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 σ_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 (Δt) 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);
 α_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 λ 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

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

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

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

α = thermal diffusivity;

ρ = 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;
 γ_L = liquid surface tension;
 μ_L = dynamic liquid viscosity;
 ε = 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

ShL = 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_{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/m² s) when multiplied by the chemical's heat of evaporation, ΔH_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_{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_{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_{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 κ_{surf} = thermal diffusivity of the surface; and
 κ_{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_p = 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_r = reduced temperature ($=T/T_c$);
T = temperature of liquid (K);
 T_c = 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_b = 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;
- 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 vapor; 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);
 E₀ = initial emission rate; and
 t_e = total time of emission.

The amount of mass emitted (GM) between times t₁ and t₂ (where t₂ = t₁ + Δt) 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 t₁ and t₂ 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.

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, 7th Edition, 1997

Container/Surface Description Release

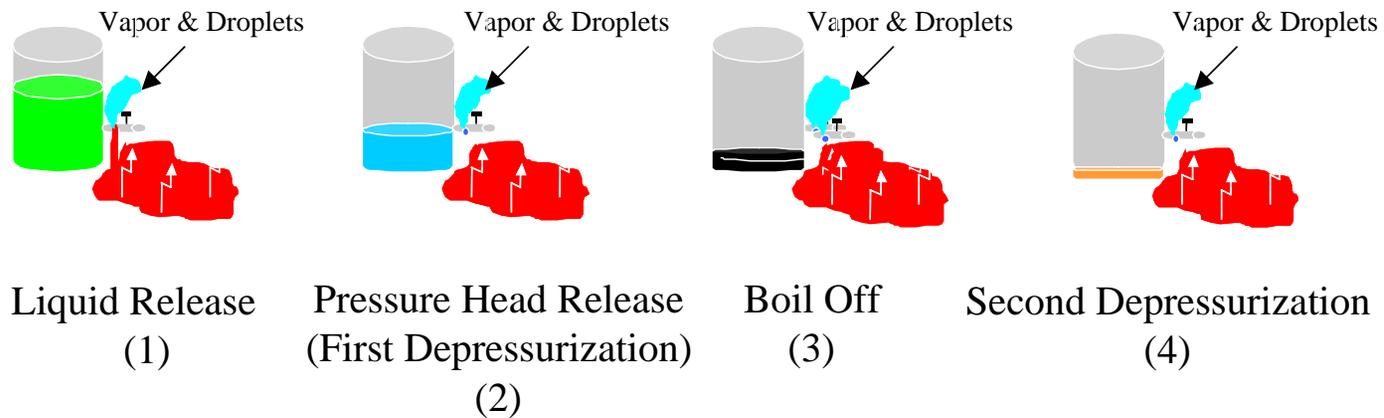


Figure 2-1. Schematic of Release Phases for Container/Release Description.

Phases of Emission

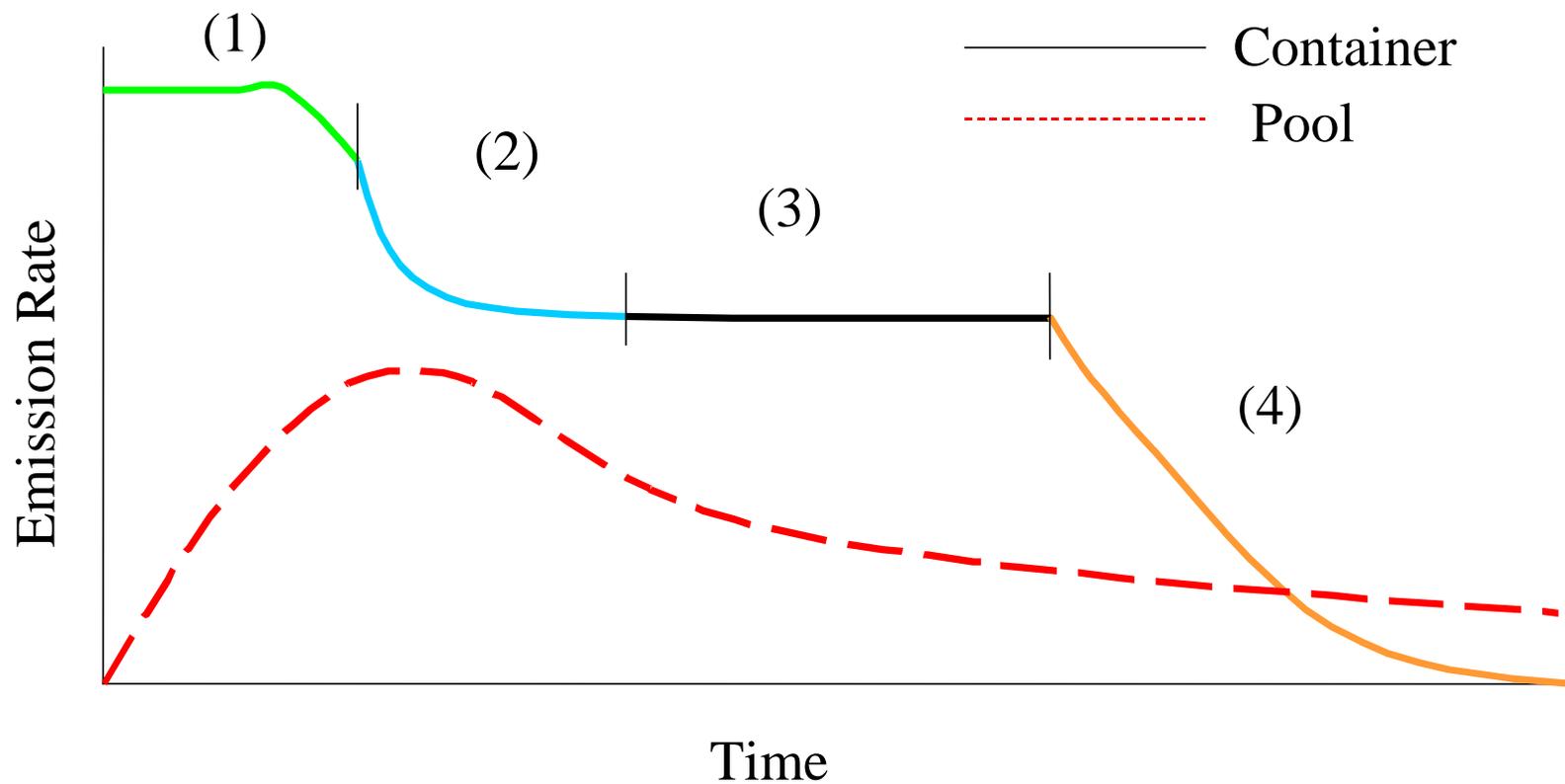


Figure 2-2. Example Emission Rate Over Time For Container Release With Pool Formation.

Liquid Release Fates

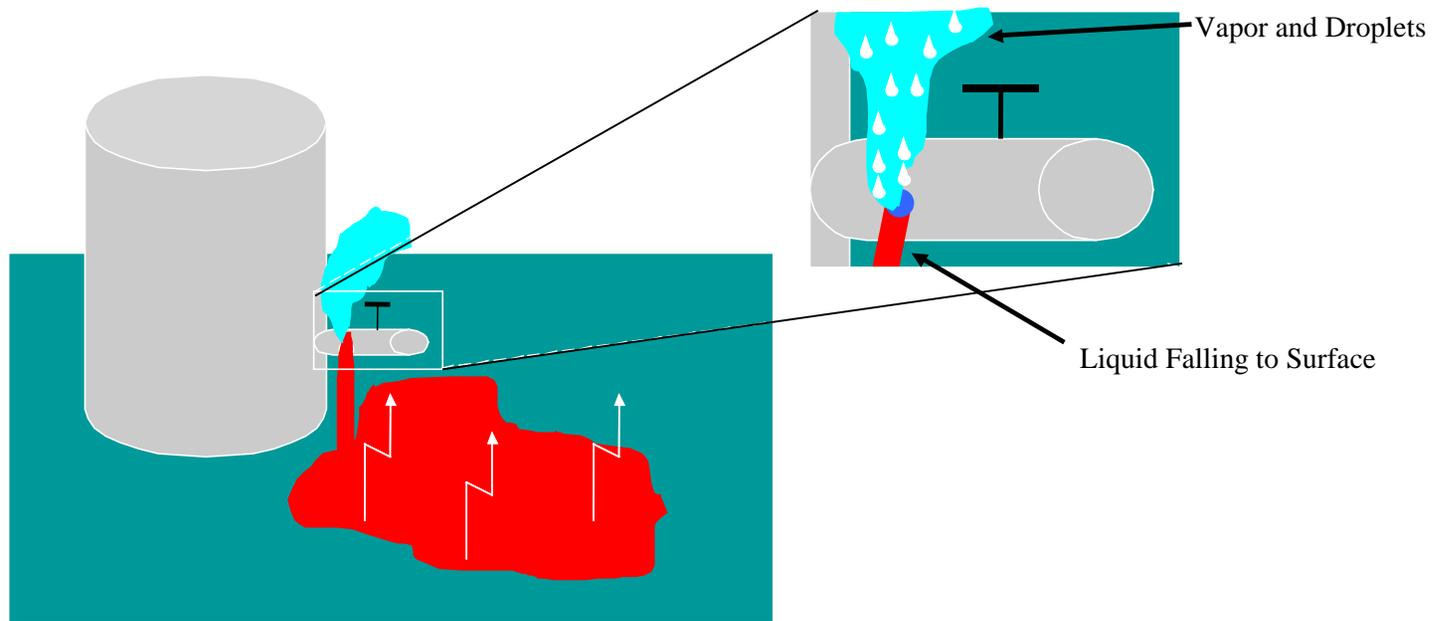


Figure 2-3. Closeup of Liquid Release Phase.

3.0 CHARM FORMULATION

There are a number of parameters calculated in CHARM as they move throughout the atmosphere. These parameters include, momentum, energy, gas concentration, particle concentration, and particle number. The advection and dispersion calculation for each of these parameters are essentially identical. Some of the parameters have extra terms to calculate processes that are particular to a parameter. The basic equations are given here. More detail on the particular terms for some of the parameters follows.

Conserved parameters (p – momentum and energy) governing equation:

$$\begin{aligned} & -\frac{\partial up_i}{\partial x} - \frac{\partial vp_i}{\partial y} - \frac{\partial wp_i}{\partial z} && \text{advection} \\ \frac{\partial p_i}{\partial t} = & + \frac{\partial}{\partial x} K_x \frac{\partial p_i}{\partial x} + \frac{\partial}{\partial y} K_y \frac{\partial p_i}{\partial y} + \frac{\partial}{\partial z} K_z \frac{\partial p_i}{\partial z} && \text{diffusion} \\ & + S_i && \text{source} \end{aligned} \quad (3-1)$$

Gas concentration equation

$$\begin{aligned} & -\frac{\partial uc_i}{\partial x} - \frac{\partial vc_i}{\partial y} - \frac{\partial wc_i}{\partial z} && \text{advection} \\ \frac{\partial c_i}{\partial t} = & + \frac{\partial}{\partial x} K_x \frac{\partial c_i}{\partial x} + \frac{\partial}{\partial y} K_y \frac{\partial c_i}{\partial y} + \frac{\partial}{\partial z} K_z \frac{\partial c_i}{\partial z} && \text{diffusion} \\ & + S_i && \text{source} \\ & - P_{cond}_i && \text{condensation onto particles} \\ & + P_{evap}_i && \text{evaporation of particles} \end{aligned} \quad (3-2)$$

Particle concentration equation

$$\begin{aligned} & -\frac{\partial un_i}{\partial x} - \frac{\partial vn_i}{\partial y} - \frac{\partial wn_i}{\partial z} && \text{advection} \\ \frac{\partial n_i}{\partial t} = & + \frac{\partial}{\partial x} K_x \frac{\partial n_i}{\partial x} + \frac{\partial}{\partial y} K_y \frac{\partial n_i}{\partial y} + \frac{\partial}{\partial z} K_z \frac{\partial n_i}{\partial z} && \text{diffusion} \\ & + S_i && \text{source} \\ & + \frac{\partial V_s n_i}{\partial z} && \text{sedimentation} \\ & \pm C_i && \text{coagulation} \end{aligned} \quad (3-3)$$

where V_s = the sedimentation velocity of particle of radius r_i :

$$V_s = \frac{2\rho_{\text{part}} r_i^2 g}{9\eta} \left\{ 1 + \text{Kn}_i \left[A + B \exp\left(\frac{-C}{\text{Kn}_i}\right) \right] \right\} \quad (3-4)$$

where

$$\text{Kn}_i = \text{Knudsen number} = \frac{\lambda_g}{r_i}$$

ρ_{part} = particle density

g = gravitational acceleration

η = dynamic viscosity of air

A, B, C = corrections for particle resistance to motion (Millikan, 1923)

A, B, C = 1.246, 0.42, 0.87 (Kasten, 1968)

The mean free path of a gas molecule (λ_g) is given in terms of viscosity and air density (ρ_g) as:

$$\lambda_g = \frac{2\eta}{\rho_g \bar{v}_g} \quad (3-5)$$

The value of \bar{v}_g is given by:

$$\bar{v}_g = \sqrt{\frac{8k_B T}{\pi m_{\text{air}}}} \quad (3-6)$$

where k_B = Boltzmann's constant

T = temperature

m_{air} = mass of an air molecule

Particle mass equation

$$\begin{aligned} & -\frac{\partial u m_i}{\partial x} - \frac{\partial v m_i}{\partial y} - \frac{\partial w m_i}{\partial z} && \text{advection} \\ \frac{\partial m_i}{\partial t} = & + \frac{\partial}{\partial x} K_x \frac{\partial m_i}{\partial x} + \frac{\partial}{\partial y} K_y \frac{\partial m_i}{\partial y} + \frac{\partial}{\partial z} K_z \frac{\partial m_i}{\partial z} && \text{diffusion} \\ & + S_i && \text{source} \\ & + P_{\text{cond}_i} && \text{condensation} \\ & - P_{\text{evap}_i} && \text{evaporation} \end{aligned} \quad (3-7)$$

3.1 Grid Definition

A 3D grid is required for the calculation. For each grid column (at an x, y location) two parameters are required. One is the elevation of the terrain in that column, the second is the surface roughness.

The CHARM Editor (CharmEd) has the capability of reading in DEM files and Globe data files to determine the terrain elevations over a grid once the position and size of the grid has been set. CharmEd also has the capability of reading in USGS land use files. The land use classifications are set to various surface roughnesses. The user can modify the relationship between land use and surface roughness. Of course, surface roughness and elevation can be set by the user for each grid cell.

It is suggested that the number of cells in the vertical should be sufficient so that the highest terrain is within the grid. That is, it is best if there are no grid columns that are completely within the terrain.

3.2 West Wind Field Model

CHARM is designed to be used with as little or much meteorological data as are available, since possible applications range from unmonitored wilderness to intensively instrumented research areas. Thus, the wind field uses any and all available data, with its accuracy improving with increased, usable data.

Atmospheric stability data are interpolated via a $1/r^2$ weighting to produce a stability field over the computational domain (1.0 = A stability, 7.0 = G stability). Wind observations are projected upwards from the measurement point through the portion of the grid without any measurement. Such projected data are weighted as 0.001 compared with user-specified weighting of from 0.0 to 1.0.

The projections are based on a power law extrapolation of the form

$$S = S_0 \left(\frac{z}{z_0} \right)^P \quad (3-8)$$

for speeds S and S_0 at vertical coordinates z and z_0 , respectively, with P determined by linear interpolation from the following table:

Stability	A	B	C	D	E	F	G
Category	1	2	3	4	5	6	7
P	0.15	0.17	0.20	0.26	0.39	0.48	0.54

The maximum wind speed allowed is 20 m/sec and the initial z_0 is assumed equal to $\Delta z/2$. After the wind speeds are projected upwards, the wind speed and direction are resolved into u and v vector components at every wind data site. Next, the entire wind field is developed via a weighted $1/r^2$ interpolation of the vertical profiles for each horizontal plane. Up to this point, terrain has not been considered. Terrain first enters by shifting the interpolated winds upward to clear the terrain. Thus, a complete wind field is calculated. However, this wind field is not satisfactory since it is not divergence-free (and it has no vertical components). Before the winds are made divergence-free, the velocity fluxes in and out of the boundaries of the computational domain are adjusted such that the flux in equals the flux out. If the wind field were to be made divergence-free at this point, the effects of atmospheric stability would be lost. Atmospheric stability has the effect of varying the relative response to terrain of horizontal and vertical motion. This is accomplished by varying the relative transparencies of the horizontal and vertical cell faces. The assignment of transparency was developed on the basis of simulations of idealized problems and appears to be qualitatively correct. The assignment of transparency is as follows:

Stability Category		1	2	3	4	5	6	7
Horizontal Transparency	T_x, T_y	1.0	1.0	1.0	1.0	200.	500.	1000.
Vertical Transparency	T_z	1.6	1.4	1.2	1.0	0.8	0.6	0.4

Terrain cells are assigned zero transparency.

The non-divergence of the wind field is imposed by an interactive solution based on calculating the divergence such that:

$$\nabla U = \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = \mathfrak{D} \quad (3-9)$$

and readjusting the velocity to minimize the divergence.

$$\begin{aligned} u &= u + \alpha \mathfrak{D} \\ v &= v + \alpha \mathfrak{D} \\ w &= w + \alpha \mathfrak{D} \end{aligned} \quad (3-10)$$

In finite difference, these expressions are written as:

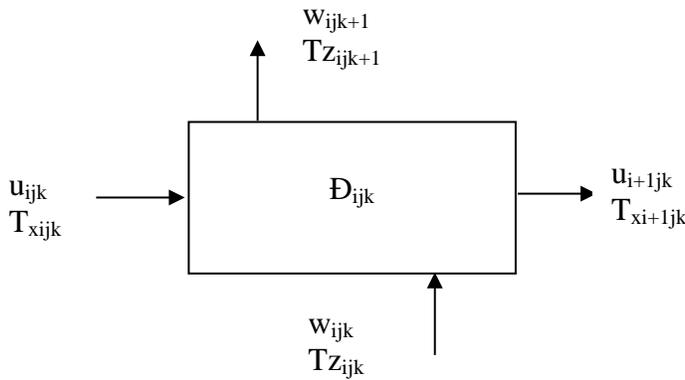
$$\frac{u_{ijk} - u_{i-1jk}}{\Delta x} + \frac{v_{ijk} - v_{ij-1k}}{\Delta y} + \frac{w_{ijk} - w_{ijk-1}}{\Delta z} = \mathfrak{D}_{ijk} \quad (3-11)$$

$$\begin{aligned}
u_{ijk} &= u_{ijk} - \frac{\alpha}{\Delta x} \mathcal{D}_{ijk} T_{xijk} \\
v_{ijk} &= v_{ijk} - \frac{\alpha}{\Delta y} \mathcal{D}_{ijk} T_{yijk} \\
w_{ijk} &= w_{ijk} - \frac{\alpha}{\Delta z} \mathcal{D}_{ijk} T_{zijk}
\end{aligned}
\tag{3-12}$$

where

$$\alpha = \frac{\beta}{\left\{ \frac{(T_{xijk} + T_{xi+1,jk})}{\Delta x^2} + \frac{(T_{yijk} + T_{yij+1k})}{\Delta y^2} + \frac{(T_{zijk} + T_{zijk+1})}{\Delta z^2} \right\}}
\tag{3-13}$$

where β is an over-relaxation factor ($1.0 \leq \beta < 2.0$) and is set to 1.25. The positioning of the variables is illustrated below:



The subroutine sweeps through the grid from each of the eight corners for fifteen cycles. After each cycle, the wind data profiles are incorporated in the wind field by a weighted averaging of the iterative solution. At the completion of the iterative cycles, all residual divergences are swept out the top of the grid. This completes the wind field development.

3.3 Myrup-Ranzieri Diffusivity Model

CHARM uses the Myrup/Ranzieri (M/R) (Myrup and Ranzieri, 1976) model for calculating the diffusivity of the atmosphere. The model calculates the surface wind speed and the Monin-Obukhov length (L) based on the surface stability and surface roughness parameter (Z_0). The determination of the Monin/Obukhov length is based on a three-part linear fit to the curves presented in the original M/R paper. The fitted curves are shown in Figure 3-1. A linear interpolation between integerized stability classifications is performed.

The top and bottom of the inversion (if any) is determined as follows. The inversion base height relative to the terrain (ZI_{base}) is calculated from:

$$ZI_{\text{base}} = \begin{cases} (k_2 - k_1 + 0.5)\Delta z & k_1 \neq k_2 \\ 0 & k_1 = k_2 \end{cases} \quad (3-14)$$

where k_1 is the k-coordinate of the first cell lying above the terrain and k_2 is the k-coordinate of the first cell that has a stability number greater than 4.5. If there are no cells with a stability category number greater than 4.5, ZI_{base} is set equal to -99.00.

The top of the inversion relative to the terrain (ZI_{top}) is calculated from:

$$ZI_{\text{top}} = (k_4 - k_1 + 0.5)\Delta z \quad (3-15)$$

where k_4 is the k-coordinate of the first cell above the inversion base with a stability category number less than 4.5. If no such cell is found, ZI_{top} is set equal to 10^6 . The vertical diffusivities are calculated by looping over the vertical cells and determining if the cell is:

1. below the inversion base or inside a surface inversion,
2. inside the elevated inversion, or
3. above the top of the inversion.

For the first case,

$$D = \begin{cases} 0.35 U_* z \left(1 + 4.7 \frac{z}{L} \right) & L \geq 0 \\ 0.35 U_* z \left(1 - 15 \frac{z}{L} \right)^{\frac{1}{4}} & L < 0 \text{ and } \frac{z}{L} < 27.6 \\ 0.5 U_* z \left(-\frac{0.4}{0.35} \frac{z}{L} \right)^{\frac{1}{3}} & L < 0 \text{ and } \frac{z}{L} \geq 27.6 \end{cases} \quad (3-16)$$

where z = the height above the ground
 L = the Monin-Obukhov length, and
 U_* = the friction velocity

$$U_* = \begin{cases} \frac{0.35 U_0}{\ln\left(\frac{z}{z_w}\right) + 4.7\left(\frac{z_w - z_0}{L}\right)} & L \geq 0 \\ \frac{0.35 U_0}{\ln\left(\frac{z'_w - 1}{z'_w + 1}\right) + 2 \tan^{-1}(z'_w) - \ln\left(\frac{z'_0 - 1}{z'_0 + 1}\right) - 2 \tan^{-1}(z'_0)} & L < 0 \end{cases} \quad (3-17)$$

$$z'_w = \left(1 - 15 \frac{z_w}{L}\right)^{\frac{1}{4}} \quad (3-18)$$

$$z'_0 = \left(1 - 15 \frac{z_0}{L}\right)^{\frac{1}{4}} \quad (3-19)$$

U_0 is wind speed at a height z_w above the surface and

$$z_w = \frac{\Delta z}{2} \quad (3-20)$$

The parameter z_0 is the surface roughness.

The vertical diffusivity D is further modified by the function

$$D = D \left(1.1 - \frac{z}{ZI_{\text{base}}}\right)^{\frac{1}{4}} \quad (3-21)$$

when

$$0.1ZI_{\text{base}} < z < 1.1ZI_{\text{base}} \quad (3-22)$$

For the second case (inside an elevated inversion), the surface wind speed is set to 3.0 m/sec, the Monin-Obukhov length is set to 20.0, and z (the height above the surface) is measured from ZI_{base} .

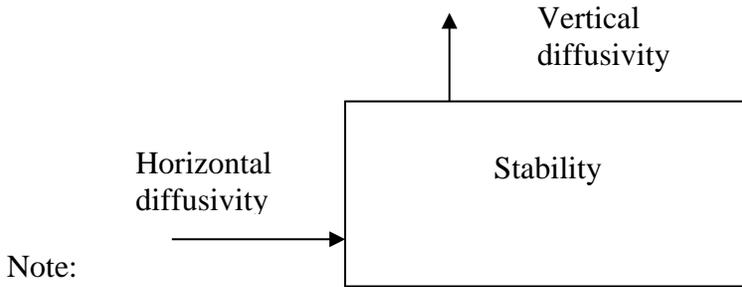
Above the elevated inversion, the third case, neutral stability is assumed and z is measured from the top of the inversion ZI_{top} . The vertical diffusion is then limited by

$$0.001 \frac{\text{m}^2}{\text{sec}} < D < 1000 \frac{\text{m}^2}{\text{sec}} \quad (3-23)$$

and assigned to the top face of the cell.

The horizontal diffusivities are calculated using the relation $D_H = \alpha D_V$ where α is 2 for all stability classes. The value of 2 was selected for two reasons. First, it seemed to be a reasonable average for cases of vertical shear (Jacobitz, 2000). Second, if it is assumed that the square of the Pasquill-Gifford coefficients (σ) are proportional to D times time since release, the average ratio of diffusivities appear to approach 1.5 to 3 across all stability classes as time since release approaches zero.

The location of the related stability vertical diffusivity and horizontal diffusivity parameters are indicated below:



Because the diffusivities are face-centered, the vertical stability is offset one-half cell above the cell center; the horizontal diffusivity is offset one-half cell to the left of the cell center.

3.4 Advection and Diffusion

The advection and diffusion formulation is the same for all constituents simulated: gases, aerosols, momentum, and energy. The advection/diffusion time step is calculated such that the maximum normalized flux across any cell is less than alpha, i.e.:

$$\Delta t = \frac{\alpha}{F_{\max}} \quad (3-24)$$

where

$$F_{\max} = \text{Maximum} \left(\frac{U_i}{\Delta x_i} + 2 \frac{K_{x_i}}{\Delta x_i^2} \right) \quad i = 1, 2, 3 \quad (3-25)$$

The time step is limited to no less than the default time of 0.01 seconds. Adding a statement in the initialization file can change this value.

The model solves the differential equation describing advection and diffusion of a parameter (C), i. e.:

$$\frac{\partial C}{\partial t} = -\nabla u C + \nabla^2 K C \quad (3-26)$$

The solution is performed separately in each direction with the form

$$\frac{\partial C}{\partial t} = -\frac{\partial u C}{\partial x} + \frac{\partial}{\partial x} K_x \frac{\partial C}{\partial x} \quad (3-27)$$

The value of u to be used is determined from the ambient wind velocity and modifications to that velocity due to the presence of mass that has been emitted into the grid. The first modification is due to the emitted momentum in each direction:

$$u' = \frac{m_a u + p_e}{m_t} \quad (3-28)$$

where u' = the new wind speed
 u = the atmospheric wind speed
 m_a = the mass of air in a cell
 m_t = the total mass in a cell
 p_e = the momentum in a cell from an emission

The mass from an emission is tracked for each cell as well as the fraction that may be in droplet form. The volume occupied by the mass from an emission can then be calculated. Whatever volume remains in a cell is assumed to be air.

The next modification is only to the vertical component of the velocity and is due to buoyancy. If the difference of the cell's density (ρ) with the ambient density (ρ_a) is greater than one percent of ρ_a then the vertical velocity may be modified. If the cell's bottom is not in contact with terrain the vertical velocity is assumed to be changing by:

$$\frac{dw}{dt} = g \left(\frac{\rho_a}{\rho} - 1 \right) \quad (3-29)$$

where g = gravitational acceleration = 9.8 m/sec²

If the bottom of the cell is in contact with the ground and the density difference is less than -0.01, the vertical motion due to slump is assumed to be transferred to horizontal motion. The horizontal velocity due to the downward motion is given by:

$$u' = \sqrt{-2g \left(\frac{\rho_a}{\rho} - 1 \right) \Delta z} \quad (3-30)$$

The finite difference solution is based on a flux-corrected version of Crowley's (1968) second-order advection scheme (Sklarew and Wilson, 1976). For the n^{th} time step of the concentration (C) of the i^{th} species in the x direction:

$$C_i^{n+1} = C_i^n + \left(F_{i-\frac{1}{2}}^n - F_{i+\frac{1}{2}}^n \right) \frac{\Delta t}{\Delta x} \quad (3-31)$$

where

$$F_{i+\frac{1}{2}}^n = \frac{\Delta x}{2\Delta t} \left\{ (C_i^n + C_{i+1}^n) \alpha_{i+\frac{1}{2}} + (C_i^n - C_{i+1}^n) \alpha_{i+\frac{1}{2}}^2 \right\} + K_{xi+\frac{1}{2}} \left(\frac{C_i^n - C_{i+1}^n}{\Delta x} \right) \quad (3-32)$$

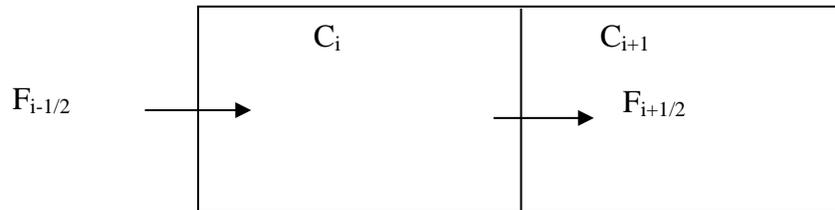
and

$$\alpha_{i+\frac{1}{2}} = u_{i+\frac{1}{2}} \frac{\Delta t}{\Delta x} \quad (3-33)$$

The flux corrector prohibits the calculation of negative concentrations and by an adjustment of the flux, as follows:

$$F_{i+\frac{1}{2}} = \begin{cases} \min \left(F_{i+\frac{1}{2}}, \frac{\Delta x}{\Delta t} C_i, \frac{\Delta x}{\Delta t} C_i + F_{i-\frac{1}{2}} \right) & F_{i+\frac{1}{2}} \geq 0 \\ \min \left(-F_{i+\frac{1}{2}}, \frac{\Delta x}{\Delta t} C_{i+1} \right) & F_{i+\frac{1}{2}} < 0 \end{cases} \quad (3-34)$$

The location of the related concentrations and fluxes are indicated below:



3.5 Cell Temperature

The temperature in each cell is calculated for each time step. The calculation is given by:

$$T_c = \frac{E_e + m_{\text{air}} C_{\text{pair}} (T_{\text{amb}}) T_{\text{amb}}}{m_{\text{air}} C_{\text{pair}} (T_c) + \sum_{i=1}^{i=n_c} m_i \left((f_{\text{di}} C_{\text{pli}} (T_c) + (1 - f_{\text{di}}) C_{\text{pvi}} (T_c)) \right)} \quad (3-35)$$

where T_c = cell temperature;
 E_e = energy in the cell from the emissions;
 m_{air} = mass of air in the cell;
 n_c = number of emitted species;
 $C_{pair}(T)$ = heat capacity of air at temperature T;
 $C_{pli}(T)$ = heat capacity of the liquid i^{th} species at temperature T;
 $C_{pvi}(T)$ = heat capacity of the vapor i^{th} species at temperature T;
 f_{di} = mass fraction of the i^{th} species in droplet form;
 T_{amb} = ambient temperature;
 m_i = mass of the i^{th} species in cell.

The equation needs to be solved iteratively since the term T_c cannot be totally isolated.

For each time step energy is added to the source's grid cells. The energy is then allowed to advect and disperse according to Equation 3-1. The amount of energy added to a source's grid cell (ΔE_e) in a time step (dt) is defined as:

$$\Delta E_e = \sum_{i=1}^{i=n_c} R_i \left((f_{di} C_{pli}(T_e) + (1-f_{di}) C_{pvi}(T_e)) \right) dt \quad (3-36)$$

where T_e = emission temperature
 R_i = emission rate of the i^{th} species

3.6 Convective Heat Transfer

Heat can be transferred between the plume just above the terrain and the terrain itself. The heat transfer is allowed only when that portion of the plume that is not at the source location and is in contact with the ground.

The rate that energy (q) is transferred between the plume and the ground is given by:

$$\frac{dq}{dt} = h A (T_g - T_c) \quad (3-37)$$

where h = convective heat transfer coefficient (assumed to be 100 W/m² K)
 A = surface area shared by the cell and ground
 T_g = surface or ground temperature (assumed to be ambient)
 T_c = cell temperature

The addition or loss of energy can raise or lower the cell temperature to a new value. After the heat is added or depleted from the cell a new cell temperature is calculated.

3.7 Surface Deposition of Chemical Vapor

The vapor state of an emitted chemical is allowed to be deposited on any surface that it comes in contact with. This means that vertical as well as horizontal surfaces can be sinks for a species. If an open (no terrain or building in it) grid cell abuts another cell that is solid, that side of the cell can be a deposition point.

It is assumed that all mass that diffuses to a surface is available for deposition. The rate that the species is taken up by the surface is assumed to be instantaneous. A simple expression for the rate of concentration change due to mass transfer limited deposition can be derived from Grove, 1967 as:

$$\frac{dc}{dt} = \frac{D_{AB}}{\delta} \frac{A}{V} (C_g - C_s) \quad (3-38)$$

where m = mass in a cell
 D_{AB} = binary diffusion coefficient for the chemical in air
 δ = depth of boundary layer above solid cell
 A = surface area of the cell side abutting a solid cell (dx dy, dx dz, or dy dz)
 V = volume of grid cell (dx dy dz)
 C_g = concentration of the gas in the cell
 C_s = concentration of the gas immediately at the surface (assumed zero, immediate reaction with surface)

The value for the diffusion layer thickness (δ) is estimated from the expression in Sverdrup, 1951 as:

$$\delta = \lambda \frac{V}{u_*} \quad (3-39)$$

where λ = factor from Von Karman = 11.5
 ν = kinematic viscosity of chemical-air mixture
 u_* = friction velocity = $k z_{ref} \frac{du}{dz}$
 u = wind speed at altitude z_{ref}
 k = von Karman's constant = 0.4
 z_{ref} = reference altitude = minimum of 6 cm (from Mangarella, et al, 1973) and z_0
 z_0 = surface roughness

If a cell's dimensions are dx, dy, and dz, the A/V term in the deposition rate calculation is dependent on the surface on which the deposition is occurring. If the surface is perpendicular to the x-axis it becomes 1/dx. If perpendicular to the y-axis it becomes 1/dy. If perpendicular to the z-axis it becomes 1/dz. The values of the rate of change

concentration due to deposition onto a surface are added together for each surface that may be abutting a cell.

The user can specify an efficiency of the deposition. The rate of change of concentration is multiplied directly by that efficiency. If the efficiency is zero, then no deposition is assumed to occur. Currently the deposition efficiency is allowed to be any value. Because the efficiency can be any value it could be negative which would then treat the reverse of deposition or out-gassing from the surface. However, since the deposition term is a function of the concentration in the cell it would be better to use a normal source in the cell.

If the efficiency factor is greater than 1, the deposition is enhanced. If this is the case, for example, due to something like electric forces, an attempt at considering those effects can be made. Normally the deposition efficiency should be zero (no deposition) or one (deposition due solely to diffusion to surface and instantaneous and complete reaction).

3.8 Source Terms

The grid cells that have sources in them have mass, momentum, and energy added to them at the beginning of each time step. Complete mixing is assumed to occur in the grid cell in which the emission occurs.

3.9 Particles

Particles or aerosols are modeled as existing in a number of size bins. The size bins are geometric in nature. That is, the particle volume in a size bin (v_i) is equal to the next smaller volume bin (v_{i-1}) times a constant value (V_{rat}). In terms of the bin with the smallest volume (v_0), the volume of the i^{th} bin is given as:

$$v_i = v_0 V_{rat}^i \quad (3-40)$$

The particle radius for the i^{th} bin is then given as:

$$r_i = r_0 V_{rat}^{\frac{i}{3}} \quad (3-41)$$

If there is more than one definition of the size bins from the input (each release can have its own size distribution), the model uses the smallest value of V_{rat} , the smallest value of v_0 and the largest bin volume to determine a new size bin distribution.

When two particles of volumes v_i and v_j collide and stick the volume ($V_{i,j}$) of the resulting particle is:

$$V_{i,j} = v_i + v_j \quad (3-42)$$

The volume of the resulting particle is partitioned between the two size bins k and $k+1$. The partitioning is performed in the manner described by Jacobson, et al., 1994.

$$f_{i,j,k} = \begin{cases} \left(\frac{v_{k+1} - V_{i,j}}{v_{k+1} - v_k} \right) \frac{v_k}{V_{i,j}} & v_k \leq V_{i,j} < v_{k+1} & k < (N_B - 1) \\ 1 - f_{i,j,k-1} & v_{k-1} < V_{i,j} < v_k & k > 0 \\ 1 & V_{i,j} \geq v_k & k = (N_B - 1) \\ 0 & \text{all other cases} \end{cases} \quad (3-43)$$

where N_B = the number of size bins

Following Jacobsen and Turco, 1995, the general formula for calculating the number concentration change of particles due to coagulation is given by:

$$\frac{dC_k}{dt} = \frac{1}{2} \sum_{j=0}^k \left(\sum_{i=0}^{k-1} f_{i,j,k} \beta_{i,j} C_i C_j \right) - C_k \sum_{j=0}^{N_B} (1 - f_{k,j,k}) \beta_{k,j} C_j \quad (3-44)$$

Jacobsen, et al., 1994 provides the formula for the volume-conserving calculation of the coagulation of particles of uniform composition as:

$$\frac{d(C_k v_k)}{dt} = \sum_{j=0}^k \left(\sum_{i=0}^{k-1} f_{i,j,k} \beta_{i,j} C_i V_{i,j} C_j \right) - C_k \sum_{j=0}^{N_B} (1 - f_{k,j,k}) V_{k,j} \beta_{k,j} C_j \quad (3-45)$$

The Brownian diffusion kernel ($\beta_{i,j}$) used in the calculation is from Fuchs (1964):

$$\beta_{i,j} = \frac{4\pi(r_i + r_j)(D_i + D_j)}{r_i + r_j + \sqrt{\delta_i^2 + \delta_j^2} + \frac{4(D_i + D_j)}{(r_i + r_j)\sqrt{\bar{v}_{pi}^2 + \bar{v}_{pj}^2}}} \quad (3-46)$$

where the particle diffusion coefficient (D_i) is defined by:

$$D_i = \frac{k_B T}{6\pi r_i \eta} \left\{ 1 + Kn_i \left[A + B \exp\left(\frac{-C}{Kn_i}\right) \right] \right\} \quad (3-47)$$

The value of \bar{v}_p is given by the general formula:

$$\bar{v}_p = \sqrt{\frac{8k_B T}{\pi m_{part}}} \quad (3-48)$$

where m_{part} = the mass of a particle

The mean distance (δ) traveled by a particle leaving a sphere's surface and going the particles mean free path distance (λ_{pi}) is given by Fuchs (1964) as:

$$\delta_i = \frac{\left\{ (2r_i + \lambda_{\text{pi}})^3 - (4r_i^2 + \lambda_{\text{pi}}^2)^{\frac{3}{2}} \right\}}{6r_i \lambda_{\text{pi}}} - 2r_i \quad (3-49)$$

where

$$\lambda_{\text{pi}} = \frac{8D_i}{\pi \bar{v}_{\text{pi}}} \quad (3-50)$$

Condensation and evaporation is calculated using the expression given by Fleagle and Businger (1963) for droplets in the atmosphere:

$$\frac{dm_d}{dt} = 4 \pi \frac{r D MW}{R T} (e_{\infty} - e_{\text{sc}}) \quad (3-51)$$

where m_d = mass of a drop in a size bin;
 r = drop radius;
 D = the diffusion coefficient;
 MW = molecular weight of the material in the drop;
 R = universal gas constant;
 T = temperature of air surrounding the drop;
 e_{∞} = vapor pressure of the material in the drop surrounding the drop;
 e_{sc} = saturation vapor pressure of the material in the drop.

The value of e_{sc} is the value of the saturation vapor pressure of the material in the drop over a flat surface (e_s), corrected for the curvature of the drop. It is given as:

$$e_{\text{sc}} = e_s \exp\left(\frac{2 \sigma MW}{\rho R T r}\right) \quad (3-52)$$

where σ = surface tension of the material in the drop;
 ρ = density of the drop.

Once mass has been evaporated or condensed the particles in the i^{th} size bin move to another size bin because the volume has changed. Since the number of droplets have not changed the new volume of the droplets (V_{di}) is given by:

$$V_{di} = \frac{M_i^{t+\Delta t}}{C_i^{t+\Delta t} \rho_{\text{drop}}} \quad (3-53)$$

where ρ_{drop} = the density of a particle.

The particles with a new volume can be allocated as above using the fraction $f_{i,j,k}$ with $V_{i,j}$ replaced by V_{di} .

When condensation or evaporation occurs latent heat and sensible heat can be exchanged. The exchanged energy (dE) can be given as:

$$\frac{dE}{dt} = L_v \frac{dm_d}{dt} \quad (3-54)$$

where L_v = latent heat of drop component.

3.10 Chemical Reactions

Chemical reactions can be taken into account for each grid cell of the calculation region. The chemical reactions are assumed to be of the form:



where A = mole concentration of reactant species A (moles/m³);
 B = mole concentration of reactant species B (moles/m³);
 C = mole concentration of product species C (moles/m³);
 D = mole concentration of product species D (moles/m³);
 a = the amount of species A consumed in the reaction;
 b = the amount of species B consumed in the reaction;
 c = the amount of species C produced in the reaction;
 d = the amount of species D produced in the reaction;
 K = the reaction rate (moles/m³ second).

There can be unlimited reactants and products; however, each reactant and product must exist in the chemical database. The reactions can be entered for use in the Charmed program. The reactions can be grouped into sets for use in the calculation.

The value for K is calculated using the expression:

$$K = k [A]^m [B]^n \quad (3-56)$$

where k = the rate constant;
 m = the order of the reaction for species A;
 n = the order of the reaction for species B.

The values for m and n are normally determined experimentally. The order for the reaction may also be available from the literature.

Using the reaction stoichiometry, the rate of disappearance for species B (r_B) and the rates of appearance for species C and D (r_C and r_D) are defined in terms of the stoichiometric coefficients as shown below, assuming a is the largest coefficient:

$$\begin{aligned} r_B &= K \frac{B}{A} \\ r_C &= K \frac{C}{A} \\ r_D &= K \frac{D}{A} \end{aligned} \quad (3-57)$$

The heat of reaction (H_r) can also be entered. The default is that the heat is zero. Exothermic reactions should have heats entered as negative numbers. Endothermic reactions should have heats entered as positive numbers. The heat value should be entered in kiloJoules (kJ) for the reaction as given. The reaction stoichiometry is used to determine the actual heat transfer rate (dH/dt). That is:

$$\frac{dH}{dt} = \frac{K}{A} H_r \quad (3-58)$$

where A is the largest species coefficient in the reaction.

A number of dependencies are allowed for k. These are:

$$k = \left\{ \begin{array}{l} A \\ A e^{\frac{b}{T}} \\ A (UV)^b \\ A (TSR)^b \\ A (Air)^b \\ A (Water)^b \\ A (AerosolNumber)^b \\ A (AersolArea)^b \\ A (AerosolVolume)^b \end{array} \right. \quad (3-59)$$

where A = a user supplied constant;
b = a user supplied constant;

T	= temperature in Kelvin;
UV	= ultraviolet radiation in kW/m ² ;
TSR	= total solar radiation in kW/m ² ;
Air	= concentration of air in moles/m ³ ;
Water	= concentration of water vapor in moles/m ³ ;
AerosolArea	= surface area concentration of particles in m ² /m ³ ;

There is a special case usage for the value of k. Rather than being treated as a rate constant it is used as a mole concentration of a species. The special case is indicated to the model by having no reactants. One or more products can be defined, each of which will be assigned a constant concentration equal to the value of k. For example, if a constant supply of O₂ is wanted in a set of reactions, the following reaction could be defined:



The O₂ concentration can then be defined to be 20 percent of the air available to the reaction by using the expression $k = A (\text{Air})$ and assigning the value of A to be 0.2.

3.11 Liquid Flow Over Terrain

The flow of liquid over terrain is built around a modified Manning Equation for open channel flow:

$$U = \frac{D_{\text{liq}}^{\frac{2}{3}} \sqrt{s} \rho_{\text{liq}} \eta_{\text{water}}}{n \eta_{\text{liq}} \rho_{\text{water}}} \quad (3-61)$$

where U	= the average speed of the liquid flow;
D _{liq}	= the liquid depth;
s	= the slope of the terrain;
n	= the Manning Roughness Coefficient (set to 0.025);
ρ _{liq}	= the flowing liquid density;
η _{liq}	= the viscosity of the flowing liquid;
ρ _{water}	= water density; and
η _{water}	= the viscosity of water.

The flow speed from the Manning Equation is compared to the speed that would be expected if the liquid were spreading due to gravitational spread. The gravitational spread speed (U_g) is given by:

$$U_g = \sqrt{2D_{\text{liq}}g} \quad (3-62)$$

If the gravitational spread speed is greater than the Manning speed it is used. The gravitational spread speed is normally only greater on a flat surface.

Much of the liquid flow calculation is taken up in determining boundary conditions such as the liquid is not allowed to flow uphill. For any one grid cell the liquid is allowed to flow in eight directions (each corner and the center of each side).

As the flow continues the heat and mass transfer and porosity terms for an evaporating pool as described in Chapter 2 are used to determine mass loss terms. These loss terms become the source terms into the atmosphere.

3.12 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

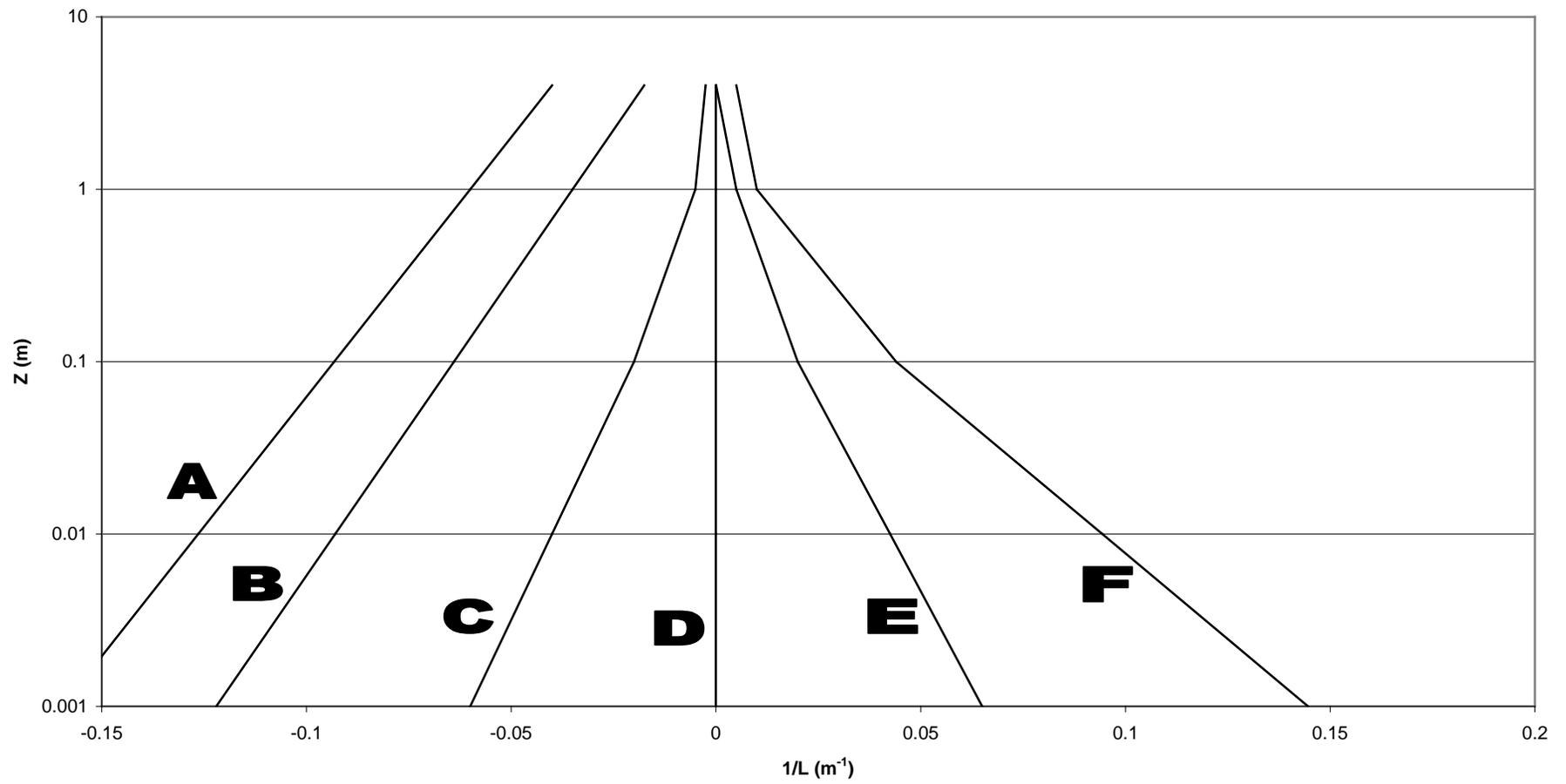


Figure 3-1. $1/L$ as a Function of Pasquill Stability Class.

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.

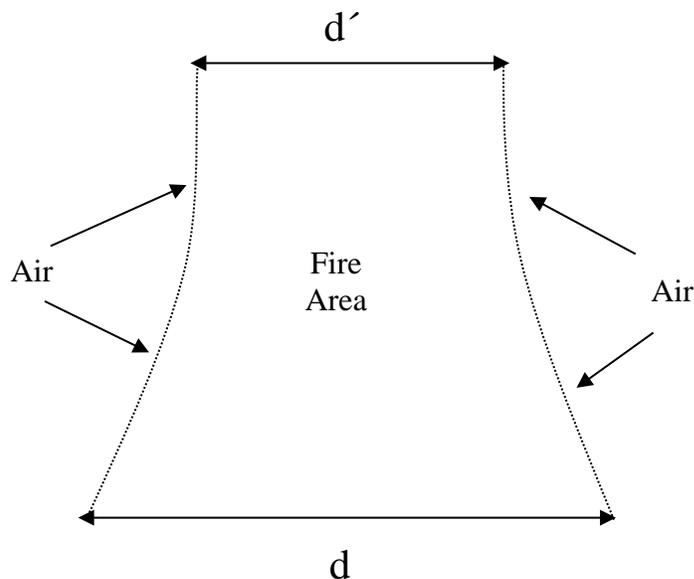


Figure 4-1. General Appearance of a Liquid Pool Fire

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 smokey. 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_{∞} = 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.

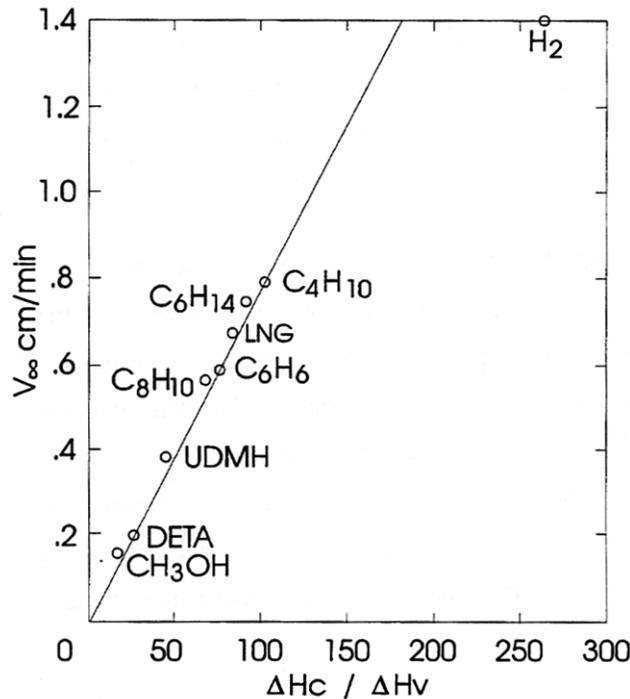


Figure 4-2. Relationship between liquid-burning rate (large pool diameter) and ratio of net heat of combustion to sensible heat of vaporization.

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.

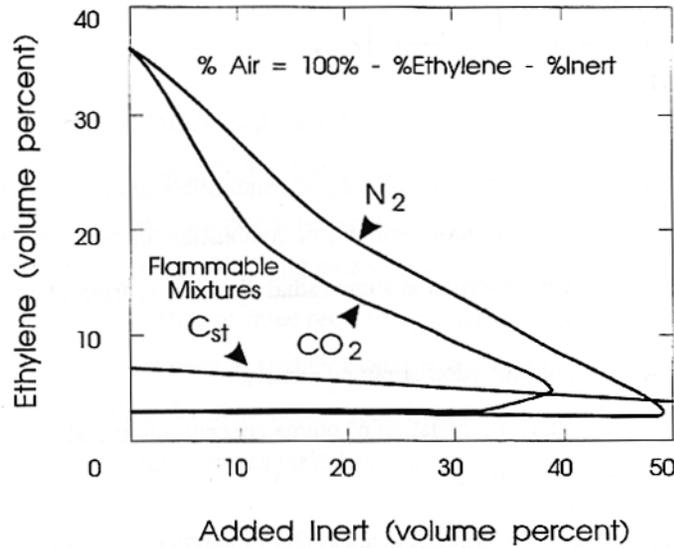


Figure 4-3. Limits of flammability of ethylene-carbon dioxide-air and ethylene-nitrogen-air mixtures at atmospheric pressure and 26° C.

This figure shows the effect of N₂ diluent and CO₂ 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_NH_MO_LF_K, 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_{ST} = 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_{ST} should lie between the lower and the upper flammable limits. Above the lower flammable limit and below C_{ST} all is burned. Above C_{ST}, too much organic is present to burn entirely. One hundred percent is assumed to be burned at C_{ST}, and zero percent is assumed burned at the upper flammable limit. Between C_{ST} 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_B) 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 CO₂ in the gas stream would be about 1:1, and 1/2 mole of H₂ would be present for each mole of CO and CO₂ 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:CO₂ is accurate to $\pm 30\%$ and the 0.5-to-one ratio for H₂ to (CO + CO₂) is accurate to about $\pm 50\%$. There will be some CO and some H₂ 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 CO₂-H₂O-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 (ΔF 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.

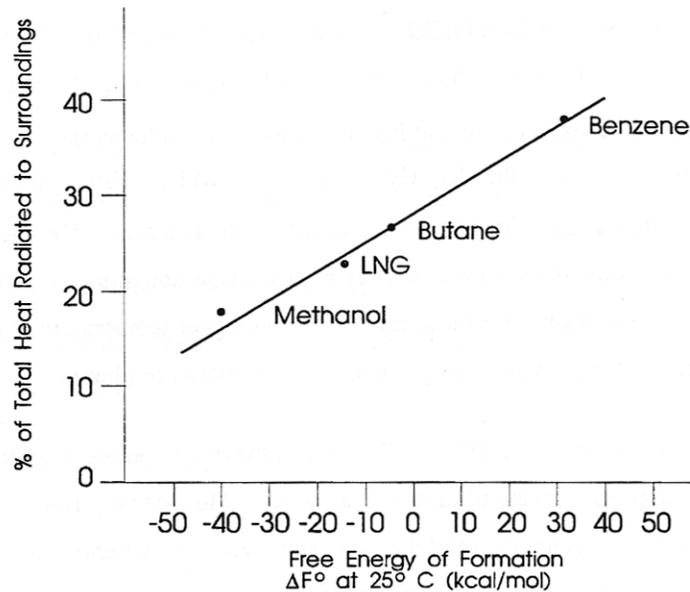


Figure 4-4. Relationship between percent of total heat radiated to the surroundings and free energy of formation.

The developed equation is:

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

where R = percent of total heat release radiated to surroundings; and
 ΔF = 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_{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 ΔT_{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_{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_{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 = $2 m c + b z$;

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

$$P_O = \sqrt{c}$$

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

Θ = 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:

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

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

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;
 - γ_1 = C_p/C_v for gas in sphere;
 - γ_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.

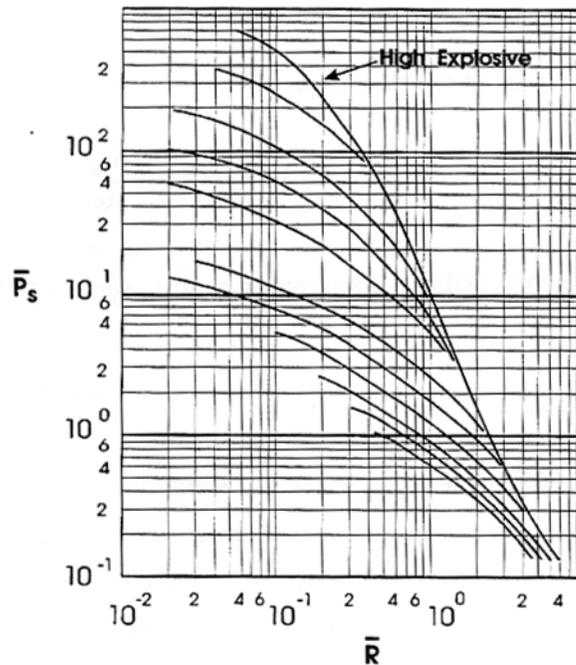


Figure 7-1. \bar{P}_s Versus \bar{R} for Sphere Burst Overpressure Calculations.

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.

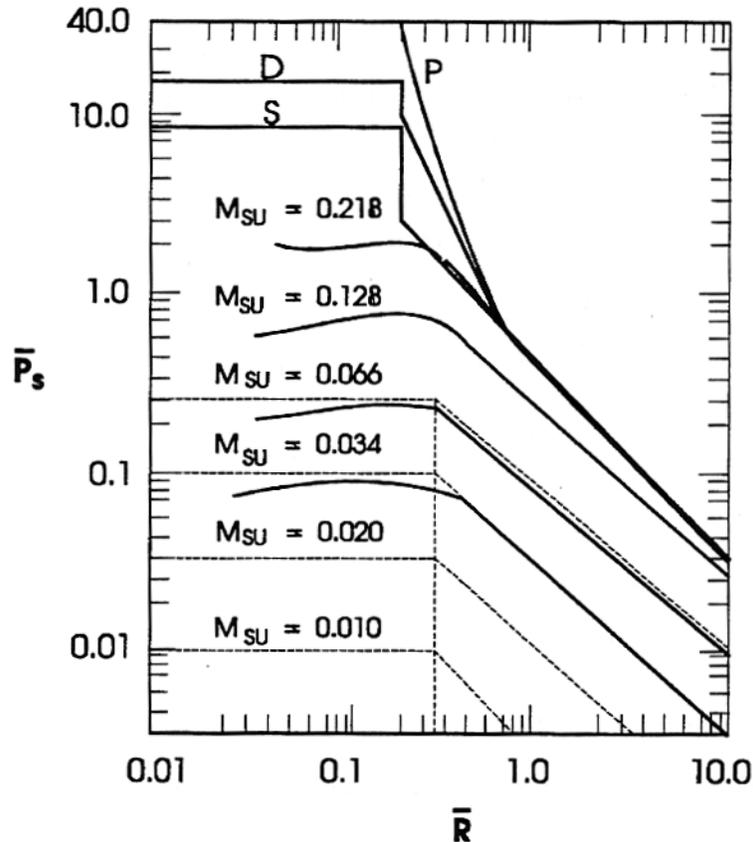


Figure 7-2. Maximum Wave Overpressure Versus Energy-Scaled Distance for Explosions With an Energy Density $q = 8$ and Various Normal Burn Velocities.

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

H_{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_{lel} = mass above LEL; and
 ε = 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 ρ_1 = density ahead of the flame;
 ρ_2 = density behind the flame; and
 M_{SU} = flame speed in Mach.

The ratio of ρ_2/ρ_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} .

8.0 NUCLEAR RADIATION

CHARM calculates nuclear radiation exposure and dose for all scenarios. A nuclide may be specified as making up a given mass fraction of the emission. Once an isotope is given CHARM will use a database to determine the decay chain for that nuclide. During the calculation the amount of energy released from decay of the nuclide and daughters is carried out. The time used in the decay calculation is the display time or time needed to get to the location of the calculation from the source, whichever is smaller, until the emission has completed. Once the emission is over the time used is the time needed to get to the location from a source or the time beyond the emission duration, whichever is greater. The exposure is reported in Roentgens per hour (R/hr) and Grays per hour (Gy/hr). The dose is given in Roentgens ® and Grays (G).

CHARM only reports the exposure and dose from the energy of emitted photons. Emitted energy from Alpha and Electron radiation is not used. The reported values are actually for the arbitrary distance of 1 meter from the source. A source is the point at the center of a grid cell. The source strength is directly proportional to the mass concentration at the center of the grid cell.

8.1 Nuclide Database

The database being used is from the International Commission on Radiological Protection (ICRP), Publication 107 (2008). In that publication a list of 1252 radionuclides along with half-life, decay mode, and emitted energy for Alpha, Electron, and Photon radiation is provided. The database includes the daughter nuclides and their fractions of nuclear transformation (nt) of the parent going into their creation.

When a nuclide is specified as part of a release CHARM determines the complete chain of daughter creation. This chain is used to get the total photon energy emitted.

8.2 Decay Chain Calculation

The number of a single decaying nuclide is given by:

$$N(t) = N(0)e^{-\lambda t} \quad (8-1)$$

where $N(t)$ = the quantity of the isotope at time t ;
 $N(0)$ = the quantity of the isotope at time 0;
 λ = the decay constant;
= $\frac{\ln(2)}{t_{1/2}}$; and
 $t_{1/2}$ = half-life of an isotope.

The rate of radiation is then given by:

$$\frac{dN(t)}{dt} = -N(t)\lambda \quad (8-2)$$

The formula used to calculate the number of the kth daughter isotope in the decay process is the Bateman (1910) equation:

$$N_k(t) = N_1(0) \left(\prod_{i=1}^{k-1} b_{i+1,i} \lambda_i \right) \sum_{j=1}^k \frac{e^{-\lambda_j t}}{\prod_{\substack{i=1 \\ i \neq j}}^k (\lambda_i - \lambda_j)} \quad (8-3)$$

where $N_k(t)$ = the quantity of isotope k at time t;
 $N_1(0)$ = the quantity of isotope 1 at time 0; and
 $b_{i+1,i}$ = the branching fraction of the parent isotope to a daughter.

Once the number of each isotope is known at a given time the contribution of its energy to the total radiated can be determined.

8.3 Exposure Rate Calculation

The rate of exposure is calculated using an expression provided by George Chabot of the Health Physics Society. After some minor alteration of Chabot's expression the one used in CHARM is:

$$Rate = 5.263 \times 10^{-10} \frac{\sum_{i=1}^{N_{isotopes}} N_i E_i \left(\frac{\mu_{ep}}{\rho} \right)_i}{r^2} \quad (8-4)$$

where $Rate$ = the exposure rate in R/hr;
 N_i = the number of nt the ith isotope has had in Bq ;
 E_i = the energy of the ith isotope released during an nt in MeV;
 $\left(\frac{\mu_{ep}}{\rho} \right)_i$ = mass energy absorption coefficient for the ith isotope in cm²/g;
 and
 r = distance from the source to the receptor in m. Assumed to be 1.

The Rate calculated in the equation is the exposure rate per nt. To get the total rate ($Rate_{total}$ in R/h per m³) the number calculated above needs to be modified:

$$Rate_{total} = Rate A_{mass} Conc \quad (8-5)$$

where A_{mass} = the activity per unit mass in Bq/kg ;
 $= 6.0221413 \times 10^{23} \frac{\lambda}{0.001 MW}$
 λ = the decay rate for the first nuclide in inverse seconds;
 MW = molecular weight of the first nuclide in grams per gram mole;

and
Conc = concentration of the material emitted that is the first nuclide in kg/m³.

8.4 Exposure Rate From Rectangular Ground Source

In the rate equation given above the assumption is that the source is at a point. Thus the inverse square relationship for determining the exposure rate at a distant point is present. This is a good assumption for air concentrations. However, if particles are deposited on the ground, that is not acceptable. In CHARM particles fall on grid rectangles on the surface. The pattern of the radiation above the grid cell does not go as inverse square. However, the pattern can be derived by assuming each part of the cell emits with an inverse square pattern. The exposure rate would be given by:

$$\text{Rate} = K \int_{-\frac{H}{2}}^{\frac{H}{2}} \int_{-\frac{W}{2}}^{\frac{W}{2}} \frac{dx dy}{(x-x_p)^2 + (y-y_p)^2 + z_p^2} \quad (8-6)$$

where *H* = the Height of the grid cell in the y direction;
W = the Width of the grid cell in the x direction;
x_p = the x location of the point of impact. WRT cell center;
y_p = the y location of the point of impact. WRT cell center;
z_p = the z location of the point of impact. WRT cell surface; and
K = the rate in Chabot's expression without inverse square r.

By substituting:

$$\begin{aligned} x' &= x - x_p \\ y' &= y - y_p \end{aligned}$$

And integrating in the x direction the following expression is derived:

$$\text{Rate} = K \int_{-y_p}^{H-y_p} \frac{1}{\sqrt{y'^2 + z_p^2}} \tan^{-1} \frac{\frac{W}{2} - x_p}{\sqrt{y'^2 + z_p^2}} dy - K \int_{-y_p}^{H-y_p} \frac{1}{\sqrt{y'^2 + z_p^2}} \tan^{-1} \frac{\frac{-W}{2} - x_p}{\sqrt{y'^2 + z_p^2}} dy \quad (8-7)$$

The two integrals are solved numerically. The solution replaces the inverse square r in the point version of the rate calculation.

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