Toxic Industrial Chemical (TIC) Source Emissions Model Improvements for Pressurized Liquefied Gases

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Abstract

The objective of the study is to update and expand toxic industrial chemical (TIC) source emissions models used in U.S. Department of Defense (DoD) atmospheric comprehensive risk assessment models so as to represent state-of-the-art knowledge. Revisions focus on high-priority scenarios, including two-phase releases of pressurized liquefied gases such as chlorine from rail cars. The study included all types of TIC releases, including gas and liquid releases, but the current paper addresses scenarios such as chlorine with the most dangerous potential consequences. The total mass released and the release duration are major parameters, as well as the velocity thermodynamic state, and amount and droplet sizes of imbedded aerosols of the material at the exit of the rupture, which are required as inputs to the subsequent jet and dispersion modeling. Because of the many possible release scenarios that could develop, a suite of model equations has been developed. These allow for gas, two phase or liquid storage and release through ruptures of various types including sharp edged and “pipe-like” ruptures. We have adopted the \( \omega \) – method (in various forms). Model equations for jet depressurization and phase change due to flashing are available. The breakup of the jet into fine droplets and their subsequent suspension and evaporation, or rain out is still a significant uncertainty in the overall modeling process. The recommended models have been evaluated with data from various TIC field experiments, in particular recent experiments with pressurized liquefied gases. It is found that there is typically a factor of two error in models compared with research-grade observations. In particular, biases are present in models’ estimates of the droplet size distributions resulting from flashing releases.

1. Introduction

In this paper, models are addressed that can calculate toxic industrial chemical (TIC) emission rates and other source parameters at the point where the emissions are “handed off” to atmospheric transport and dispersion models. Generally what are required are models that are of the right quality, i.e. models that are “fit-for-purpose”. The generic approach for the modeling of the source term for a TIC release is outlined in the four points below.

1. There are various specific scenarios of interest and these depend upon

The stored material - Each TIC material has its own thermodynamic, fluid mechanical and transport properties, and the degree of detail within various models may require more or less property information.
The type of storage (geometry) - Models may be required that can accommodate any shape of storage vessel. However two particular shapes are fairly common, that is the cylindrical storage vessel with either vertical or horizontal axis.

The type of storage (thermodynamic state) - Generally there are only a limited number of cases and these are:

- Material stored as a vapor only; consequently the material must be saturated or superheated (with respect to the saturated state at the storage pressure); e.g. water vapor/steam stored at 120 C at 1 atm pressure. (See glossary for the definition of terms).
- Material stored as a liquid only; the material must be saturated or subcooled (with respect to the saturated state at the storage pressure). This includes the case of material stored as a liquid at ambient temperature and pressure; e.g., water stored at 20 C and 1 atm pressure. Alternatively it could be a material stored as a liquid at a pressure that is equal to or above the saturated vapor pressure for the storage temperature; e.g., water stored at 100 C and 1.2 atm pressure. In this case the liquid is stored under a pad (e.g. nitrogen) pressure.
- Material stored as a vapor and liquid together at saturation condition, that is at a pressure and temperature that lie on the saturated vapor line; e.g., water and steam stored together at 100 C and 1 atm pressure.

The type of rupture - There are five broad categories:

- Catastrophic failure
- Those that resemble a sharp-edged orifice
- Those that resemble many sharp-edged orifices
- Those that resemble a short pipe. This last case may be pipelike just because of the width of the containing vessel.
- Those from a rupture in a long pipe connected to a vessel

Three accidental chlorine releases from railcars have been studied in some detail (e.g., Hanna et al., 2009). At the Macdona and Graniteville accidents the ruptures were jagged holes of rough dimension 10 cm by 30 cm. These would be classed as resembling sharp edged orifices unless the storage vessel wall was thicker than 0.1 m. The storage vessel wall was estimated to be of the order of 0.1 m for these accidents. For the Festus accident the rupture was at the end of a long, narrow pipe connected to a storage vessel.

From knowledge of the stored material, the type of storage (geometrical and thermodynamic) and the type of rupture the model(s) must calculate:

- The release rate and other characteristics of the release at the rupture
- The resulting response of the storage vessel
- The near source depressurization to atmospheric pressure
• The partition of the material into vapor, suspended liquid aerosol and liquid rainout close to the release

2. For the special case where some of the liquid pools on the underlying surface, there is a requirement for a model for any resulting evaporating pool

3. And there is then the requirement for an atmospheric dispersion model to treat both the airborne sources directly from the rupture and from any evaporation from the liquid pool that may have formed.

4. Finally there is the incorporation, if appropriate, of several complicating factors such as nearby buildings, topography, material removal, etc.

Our approach requires the selecting, from the various available models, models that will address adequately the processes above. An important issue here is to ensure that the selected models are well-balanced in the sense that they all have similar accuracy and similar speeds and similar complexity or simplicity. These are often matters of judgment and pragmatism and should be guided by the overall model “purpose” and also by the current state of development or development intent of existing operational models.

In this paper we focus on pressurized liquefied gases and consider the following parts of the modeling process in turn:

• Fluid property information
• Release rate and exit thermodynamic conditions
• Vessel response
• Flow after exit from the storage vessel

2. Fluid property information

The TICs are principally of concern as inhalation hazards. The scale over which health effects occur will depend upon the toxicity of the material, the amount of material likely to be released in an incident, and whether their boiling point is low enough so that they rapidly become gases or suspended aerosols upon release. There are many toxic chemicals stored as gases and these must also be considered however the mass stored is likely to be less than for the storage of liquefied gases. Hanna et al. (2009) indicate the comparative health impacts in one particular region that may result from releases of various stored and transported TICs taking into account the above features. The “top 13” are:
- Chlorine, Sulfur Dioxide, Ammonia (anhydrous), Hydrogen Chloride (anhydrous), Phosgene,
- Bromine, Acrolein, Hydrogen Cyanide, Chlorine Trifluoride, Methyl Chloroformate, Oleum (65% SO₃), Hydrogen Fluoride, Phosphorus Trichloride

It is clear that common chemicals such as chlorine, ammonia and sulfur dioxide top this list reflecting the large amounts of the chemicals being stored and transported. Because many TICs of interest are commonly stored as liquids and will commonly disperse as gases, the study of TIC
releases will also commonly involve the fluid mechanics and thermodynamics of multi-phase flows. The material properties play an important role in such flows.

The nature of much of the fluid information required is obtained within the liquid-vapor phase diagram. Various forms of this diagram are available of which the most easily interpreted is that using pressure and specific volume (inverse of density) as axes and temperature as the parameter. However, because pressure and temperature are not independent in a two-phase region this form of phase diagram is less useful. The preferred version is the temperature-entropy form with pressure as the parameter, shown in Figure 1, which applies to chlorine. The quantitative data are available in tabular/electronic form from various standard sources and some of these are listed in the next section.

![Figure 1. Temperature-Entropy Diagram for Chlorine. Colored lines are pressure in units of MegaPascals.](image)

The lines shown are constant pressure lines in units of MegaPascals. The “hump” shape in the middle is the saturation line that demarcates the two-phase region. A depressurization, at a commonly-assumed constant entropy, will produce a vertical line indicating a temperature reduction. The area to the left of the “hump” is referred to as sub-cooled liquid while the area to the right of the hump is referred to as superheated vapor. These terms are used here solely to indicate that the
material is a liquid or a vapor respectively and is not within the two phase region or on the saturation line. These terms are often used when referring to the state of the material within a storage vessel. To the left of the curve the storage temperature is lower than the saturation temperature at the same pressure while to the right the temperature is greater than the saturation temperature at the same pressure. Here we are using the terms subcooled and superheated to describe the storage conditions.

The terms subcooled or superheated are also used when the temperature of the fluid is compared with the saturation temperature at ambient (atmospheric) pressure also known as the normal boiling point. This will affect the state of the material as it exits from the storage vessel. If the fluid temperature is above the normal boiling point then the fluid is superheated and will change phase upon depressurization down to atmospheric pressure. If the fluid temperature is less than the normal boiling point then the fluid is subcooled and will not change phase upon depressurization down to atmospheric pressure.

So a material could be a subcooled liquid relative to saturation conditions at the storage pressure but a superheated liquid relative to saturation conditions at atmospheric pressure. The terminology used throughout this paper is to explicitly state whether the reference is to the saturation temperature at the storage pressure or at ambient pressure.

Because pressure and temperature are not independent variables (for single-component fluids) when two phases are present, the two-phase region in Figure 1 collapses to a single curve when the phase diagram is presented on pressure-temperature axes as in Figure 2.

Figure 2. The saturation curve of pressure against temperature for chlorine; definition of terms.
In this plot the “hump” of the two-phase region in Figure 1 has collapsed to the single line. Note that the red dot in Figure 2 shows material that is a subcooled liquid relative to the saturation line (at the same pressure) but is a superheated liquid relative to the saturation line (at ambient or atmospheric pressure).

The National Institute of Standards and Technology (NIST) database is currently used in many models for many materials. Alternatively, DIPPR is a widely used property database. Currently NIST is a sponsor of DIPPR 801 (BYU DIPPR 801 ver website). Where the chemical is not found in either NIST or DIPPR, then one has to resort to estimation methods. In this case significant discrepancies may arise depending upon how the estimations are made.

Properties of interest include
- Antoine coefficients (for saturation vapor pressure)
- Molecular weight
- Liquid density (plus variation with temperature)
- Specific heats (liquid and vapor)
- Surface tension (for droplet deformation)
- Liquid viscosity (for droplet absorption into substrate)

3. Release rate and exit thermodynamic conditions

For most cases with a rupture of a container full of pressurized liquefied gas, the mass release rate will vary strongly with time. The optimum input for the dispersion model is the release rate as a function of time with a resolution of a few seconds. However, many dispersion models cannot use that much detail, and the mass release rate will, at best, be a set of piecewise constant values, with each piece averaged over say 1 to 10 minutes or more. Some models can take only a constant release rate (although perhaps for a finite duration) or a single total mass released. Thus the total mass released is also a major parameter. The thermodynamic state of the material at the exit of the rupture is required as an input to the subsequent jet and dispersion modeling. Also because the flow may be choked at the exit the pressure at the exit may be above atmospheric pressure. Consequently the jet material will accelerate after the exit. This requires the calculation of the momentum flow rate of the jet including any acceleration due to an elevated pressure at the exit plane.

3.1 Introduction

In order to calculate the mass flow rate from the storage container and the thermodynamic condition of the released material at the rupture plane it is common to consider the flow as in Figure 3. Within the storage container there exists essentially stagnant fluid and this accelerates towards the rupture plane. The pressure at the rupture plane (or at the vena contracta if one exists) will be atmospheric pressure if the flow is unchoked or will be above atmospheric pressure if the flow is choked. The pressure at the rupture plane is an important input to the subsequent jet modeling.
Currently we are only interested in going from the stagnant (stationary, stagnation) conditions “o” to those at or just after the rupture plane “1”. In all scenarios the pressure will reduce from the storage pressure to atmospheric pressure. However this may occur directly to atmospheric pressure at the rupture plane or it may occur with an important intermediary pressure at the rupture plane that is above atmospheric pressure (a “choking” condition). In this case there would be a further depressurization down to atmospheric pressure downstream of the rupture plane. The mass flow rate of a compressible fluid through a rupture is often thought to depend upon the pressure difference across the rupture. This statement is only partially correct.

For a fixed pressure in the storage vessel the mass flow rate does increase for smaller and smaller downstream pressures. However there is a limiting mass flow rate that beyond which the downstream pressure has no influence. In this case the mass flow rate depends on the pressure in the storage vessel and not on the difference in pressure across the rupture. This condition is called “choked flow” and is commonly met in single phase high speed gas dynamics. The maximum exit velocity will be the sonic velocity of the fluid (of the order of several 100’s of m/s) at the thermodynamic conditions at the rupture plane. If the fluid is made up of gas and liquid then this can be considered a pseudo compressible fluid and will also experience a choking condition. Somewhat surprisingly the maximum exit velocity for a two phase fluid can be much smaller than the maximum exit velocities of either phase individually. Physically this is because the “sonic” velocity depends on the compressibility and the inertia (density) of the fluid. For the two phase flashing fluid the phase-change process in effect increases the two-phase mixture compressibility, hence yielding a low sonic velocity. Maximum exit velocities of the order of only several 10’s of m/s are often found.

The types of releases may be categorized as coming from containers in which material is stored as a:

1. Liquid in a subcooled state (with a storage temperature that is lower than the saturation temperature at the storage pressure). This includes refrigerated liquefied gases (stored at atmospheric pressure) and pressurized and partially refrigerated liquefied gases (often done with anhydrous
ammonia). It is important to note that if the material is subcooled then, by definition, there cannot be both phases of the material present unless there is an imposed pad gas.

2. Gas in a superheated state (with a storage temperature that is higher than the saturation temperature at the storage pressure)

3. Either liquid or gas under saturation conditions (at the ends of the horizontal lines in Figure 1) or liquid and gas together (somewhere along the horizontal lines in Figure 1). The last case is commonly met with both liquid and gas being present within the storage vessel. What is being considered specifically here is that, during the release, part of the liquid and vapor within the vessel may mix and appear to be like a stored mixture at saturation conditions.

It is useful to consider the list of TICs mentioned earlier and refer to them in the three categories above. The 13 TICs on the list are inhalation toxics that are shipped in large quantities. The most dangerous category of TICs includes those with low boiling points (i.e., they are gases at ambient conditions) that are transported as pressurized liquids. The “top three” in this group are chlorine, ammonia (anhydrous), and sulfur dioxide, which all have boiling points less than -10 C and are shipped in large quantities in rail cars. Other high-priority TICs in this group include chlorine trifluoride, hydrogen chloride anhydrous, hydrogen fluoride, and phosgene. As an example chlorine is typically stored under saturation condition with liquid and vapor together. Consequently the pressure and temperature are not independent. The pressure in the storage vessel will be that determined by the temperature of the contents of the vessel. If the contents increase in temperature due to heat transfer from the storage vessel to the contents then some of the contents will change phase to a gas and thereby increase the pressure until the temperature and pressure are back together on the saturation line. Some of these chemicals may be stored as partly pressurized and partly refrigerated, and some may have a pad gas introduced under particular situations.

A less dangerous category of TICs on the list includes those that are liquids at ambient conditions (e.g., acrolein, bromine, hydrogen cyanide, and methyl chloroformate), which are most likely to be emitted to the atmosphere primarily by evaporation from a liquid pool. The mass is emitted over a relatively long time period and the downwind concentrations are relatively low. These four liquids were selected for the high-priority list because of their relatively low toxic concentration criteria and the fact that they are transported in relatively large amounts. These are subcooled liquids under both storage conditions and ambient conditions.

Finally, two of the TICs on the list are also liquids at storage and ambient conditions (e.g., oleum (65% sulfur trioxide) and phosphorous trichloride) are in the category of “fuming liquid”, meaning that they may react with water vapor in the atmosphere, with the release of heat and conversion to secondary chemicals.

We see that only the first set of chemicals carries across to categories 1 and 3 above. The source emission models for releases of the other chemicals involve liquid pool formation and subsequent evaporation.

Most importantly, it may well be the case that more than one type of release may be evident in the one incident and the one rupture. During depressurization of the storage vessel the vessel may
contain regions of vapor only, liquid only and a, roughly homogeneous, vapor-liquid mixture. Depending on the geometric location of the rupture different release types will occur. The evolution of the internal state of the storage vessel during depressurization may mean that a fixed geometrical location of the rupture will experience three or more different release types. For example, consider a mid-level rupture in a storage vessel that contains material stored under saturation conditions and predominantly liquid. Initially the rupture will be in the liquid space. After rupture the tank contents might appear as a liquid phase at the bottom, a vapor phase at the top and a liquid-vapor mixture between the two. As time proceeds and the tank empties the released material (at the rupture plane) may be all liquid, a two-phase mixture and all vapor.

For the cases labeled 1) and 2) above and provided the material does not change phase prior to exiting the rupture and when the release process is one that always maintains thermodynamic equilibrium, the release problem is relatively straightforward.

3.2 Recommended approach where the liquid is subcooled referenced to the saturation temperature at both the storage pressure and atmospheric pressure.

In this case the liquid in the storage vessel is initially at a temperature below its normal boiling point (that is below the saturation temperature at ambient pressure so there is no phase change upon release). It must be stored under a pad gas which is at a pressure higher than ambient pressure. The relevant equation is the Bernoulli equation

\[ G = C_D \left(2 \left(P_0 - P_a \right) \rho_f g h \right)^{1/2} \]

Recommended equation 1

where:
- \( G \) = mass flow rate per unit rupture area (kg s \(^{-1}\) m \(^{-2}\))
- \( \rho_f \) = liquid density in storage tank (kg m \(^{-3}\))
- \( P_0 \) = storage pressure (N m \(^{-2}\))
- \( P_a \) = atmospheric pressure (N m \(^{-2}\))
- \( C_D \) = discharge coefficient (dimensionless); discussed in detail in Section 3.5
- \( g \) = acceleration due to gravity (m s \(^{-2}\))
- \( h \) = height of liquid above the rupture position (m)

3.3 Recommended approach where the vapor is superheated referenced to the saturation temperature at both storage and atmospheric pressure

For the superheated vapor case, the relevant equations are the compressible gas flow equations and these allow for the important phenomenon of choked or critical flow. Consider a gas jet coming from a rupture in the vapor space of a pressurized liquid storage tank. When the rupture occurs, the velocity, and the mass flow rate, of the exiting fluid will depend on the pressure inside and the pressure outside of the container. When these pressures are not too different the flow is unchoked. However the gas can exit the rupture only as fast as its sonic velocity and at larger pressure differences there is a "choked" condition at the exit. Choked flow simply means that the gas is moving through the puncture at its maximum possible speed, namely the local speed of sound in the gas.
The discharge rate equations for an ideal (note that non-ideal gas behavior may be expected when the flow approaches the saturation curve) gas jet release are well known. Whether or not the flow is choked depends on the ratio of atmospheric pressure to tank pressure relative to the critical pressure ratio as defined below:

\[ r_{crit} = \left( \frac{P_a}{P_0} \right)_{crit} = \left( \frac{2}{\gamma + 1} \right)^{\frac{\gamma}{\gamma-1}} \] (2)

where

- \( P_0 \) = absolute tank (stagnation) pressure (N m\(^{-2}\))
- \( P_a \) = absolute ambient atmospheric pressure (N m\(^{-2}\))
- \( \gamma \) = gas specific heat ratio = \( c_p/c_v \) (dimensionless)

For a typical gas, values of \( \gamma \) range from 1.1 to 1.5, and \( r_{crit} \) values range from 0.5 to 0.59. Thus, the releases of most diatomic gases (\( \gamma = 1.4 \)) will be a choked or critical flow at a critical pressure ratio of 0.528 (i.e. a tank pressure above approximately twice atmospheric pressure). Note that the critical pressure ratio \( r_{crit} \) will be given the symbol \( \eta_c \) when addressing two phase flow later.

For an ideal gas exiting through an orifice under isentropic conditions, the gas mass discharge rate is given by:

\[ m = G A_h \] (3)

\[ G = C_D \sqrt{\frac{2 P_a}{\gamma}} \left[ \left( \frac{P_a}{P_0} \right)^{\gamma} - \left( \frac{P_a}{P_0} \right)^{\frac{\gamma+1}{\gamma-1}} \right] \] for subsonic or unchoked flows \( \left( \frac{P_a}{P_0} \geq r_{crit} \right) \) (4)

**Recommended equation 2a**


\[ G = C_D \sqrt{\frac{P_a}{\gamma}} \left( \frac{2}{\gamma+1} \right)^{\frac{\gamma+1}{\gamma-1}} \] for choked flows \( \left( \frac{P_a}{P_0} \leq r_{crit} \right) \) (5)

**Recommended equation 2b**

where

- \( P_0 \) = absolute tank (stagnation) pressure (N m\(^{-2}\))
- \( P_a \) = absolute ambient atmospheric pressure (N m\(^{-2}\))
- \( \gamma \) = gas specific heat ratio = \( c_p/c_v \) (dimensionless)
- \( m \) = gas discharge rate (kg s\(^{-1}\))
- \( C_D \) = discharge coefficient (dimensionless)
- \( A_h \) = hole or rupture area (m\(^2\))
\( v_0 = \) specific volume of gas within the vessel

Some care is needed when considering flows that come near to the saturation curve. The use of perfect gas laws will not be applicable even if there is no phase change. Furthermore if the release changes phase e.g. a superheated vapor cools as it depressurizes then it may condense and the condensation will affect the flow. In addition caution should be shown by the user about non-ideal gas behavior that will occur at high pressures. Note that the \( \omega \) – method addressed in Sec. 3.4.1 can be used in the case with condensation phenomena.

3.4 Recommended approach for the release of material that is initially, or becomes, two-phase

There are several approximate methods available to describe the depressurization of a material that is initially two phase or that becomes two phase during depressurization that do not have demanding data requirements. Most of these rely on treating the two phase fluid as a compressible pseudo-fluid whose compressibility can be determined based on the bulk properties of the two phase fluid. Several scenarios can be envisaged for which a model for the source emission rate is required. The two main categories are: i) Storage at saturated conditions as a liquid, as a gas or as a mixture of the two, and ii) Storage as a liquid at subcooled conditions but such that the material would be superheated at atmospheric pressure.

3.4.1 Release from storage at saturated conditions as a liquid, as a gas or as a two-phase mixture of the two

The model recommended here is the \( \omega \) – method (Leung, 1986, 1990, 1996a). This is a widely used simple model and has been extensively tested e.g. see Richardson et al (2006). The model can be used for estimating flow rates and exit pressures. The initial state can be all (saturated) liquid, all (saturated) vapor or a mixture of the two but saturated conditions must apply. The \( \omega \) – method was first proposed for flashing two-phase flow in 1986, and in subsequent years was extended to non-flashing two-phase flow (Leung 1990), subcooled liquid flow (Leung 1988), two-phase pipe flow (Leung 1987, Leung 1994), and the local speed of sound in two-phase mixture (Leung 1996b). The \( \omega \) – method is an (isentropic) homogeneous equilibrium model (HEM) for the flow of a saturated two-phase mixture initially at a storage pressure \( P_0 \) equal to \( P_v(T_0) \), the vapor pressure at the storage temperature \( T_0 \).

The “\( \omega \)-method” is based on three approximations or assumptions:

- The liquid vapor mixture is homogeneous i.e. there is no slip between the phases
- The phases are in thermodynamic equilibrium
- The expansion is isentropic. This last assumption will likely be valid prior to the fluid exiting through the rupture; between “0” and “1” in Figure 3.

It is applicable to cases where the initial state is two phase or on the saturation line as a liquid or a vapor. For example it can treat the case of a saturated vapor; a case in which condensation would occur through the flow passage. As with Section 2.4 where the compressible gas equations were appropriate, here the two phase material might be considered as a type of “compressible gas”. Consequently the phenomenon of choking will also be relevant. That is, the flow may be choked.
(quite common for TIC releases) or unchoked depending upon the material properties and the storage conditions. Because the “sonic velocity” for a two phase mixture is typically well below the speed of sound for either the liquid or the vapor phase, smaller exit velocities are expected for the two phase scenario.

The critical or choked flow rate for various storage conditions can be found once the pressure $P$ vs. specific volume ($v$) relationship is available as tables or formulae. This can be obtained from isentropic flashing calculations at varying pressure, as discussed in the DARPA report (Hanna Consultants, 2006), in the AIChE/DIERS report (Fisher et al., 1992), and by Richardson et al. (2006). In fact, this is the essence of an exact approach for the two phase case and an example of this is provided at the end of this section as 3.4.6. However this exact approach requires fluid property data that may not be commonly available and adequately accurate for a wide range of chemicals.

The “$\omega$-method” is based on a one-parameter approximation of the $P$ vs. $v$ relationship using:

$$\frac{v}{v_0} - 1 = \omega \left( \frac{P}{P_0} - 1 \right)$$

and

$$\omega = \alpha_0 \left[ 1 - 2 \frac{P_0 v_f g_0}{h_{f g_0}} \right] + \frac{T_0 c_{p_0} P_0}{v_0} \left( \frac{v_{f g_0}}{h_{f g_0}} \right)^2$$

where the subscript “0” denotes the values in the tank at stagnation condition, the derivative is at constant entropy and

- $\alpha_0$ = volume fraction of TIC vapor
- $c_{p_0}$ = heat capacity of the (liquid) material at $T_0$ (J kg$^{-1}$ °K$^{-1}$)
- $h_{f g_0}$ = heat of vaporization at $T_0$ (J kg$^{-1}$)
- $P$ = downstream pressure (N m$^{-2}$)
- $P_0$ = stagnation (storage) pressure (N m$^{-2}$)
- $T_0$ = storage tank temperature (°K)
- $v$ = specific volume of the material at $P$ (m$^3$ kg$^{-1}$)
- $v_0$ = specific volume of the material at $P_0$ (m$^3$ kg$^{-1}$)
- $v_{f g_0}$ = specific volume difference between liquid and vapor at $T_0$ (m$^3$ kg$^{-1}$)

and $v_0 = v_{fo} + x_o v_{g0}$ where $x_o$ is the inlet vapor mass fraction or quality

Leung describes the parameter $\omega$ as consisting of two distinct terms: the first reflects the compressibility of the two-phase mixture due to the existing vapor/gas volume, and the second concerns the compressibility due to phase change upon depressurization or flashing. The larger the value of $\omega$, the more volume expansion or compressible behavior the mixture exhibits. As noted in Leung (1996a), flashing flow occurs for $\omega > 1$ and non-flashing flow for $0 < \omega < 1$.) $\omega$ depends only on conditions at stagnation in the tank. The $\omega$-method is presented in the design chart in Leung (1986, 1990) and Figure 4. The critical mass flux per unit rupture area,
$G_c$, and the critical pressure, $P_c$ (the pressure at the exit plane for choked flow), can be found as follows:

1. Find $\omega$ from its definition equation above
2. Find $\eta_c$ from Figure 4 or from a solution to the critical pressure ratio $\eta_c$

$$\eta_c^2 + \omega (\omega - 2) (1 - \eta_c)^3 + 2 \omega^2 \ln(\eta_c) + 2 \omega^2 (1 - \eta_c) = 0 \quad (8)$$

3. Find $G_c^*$ from Figure 4 or
a) For choked flow simply use the following formula

$$G_c^* = \eta_c / \sqrt{\omega} \quad (9)$$

b) For unchoked flow where $\eta > \eta_c$

$$G_c^* = \left[ -2 (\omega \ln \eta + (\omega - 1) (1 - \eta)) \right]^{\frac{3}{2}} \left[ \omega \left( \frac{1}{\eta} - 1 \right) + 1 \right] \quad \text{where } \eta = \frac{P_c}{P_o} \quad (10)$$

4. Then $P_c$ and $G_c$ are found from

$$P_c = \eta_c P_o \quad (11)$$

$$G_c = G_c^* \left( \frac{P_c}{P_o} \right)^{\frac{3}{2}} \quad (12)$$

The following figure is assumed to apply to all two-phase fluids; an assumption supported by the data presented in Fig. 2 of Leung (1986); the figure covered chlorine, ammonia, carbon tetrachloride, water and several other chemicals.

The temperature along a saturation line (as shown in Figure 2 for chlorine) can be found using the Clapeyron equation (Perry and Green, 1997). That is

$$\frac{dT}{dP} = \frac{v_g}{(h_g - T)} \quad (13)$$

Thus the temperature $T_c$ corresponding to $P_c$ can be found. Additionally since most chemicals should have accurate vapor pressure-temperature relationships or correlations, one could in fact be more precise in using them for determining the temperature $T_c$ corresponding to $P_c$ at the choking location.
Figure 4. Design chart for critical flow parameters of a two-phase mixture; that is, initially at saturation conditions

The vapor quality (vapor mass fraction), $x$, at temperature $T = T_c$ is:

$$x = \frac{T}{h_x} \left( c_p \ln \frac{T_c}{T} + x \frac{h_g}{T_o} \right)$$

(14)

From the vapor mass fraction the density or the specific volume of the two phase fluid can be calculated.

$$\nu_m = (1-x) \nu_f + x \nu_g = \nu_f + x \nu_g$$

(15)

If the chemical has reasonable enthalpy data, the flash calculation can be performed directly without resorting to the above approximate equation.

Note that $x$, the vapor mass fraction, is related to the vapor volume fraction, $\alpha$, by
In summary, we calculate $\omega$ and then determine $\eta_c$ and $G^*_c$. These are then converted to the critical mass flow/unit rupture area $G_c$ and the exit plane pressure $P_c$ which are the required unknowns. We can also calculate the temperature at the exit plane and the vapor mass fraction there, and thus the fluid density or specific volume and finally the exit velocity at the rupture plane.

Examples where this exercise is gone through, step by step, for specific TICs and scenarios are provided later.

Note that there is no discharge coefficient in the above analysis. A discharge coefficient of unity could be assumed though see Leung (2004) and Section 3.5 for further guidance.

The above set of equations (Recommended equation set 3) is generally applicable to releases of material under saturated conditions whether saturated liquid, saturated vapor or saturated two phase storage.

There are several widely used simplified methods such as the Equilibrium Rate Model (ERM) model by Fauske and Epstein (1988). Though this approach is now thought to be less appropriate and more limited than the $\omega$-method for the problems at hand the results for that model are included here as they may be useful for very simple calculations. The ERM can be derived from the “$\omega$” method above with the initial vapor fraction ($\alpha_0$) set equal to zero.

$$\alpha = \frac{x v_e}{v} \quad (16)$$

where

$$G_{ERM} = \frac{h_{fgo}}{v_{fgo}} \frac{\left(\frac{dT}{dT}\right)_s}{c_{pf0}} \left(\frac{T_o}{c_{pf0}}\right)^{1/\eta_c}$$ \quad (17)

provided that $x < \frac{P_{v/\rho} T_o}{h_{fgo}^2} c_{pf0}$ \quad (18)

This provides a good estimate of the flow rate without the need to specify the liquid-to-vapor ratio involved in the discharge. However the only difference between “$\omega$” method (with the initial vapor fraction ($\alpha_0$) set equal to zero) and the ERM model is the $\eta_c$ value which ERM assumes 1.0. According to Fig 4, for $\omega > 10$, i.e. low-quality two-phase flow, $\eta_c$ is about 0.9. So the real
difference is only about 10% between the two models. Since ERM has other limitations such as assuming the critical pressure ratio is 1.0 all the time the \( \omega \) method is preferred.

### 3.4.2 The non-equilibrium flow of a saturated liquid through a rupture

When the length of the rupture is very short, say like a sharp edged orifice, the stored liquid may be able to exit the storage vessel quickly enough so that thermodynamic equilibrium is not maintained. There is not time enough for the material to change phase until well after the material has exited the vessel.

The non-equilibrium nature of the flow is often thought of in terms of the “length” of the “orifice”, in that a sharp edged orifice will have a small length and short residence time while the flow through a pipe-like orifice will have a long length and a long residence time. The latter flow will appear more like an equilibrium flow and the former like a non-equilibrium flow. A delimiter of a length of 0.1 metre is often quoted.

The use of a dimensional criterion rather than a dimensionless one is often queried. However experimental data support the dimensional result (Moody, 1975; Fauske, 1985). The residence time that is of primary importance, but other physical properties such as surface tension and Jakob number could play a part in the bubble growth dynamics. Moody argued that the bubble growth time is typically about 1 millisecond, and that that residence time would translate approximately to a 0.15 m length. Among the short nozzle data, there are very few data sets that would allow one to examine the effect of L (or L/D) in detail in the \(< 0.1 \) m region; two exceptions are illustrated later in Figures 7 and 8.

A model for this type of problem is sometimes called a Homogeneous Non-Equilibrium (or Frozen) Model (HNEQ). There are also more complex homogeneous non-equilibrium models.

For flow lengths less than 0.1 m (the non-equilibrium regime), the flow rate increases strongly with decreasing length. As the length approaches zero an all liquid flow occurs and

\[
G_{c,L=0} = C_D \left( \frac{2(P_s - P_a)}{\nu_{f0}} \right)^{1/2}
\]

where:

- \( C_D \) = discharge coefficient (dimensionless and typically 0.6 for an orifice)
- \( P_s \) = vapor pressure at the stagnation/storage temperature \( T_0 = P(T_0) \) (N m\(^{-2}\))
- \( P_a \) = ambient pressure (N m\(^{-2}\))
- \( \nu_{f0} \) = specific volume of the liquid at saturation condition

That is, the Bernoulli equation for an incompressible liquid with pressure drop, \((P_s - P_a)\), available for flow. In this case the storage pressure and the saturation pressure are equal so \((P_s - P_a) = (P_0 - P_a)\)
Figure 5. Typically flashing discharge data of initially saturated water

Figure 5 taken from Fauske (1985) shows the equilibrium and non-equilibrium results for the mass flux (for saturated conditions). When L is large the mass flow rates are small and the ERM is within 20% of the more exact HEM. Much larger release rates are apparent when L is small and the flow near the rupture is a non-equilibrium one.

Fauske (1985) proposed an interpolation formula linking the ERM model and the non-equilibrium model for the discharge rate of saturated liquid and produced the supporting figure 6 below:

Figure 6. Saturated F-11 mass flux variation with L/D for D = 3.2 mm
A similar interpolation was developed by Leung between the “ω” method (as our recommended example of an HEM model) and the orifice model by defining a non-equilibrium parameter N in terms of the flow length L as:

\[ N = \left( \frac{G_\omega}{G_{c,L=0}} \right)^2 (1-L/L_E) + \frac{L}{L_E} \quad L \leq L_E \]  

(20)

and

\[
G = G_\omega \text{ for } L > L_E 
\]

(21)

\[
G = \frac{G_\omega}{N^{1/2}} \text{ for } L \leq L_E
\]

(22)

where \( G_\omega \) and \( G_{c,L=0} \) are mass flux per unit rupture area given by the \( \omega \)-method and by the all liquid orifice model respectively. For equilibrium flow to be attained, the flow length has to exceed 0.1 m (a relaxation phenomenon) and the corresponding \( C_0 \) is taken to be 1.0 (i.e. with no vena contracta).

As first pointed out by Fletcher (1984), van den Akker (1983), and Moody (1975), the proper scaling in this non-equilibrium region is the pipe length and not the length-to-diameter ratio (L/D) of the pipe. A constant relaxation length ranging from 75 mm to 150 mm has been proposed by these early researchers. Figures 7 and 8 illustrate the present correlation for the saturated discharge of water and Freon, respectively using a constant equilibrium length of 100 mm. Both the equilibrium regime and the non-equilibrium region are illustrated here. For the saturated water case, an inlet pressure \( P_o \) of 55 bar was used in the prediction (a lower \( P_o \) would raise the prediction due to the higher liquid density).

When there is full non-equilibrium and L approaches zero the velocity of the jet exiting the rupture plane will be determined directly from the Bernoulli equation. There has been some argument about what the pressure at the rupture plane (or the vena contracta) must be. It appears that it must be atmospheric pressure, with the exiting liquid in a non-thermodynamic equilibrium state. The important point is that the jet will not accelerate further due to any pressure excess at or downstream of the rupture plane. There will be an expansion, and hence acceleration, due to the subsequent flashing process. What the exit plane pressure will be in the region where L is larger than 0.1 m has not been clarified.

This would obviously be relevant if the rupture was to be in the form of a “short” pipe attached to the storage vessel i.e. the breakage of pipework attached to the storage vessel.

**3.4.3 The release of a subcooled liquid through a rupture**

The \( \omega \)-method, as described earlier, is restricted to materials that are initially at saturation conditions, be they vapor only, liquid only or vapor and liquid together. The case of sub-cooled liquids is not treatable with that approach. However Leung (1988, 1995) does provide a modified form of the \( \omega \) method for subcooled liquids. Subcooled liquids may arise due to cooling of the material or to the “padding” of the stored material with another gas. The subcooled liquid release is of particular interest as “Even a moderate subcooling may …..cause a much larger mass flow” Nyren and Winter (1987).
**Figure 7.** Prediction of saturated water discharge using present correlation (data as presented in Fletcher, 1984 paper). $G_E$ and $G_{NE}$ are the equilibrium and non-equilibrium solutions respectively.

**Figure 8.** Prediction of saturated Freon discharge using present correlation (data as presented in Fletcher, 1984 paper). $G_E$ and $G_{NE}$ are the equilibrium and non-equilibrium solutions respectively.
The extension of the $\omega$-method to subcooled liquid discharge is facilitated by removing the first term in equation 3.7 and defining a “saturated” $\omega$ parameter as:

$$\omega_s = -\frac{C_{p_0}}{v_{f_0}} \left( \frac{v_{\text{sat}}}{h_{\text{fg}}} \right)^2$$  \hfill (23)

where $P_s$ = vapor pressure corresponding to inlet temperature $T_o$ (N/m²)
$v_{f_0}$ = liquid specific volume (m³/kg)

Again all the properties are to be evaluated at $T_o$, the inlet stagnation temperature. The generalized solutions are divided into low and high subcooling regions, delineated by a transition saturation pressure ratio ($P_s/P_o$):

$$\eta_s = \frac{P_s}{P_o} = \frac{2\omega_s}{1 + 2\omega_s}$$  \hfill (24)

In the low-subcooling region where $\eta_s = \eta_{st}$ or $P_s > \eta_{st}P_o$, the fluid attains flashing (two-phase) flow prior to the exit plane (throat) location and the dimensionless mass flux is given by

$$\frac{G}{\sqrt{P_s/v_{f_0}}} = \left[ \frac{2(1 - \eta_s) + 2\omega_s\eta_s \ln \left( \frac{\eta_s}{\eta} \right) - (\omega_s - 1)(\eta_s - \eta)}{\omega_s \left( \frac{\eta_s - 1}{\eta} \right) + 1} \right]^{1/2}$$  \hfill (25)

and for choking conditions to occur, the following equation yields the critical pressure ratio $\eta_c$:

$$\left( \frac{\omega_s + \frac{1}{\omega_s} - 2}{2\eta_c} \right)^2 \eta_c^2 + 2(\omega_s - 1)\eta_c + \omega_s\eta_c \ln \left( \frac{\eta_c}{\eta} \right) + \frac{3}{2} \omega_s\eta_c - 1 = 0$$  \hfill (26)

Note that above two equations, Eqs. (25) and (26) reduce exactly to Eqs. (9) and (10) in section 3.4.1, respectively, for the saturated liquid inlet case with $\eta_s = 1$ (i.e. $P_s = P_o$).

In the high subcooling region where $\eta_s < \eta_{st}$ or $P_s < \eta_{st}P_o$, no vapor is formed until the exit plane is reached, and Eq. (25) reduces to a Bernoulli-type formula,

$$\frac{G}{\sqrt{P_s/v_{f_0}}} = \sqrt{2(1 - \eta_s)}$$  \hfill (27)

or

$$G_e = \sqrt{2 \rho_{f_0} \left( P_o - P_s \right)}$$  \hfill (28)

Recommended equation 4
where $\rho_{fo} = 1/\nu_{fo}$, the inlet liquid density at $T_o$. The critical pressure ratio is given by

$$\eta_c = \frac{p}{p_s}$$  \hspace{1cm} (29)

or choking simply occurs at the saturation pressure corresponding to the inlet temperature $T_o$.

Figure 9 illustrates the graphical solutions for inlet subcooled liquid discharge. The point of consequence here is that the pressure at the rupture exit plane is the saturation vapor pressure corresponding to the storage temperature and this will be in excess of ambient pressure. Thus the phase change occurs outside the storage vessel.

In figure 9 all liquid discharge will be expected where “high sub-cooling” is indicated. Where “low subcooling” is indicated there will be some phase change within the vessel and a reduced mass flux discharge. Roughly speaking, if the storage pressure is more than about 10% larger than the saturation pressure at the storage temperature an all liquid release is expected; reflecting the maximum discharge rate possible.

As the stagnation pressure approaches the saturation pressure at the storage temperature the equation for the strongly sub cooled mass flux is not consistent with that obtained based on an homogeneous equilibrium model (HEM) or an (ERM) model for saturated liquid storage conditions. A pragmatic solution to this is to use the interpolation proposed by Fauske and Epstein. (1988, 1989) that takes the “vector sum” of, say, the ERM model and strongly sub cooled model above. Fauske and Epstein (1988) present three experimental results that, they argue, support the formulae. However it is thought that this may underestimate the flow rate for slightly subcooled liquids and DIERS/AIChE (Fisher et al., 1992) recommends the method given in Leung and Grolmes (1988). But we note again that these arguments and the interpolation will not produce an exit plane pressure. Of considerable importance is that the $\omega$-method when extended to subcooled materials provides both the discharge rate and the exit plane pressure, as well as a smooth transition.

### 3.4.4 A non-equilibrium flow of a subcooled liquid through a rupture

A similar non-equilibrium correlation as suggested for the saturated liquid discharge can be employed for the subcooled liquid case. Here the equilibrium mass flux is evaluated using the subcooled liquid extension to the $\omega$ method as presented in Section 3.4.2, and is closely approached when $L = 0.1$ m. When $L$ approaches zero length the orifice liquid discharge with a typical $C_D$ of 0.6 would be applicable.

### 3.4.5 The effect of a rupture in a longer pipe connected to a vessel

If the pipework was “longer” then calculation of the release rate would need to account for frictional losses in the pipe and these would depend upon $L/D$ and the reduction in flow rate due to the phase change occurring within the pipe rather than close to the end. Of course the exit pressures and velocities would be altered also. Fauske and Epstein (1988) provide simple estimates of the effects of friction for modest pipe $L/D$ s on the mass flow rate from the storage vessel and the exit pressure that may be useful directly or as an indicator of the magnitude of this effect.
Figure 9. Critical discharge of inlet subcooled liquid based on ω method.

The ω-method has also been extended to similar discharges but through more extensive pipework and for two-phase inlet conditions including saturated liquid and subcooled liquid (Leung and Grolmes, 1987, Leung and Ciolek, 1994). For the former the analytical results can be illustrated by Fig. 10 where the effect of L/D – shown in horizontal axis as 4fL/D where f is the Fanning friction factor – is to reduce the mass flux $G_c$ relative to the equilibrium nozzle case $G_{oc}$. Figures 7 and 8 illustrate the success of the omega model as applied to pipe discharges where both saturated liquid inlet data for R-11 and water were closely predicted at length satisfying the equilibrium (relaxation) criterion.
As for the subcooled liquid pipe discharge, the bounding equilibrium flow is given by a simple Bernoulli type formula (Leung, 1994),

$$G = \sqrt{\frac{2 \rho_{ls} (P_e - P_s)}{1 + 4f} \frac{L}{D}} \quad (30)$$

By bounding it is meant that this will be the maximum discharge rate; a maximum when the phase changes at the very end of the pipe and so it is essentially an all-liquid flow throughout the pipework.

3.4.6 An exact alternative exact approach for the two phase case

An interesting and possibly operationally useful approach has been provided by Richardson 2006. For this problem Richardson et al. (2006) made the very important, though not new, observation that the simplified approximate solutions for this problem as provided by Fauske and Epstein (1988, 1999) and, more substantially, by Leung (1996) may be an unnecessary approach. Direct and exact calculation may be just as efficient. The simplified approaches are of course extremely
useful for directly determining the relative influence of the various input variables and for
determining output trends with the input variables. Simplified methods, like the $\omega$-method, were
meant to circumvent the hard-to-get thermodynamic properties for industrial chemicals. If detailed
thermodynamic properties are available there be no need to use the “$\omega$ method”, and a classical
HEM calculation such as this can be made.

All that is required for an exact solution is to satisfy three conditions that connect the flow from
the storage tank to the rupture/exit plane. The conditions are:

- The specific entropy, $s$, is the same at both places (flow is reversible)
- The sum of the specific enthalpy, $h$, and $U^2/2$ is the same at both places (flow is adiabatic)
- The velocity at the exit plane $u_0$ is the “speed of sound” and is given by \((\partial P/\partial \rho)^{1/2}\) where
  the derivative is taken at constant entropy evaluated at the conditions at the exit plane (the
  flow is choked at the exit/rupture plane)
- If no solution is found then the flow will be non-choking. In this case the condition at the
  rupture plane should be that the pressure is atmospheric.

The solution relies on an iteration based around the thermodynamic properties of the material.
These should be accessible for many TICs. A solution procedure is referred to in Richardson et al.
(2006). There is substantial concern regarding the need for constant entropy flash calculations; the
tools for this are available (a robust flash routine or simulation package such as ASPEN) and
further consideration may be worthwhile depending, in part, on what particular scenarios are of
interest.

Richardson states that the $\omega$-method (a homogeneous equilibrium model, HEM) is within 1% of
exact calculations. The recommendation here is that the use of an exact approach should be
considered further; particularly the availability of the necessary chemical data. Of course, from an
engineering standpoint, if the $\omega$-method is within 1%, there may be little good reason to use
anything more complex!

3.5 The discharge coefficient $C_D$

The dimensionless discharge coefficient, $C_D$, accounts for reductions below the theoretical exit
velocity due to frictional losses arising in the flow near the rupture and the possibility of the flow
area being smaller than the rupture area (a phenomenon called the vena contracta). The
combination of these two components means that $C_D$ accounts for the reduction in flow rate due
to both the effect of friction and the reduction in the jet area being smaller than the rupture area. It
depends upon nozzle shape and Reynolds number, and graphical relationships of $C_D$ for various
types of orifices can be found in handbooks and fluid mechanics textbooks (e.g., Perry and Green,
1997). In the context of this document, $C_D$ is entirely due to the flow field or vena contracta effect
and is not affected by frictional loss or L/D.

It is typically 0.6 for incompressible flow of liquids or vapors flowing through circular sharp-
 edged orifices. For thin slit orifices the theoretical discharge coefficient is $\pi/(\pi+2) = 0.61$
(Batchelor, 1967). For sharp edged orifices a discharge coefficient of 0.60 is recommended.
For gas flows through orifices, the observed discharge coefficient varies from 0.6 at low pressure drops (the incompressible flow case) to slightly less than 0.9 at large pressure drops (the compressible flow case) – 0.85 has been quoted, Shapiro “Compressible Fluid Flow”, fig 4.17.

Discharge coefficients for a comprehensive range of industrially relevant scenarios are available in Wirth (1983) (in German).

Leung (2004) presents results for discharge coefficients for orifice flow and its application to safety relief valves under two-phase conditions. He also provides theoretical results using $\omega$-method for the discharge coefficient. It varies monotonically from 0.60 through 0.88 to unity as $\omega$ varies from near zero (liquid flow) through unity (near (compressible) gas/vapor flow) to very large (saturated liquid inlet). These results have been supported by the work of Richardson et al. (2006). Leung (private communication) argues that the saturated liquid case provides a more compressible mixture due to its ability to flash and greatly increase its specific volume, yielding a lesser contraction at the vena contracta location; a plausible argument and consistent with the $\omega$-method.

We recommend:

- the use of a value of $C_D = 1$ for all scenarios if a truly conservative estimate is essential
- If this is not the case and a more accurate result is desired then we recommend the use of $C_D = 0.60$ for all-liquid flows and for all-gas flows where incompressibility can be assumed (at Mach numbers less than 0.3)

• For all other cases we recommend the use of $C_D = 1$

**Recommended equations 6**

If more detailed information is required then the following may be considered:

- The result from Leung (2004) above
- Extensive research has been done on discharge coefficients for incompressible, compressible, two-phase fluids in various flow geometries (Jobson, 1955; Bragg, 1960; Chisolm, 1983, Idelchik, 1986; Morris, 1989; Wirth, 1983).
- The effect of some other geometry can produce discharge coefficients from below 0.50 for incompressible fluids as shown below. Note that case d) below has the lowest discharge coefficient and has a re-entrant shape that is possibly similar to penetration from outside.
4. Storage vessel response

4.1 Introduction

Following a rupture of a storage vessel there will be a mass flow rate from the vessel and this may be gas, liquid or a mixture of gas and liquid depending upon the contents, their disposition and the rupture position. The vessel response (called blowdown in the chemical engineering community) will depend upon the fundamental equations for mass, momentum, enthalpy and entropy including heat transfer to or from the vessel contents, transfers between different phases within the storage vessel and the thermodynamic equilibrium or not of the vessel contents. These changes will lead to a change in the phase fractions in the vessel and the temperatures and pressure within the vessel.

The chemical engineering community defines blowdown as the time-dependent (transient) discharge from a vent or hole in a pressurized vessel containing liquefied gas, as the tank depressurizes to
ambient conditions. Generally there are several different scenarios that are considered based on the storage conditions, the thermodynamic properties of the stored material and the type of rupture.

One specific scenario is of particular interest in the context of this study; the scenario where the material is stored under “saturated” conditions where both liquid and vapor are present within the storage vessel (and are initially in thermal equilibrium). Under these conditions the storage pressure and the storage temperature (both assumed uniform) are not independent; knowing the pressure or temperature determines the other (for example, water boils at 100°C at 101,325 N/m² pressure). This scenario is typical of several possible releases of concern. A related, though different, scenario is when the storage vessel also contains an inert “pad” gas, such as nitrogen. The nitrogen can be used to keep the stored material as solely liquid by ensuring that the storage pressure is in excess of the saturated vapor pressure corresponding to the storage temperature. Often tanks are pressurized with 

Evidence shows that if the blowdown is due to a top opening, then the “pad” gas will be vented out initially and subsequent blowdown will follow the saturation curve. On the other hand, if the blowdown is from a bottom hole, then the “pad” gas will exert its influence on the discharge rate – a subcooled liquid discharge regime. Note that the “pad” gas pressure will continue to diminish due to the increasing head space as inventory drops. This can easily be accounted for in a simulation code.

When a tank ruptures or a hole develops in the tank material exits the tank and the pressure decreases within the tank. If the hole is well above the vapor/liquid interface then vapor will exit the tank. If the hole is well below the vapor/liquid interface then liquid will exit the tank. In both cases the material approaching the hole, at the hole and just downstream of the hole will maintain its state of either vapor or of liquid. The decrease of pressure within the tank will lead to the liquid within the tank changing phase by homogeneous and/or heterogeneous nucleation and the liquid boils sometimes violently. The region of two phase fluid within the tank will be near to the initial position of the fluid interface. This region of the tank contents will swell. If the hole is within this two phase region of the tank contents then there will be two phase fluid approaching, at and immediately downstream of the hole. Experimental data including those of the large-scale DIERS experiments (500 gal or 2 m³) demonstrated that the void (or bubble volume) distribution is skew, more void at top than at bottom. However the void profile would very much depend on the size of the rupture (opening) and location. A large opening at the top can induce so much flashing (phase change) inside the tank as a result of rapid depressurization that can cause the level swell to the top, resulting in a two-phase release.

For an arbitrary hole position and initial fluid interface position various time dependent flows will evolve. For example:

- A hole at the top of a tank, well above the vapor/liquid interface, will initially discharge vapor. As the pressure in the tank begins to decrease, some of the liquid will vaporize (and eventually exit the tank) and slow the pressure decrease. This may be a substantial fraction of the tank mass. The vaporizing phase change within the tank cools the tank contents by auto refrigeration, and eventually the vapor pressure falls to atmospheric pressure and discharge ceases. More commonly there will be a continued release after pressure has come down to equilibrate with the outside ambient pressure heat transfer because of the heat transfer to the tank contents from the tank walls and from outside the tank. Note that heat transfer from the
tank walls may influence the blowdown process but heat transfer from outside will be too slow to play an important role in the blowdown phase.)

- With a hole at the bottom of a tank, well below the vapor/liquid interface then the discharge will be all liquid. It will remain an all liquid release until the two phase region within the tank descends to the position of the hole.

- If the hole is initially near the liquid/vapor interface there will be a two phase release closely following the rupture and this will remain so until the two phase region within the tank drops below the hole position.

The overall picture is best considered for a hole initially well below the vapor/liquid interface. The sequence of events (at the plane of the rupture) would be an initial all-liquid release, then a two-phase release and then a single phase release. The pressure would remain relatively constant but slightly decreasing until all the liquid had vaporized. The mass flow rates would be largest for the all liquid release, less for the two phase release and smallest for the single phase vapor release. The exit velocities (and possibly the momentum fluxes) would be in the reverse order. The all liquid release produces the smallest velocities and the all vapor releases produces the largest velocities.

The most prevalent release scenarios involve pressurized liquefied gas of TICs such as chlorine, anhydrous ammonia, and sulfur dioxide, which would lead to two-phase jet releases. Two-phase flow stops when the inventory depletes sufficiently for the frothy level to drop below the bottom of the puncture. The blowdown stops when the pressure in the tank reaches atmospheric.

An example of a particularly simple blowdown model (from Joseph C. Leung) follows. This is included in this report as indicative of what might be developed.

4.2 On level swell and discharge exit conditions during vessel blowdown

The purpose of this section is to summarize the methodology and underlying equations describing the level swell and the discharge exit conditions during a vessel blowdown. The discussion is necessarily brief and should provide a good-enough first approximation to the rather complex in-vessel hydrodynamic behavior during blowdown.

In this treatment the model assumptions are:

1. Neglect transient level swell associated with pressure undershoot or delayed bubble nucleation during the initial blowdown.
2. Thermodynamic equilibrium between vapor and liquid phases.
3. One-dimensional model allowing vertical void distribution.
4. Constant cross-sectional area vessel.
5. Uniform vapor generation from blowdown (depressurization).
6. Churn-turbulent flow regime with $C_o$ (void distribution parameter) of 1.0 in terms of the drift-flux model.
7. Uniform pressure and temperature in vessel
4.2.1 Basic relations in level swell analysis

The level swell inside a vessel is a buoyancy-driven flow phenomena where the rising of swarms of vapor bubbles through the liquid bulk results in the level swell. This phenomena is best described by the so-called drift-flux model (Wallis, 1969; Zuber and Findlay, 1965). Applications of the drift-flux model can be found in blowdown analysis of nuclear reactor components and chemical equipments. The DIERS work utilized the drift-flux model extensively in describing the hydrodynamics of both chemical runaway reactions and storage vessels during pressure relief conditions (DIERS report, 1983; Fisher, 1992). It suffices here to just summarize the key results. During a vessel blowdown, the superficial vapor velocity at the top $j_\infty$ and the average void fraction in the liquid pool $\bar{\alpha}$ are related via:

$$ \frac{j_\infty}{U_c} = \frac{2\bar{\alpha}}{1 - \bar{\alpha}} $$

where $U_c$ is the individual bubble rise velocity (m/sec) given by Wallis (1969).

$$ U_c = 1.53 \left[ \frac{\sigma g (\rho_f - \rho_g)}{\rho_f^2} \right]^{1/4} $$

Here $\sigma$ is the liquid surface tension (N/m), $\rho_f$ is the liquid density (kg/m$^3$) and $\rho_g$ is the vapor density (kg/m$^3$). In most cases, $\rho_g << \rho_f$ such that Eq. (32) can be simplified to

$$ U_c = 1.53 \left[ \frac{\sigma g}{\rho_f} \right]^{1/4} $$

The void fraction at the top of the pool $\alpha_f$ can be related to the average $\bar{\alpha}$ via,

$$ \alpha_f = \frac{2\bar{\alpha}}{1 + \bar{\alpha}} $$

If one invokes a simple linear void distribution profile, the void fraction at the bottom $\alpha_B$ would be given by

$$ \alpha_B = 2\bar{\alpha} - \alpha_f $$

Now define $H_v$ as the vessel height (m), $H_L$ as the collapsed liquid height (m), and $H_{2P}$ as the two-phase swell height (m).

Here $H_v$ is related to the liquid mass $M_L$ (kg) via:
where $A_x$ is the vessel cross-sectional area ($m^2$). Also $H_{2P}$ is related to $H_L$ via:

$$H_{2P} = \frac{H_L}{1 - \alpha}$$

Finally the void fraction in the vessel $\alpha_o$ is related to $H_o$ and $H_L$ via:

$$\alpha_o = \frac{H_o - H_L}{H_o}$$

### 4.2.2 Complete vapor-liquid (V/L) disengagement (top vent)

In a top-vented vessel, the complete V/L disengagement criterion is simply stated as

$$\bar{\alpha} < \alpha_o$$

It can be easily shown that this inequality requires that $H_{2P} < H_o$ as expected, i.e., the two-phase swell height being less than the vessel height. Here the superficial vapor velocity $j_{g\infty}$ at the top of the liquid pool is related to the vapor discharge rate at the top hole,

$$\rho_g j_{g\infty} A_x = W x_1 = W_g$$

where $x_1$, the exit quality, is 1.0 for vapor discharge, $W$ is the mass discharge rate, and $W_g$ designates vapor mass flow rate (kg/s). This $j_{g\infty}$ is used in Eq. (31) to determine the level swell or $\bar{\alpha}$. On the other hand, if $\bar{\alpha} > \alpha_o$, that would imply a level swell to the vessel top resulting in partial V/L disengagement for a top-vented configuration.

### 4.2.3 Partial V/L disengagement (top vent)

In a top-vented vessel when the level swell reaches the top vent, the vessel exit quality or vapor mass fraction is given by Leung (1987):

$$x_1 = \frac{\rho_x U_x A_x + \rho_g}{W \rho_L}$$

where $W$ is the mass discharge rate (kg/sec). Note that $W$ is dependent on $x_1$, the inlet quality to the hole opening, via
\[ W = C_d A_o G(x_1) \]  \hspace{1cm} (42)

where \( C_d \) is the discharge coefficient, \( A_o \) is the hole area \((m^2)\) and \( G \) is the discharge mass flux \((kg/m^2\cdot sec)\) with \((x_1)\) indicating its dependency on \( x_1 \) in above equation. Thus Eqs. (41) and (42) have to be solved simultaneously for both \( W \) and \( x_1 \). Numerically successive substitution scheme for \( x_1 \) has been found to converge in a few iterations.

### 4.2.4 Exit conditions for side and bottom vents

For side and bottom vent, the exit conditions can be determined in accordance to the void distribution profile. For complete \( V/L \) disengagement, i.e. only vapor exiting the hole at an elevation \( Z \) (above vessel bottom), it requires the hole to be above the swell liquid level, i.e.

\[ Z > H_{sp} \quad \text{or} \quad \frac{H_t}{1 - \alpha} \]  \hspace{1cm} (43)

Otherwise for \( Z < H_{sp} \), i.e. vent located below swell liquid level, the local void fraction can be approximated by

\[ \alpha_Z = \alpha_g + \left( \alpha_f - \alpha_g \right) \frac{Z}{H_{sp}} \]  \hspace{1cm} (44)

where \( Z \) \((m)\) is the elevation of the vent above the vessel bottom and \( \alpha_Z \) denotes the void fraction at elevation \( Z \).

The exit quality \( x_1 \) is simply

\[ x_1 = 1 \quad \text{if Eq. (43) is satisfied, otherwise} \]

\[ x_1 = \frac{\frac{\alpha_g \rho_g}{\alpha_g \rho_g + (1 - \alpha_Z) \rho_i}} \]  \hspace{1cm} (45)

Again since \( W \) depends on \( x_1 \) via Eq. (42), both Eqs. (45) and (42) have to be solved simultaneously for both \( W \) and \( x_1 \).

Here the superficial vapor velocity \( j_g \) at the top of the liquid pool is also related to the volumetric discharge rate via

\[ j_g A_x = \frac{W}{\alpha_g \rho_g + (1 - \alpha_Z) \rho_i} \]  \hspace{1cm} (46a)

or

\[ \rho_j j_g A_x = \frac{Wx_1}{\alpha_Z} \]  \hspace{1cm} (46b)

The above two equations are identical but Eq. (46a) avoids the division by zero when \( \alpha_Z \) is 0.
5. Flow after exit from the storage vessel

In all model systems, it is essential that total plume or puff fluxes be conserved at any transition from one model component to another (such as from the source emission model (SEM) to the atmospheric dispersion model (ADM). The most important of these is the mass flux, since it is directly used to calculate the concentrations. Other fluxes to be conserved are momentum flux, enthalpy flux, and aerosol drop mass flux and drop size distributions.

For TICs such as chlorine, there is a significant jet that extends from the hole in the storage tank to some downwind distance (10’s to 100’s of meters) where the jet speed reduces and approaches the ambient wind speed. Close to the rupture the jet may be at pressures many times atmospheric and the material in a superheated state. Downstream the jet pressure reduces to atmospheric, the superheated material may flash as liquid changes phase to gas and the jet will entrain ambient air. These processes are commonly artificially split into two distinct processes. Very close to the rupture (within a few meters) the flashing and the depressurization of the jet down to atmospheric pressure occur but without any entrainment of ambient air. Subsequently the jet is assumed to be at atmospheric pressure and entrainment of ambient air takes place. Across these two artificial processes the various fluxes are required to be continuous. Of great importance is that within the near rupture region the liquid that has not flashed will be forming small droplets due to both mechanical shear and the thermodynamic flashing processes. Not all of these effects are included in all widely-used models, and sometimes one or both parts of the jet are included in the SEM. Often the second part of the jet is included in the ADM. Consequently the transition from SEM to ADM occurs at different locations for different models. Many publicly-available models ignore some of the jet effects or only roughly parameterize them.

When the concentrations are needed very near the source location (say, within 100 m) it is necessary to account for more of the source details than if the concentrations are needed at farther distances (say beyond a few hundred meters). For example, by the time the plume reaches a distance of 1 km, the aerosol generation and evaporation processes are much less important, as long as the rainout (and reduction of plume mass flux) can be approximated. Sensitivity studies can assist in decided which details are necessary.

The material exiting through the rupture plane will eventually form a conventional momentum jet at atmospheric pressure. The requirement is to model the flow between the rupture plane and the momentum jet at atmospheric pressure. This is commonly attempted by finding an equivalent source condition for the momentum jet that is consistent with the conditions at the rupture plane. If the flow is unchoked at the rupture plane then the pressure is atmospheric and there is no further depressurization. If the flow is choked at the rupture plane then there will be an acceleration of the released material as it depressurizes. Additionally the depressurization will allow further liquid to change phase to a vapor and cool the jet. This process is commonly called “flashing”. Accompanying this process will be a breakup of the liquid part of a jet into smaller droplets as a result of mechanical shear instability and the thermodynamic flashing process. Finally, there will also be mixing between the momentum jet and the surrounding atmosphere.

All these effects must be subsumed into an alternative initial condition for the momentum jet at atmospheric pressure. This is often done by assuming that there is a depressurization to atmospheric pressure.
pressure and there is no mixing between the momentum jet and the surrounding atmosphere until after the depressurization has been accounted for.

In this section we are considering the processes between planes 1 and 2 in Figure 3, but not allowing any mixing of the surrounding atmosphere into the jet.

There are three distinct though related phenomena here.

5.1 Jet depressurization to atmospheric pressure

The first of these is the acceleration of the jet downstream of the rupture as the fluid depressurizes to atmospheric pressure.

Considering a flow from a hole (subscripted “1”) to the end of expansion (subscripted “2”), the following approaches are mostly used in the literature:

\[
\dot{m}_1 + (P_1 - P_2)A = \dot{m}_2
\]

\[
u_2 = \frac{(P_1 - P_2)A}{\dot{m}} = u_2 + \frac{P_1 - P_2}{G_1}
\]

where
- \( \dot{m} \) = mass flow rate (kg s\(^{-1}\))
- \( G_1 \) = mass flux (kg m\(^{-2}\) s\(^{-1}\))
- \( u \) = velocity (m s\(^{-1}\))
- \( P \) = pressure (Pa)
- \( A \) = flow area (m\(^2\))

Enthalpy Balance

\[
H_1 + \frac{1}{2} u_1^2 = H_2 + \frac{1}{2} u_2^2
\]

where \( H \) is enthalpy (expressed as \( c_p T \) for ideal gases).

Recommended equations 7

5.2 Flashing of superheated liquid to vapor

The second phenomenon is the phase change from liquid to vapor immediately downstream of the rupture plane. The mass fraction that initially changes phase by flashing is determined by direct thermodynamic calculations. The flash fraction arising from an all-liquid release is

\[
x_g = C_p(T_0 - T_b) / h_{fg}
\]
where \( C_{pl} \) is the liquid specific heat, \( T_0 \) and \( T_b \) are the temperatures in the storage vessel prior to flashing and the boiling point of the material at atmospheric pressure respectively, \( h_{fg} \) is the phase change enthalpy at atmospheric pressure. This formulation may be found in Fauske and Epstein (1988) and may be traced back to the application of the steady flow energy equation while ignoring the kinetic energy terms. Their inclusion leads to

\[
x_g = \frac{C_{pl}(T_0 - T_b)}{h_{fg}} - \frac{1}{2} \frac{(U_1^2 - U_2^2)}{h_{fg}}
\]

Recommended equation 8c

The third phenomenon is the breakup of the remaining liquid into small droplets with a particular probability density function for their sizes. The larger droplets will fall out to make a “pool” on the ground while the smaller droplets remain suspended and will evaporate in the plume. The characteristic droplet diameter is often to be determined from correlations. From this the rainout fraction may be estimated though this should be influenced by the fluid dynamics of both the jet flow from the rupture and the ambient wind conditions.

An important aspect of this section and the next, in the context of real scenarios, is that the release and jet may have many orientations and may hit and be influenced by various obstructions. Additionally they may not be directed into regions of clear air but may be submerged within large clouds formed by material released earlier and remaining near to the material source. This is very possible when the local wind speed is small.

In the case of a flashing liquid jet, such as a release of chlorine or ammonia or HF from a pressurized container, the chemical will flash partially to vapor when released to atmospheric pressure as described above. For ammonia, about 80 % of the released mass remains as liquid. Thus, the “quality”, or mass fraction that is vapor, is 100% - 80% = 20%. The liquid component in the aerosol is often parameterized to consist of spherical droplets with sizes distributed around some mean diameter. The droplets are assumed to be surrounded by a mixture of air and evaporated vapor. Some large liquid drops may rainout (i.e., may fall) immediately onto the ground, some drops may move under gravity and drag force while vaporizing and may rainout later, and some may remain in
the plume as an aerosol. However, the fraction of liquid that rains out versus the fraction that remains suspended in the plume as an aerosol is not well known. This fraction is important because the greatest hazard range is likely to occur when all the release remains suspended as is the maximum possible source emission rate for the subsequent dispersion modeling. Additionally, the evaporation of the suspended aerosol produces an increased negative buoyancy and this can affect the downwind plume greatly. The liquid that rains out is likely to form a boiling pool that will continuously evaporate and add vapor mass into the dispersing jet. The evaporation may continue long after the jet release ceases. This process is controlled by the heat transfer to the liquid pool.

The breakup of the liquid into droplets occurs by two mechanisms; a mechanical breakup dominant for releases that are subcooled relative to ambient conditions and a thermodynamic breakup dominant for liquid or two phase releases that are superheated relative to the ambient conditions though both effects may also occur together.

The modeling of these processes is complex and the results are typically in the form of correlations. It is sometimes forgotten that the essential information required is the amount of released material that rains out. Additionally, knowledge of where the rainout occurs may be required for input to the pool evaporation modeling but pragmatically all that may be required is knowledge of where the mean particle diameter rains out.

By definition whatever does not rain out must remain within the jet/plume and be subsequently be evaporated within the jet/plume. Most jet/plume models can accommodate this evaporation process either in bulk due to air entrainment or by considering evaporation of individual droplets. In the latter case knowledge of the mean droplet diameter of the liquid in the jet/plume or the actual particle size distribution is required. Whether such detailed knowledge of the evaporation process is required in operational models could be argued.

However, the approach commonly taken is to determine a mean particle diameter, assume a particle diameter distribution and then track the fate of particles within the jet/plume downstream of the rupture, with some of the particles raining out and some evaporating. Of course, this all hinges on whether an appropriate two-phase jet model is available and whether this is correctly linked to the (possibly multi-phase) plume model.

The mean diameter and/or the size distribution of the liquid drops has to be input to the models for droplet motion and vaporization. In some models, this is provided by the Wolfe and Anderson (1964) shattering formula, which gives the droplet size based on an assumption of an aerodynamic or mechanical breakup mechanism (e.g., the shattering of initial drops into smaller droplets due to aerodynamic forces. The stable droplet size is determined by the ratio of the disruptive hydrodynamic forces to the stabilizing surface tension force. The ratio is the Weber number, We:

\[
We = \frac{\rho_g u_{rel}^2 d_p}{\sigma}
\]  

where

- \(\rho_g\) = surrounding gas density, usually ambient air (kg m\(^{-3}\))
- \(u_{rel}\) = relative velocity between the jet and gas (ambient air) (m\(^2\) s\(^{-2}\))
It is generally accepted that there is a critical Weber number, $\text{We}_c$, below which drop breakup does not occur. Figure 8 shows that the $\text{We}_c$ is approximately 12 for small Ohnesorge number, which is the ratio of the viscous force to the surface tension force, and is also known as the viscosity number. Drop breakup at higher Ohnesorge number is progressively more difficult and is ultimately impossible.

**Figure 8.** Observations of critical Weber number as a function of Ohnesorge number (Brodkey, 1969)

The assumption of a mechanical breakup mechanism leads to the following estimate of the mean droplet diameter, $d_{pm}(m)$:

$$d_{pm} = \text{We}_c \frac{\sigma}{\rho u_{st}^2} \quad (54)$$

The TNO (1997) Yellow Book recommends values of between 10 and 20 for $\text{We}_c$, and most models use 12.5.

The thermodynamic breakup occurs when the liquid is superheated relative to atmospheric conditions, with a degree of superheat defined as $\Delta T_{sh} = T_o - T_{sat}(P_o)$, where $T_o$ is the temperature at stagnation, typically the storage temperature. The superheat, if sufficient, nucleates bubbles which grow until they agglomerate with neighbors, thereby breaking the liquid apart (Brown and York, 1962). This flashing droplet breakup is a dominant mechanism in releases of pressurized chlorine or ammonia. A method for estimating the size of the droplets formed by the flashing mechanism is
given by Woodward (1995). After correlating published experimental drop sizes against a number of differing parameters, he concluded that the partial expansion energy, $E_p$ (J/kg), was the most effective correlator for droplet size:

$$E_p = -\Delta H - \nu_s (P_s - P_f) + \nu_s \left| P_1 - P_f \right|$$  \hspace{1cm} (55)

where

- $\Delta H =$ Change in enthalpy from exit to expansion (from plane 1 to plane 2 in Figure 8) (J kg$^{-1}$)
- $P_s =$ saturation pressure at the storage or stagnation temperature (N m$^{-2}$)
- $\nu_s =$ mixture specific volume at $T_s$ ($P_s$) (m$^3$ kg$^{-1}$)
- $P_1 =$ exit pressure (N m$^{-2}$)

The drop diameter, $d_{pf}$ (m), is given by the formula:

$$d_{pf} \times 10^6 = \begin{cases} 1000 & E_p \leq 0.1 \\ 833 - 73.4 \ln(E_p) & 0.1 < E_p \leq 6000 \\ 498 - 43.0 \ln(E_p) & 6000 < E_p \leq 15000 \\ 0.85 & 15000 < E_p \end{cases}$$

where $E_p$ has units of J/kg.

Figure 9 shows diameters of liquid Cl$_2$ drops in the CCPS experiment vs. $E_p$ (Woodward, 1995; CCPS/AIChE, 1999). Unfortunately, the drop sizes were not measured in the CCPS experiment. Woodward (1995) assumed the drop sizes, as the $y$-axis title indicates, calculated the trajectories of the drops, compared calculated amount of rainout against experimental liquid capture data. Therefore, the value of $E_p$ as a correlator is demonstrated. But the relationship in the equation above is specific only to the models of drop motion and vaporization Woodward used in arriving at it. Witlox, et al. (2007) has proposed similar correlations. But all these correlations can only be used together with the droplet motion, vaporization, and rainout models the correlations are based on.

Finally the smaller drop size of $d_{pm}$ and $d_{pf}$ is recommended for use as the average drop size at the end of expansion.
The CCPS/AIChe performed experiments to gather data on aerosol rainout from superheated liquid release, so that these could be used to validate the CCPS RELEASE model (CCPS/AIChe, 1999). The tests were carried out in two phases, Phase 1 consisting of water and CFC-11 and Phase 2 of chlorine, monomethylamine (MMA) and cyclohexane (Cyc6) releases. The results reported by Energy Analysts (1990) and Quest Consultants (1992) are available on CD-ROM that was attached to the CCPS/AIChe (1999) report. The experimental data were later modified to allow for evaporation of liquid drops during their flight and also evaporation in the liquid capture pans. The experiments, in spite of some criticisms (Ramsdale and Tickle, 2000), provide valuable data with which to validate rainout models. Apart from these experiments, very few rainout data exist, except for Rohm & Hass (R&H) MMA data (Lantzy et al., 1990). Chemicals were released 1.22 m above the liquid capture pans in CCPS and 1.73 m in R&H experiments.

Figure 10 shows the “corrected” rainout in the CCPS experiment vs. “needed drop diameter” (Woodward, 1995; CCPS/AIChe, 1999). Because drop sizes were not observed in the experiment, the term “needed drop diameter” refers to a parameterization of the expected drop diameter. This corroborated an independent analysis by Melhem et al. (1995) of the same data, shown in Figure 12. The experimenters have questioned the quality of water data because the water experiments were done in a semi-enclosed greenhouse that might have become saturated with water vapor during experiments. Except for water, all tested chemicals seem to show good correlations between rainout and droplet size. It shows approximately 45% rainout of liquid with droplet size.
diameter of 300 microns. However, this may be an acceptable estimate only for the particular CCPS experimental conditions.

Initial Drop Size and Its Distribution - Suppose the dispersion model requires specification of the PSD, the liquid mass fraction, and the temperature for all liquid releases. At present, no deterministic models are available that can predict stable droplet sizes for various release conditions. Correlations based on observations are the best alternatives. Having reviewed those in the literature, Melhem et al. (1992, 1995) proposed the use of specific available energy, \( A_E \) (J/kg), as the correlation parameter:

\[
d_p = f \left( \frac{P_o - A_E}{\sigma_d} \right)
\]

and

\[
A_E = -\Delta U - P_o(v_o - v_2) = -(H_2 - H_o) - v_o(P_o - P_a)
\]

where

- \( d_p \) = droplet diameter (m)
- \( \rho_v \) = vapor density at “2” (kg m\(^{-3}\))
- \( \sigma_d \) = surface tension of the droplet liquid (N m\(^{-1}\))
- \( \Delta U \) = Change in internal energy from storage to expansion (J kg\(^{-1}\))

Later Woodward (1995) and CCPS/AIChE (1999) reviewed the literature correlations for droplet size. They concluded that the partial expansion energy, \( E_p \) (J/kg), was the most effective correlator for droplet size:

\[
E_p = -\Delta H - v_o(P_o(T_o) - P_a) + v_o(P_o - P_a(T_o))
\]

where

- \( \Delta H \) = Change in enthalpy from stagnation to expansion (J kg\(^{-1}\))

Both correlators, \( A_E \) and \( E_p \), are related to the same measure of kinetic energy “available” when the flashing liquid expands from stagnation to ambient pressure. Previously we recommended the most widely recommended \( E_p \)-based CCPS correlations for the Sauter mean diameter (SMD) of the droplet size:

\[
d_{pm} \times 10^6 = 833 - 73.4 \ln(E_p)
\]

The CCPS/AIChE (1999) recommends the smaller of \( d_{pm} \) (based on mechanical break-up) and \( d_{pf} \) (based on flashing break-up) as the average drop size at the end of expansion. This is in error – it leads to using \( d_{pm} \) at low superheats and \( d_{pf} \) at high superheats. This has been pointed out also by Witlox et al. (2007). For many scenarios of interest, using the correlation as is may be sufficient.

A recent correlation (called here “DNV-JIP”) proposed by Witlox et al. (2007) is sometimes used. It has been recommended that the Witlox et al. correlation be carefully re-evaluated for the following reasons:
The DNV-JIP correlation uses the correlation developed by Kitamura et al. (1986) to find the superheat for transition from mechanical break-up to flashing break-up. Witlox et al. however use $\rho_v$ at $T_o$ in place of the equilibrium vapor density at ambient pressure that Kitamura et al. have used. This would produce significant errors in predicting drop size.

Table 2 and Figure 7 in Witlox et al. (2007) show the DNV-JIP correlation predicts much larger drop sizes, more rainout accordingly, than the CCPS/AIChe (1999) model. This is not expected by the experimenters, industry experts, and accident investigators.

The DNV-JIP correlation is based on a few experimental data. In fact, the DNV-JIP is involved in Phase III for more experiments.

Figure 10. Rainout % plotted versus needed (parameterized) drop size in CCPS experiments
Once a model is implemented with proper droplet motion and vaporization models with the initial drop size discussed here, it may be able to predict rainout. But at present, there is not an accepted model that performs consistently well against the limited set of experiments done by CCPS/AIChE (1998), Rohm and Haas (Witlox et al., 1990), and Witlox et al. (2007). The lack of an acceptable model may be also due to the need for more experimental data, especially for full-scale releases.

CCPS/AIChE experimental data were useful but the range of scenarios should be expanded.

It may be worthwhile to see what can be summarized as “known”.

- There is both mechanical and thermodynamic breakup
- Witlox has argued that the problem is generally more complex than can be treated with very simple parameterizations; this may be less important if only a smallish number of TICs are being considered
- Two approaches have been followed for rainout; direct correlations or following individual particles
- In both cases the near rupture jet characteristics must play a part.
- The treatment of the liquid that is not rained out is relatively straightforward and there are several levels of approximation that have been used.
- Witlox (2002) argues that a case could be made that all particles below 20 micron would not rain out. Figure 10 suggests that maybe a figure of 100 microns might be acceptable. Figures 10 and 11 suggest that “roughly” there is “always” some substantial rainout (around 80%) for all particles above 400 microns. Are there not some simple parameterizations hidden away here that could be operationally useful (given some set accuracy threshold)
• There are several correlations for the probability density function of droplet sizes together with the accompanying characteristic diameter.

The breakup of the jet into fine droplets and their subsequent suspension and evaporation, or rain out, is a significant uncertainty in the overall modeling process. What has not yet been done is to recommend the RELEASE approach, the more recent and “still being developed” Witlox effort or what can be discerned from the also recent FLIE project. Weaknesses of the RELEASE model and the lack of completeness of the Witlox JIP experimental and model development make it difficult to offer specific recommendations. What can be said is that there is nothing inherently poor about the Witlox JIP model and this model could be used though the uncertainty of this modeling process must be kept in mind.

6. Evaluation of the Modeling

6.1 Discharge conditions

6.1.1 Evaluation of the modeling of the mass discharge rate: single phase release

An evaluation of the emission model estimates has been conducted to test their applicability. The evaluation is limited to single component fluids and single phases, either gases or liquids in an orifice flow. Upon exiting the orifice, the liquids analyzed transition rapidly to two-phase flows. The evaluation is limited to only a few comparisons since the single phase models have been evaluated elsewhere (e.g., Richardson et al., 2006; Spicer et al., 2003; Nyren and Winter, 1987), perform well, and are rather well understood. We first consider a compressible gas flow and then liquid flows through an orifice.

Richardson et al. (2006) carried out well-designed experiments for the measurement of single and two-phase flows of hydrocarbons through an orifice. The experiments, conducted for the UK Energy Institute, were made for volatile mixtures of natural gas, propane, and condensates and were aimed primarily at testing models for restricted flow (through relief valves, etc.) in the oil and gas industry. The experiments were significant in their precise determination of the mixture composition, mass flow, and thermodynamic state including the fluid temperature and pressure. Moreover, the apparatus used allowed higher flow rates (up to 4 kg/s) than usually possible in laboratory-scale experiments and at storage pressures approaching 100 bar. Here, we only use their natural gas data for testing mass flow based on the perfect gas law (Eq. 4).

In addition to measurements, Richardson et al. calculated the flow rate for single- and two-phase flow using a simple model based on isentropic choked flow with the “sound speed” determined for either a single- or two-phase fluid. A key component of this was an equation of state model for determining the pressure, temperature, and mixture composition based on a “principle of corresponding states,” which was purported to be more accurate than a cubic equation of state model such as the Peng-Robinson (1976) approach. A more complete equation of state model is particular useful for two-phase mixtures and at pressures near and above the critical pressure \( P_c \), where compressibility effects for non-ideal gases become important.

For natural gas, an analysis of the simple emissions estimate based on the perfect gas model (Eq. 4)
has been made by determining the discharge coefficient, \( C_D = \frac{\text{observed flow rate}}{\text{predicted flow rate}}, \) and comparing it with the Richardson et al. results and the \( C_D \) ranges discussed in Section 3.5. In the perfect gas formulation, the natural gas was assumed to be all methane, which should be a good first approximation since natural gas is 90% methane, 9% ethane, and 1% propane by weight. In the natural gas experiments, the orifice diameter ranged from 8 to 15 mm, the pressure from 10 to 82 bar, and the measured flow rate from 0.3 to 2.82 kg/s.

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![Graph](image)

**Figure 12.** The discharge coefficient for the perfect gas and Richardson et al. (2006) emissions models for natural gas as a function of a) the measured flow rate, and b) the ratio of storage pressure to critical pressure. The flow rate measurements are from Richardson et al. (2006).

Figure 12 shows the discharge coefficient for the natural gas data where the open and enclosed circles are the results for the perfect gas approach (Eq. 4) and the Richardson et al. model, respectively. As can be seen, the Richardson et al. model leads to an approximately constant \( C_D = 0.9 \) (average value), whether plotted versus the measured mass flux or the pressure ratio \( P_0/P_c \). The perfect gas approach (open circles) gives higher \( C_D \) values that range from about 0.9 to 1.1, and this is believed due to two causes. The first is the assumption that the natural gas is 100% methane, which may explain the higher \( C_D \) values (average of 0.97) for the “lower” pressures \( P_0/P_c < 1 \),
where non-ideal gas effects are not a large issue. Second, the \( C_D \)'s show systematically higher values for the larger pressure ratios \( (P_0/P_c > 1) \) where non-ideal gas effects are probably important. The \( C_D \)'s are as much as 20\% greater than the Richardson et al. \( C_D \) (0.9) at \( P_0/P_c = 1.8 \), where \( P_0 = 82 \text{ bar} \). This is probably due to the failure of the perfect gas law to perform well at such high pressures.

Leung (private communication) made a corroborative check on the above speculated effect of pressure using a non-ideal gas flow model (Leung and Epstein, 1988), which accounts for compressibility at high pressure. Assuming the natural gas to be 100\% methane, he obtained a theoretical mass flow rate of 2.85 kg/s versus the measured value of 2.72 kg/s at the highest pressure \( (P_0 = 82 \text{ bar}) \). This resulted in a \( C_D = 0.95 \), which is considerably closer to the Richardson et al. value (0.9) than the perfect gas model \( (C_D = 1.1) \) at that pressure. Thus, the non-ideal gas model indeed explained most of the difference between the perfect gas and Richardson et al. model results. Leung also found that for a mixture of 90\% methane and 10\% ethane, the \( C_D \) was 0.93 or slightly closer to the reported 0.9 value.

In summary, the perfect gas model combined with the recommended \( C_D = 1 \) (Section 3.5) would slightly overestimate the Richardson et al. flow rate data for \( P_0/P_c < 1 \) and underestimate the flow rate by about 10\% at the highest pressures in those experiments. This accuracy is considered sufficient for TIC modeling.

For liquids, we evaluated the predicted mass flow rate or discharge coefficient using experimental data collected in testing the RELEASE model (Johnson and Woodward, 1999). Since the \( C_D (= 0.6) \) for liquid discharges is well documented (Section 3.5), the evaluation was only conducted for two of the liquids, water and CFC-11, used in the RELEASE/CCPS experiments. The comparisons were expected to be a confirmation of the above \( C_D \) value. For these experiments, the liquids were released through an orifice connected to a heated storage tank, which was pressurized to ensure that the fluid in the orifice was 100\% liquid. The release rate was determined from the change with time of the liquid level in the tank. The water releases were conducted for storage temperatures ranging from 378 to 488 K and orifice pressures of 184 to 2140 kPa, whereas the CFC-11 releases involved lower temperatures (295 to 355 K) and pressures (162 to 554 kPa). The lower end of the temperature range was near the boiling point of the liquids. The measured release rates ranged from 0.07 to 3.11 kg/s (water) and 0.27 to 0.67 kg/s (CFC-11).

Figure 13 shows the discharge coefficient as a function of the pressure difference, \( P_0 - P_a \), driving the flow. The average \( C_D \)'s for water and CFC-11 are 0.59 and 0.61, respectively, and are in close agreement with the \( C_D (= 0.6) \) reported for liquids in Section 3.5. Aside from three \( C_D \) values (≥ 0.69) for water, the individual \( C_D \)'s exhibit relatively little scatter and have small rms deviations about the average: 0.05 for water and 0.02 for CFC-11. The agreement between the average \( C_D \)'s and the expected one (0.6) is representative of that for the other liquids—chlorine, methylamine, and cyclohexane—in the CCPS experiments. This was demonstrated by Spicer et al. (2006) in a comparison between the predicted and measured flow rates.
Figure 13. The discharge coefficient for a) water and b) CFC-11 based on the mass flow rate obtained from the incompressible flow rate model (Eq. 1). The measured flow rates are from the CCPS experiments (Johnson and Woodward, 1999).

6.1.2 Evaluation of the modeling of the mass discharge rate: two phase release

Richardson et al. (2006) also undertook an extensive set of experiments, again with what might be considered as sharp-edged orifices, using highly volatile mixtures of hydrocarbons at pressures up to 100 bar and flow rates of up to 4 kg/s under saturation conditions. What is of particular interest for this report was that Richardson et al. compared their experimental results with predictions provided by an HEM model (described in Section 3.4.6). The expected flow rate was calculated from the exact iterative technique and compared with the measured flow and the discharge coefficient calculated as the ratio of the two. Several hundred experiments were undertaken.

Richardson et al. (2006) also compared the results from their HEM model and the ω-method recommended in this report and concluded that “for wide-boiling mixtures in which the upstream
condition is two-phase …… the ω-method agrees with the exact, iterative method to within 1%.” Thus we can interpret the comparison made with the exact HEM model as being equivalent to a comparison made with the ω-method. The liquid mass fractions upstream of the orifice varied from 0.0 to 1.0.

However the ω-method omega did produce significantly larger errors when the fluid stream is single phase at the orifice, but two phase within the throat.

There were two situations for which two particular (simple) model types were applicable

1. For flows of compressed volatile liquids … the incompressible flow model provides a good approximation with a discharge coefficient of 0.60. This simple model progressively breaks down as the volatile gas content increases. This is the Bernoulli equation approach.

2. For two-phase flows (that must of course be at the appropriate two-phase state) and the liquid mass fraction is below 0.8 then the homogeneous equilibrium model (HEM) provides a good approximation; with the discharge coefficient varying from 0.90 for a pure single-phase gas flow to about 0.98 when the upstream liquid fraction is 0.8.

3. The transition from incompressible-flow to HEM is not sharp as the upstream state crosses the saturation boundary.

Also of importance is the observation that the variability of the calculated discharge rates using the above arguments seemed quite modest (order 10%) compared with our accuracy requirements.

6.1.3 Evaluation of the modeling of the thermodynamic state of discharge

There is little specific data to be used here presumably because of the strong assumption that the thermodynamic state will be provided by basic thermodynamic relationships. The data from Richardson et al. (2006) for two phase releases was consistent with that anticipated from the model used by Richardson et al. (2006) or by that anticipated from the use of the ω – method, reflecting that the appropriate thermodynamics was being utilized.

Of interest from the FLADIS study of Nielsen et al. (1997) was that for a sub-cooled storage of ammonia and a discharge through a long nozzle (for which an equilibrium model would be appropriate) then the pressure at the nozzle exit was well above atmospheric pressure and close to the saturated vapor pressure at the temperature at the nozzle.

This is to be contrasted with the data from the studies of Spicer et al. (2006) that were for sub-cooled liquids and a sharp edged orifice release. In all these latter cases, except one, the results were consistent with the pressure at the exit being atmospheric and the flow near the rupture being a non-equilibrium one. The exceptional case was an ammonia release.

6.1.4 Evaluation of the modeling of the exit velocity and momentum
There is little data to evaluate the modeling of the exit velocity and momentum of the jet. The results from Nielsen et al. (1997) and from Spicer and Havens (2005) for sub-cooled liquids indicates that the pressure at the exit plane would be atmospheric if the flow was a non-equilibrium one and the saturated vapor pressure at the nozzle (or approximately the storage) temperature if the flow was an equilibrium one. These differences will directly influence the momentum of the flow and the effective velocity of the release.

The modeling anticipates an increase of velocity during the flashing. However this was not seen when studying droplet data at different positions downstream. However the question was then asked as to whether the flow acceleration had already taken place prior to the measurements of the droplet velocities. The important comparison would be between the actual liquid exit velocity and the downstream flow and droplet velocities.

In an interim calculation, an example was described of a droplet velocity starting from 45 m/s at x/D = 20, and decreasing to 20-25 m/s further downstream. However other calculations indicated that the liquid exit velocity was of the order of less than 25 m/s for propane, and even less than this for butane. This was then rechecked. It was argued that, assuming all liquid at the orifice exit, that the velocity was 24 m/s. The droplet velocities at x/D = 20 (first measurement position) showed a mean droplet velocity of 43 m/s.

To complicate the issue it was found from the computations of the mass flow rate at the exit that the exit pressure is atmospheric (that is, the atmospheric exit pressure gives better results than the saturation pressure at the stagnation temperature).

Additionally data from VKI experiments do show an acceleration and this acceleration occurs before x/D = 20 and this seems consistent with the FLIE result.

It is unclear whether this process is linked to “flashing” or the excess pressure above ambient at the exit plane for choked flows. The latter phenomenon is also anticipated for underexpanded single phase jets. The acceleration in that case is directly attributed to the excess pressure at the exit plane.

6.2 Evaluation of the modeling of jet break up, droplet particle size and rainout

6.2.1 RELEASE model

The RELEASE model (Johnson and Woodward, 1999) for droplet size and rainout is based on six key assumptions listed below.

1) The droplet size distribution is assumed to follow a lognormal probability density function (PDF) with a geometric mean (GM) diameter, hereafter called the mean diameter $d_{pm}$, for given exit or orifice conditions and a constant geometric standard deviation (GSD), $\sigma_{G} = 1.8$.

2) The mean diameter $d_{pm}$ is given by the smaller of two estimates $d_{pm} = \text{Min}(d_{p1}, d_{p2})$ where $d_{p1}$ is based on a mechanical or aerodynamic breakup model using the critical Weber number ($We_c$)
criterion: \( d_{p1} = \text{We}_c \sigma_L/(\rho_a u_{exp}^2) \) and where \( \text{We}_c \) is set to a “base value of 10,” \( \rho_a \) is the air density, and \( u_{exp} \) is the expansion velocity; the \( u_{exp} = u_2 \) is the value at section 2 in Fig. 8. The \( d_{p2} \) is based on a flash breakup model using the same \( \text{We}_c \) but with \( \rho_a \) and \( u_{exp} \) replaced by \( \rho_v \) and \( u_{rel} \), respectively. Here, \( \rho_v \) and \( u_{rel} \) are the flash vapor density and the “relative velocity,” which is found from \( u_{exp} \), the exit or discharge velocity \( u_e \), and a bubble velocity in the drops. For the CCPS experiments, the smaller predicted drop size was always the \( d_{p1} \) (Johnson and Woodward, 1999).

3) The expansion velocity is found from the mass and momentum balance discussed in Section 5.1: \( u_2 = u_1 + (P_1 - P_2)/G_1 \), where \( P_2 \) is the ambient pressure.

4) There is no evaporation of the rainout droplets along their trajectory to the surface.

5) The mass fraction of droplets that rain out is found by integrating over the droplet mass distribution or PDF from a droplet diameter \( d \) equal to the “critical diameter” \( d_c \) to \( \infty \).

6) As presented by Johnson and Woodward (1999), the critical drop size is the diameter \( d_c \) with a critical settling velocity \( u_e \), equal to the radial velocity \( u_r \) of the spreading jet, where \( u_r = u_{exp} \tan \theta_j \) and \( \theta_j \) is the jet spread angle which they take as 4.46°. Droplets larger than \( d_c \) will have greater settling velocities and fall faster than \( u_e \) and thus rain out. We note that this assumption ignores the effects of jet turbulence on the droplet trajectories and the distance dependence of the jet velocity following the expansion zone.

The RELEASE model also was used to determine the “needed diameter for a match” to explain or be consistent with the rainout data. The needed diameter was an inferred value of \( d_{pm} \) found from the calculated \( d_c \) above and the observed rainout. We developed an analytical expression for the rainout fraction \( R \) by integrating over the droplet mass distribution as indicated in 5) above and dividing the result by the total mass. The expression is

\[
R = 0.5(1 - \text{erf}(\phi_c))
\]

where \( \text{erf} \) is the error function,

\[
\phi_c = \ln(d_c/d_{pm})/(2^{1/2} \sigma) - (3 - 2^{1/2}/2) \sigma
\]

and \( \sigma = \ln \sigma_0 \). Thus, given \( R \) one can find \( \phi_c \), the ratio \( d_c/d_{pm} \), and hence \( d_{pm} \) with knowledge of \( d_c \). This \( R \) expression was not given or used by Johnson and Woodward (1999), who presumably used similar methods to obtain \( R \) in terms of \( d_c/d_{pm} \) and thus find the “needed” or observed diameter. In the following, the RELEASE model prediction of \( d_{pm} (= d_{p1}) \) was compared with these “observed” diameters, which are given in Tables 11-1 to 11-5 in Johnson and Woodward (1999).

6.2.2 RELEASE/CCPS experiments

The CCPS or RELEASE experiments for water and CFC-11 were conducted in a greenhouse to shield the tests from any wind effects; the range of storage temperatures and pressures were given in the references. For these experiments, the discharge orifice was oriented horizontally and located 1.22 m above a 15.2-m long capture system consisting of pans that collected the
falling liquid and conveyed it to collection vessels, which were weighed to determine the rainout mass. Note that the rainout depended on the particular source–collection pan geometry, i.e., the source height and the length of the collection pan. The orifice diameters ranged from 3.2 to 12.7 mm for water and was 6.4 mm for CFC-11. For the CFC-11 tests, the vessels were cooled, presumably to prevent evaporation of the captured liquid since the CFC-11 boiling point temperature (297 K) was in the ambient temperature range.

For chlorine, cyclohexane, and methylamine, the experiments were conducted using a similar test arrangement and the same geometry as for water and CFC-11. However, the experiments were performed outdoors at the DOE Test Spill Facility in Nevada due to the hazardous nature of these chemicals. Chlorine and methylamine have boiling point temperatures ($T_{\text{boil}} = 237$ K and 264 K at local conditions) below the summer ambient temperatures in Nevada, and thus, the liquid capture system was modified for these chemicals. Chlorine and methylamine were captured using basic and acidic solutions, respectively, in the capture pans with subsequent solution analysis determining the mass of the captured chemicals. The cyclohexane rainout was found by draining it directly from the capture pans to the weighing vessels.

The liquid captured in the pans or rainout varied systematically with the isenthalpic flash fraction, $x_g$ (see Eq. 8a, Section 5.2) or essentially with the superheat, $T_0 - T_{\text{sat}}(p_a)$ where $T_{\text{sat}}(p_a) = T_{\text{boil}}$. This is shown in Fig. 14 for the five liquids where the liquid captured is expressed as a percentage of the released mass. This figure also shows that the captured mass decreased systematically with a decrease in the boiling point temperature, which corresponds to an increase in the liquid volatility. Thus, the most volatile chemical, chlorine, exhibits the smallest capture and the least volatile, water, the highest. The liquid capture fractions in this figure are the raw or "uncorrected" values.

Two points should be made concerning the evaluation of the RELEASE model predictions of droplet size using the CCPS data. First, drop sizes were not measured in the CCPS experiments and instead were inferred from the rainout measurements as noted in Section 6.2.1. Thus, evaluation of the RELEASE model using these data is not a completely independent test of the model, but is nevertheless useful (e.g., to show model biases).

Second, the rainout data collected for chlorine, cyclohexane, and methylamine were corrected by Johnson and Woodward (1999) for re-evaporation from the capture pans because the experiments were conducted outdoors during the summer as already mentioned. For chlorine and methylamine, the correction accounted for the spreading, dissolution, and reaction of these chemicals in an aqueous solution. For cyclohexane, the correction was made for the capture and spreading of the liquid in a dry pan, which was cooled from below to prevent or diminish the evaporation. In the case of methylamine and cyclohexane, the corrections were relatively small with the ratio of corrected to uncorrected capture averaging $1.14 \pm 0.038$ for methylamine and $0.88 \pm 0.070$ for cyclohexane. However, for chlorine, the ratio was large---$2.72 \pm 0.28$---and thus represented a significant correction to the original data.
6.2.3 RELEASE model results

The RELEASE model predictions of the mean diameter, $d_{pm}$ or $D_{pred}$, are compared with the observed diameters, $D_{obs}$, obtained from the corrected CCPS rainout data. The ratio $D_{pred}/D_{obs}$ is analyzed for four data groupings: 1) chlorine, 2) CFC-11, methylamine, and cyclohexane, 3) water, and 4) all liquids. These groupings were selected because a) chlorine had the largest correction to the observed rainout data, b) water was suspected of being much different from the other rainout data (Fig. 14) due to the high humidity in the greenhouse, the possibility of condensation onto droplets in the discharge jet (Johnson and Woodward, 1999), and thus higher rainout, and c) the CFC-11, methylamine, and cyclohexane exhibited similar trends of $D_{pred}/D_{obs}$. 

Figure 14 Dependence of the rainout expressed as a percentage of the released liquid mass on the flash fraction ($x_g$) for the liquid discharges in the CCPS experiments (Johnson and Woodward, 1999)
Figure 15 presents the $D_{\text{pred}}/D_{\text{obs}}$ versus the superheat for the four groups where one can observe the different character of the trends in a) to c). The $D_{\text{pred}}/D_{\text{obs}}$ ratio for chlorine has a mean value (1.6) that is about double that of the other chemicals including water (see also Fig. 17), and it exhibits much more scatter than the others especially CFC-11, methylamine, and cyclohexane. We believe that this difference may be due to the large correction factor (2.7) applied to the original chlorine rainout data. With the exception of water, the chemicals exhibit a trend of a decreasing $D_{\text{pred}}/D_{\text{obs}}$ with an increase in the superheat.

Figure 16 shows the $D_{\text{pred}}/D_{\text{obs}}$ ratio versus the calculated orifice velocity $u_0$ and trends that look quite similar to those with the superheat—-a decrease in $D_{\text{pred}}/D_{\text{obs}}$ with $u_0$, here, the $u_0$ is computed from Eq. 3.1 as $u_0 = G/\rho_f$ using a $C_D = 0.6$. The similarity in the trends is not surprising since the $u_0$ increases with the storage/orifice pressure, which increases with the superheat. For $u_0$, the trend of decreasing $D_{\text{pred}}/D_{\text{obs}}$ with $u_0$ is believed due to the dependence and sensitivity of both the predicted and observed mean diameter on $u_{\text{exp}}$, which in turn depends on $u_0$ or $u_1$ (Fig. 8). We note that the expansion velocities from RELEASE ranged from about one to three times $u_0$ (Johnson and Woodward, 1999). We cannot ascertain whether the trend in the $D_{\text{pred}}/D_{\text{obs}}$ is due to the predicted or observed values or both. Results in Fig. 8.5d with the Witlox et al. (2007) data (discussed in Section 6.2.5) appear to be a continuation of the trend found with the CCPS data.

In addition to the $u_{\text{exp}}$ accuracy, there are at least two other factors that would affect the prediction of $d_{\text{pm}}$ and its inference from the rainout data: 1) the neglect of jet turbulence which would affect the droplet trajectories and the amount/location of the surface deposition or rainout, and 2) the jet axial velocity $u_j$, which should decrease downstream of the expansion zone, and also would modify the droplet trajectories and deposition. The $u_j$ decrease should be $u_j \propto 1/x$ for a turbulent jet (e.g., Schlichting, 1987), but in RELEASE the $u_j$ is taken as $u_{\text{exp}}$ or a constant. The above effects could be included with a simple rainout or deposition model that incorporated a “tilted plume” (e.g., Overcamp, 1976). We note that the Cleary et al. (2007) laser measurements of water jets and droplets clearly show the gravitational settling and “tilt” of the droplet jet/plume.

Given the simplicity of the RELEASE model, we believe that it would be useful to build a simple “simulator” model and use it to test the predicted variation of the $d_{\text{pm}}$, or $D_{\text{pred}}$ trends with $u_0$, the sensitivity of the model to $u_0$ and $u_{\text{exp}}$, other assumptions on the effects of jet turbulence, the jet axial velocity decay with distance, etc.

Figure 17 shows the statistics of the $D_{\text{pred}}/D_{\text{obs}}$ for each of the CCPS chemicals. The behavior confirms the scatter plot results in showing the overprediction of $D_{\text{obs}}$ for chlorine, a mean $D_{\text{pred}}/D_{\text{obs}} = 1.6 \pm 0.93$, and the large rms error. This mean ratio is about twice that for CFC-11, methylamine, cyclohexane, and water. For CFC-11, methylamine, and cyclohexane, the rms errors are modest or about 30% of their respective mean values, but for water the rms deviation is 0.92 or about 1.2 times the mean. The latter may partially be due to the high humidity in the greenhouse as noted earlier.
Figure 15. Variation of the predicted-to-observed droplet diameter with the liquid superheat for the RELEASE model using the CCPS data; “observed” diameter determined from the rainout data (Johnson and Woodward, 1999; Tables 11-1 to 11-5).
Figure 16. Predicted-to-observed droplet diameter versus the orifice velocity for the RELEASE model using the CCPS and Witlox et al. (2007) data.

6.2.4 JIP model

The Joint Industry Project (JIP) model developed by Witlox et al. (2007) is based on an empirical correlation from the laboratory-scale water jet experiments of Cleary et al. (2007). It predicts a Sauter mean diameter (SMD), also designated here by $d_{pm}$, and is based on the following:
1) The $d_{pm}$ is comprised of an aerodynamic breakup model prediction $d_{pa}$ valid from a zero superheat to a transition “A” superheat $\Delta T_A$ and a flashing droplet size $d_{pc} (= d_{pa}/2.4)$ achieved at a transition superheat $\Delta T_C$. For intermediate superheats ($\Delta T_A < \Delta T < \Delta T_C$), the droplet size is assumed to vary linearly with superheat. This continues until $d_{pm}$ reaches the “fully flashed” diameter of 30 $\mu$m, after which it decreases at a very slow rate.

2) The aerodynamic model prediction is given by the dimensionless empirical correlation developed by Cleary et al. (2007):

$$\frac{d_{pa}}{d_o} = 64.73 \text{We}_{L,o}^{-0.533} \text{Re}_{L,o}^{-0.014} (L/d_o)^{0.114},$$

where $\text{We}_{L,o} = \rho_L u_o^2 d_o / \sigma_L$, $\text{Re}_{L,o} = u_o d_o / \nu_o$ is the orifice Reynolds number, $L$ is the orifice wall thickness or pipe length (if there is one), and $d_o$ is the orifice diameter. Although dimensionally correct, the $\text{We}_{L,o}$ is not really a Weber number since it is based on the orifice diameter rather than a droplet diameter.

3) The superheat at the beginning ($\Delta T_A$) and end ($\Delta T_C$) of the transition to flashing are found from

$$J_{A} = 55 \text{We}_{v}^{-1/7} \quad \text{and} \quad J_{C} = 150 \text{We}_{v}^{-1/7},$$

where $\text{We}_{v} = \rho_v u_o^2 d_o / \sigma_L$ is the vapor “pseudo Weber number” (again not actually a Weber number due to the use of $d_o$), $J_A = (c_p L \Delta T_{sh}/h_{fg})(\rho_L/\rho_v)$ is the Jacob number, subscripts A and C on $J_a$ denote conditions at the superheats $\Delta T_A$ and $\Delta T_C$, $v$ denotes the vapor, and all variables ($\rho_L$, $\rho_v$, $h_{fg}$, etc.) are evaluated at the orifice temperature. The transition state beginning (A) and end (C) are based on jet droplet visualizations in the Cleary et al. experiments. The form of the Jacob number correlations are similar to the flashing correlation expression of Kitamura et al. (1986), but differ in that the use of $\text{We}_{v}$ in the latter is a true Weber number based on the droplet diameter in the post-expansion region and not the orifice diameter.

4) Evaporation of rainout droplets is not addressed as is the case for the RELEASE model.

Some further comments on the JIP model are in order. First, the correlation for the aerodynamic diameter has a very weak dependence on the orifice Reynolds number, which results in only a small deviation of $\text{Re}_{L,o}^{0.014}$ from 1 over a large $\text{Re}_{L,o}$ range. For $\text{Re}_{L,o} = 10^3$ and $10^6$, the $\text{Re}_{L,o}$ term only varies from 0.91 to 0.82 and could be taken as its average or even 1 for simplicity. We note that the Reynolds number for the Witlox et al. (2007) water jet data ranged from about $9 \times 10^4$ to $1.9 \times 10^5$, whereas the $\text{Re}_{L,o}$ in the CCPS water experiments was about an order of magnitude larger, $1.6 \times 10^5$ to $1.1 \times 10^6$.

Second, the $(L/d_o)^{0.114}$ term has a variation from 1 to 1.6 for $L/d_o = 1$ to 50, which is the $L/d_o$ range in the Cleary et al. (2007) experiments. If the $(L/d_o)^{0.114}$ term were taken as some typical value, say 1.3, the Cleary et al. correlation could be simplified to $d_{pa}/d_o = a_1 \text{We}_{L,o}^{-1/2}$, where $a_1$ is a constant. Either this simple form or the full form above for $d_{pa}/d_o$ shows that the $d_{pa}$ has a weaker dependence on $u_o$ in the JIP model, $d_{pa} \propto 1/u_o$ than the RELEASE model ($d_{pa} \propto 1/u_o^2$).
Third, as noted above, the We in the transition-to-flashing correlations is not a true Weber number but a dimensionless variable based on the orifice diameter. As a result, the Cleary et al. correlations must be regarded as specific to their particular experiments and require extensive evaluation over a broad range of conditions.

6.2.5 JIP model results

The JIP model was evaluated with the Witlox et al. (2007) dataset and some of the measurements from the CCPS experiments. The Witlox et al. data contained droplet diameters from seven experiments including the two water jet tests of Cleary et al. and those from four other sources. The experiments included flashing water, butane, and propane jets at storage pressures ranging from 3 bar to 11.5 bar, \( T_0 \) from 23 K (butane) to 167 K (water), orifice diameters from 0.75 mm to 5 mm, and orifice velocities from 20 to 36 m/s. The Cleary et al. droplet measurements were obtained using a phase Doppler anemometry system in which the Doppler frequency data gave information on the particle velocity and the signal phase shift provided data on particle size.

Witlox et al. evaluated the JIP model using 10 tests from the CCPS experiments with two tests randomly chosen for each of the five liquids. However, the “observed” CCPS diameters differed from the values reported in Johnson and Woodward (1999), and we replaced them with the Johnson and Woodward values (their Tables 11-1 to 11-5) to maintain consistency with the data used earlier (Section 6.2.3).

Figure 18a shows the \( \frac{D_{\text{pred}}}{D_{\text{obs}}} \) ratios for the JIP model as a function of the superheat with the RELEASE model results shown for reference. Overall, the JIP model exhibits a trend of over-prediction (up to almost 3) at the lower superheats (\( \Delta T_s < 30 \text{ K} \)) and under-prediction for the higher superheats, with the RELEASE model showing a similar trend. For the CCPS data only, the two models exhibit similar results with a mean ratio of \( \frac{D_{\text{pred}}}{D_{\text{obs}}} \) of 1.28 ± 0.93 for JIP and 1.14 ± 0.65 for RELEASE, the main difference being the greater scatter for the JIP model.

However, the models have consistently smaller mean ratios for the Witlox et al. data---0.48 ± 0.17 for JIP and 0.22 ± 0.10 for RELEASE; these results/trends may be related more to the dependence on the orifice velocity (below).

Figure 18b presents the \( \frac{D_{\text{pred}}}{D_{\text{obs}}} \) versus the orifice velocity for the two models and both datasets. For both models, the trend of over-prediction at lower velocities and under-prediction at higher \( u_o \)’s is consistent with the RELEASE trend for all of the CCPS data (Fig. 17d). As found there, the Witlox et al. data seemed to be a continuation of the trend found for RELEASE with the CCPS data. This trend may be caused by: 1) a deficiency in the model physics concerning the treatment of \( u_o \), 2) a difference in the measurement methods for the two datasets, and 3) a difference between the \( d_{\text{pm}} \) and SMD values. Item 3 can and will be assessed in the future. It is important to determine the cause of this trend with \( u_o \) and correct it since the RELEASE predictions of the droplet diameter are only one-fifth of the observed values for the Witlox et al. data (at high \( u_o \)).

9. References
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Glossary of Terms

**Flashing** – vapor formation due to a reduction in pressure.

**Flashing flow** – vapor formation due to a reduction in pressure (a pressure drop) in the flow.

**Saturation line** – the locus of conditions (of pressure and temperature) at which vapor and liquid co-exist.

**Saturation, saturated state** – When vapor and liquid co-exist under thermodynamic (phase) equilibrium, the respective phases are termed saturated vapor and saturated liquid.

**Saturated vapor pressure** – is the vapor pressure exerted by the co-existing liquid at the saturation temperature.

**Subcooled liquid** – refers to liquid existing below its saturation temperature at the prevailing pressure.

**Superheated vapor** – refers to vapor existing above its saturation temperature at the prevailing pressure.

**Vapor, Gas** – vapor is a gas below its thermodynamic critical temperature, while gas is one above its critical temperature; though these terms are sometimes used synonymously.
**Choked flow** – is the condition of maximum flow rate that is achieved even with further lowering of the downstream pressure.

**Enthalpy** – denoted by the symbol H is given by U (internal energy) and PV (pressure times volume), a thermodynamic state function. h,u and v are the specific enthalpy, the specific energy and the specific volume respectively.

**Entropy** – denoted by the symbol S is a thermodynamic state function, its usefulness lies in the entropy balance and the entropy change in reversible and irreversible process analysis.

**Stagnation pressure** – is the pressure when a flowing fluid is decelerated to zero via a frictionless process; it generally refers to upstream inlet condition when the fluid velocity is small or possibly zero within a storage container.

**Stefan (bulk) flow** - transport phenomenon concerning the movement of a chemical species induced by a process (e.g., evaporation, condensation, chemical reaction) at an interface.