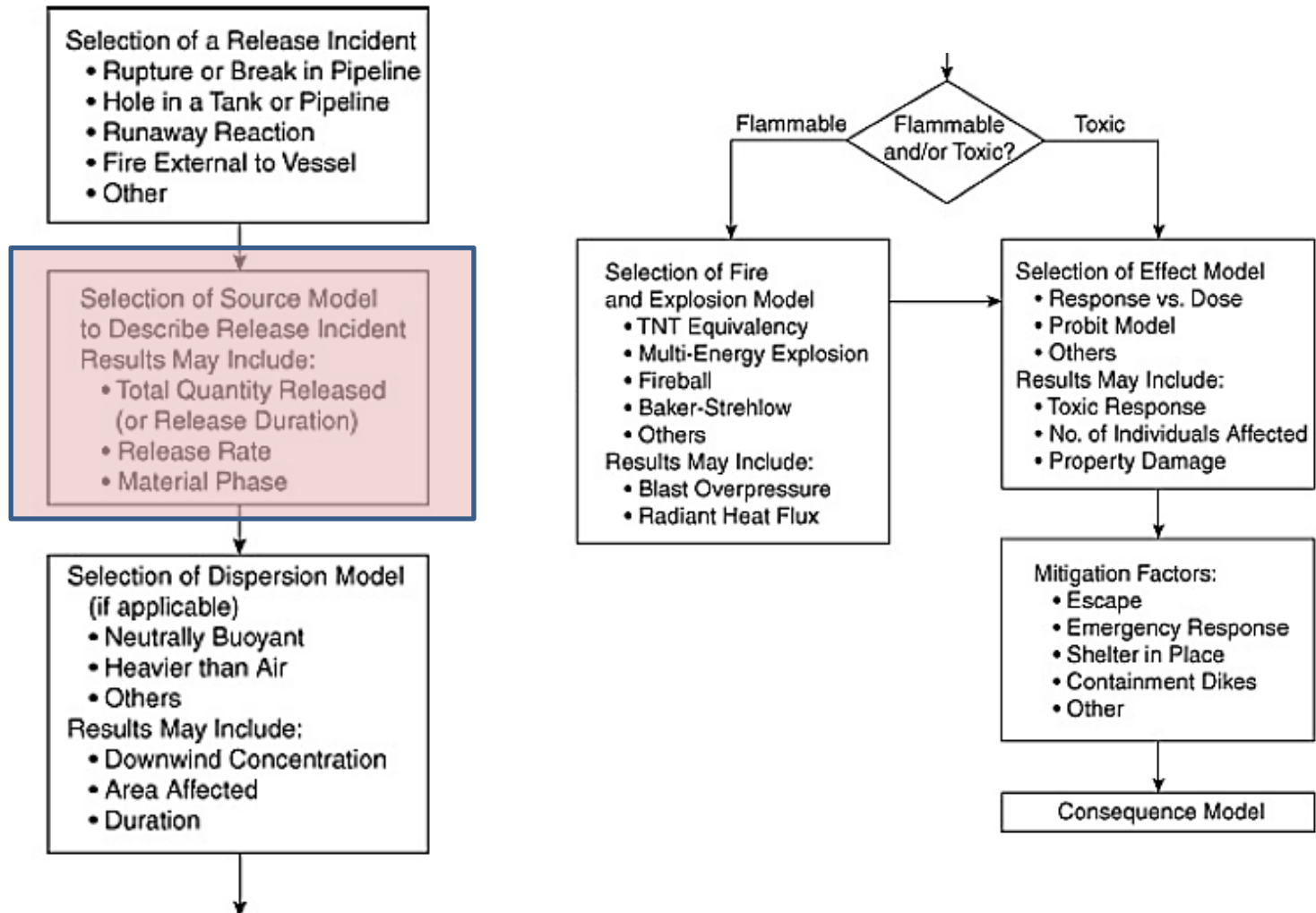


Source Models

- Most accidents in chemical plants result in spills of toxic, flammable, and explosive materials.
- Typical incidents might include the rupture or break of a pipeline, a hole in a tank or pipe, runaway reaction, or fire external to the vessel.
- Once the incident is known, source models are selected to describe how materials are discharged from the process.
- The source model provides a description of the rate of discharge, the total quantity discharged (or total time of discharge), and the state of the discharge (that is, solid, liquid, vapor, or a combination).
- A dispersion model is subsequently used to describe how the material is transported downwind and dispersed to some concentration levels.
- For flammable releases fire and explosion models convert the source model information on the release into energy hazard potentials, such as thermal radiation and explosion overpressures.

Consequence analysis procedure

Adapted from Center for Chemical Process Safety (CCPS), *Guidelines for Consequence Analysis for Chemical Releases*

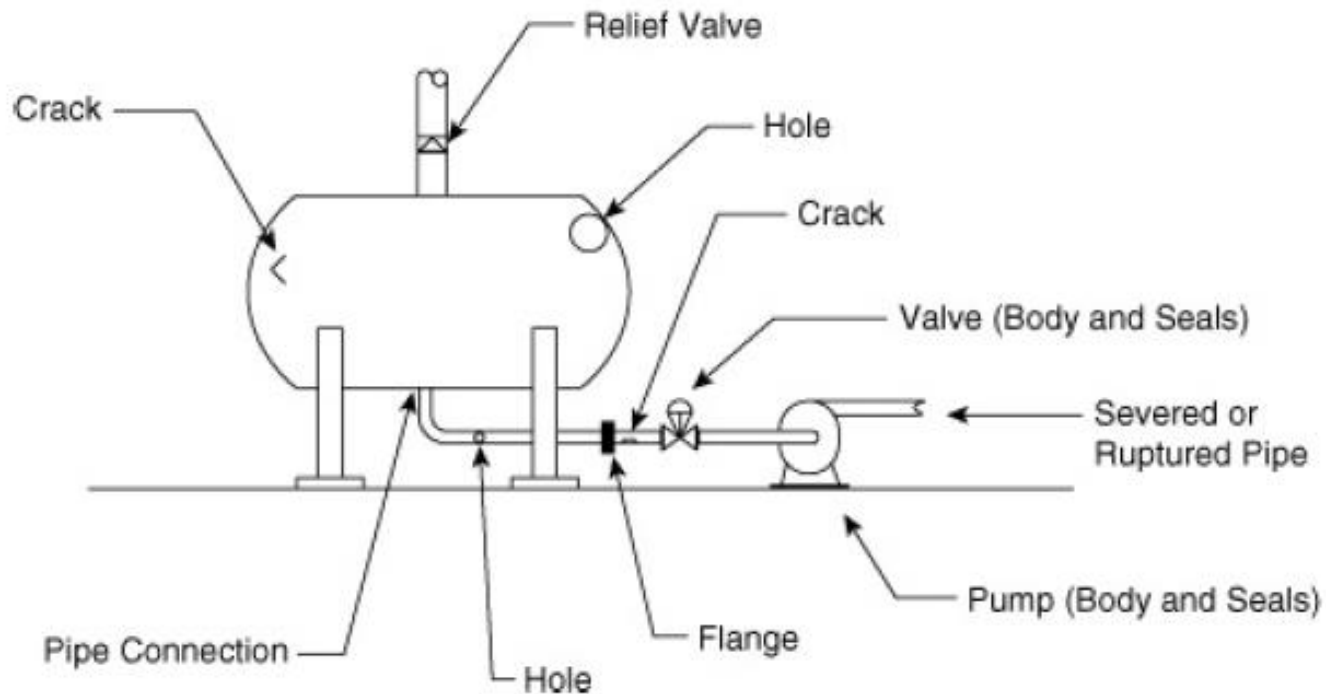


Introduction to Source Models

- Source models are constructed from fundamental or empirical equations representing the physicochemical processes occurring during the release of materials.
- For a reasonably complex plant many source models are needed to describe the release.
- Some development and modification of the original models is normally required to fit the specific situation.
- If uncertainty exists, the parameters should be selected to maximize the release rate and quantity.
- Release mechanisms are classified into wide and limited aperture releases.
- In the wide aperture case a large hole develops in the process unit, releasing a substantial amount of material in a short time.
-

- An excellent example is the over pressuring and explosion of a storage tank.
- For the limited aperture case material is released at a slow enough rate that upstream conditions are not immediately affected.
- Assumption of constant upstream pressure is frequently valid.
- For these releases material is ejected from holes and cracks in tanks and pipes, leaks in flanges, valves, and pumps, and severed or ruptured pipes.
- Relief systems, designed to prevent the over pressuring of tanks and process vessels, are also potential sources of released material.

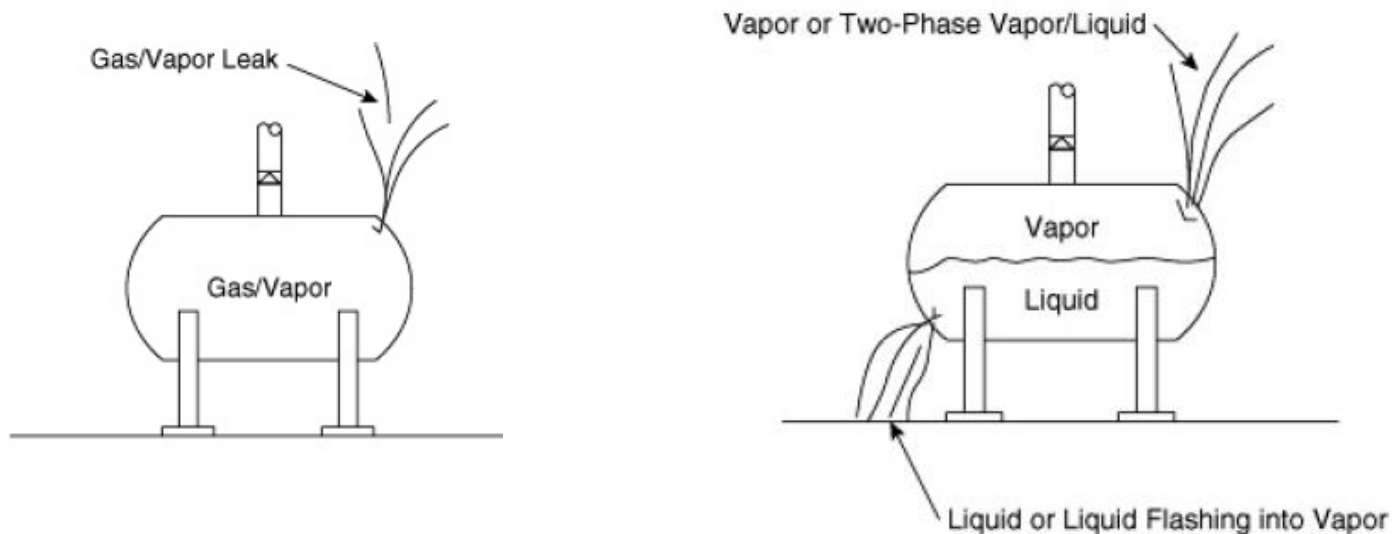
Various types of limited aperture releases



For gases or vapors stored in a tank, a leak results in a jet of gas or vapor. For liquids a leak below the liquid level in the tank results in a stream of escaping liquid.

Vapor and liquid are ejected from process units in either single- or two phase states

- If the liquid is stored under pressure above its atmospheric boiling point, a leak below the liquid level will result in a stream of liquid flashing partially into vapor.
- Small liquid droplets or aerosols might also form from the flashing stream, with the possibility of transport away from the leak by wind currents.
- A leak in the vapor space above the liquid can result in either a vapor stream or a two-phase stream composed of vapor and liquid, depending on the physical properties of the material.



There are several basic source models that are used repeatedly and will be developed in detail here. These source models are

- Flow of liquid through a hole
- Flow of liquid through a hole in a tank
- Flow of liquids through pipes
- Flow of gases or vapor through holes
- Flow of gases or vapor through pipes
- Flashing liquids
- Liquid pool evaporation or boiling

Other source models, specific to certain materials, are introduced in subsequent chapters.

Flow of Liquid through a Hole

A mechanical energy balance describes the various energy forms associated with flowing fluids:

$$\int \frac{dP}{\rho} + \Delta \left(\frac{\bar{u}^2}{2\alpha g_c} \right) + \frac{g}{g_c} \Delta z + F = -\frac{W_s}{\dot{m}},$$

Where

The Δ function represents the final minus the initial state.

P is the pressure (force/area),

ρ is the fluid density (mass/volume),

\bar{u} is the average instantaneous velocity of the fluid (length/time),

g_c is the gravitational constant (length mass/force time²),

α is the unitless velocity profile correction factor with the following values:

$\alpha = 0.5$ for laminar flow, $\alpha = 1.0$ for plug flow, and $\alpha \rightarrow 1.0$ for turbulent flow,

g is the acceleration due to gravity (length/time²),

z is the height above datum (length),

F is the net frictional loss term (length force/mass),

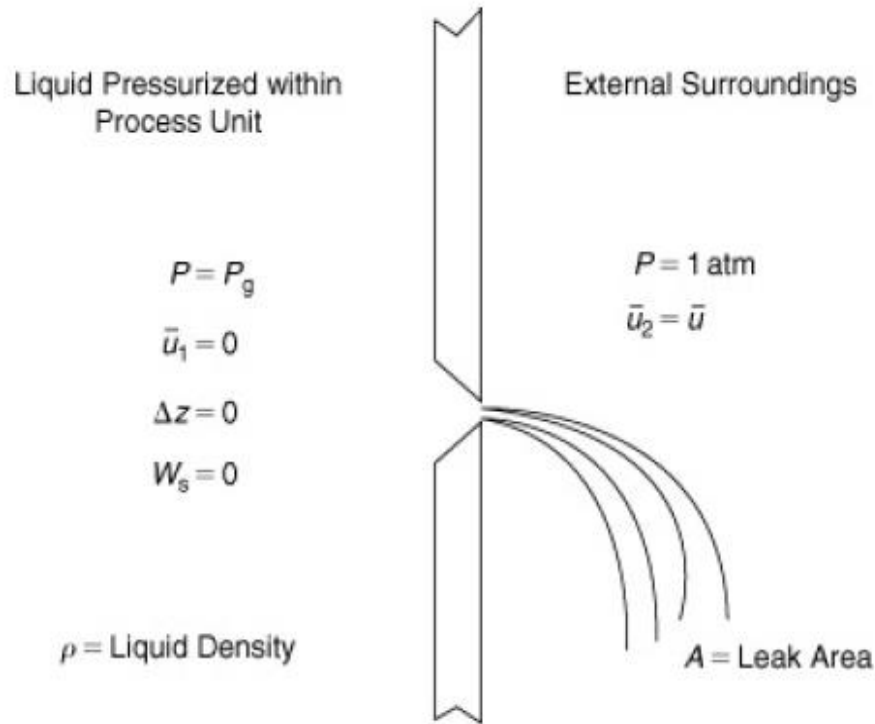
W_s is the shaft work (force length), and

\dot{m} is the mass flow rate (mass/time).

For incompressible liquids the density is constant, and

$$\int \frac{dP}{\rho} = \frac{\Delta P}{\rho}.$$

Liquid escaping through a hole in a process unit



$$Q_m = AC_o \sqrt{2\rho g_c P_g}$$

- Consider a process unit that develops a small hole,
- The pressure of the liquid contained within the process unit is converted to kinetic energy as the fluid escapes through the leak.
- Frictional forces between the moving liquid and the wall of the leak convert some of the kinetic energy of the liquid into thermal energy, resulting in a reduced velocity.

- For this limited aperture release, assume a constant gauge pressure P_g within the process unit.
- The external pressure is atmospheric; so $\Delta P = P_g$.
- The shaft work is zero, and the velocity of the fluid within the process unit is assumed negligible.
- The change in elevation of the fluid during the discharge through the hole is also negligible; so $\Delta z = 0$.
- The frictional losses in the leak are approximated by a constant discharge coefficient C_1 , defined as

$$-\frac{\Delta P}{\rho} - F = C_1^2 \left(-\frac{\Delta P}{\rho} \right)$$

- The modifications are substituted into the mechanical energy balance to determine \bar{u} the average discharge velocity from the leak:

$$\bar{u} = C_1 \sqrt{\alpha} \sqrt{\frac{2g_c P_g}{\rho}}$$

$$C_o = C_1 \sqrt{\alpha}$$

$$\boxed{\bar{u} = C_o \sqrt{\frac{2g_c P_g}{\rho}}}$$

- The mass flow rate Q_m resulting from a hole of area A is given by

$$Q_m = \rho \bar{u} A = A C_o \sqrt{2 \rho g_c P_g}$$

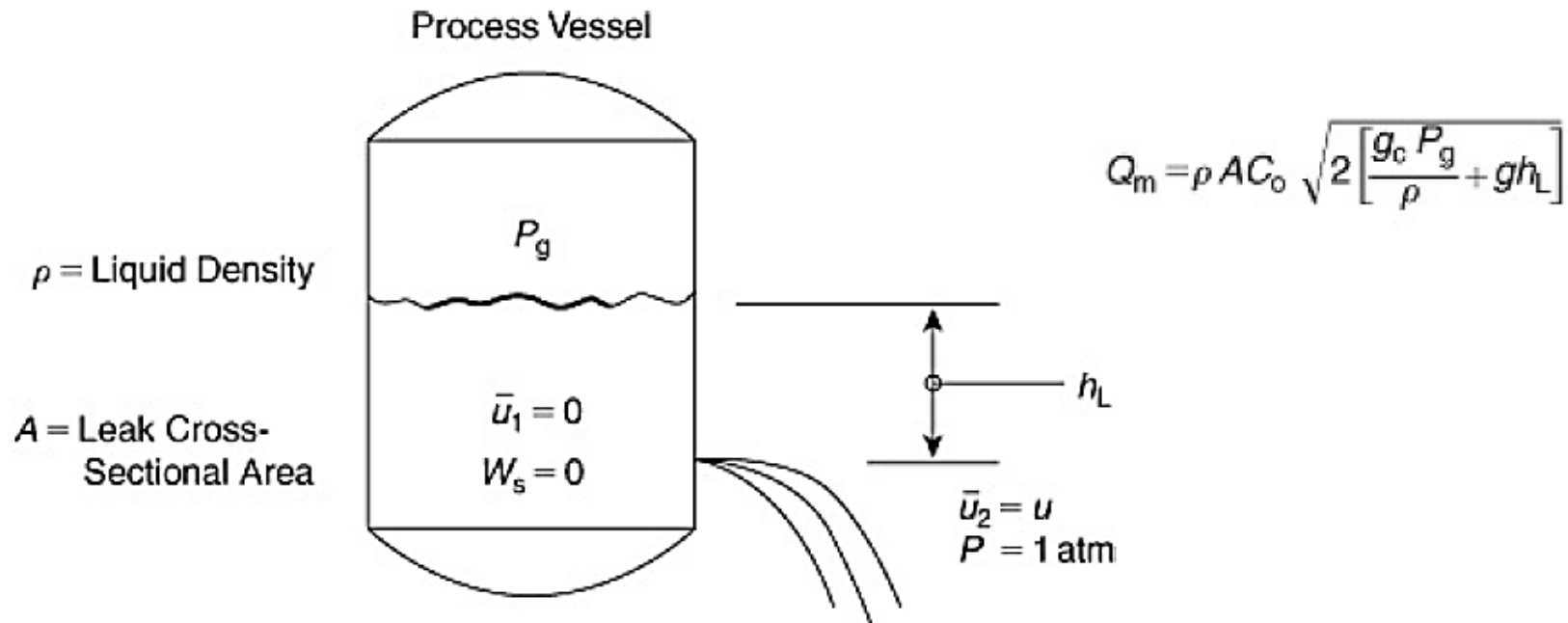
- The total mass of liquid spilled depends on the total time that the leak is active.
- The discharge coefficient C_o is a complicated function of the Reynolds number of the fluid escaping through the leak and the diameter of the hole.

The following guidelines are suggested:

- For sharp-edged orifices and for Reynolds numbers greater than 30,000, C_o approaches the value 0.61.
- For these conditions the exit velocity of the fluid is independent of the size of the hole.
- For a well-rounded nozzle the discharge coefficient approaches 1.
- For short sections of pipe attached to a vessel (with a length-diameter ratio not less than 3), the discharge coefficient is approximately 0.81.
- When the discharge coefficient is unknown or uncertain, use a value of 1.0 to maximize the computed flows.

Flow of Liquid through a Hole in a Tank

- A storage tank has a hole develops at a height h_L below the fluid level.
- The flow of liquid through this hole is represented by the mechanical energy balance and the incompressible assumption.
- An orifice-type leak in a process vessel. The energy resulting from the pressure of the fluid height above the leak is converted to kinetic energy as the fluid exits through the hole. Some energy is lost because of frictional fluid flow



- The gauge pressure on the tank is P_g , and the external gauge pressure is atmospheric, or 0.
- The shaft work W_s is zero, and the velocity of the fluid in the tank is zero.
- A dimensionless discharge coefficient C_1 is defined as

$$-\frac{\Delta P}{\rho} - \frac{g}{g_c} \Delta z - F = C_1^2 \left(-\frac{\Delta P}{\rho} - \frac{g}{g_c} \Delta z \right)$$

- The mechanical energy balance is solved for \bar{u} , the average instantaneous discharge velocity from the leak:

$$\bar{u} = C_1 \sqrt{\alpha} \sqrt{2 \left(\frac{g_c P_g}{\rho} + gh_L \right)}$$

- where h_L is the liquid height above the leak. A new discharge coefficient C_o is defined as

$$C_o = C_1 \sqrt{\alpha}$$

The resulting equation for the instantaneous velocity of fluid exiting the leak is

$$\bar{u} = C_o \sqrt{2 \left(\frac{g_c P_g}{\rho} + gh_L \right)}$$

The instantaneous mass flow rate Q_m resulting from a hole of area A is given by

$$Q_m = \rho \bar{u} A = \rho A C_o \sqrt{2 \left(\frac{g_c P_g}{\rho} + gh_L \right)}$$

As the tank empties, the liquid height decreases and the velocity and mass flow rate decrease

- Assume that the gauge pressure P_g on the surface of the liquid is constant.
- This would occur if the vessel was padded with an inert gas to prevent explosion or was vented to the atmosphere.
- For a tank of constant cross-sectional area A_t , the total mass of liquid in the tank above the leak is

$$m = \rho A_t h_L$$

- The rate of change of mass within the tank is $\frac{dm}{dt} = -Q_m$
- By substituting and by assuming constant tank cross-section and liquid density, we can obtain a differential equation representing the change in the fluid height:

$$\frac{dh_L}{dt} = -\frac{C_o A}{A_t} \sqrt{2 \left(\frac{g_c P_g}{\rho} + gh_L \right)}$$

- rearranged and integrated from an initial height h_L^0 to any height h_L

$$\int_{h_L^0}^{h_L} \frac{dh_L}{\sqrt{\frac{2g_c P_g}{\rho} + 2gh_L}} = -\frac{C_o A}{A_t} \int_0^t dt$$

- This equation is integrated to

$$\frac{1}{g} \sqrt{\frac{2g_c P_g}{\rho} + 2gh_L} - \frac{1}{g} \sqrt{\frac{2g_c P_g}{\rho} + 2gh_L^0} = -\frac{C_o A}{A_t} t$$

- Solving for h_L , the liquid level height in the tank, yields

$$h_L = h_L^o - \frac{C_o A}{A_t} \sqrt{\frac{2g_c P_g}{\rho} + 2gh_L^o} t + \frac{g}{2} \left(\frac{C_o A}{A_t} t \right)^2.$$

- Substituted to obtain the mass discharge rate at any time t

$$Q_m = \rho C_o A \sqrt{2 \left(\frac{g_c P_g}{\rho} + gh_L^o \right)} - \frac{\rho g C_o^2 A^2}{A_t} t.$$

- The first term on the right-hand side is the initial mass discharge rate at $h_L = h_L^o$.
- The time t_e for the vessel to empty to the level of the leak is found by solving for t after setting $h_L = 0$ in the upper most eq.:

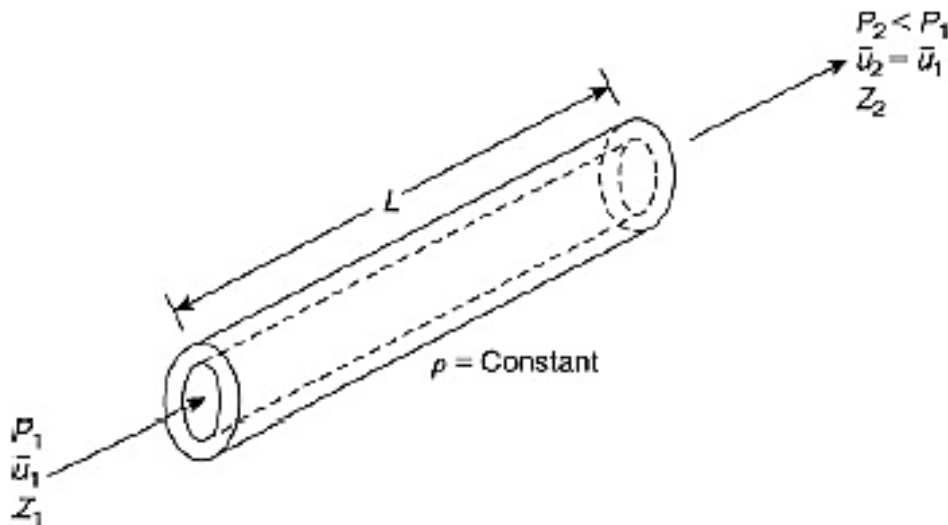
$$t_e = \frac{1}{C_o g} \left(\frac{A_t}{A} \right) \left[\sqrt{2 \left(\frac{g_c P_g}{\rho} + gh_L^o \right)} - \sqrt{\frac{2g_c P_g}{\rho}} \right]$$

- If the vessel is at atmospheric pressure, $P_g = 0$

$$t_e = \frac{1}{C_o g} \left(\frac{A_t}{A} \right) \sqrt{2gh_L^o}.$$

Flow of Liquids through Pipes

- A pipe transporting liquid and pressure gradient across the pipe is the driving force for the movement of liquid.
- Frictional forces between the liquid and the wall of the pipe convert kinetic energy into thermal energy.
- This results in a decrease in the liquid pressure.



- Flow of incompressible liquids through pipes is described by the mechanical energy balance combined with the incompressible fluid assumption

$$\frac{\Delta P}{\rho} + \frac{\Delta \bar{u}^2}{2\alpha g_c} + \frac{g}{g_c} \Delta z + F = -\frac{W_s}{\dot{m}}$$

- The frictional loss term F represents the loss of mechanical energy resulting from friction and includes losses resulting from flow through lengths of pipe fittings such as valves, elbows, orifices; and pipe entrances and exits.
- For each frictional device a loss term of the following form is used:

$$F = K_f \left(\frac{u^2}{2g_c} \right)$$

- K_f is the excess head loss due to the pipe or pipe fitting (dimensionless) and u is the fluid velocity (length/time).

- For fluids flowing through pipes the excess head loss term K_f is given by

$$K_f = \frac{4fL}{d}$$

f is the Fanning friction factor (unit less),

L is the flow path length (length), and

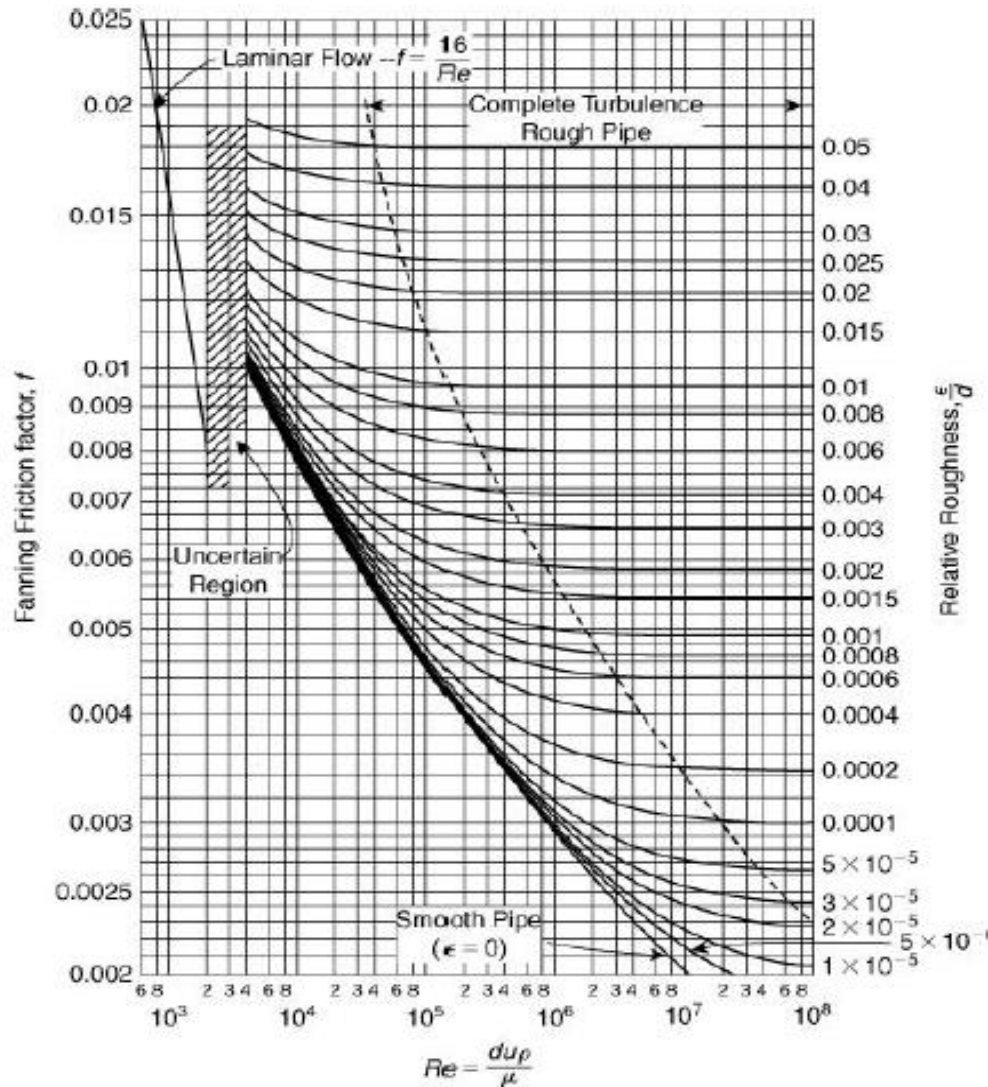
d is the flow path diameter (length).

- The Fanning friction factor f is a function of the Reynolds number Re and the roughness of the pipe ε .
- Plot of the Fanning friction factor versus Reynolds number with the pipe roughness, ε/d , as a parameter.

Roughness Factor ϵ for Pipes

| Pipe material | Condition | Typical ϵ | |
|--------------------------------|---------------------------|--------------------|---------------------|
| | | mm | inch |
| Drawn brass, copper, stainless | New | 0.002 | 0.00008 |
| Commercial steel | New | 0.046 | 0.0018 |
| | Light rust | 0.3 | 0.015 |
| | General rust | 2.0 | 0.08 |
| | Wrought, new | 0.045 | 0.0018 |
| Iron | Cast, new | 0.30 | 0.025 |
| | Galvanized | 0.15 | 0.006 |
| | Very smooth | 0.04 | 0.0016 |
| Concrete | Wood floated, brushed | 0.3 | 0.012 |
| | Rough, visible form marks | 2.0 | 0.08 |
| | Drawn tubing | 0.002 ^c | 0.0008 ^c |
| Glass or plastic | Smooth tubing | 0.01 | 0.004 |
| Rubber | Wire reinforced | 1.0 | 0.04 |
| Fiberglass ^b | | 0.005 | 0.0002 |

Plot of Fanning friction factor f versus Reynolds number



- For laminar flow the Fanning friction factor is given by

$$f = \frac{16}{Re}$$

- For turbulent flow the data are represented by the Colebrook equation:

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

- An alternative form is useful for determining the Reynolds number from the friction factor f , is

$$\frac{1}{Re} = \frac{\sqrt{f}}{1.255} \left(10^{-0.25/\sqrt{f}} - \frac{1}{3.7} \frac{\varepsilon}{d} \right)$$

2-K Method

- For pipe fittings, valves, and other flow obstructions the traditional method has been to use an equivalent pipe length L_{equiv} .
- The problem with this method is that the specified length is coupled to the friction factor.
- An improved approach is to use the 2-K method, which uses the actual flow path length.
- Equivalent lengths are not used — and provides a more detailed approach for pipe fittings, inlets, and outlets.
- The 2-K method defines the excess head loss in terms of two constants, the Reynolds number and the pipe internal diameter:

$$K_f = \frac{K_1}{Re} + K_\infty \left(1 + \frac{1}{ID_{\text{inches}}} \right)$$

- K_f is the excess head loss (dimensionless),
- K_1 and K_∞ are constants (dimensionless),
- Re is the Reynolds number (dimensionless),
- ID_{inches} is the internal diameter of the flow path (inches)

| Fittings | Description of fitting | K_1 | K_∞ |
|-----------------|--|-------------------------|------------------------------|
| Elbows 90° | Standard ($r/D = 1$), threaded | 800 | 0.40 |
| | Standard ($r/D = 1$), flanged/welded | 800 | 0.25 |
| | Long radius ($r/D = 1.5$), all types | 800 | 0.20 |
| | Mitered ($r/D = 1.5$): 1 weld (90°) | 1000 | 1.15 |
| | 2 welds (45°) | 800 | 0.35 |
| | 3 welds (30°) | 800 | 0.30 |
| | 4 welds (22.5°) | 800 | 0.27 |
| | 5 welds (18°) | 800 | 0.25 |
| Valves | Gate, ball or plug | | |
| | Full line size, $\beta = 1.0$ | 300 | 0.10 |
| | Reduced trim, $\beta = 0.9$ | 500 | 0.15 |
| | Reduced trim, $\beta = 0.8$ | 1000 | 0.25 |
| Globe | Standard | 1500 | 4.00 |

Liquid discharge through holes

- The 2-K method also represents liquid discharge through holes.
- From the 2-K method an expression for the discharge coefficient for liquid discharge through a hole can be determined.

$$C_o = \frac{1}{\sqrt{1 + \sum K_f}}$$

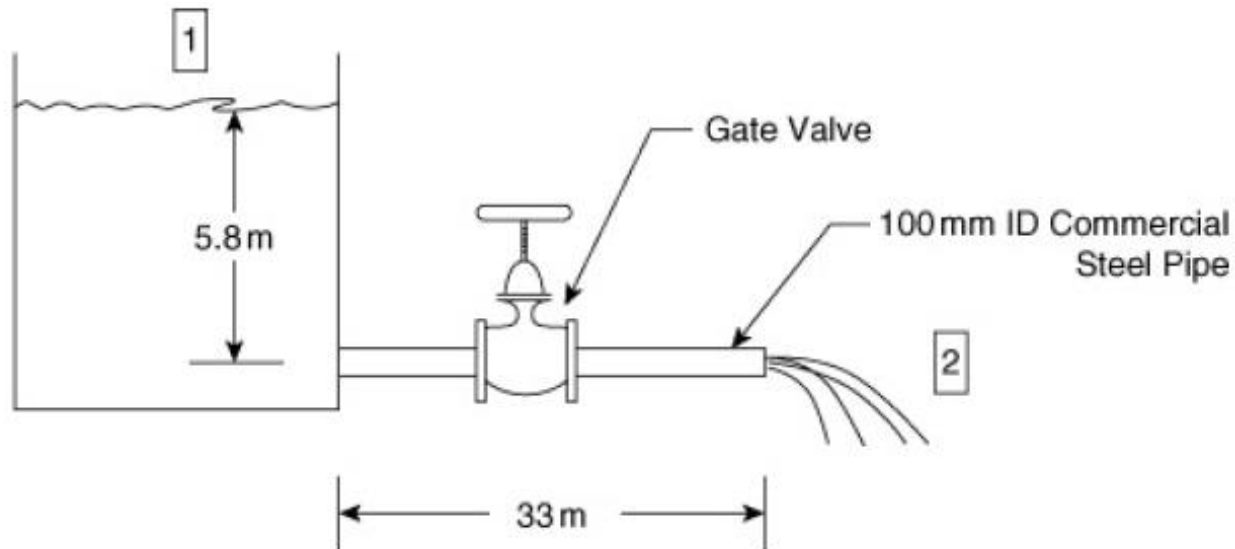
- Where $\sum K_f$ is the sum of all excess head loss terms, including entrances, exits, pipe lengths, and fittings.
- For a simple hole in a tank with no pipe connections or fittings the friction is caused only by the entrance and exit effects of the hole.
- For Reynolds numbers greater than 10,000, $K_f = 0.5$ for the entrance and $K_f = 1.0$ for the exit.
- Thus $\sum K_f = 1.5$, $C_o = 0.63$, which nearly matches the suggested value of 0.61.

The solution procedure to determine the mass flow rate of discharged material from a piping system is as follows:

1. Given: the length, diameter, and type of pipe; pressures and elevation changes across the piping system; work input or output to the fluid resulting from pumps, turbines, etc.; number and type of fittings in the pipe; properties of the fluid, including density and viscosity.
2. Specify the initial point (point 1) and the final point (point 2). This must be done carefully because the individual terms in Equation are highly dependent on this specification.
3. Determine the pressures and elevations at points 1 and 2. Determine the initial fluid velocity at point .
4. Guess a value for the velocity at point 2. If fully developed turbulent flow is expected, then this is not required.
5. Determine the friction factor for the pipe using Equations.

6. Determine the excess head loss terms for the pipe for the fittings and for any entrance and exit effects. Sum the head loss terms, and compute the net frictional loss term using the velocity at point 2.
7. Compute values for all the terms in Equation, and substitute into the equation. If the sum of all the terms in Equation is zero, then the computation is completed. If not, go back to step 4 and repeat the calculation.
8. Determine the mass flow rate using the equation. If fully developed turbulent flow is expected, the solution is direct. Substitute the known terms into Equation 4-28, leaving the velocity at point 2 as a variable. Solve for the velocity directly.

- Water contaminated with small amounts of hazardous waste is gravity-drained out of a large storage tank through a straight, new commercial steel pipe, 100 mm ID (internal diameter). The pipe is 100 m long with a gate valve near the tank. The entire pipe assembly is mostly horizontal. If the liquid level in the tank is 5.8 m above the pipe outlet, and the pipe is accidentally severed 33 m from the tank, compute the flow rate of material escaping from the pipe.



- The draining operation is shown. Assuming negligible kinetic energy changes, no pressure changes, and no shaft work, the mechanical energy balance applied between points 1 and 2 reduces to

$$\frac{g}{g_c} \Delta z + F = 0.$$

For water

$$\mu = 1.0 \times 10^{-3} \text{ kg/m s},$$

$$\rho = 1000 \text{ kg/m}^3.$$

The K factors for the entrance and exit effects are determined. The K factor for the gate valve is found in, and the K factor for the pipe length is given by Equation For the pipe entrance,

$$K_f = \frac{160}{Re} + 0.50.$$

For the gate valve,

$$K_f = \frac{300}{Re} + 0.10.$$

- For the pipe exit $K_f = 1.0$.

- For the pipe length $K_f = \frac{4fL}{d} = \frac{4f(33 \text{ m})}{(0.10 \text{ m})} = 1320f$.

- Summing the K factors gives $\sum K_f = \frac{460}{Re} + 1320f + 1.60$.

- For $Re < 10,000$ the first term in the equation is small.
Thus

$$\sum K_f \approx 1320f + 1.60,$$

- The gravitational term in the mechanical energy equation is given by because there is no pressure change and no pump or shaft work, the mechanical energy balance

$$F = \sum K_f \left(\frac{\bar{u}^2}{2g_c} \right) = (660f + 0.80)\bar{u}^2.$$

$$\frac{\bar{u}_2^2}{2g_c} + \frac{g}{g_c}\Delta z + F = 0.$$

Solving for the exit velocity and substituting for the height change gives

$$\bar{u}_2^2 = -2g_c\left(\frac{g}{g_c}\Delta z + F\right) = -2g_c(-56.8 + F).$$

The Reynolds number is given by

$$Re = \frac{d\bar{u}\rho}{\mu} = \frac{(0.1 \text{ m})(\bar{u})(1000 \text{ kg/m}^3)}{1.0 \times 10^{-3} \text{ kg/m s}} = 1.0 \times 10^5 \bar{u}.$$

For new commercial steel pipe, $\varepsilon = 0.0046$ mm and because the friction factor f and the frictional loss term F are functions of the Reynolds number and velocity, the solution is found by trial and error. The trial and error solution is shown in the following table:

$$\frac{\varepsilon}{d} = \frac{0.046 \text{ mm}}{100 \text{ mm}} = 0.00046.$$

| Gussed \bar{u} (m/s) | Re | f | F | Calculated \bar{u} (m/s) |
|---------------------------|---------|---------|-------|-------------------------------|
| 3.00 | 300,000 | 0.00451 | 34.09 | 6.75 |
| 3.50 | 350,000 | 0.00446 | 46.00 | 4.66 |
| 3.66 | 366,000 | 0.00444 | 50.18 | 3.66 |

Thus the velocity of the liquid discharging from the pipe is 3.66 m/s.

The table also shows that the friction factor f changes little with the Reynolds number.

Thus we can approximate for fully developed turbulent flow in rough pipes. Friction factor value of 0.0041. Then

$$F = (660f + 0.80)\bar{u}_2^2 = 3.51\bar{u}_2^2.$$

$$\bar{u}_2^2 = -2g_c(-56.8 + 3.51\bar{u}_2^2)$$

$$= 113.6 - 7.02\bar{u}_2^2,$$

$$\bar{u}_2 = 3.76 \text{ m/s.}$$

This result is close to the more exact trial and error solution.
The cross-sectional area of the pipe is

$$A = \frac{\pi d^2}{4} = \frac{(3.14)(0.1 \text{ m})^2}{4} = 0.00785 \text{ m}^2.$$

$$Q_m = \rho \bar{u} A = (1000 \text{ kg/m}^3)(3.66 \text{ m/s})(0.00785 \text{ m}^2) = 28.8 \text{ kg/s}.$$

- This represents a significant flow rate.
- Assuming a 15-min emergency response period to stop the release, a total of 26,000 kg of hazardous waste will be spilled.
- In addition to the material released by the flow, the liquid contained within the pipe between the valve and the rupture will also spill.
- An alternative system must be designed to limit the release.
- This could include a reduction in the emergency response period, replacement of the pipe by one with a smaller diameter, or modification of the piping system to include additional control valves to stop the flow.

Flow of Gases or Vapors through Holes

- For flowing liquids the kinetic energy changes are frequently negligible and the physical properties (particularly the density) are constant.
- For flowing gases and vapors these assumptions are valid only for small pressure changes ($P_1/P_2 < 2$) and low velocities (<0.3 times the speed of sound in gas).
- Energy contained within the gas or vapor as a result of its pressure is converted into kinetic energy as the gas or vapor escapes and expands through the hole.
- The density, pressure, and temperature change as the gas or vapor exits through the leak.
- Gas and vapor discharges are classified into throttling and free expansion releases.
- For throttling releases the gas issues through a small crack with large frictional losses;

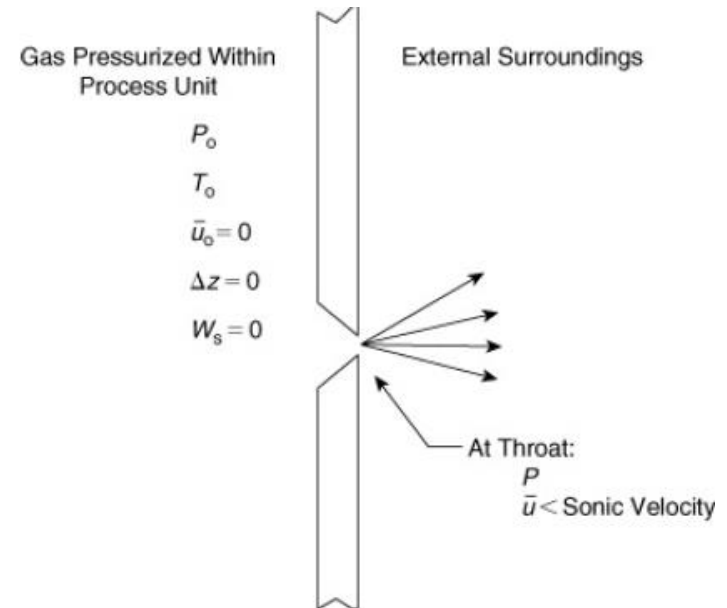
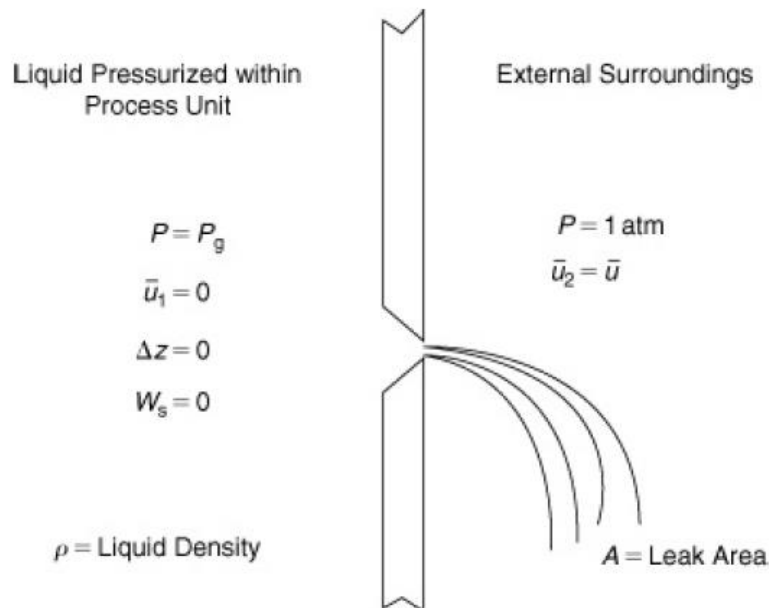
- little of the energy inherent to the gas pressure is converted to kinetic energy.
- For free expansion releases most of the pressure energy is converted to kinetic energy; the assumption of isentropic behavior is usually valid.
- Source models for throttling releases require detailed information on the physical structure of the leak.
- Free expansion release source models require only the diameter of the leak.

A free expansion leak is shown in Figure. The mechanical energy balance describes the flow of compressible gases and vapors.

Assuming negligible potential energy changes and no shaft work results in a reduced form of the mechanical energy balance describing compressible flow through holes:

$$\frac{\Delta P}{\rho} + \frac{\Delta \bar{u}^2}{2\alpha g_c} + \frac{g}{g_c} \Delta z + F = -\frac{W_s}{\dot{m}}$$

$$\int \frac{dP}{\rho} + \Delta \left(\frac{\bar{u}^2}{2\alpha g_c} \right) + F = 0.$$



- A discharge coefficient C_1 is defined in a similar fashion to the coefficient defined in

$$-\int \frac{dP}{\rho} - F = C_1^2 \left(-\int \frac{dP}{\rho} \right).$$

- The integration is carried to any arbitrary final point (denoted without a subscript). The result is

$$C_1^2 \int_{P_0}^P \frac{dP}{\rho} + \frac{\bar{u}^2}{2\alpha g_c} = 0.$$

- For any ideal gas undergoing an isentropic expansion,

$$Pv^\gamma = \frac{P}{\rho^\gamma} = \text{constant},$$

where γ is the ratio of the heat capacities, $\gamma = C_p/C_v$.

Defining a new discharge coefficient C_0 identical to that in and integrating results in an equation representing the velocity of the fluid at any point during the isentropic expansion:

$$\bar{u}^2 = 2g_c C_o^2 \frac{\gamma}{\gamma - 1} \frac{P_o}{\rho_o} \left[1 - \left(\frac{P}{P_o} \right)^{(\gamma-1)/\gamma} \right] = \frac{2g_c C_o^2 R_g T_o}{M} \frac{\gamma}{\gamma - 1} \left[1 - \left(\frac{P}{P_o} \right)^{(\gamma-1)/\gamma} \right].$$

The second form incorporates the ideal gas law for the initial density ρ_o . R_g is the ideal gas constant, and T_o is the temperature of the source. Using the continuity equation

$$Q_m = \rho \bar{u} A$$

$$\rho = \rho_o \left(\frac{P}{P_o} \right)^{1/\gamma}$$

$$Q_m = C_o A P_o \sqrt{\frac{2g_c M}{R_g T_o} \frac{\gamma}{\gamma - 1} \left[\left(\frac{P}{P_o} \right)^{2/\gamma} - \left(\frac{P}{P_o} \right)^{(\gamma+1)/\gamma} \right]}.$$

For many safety studies the maximum flow rate of vapor through the hole is required.

This is determined by differentiating Equation(Q_m) with respect to P/P_o and setting the derivative equal to zero. The result is solved for the pressure ratio resulting in the maximum flow:

$$\frac{P_{\text{choked}}}{P_o} = \left(\frac{2}{\gamma + 1} \right)^{\gamma/(\gamma-1)}.$$

- The choked pressure P_{choked} is the maximum downstream pressure resulting in maximum flow through the hole or pipe.
- For downstream pressures *less* than P_{choked} the following statements are valid:
 - (1) The velocity of the fluid at the throat of the leak is the velocity of sound at the prevailing conditions, and
 - (2) Velocity and mass flow rate cannot be increased further by reducing the downstream pressure; they are independent of the downstream conditions.

This type of flow is called *choked*, *critical*, or *sonic flow*.
- For ideal gases the choked pressure is a function only of the heat capacity ratio γ .

| Gas | γ | P_{choked} |
|------------------|--------------|---------------------|
| Monatomic | $\cong 1.67$ | $0.487P_o$ |
| Diatomic and air | $\cong 1.40$ | $0.528P_o$ |
| Triatomic | $\cong 1.32$ | $0.542P_o$ |

- For an air leak to atmospheric conditions ($P_{\text{choked}} = 14.7$ psia),
- If the upstream pressure is greater than $14.7/0.528 = 27.8$ psia, or 13.1 psig, the flow will be choked and maximized through the leak.

$$(Q_m)_{\text{choked}} = C_o A P_o \sqrt{\frac{\gamma g_c M}{R_g T_o} \left(\frac{2}{\gamma + 1}\right)^{(\gamma+1)/(\gamma-1)}},$$

where

M is the molecular weight of the escaping vapor or gas,

T_o is the temperature of the source, and

R_g is the ideal gas constant.

- For sharp-edged orifices with Reynolds numbers greater than 30,000 (and not choked), a constant discharge coefficient C_o of 0.61 is indicated.

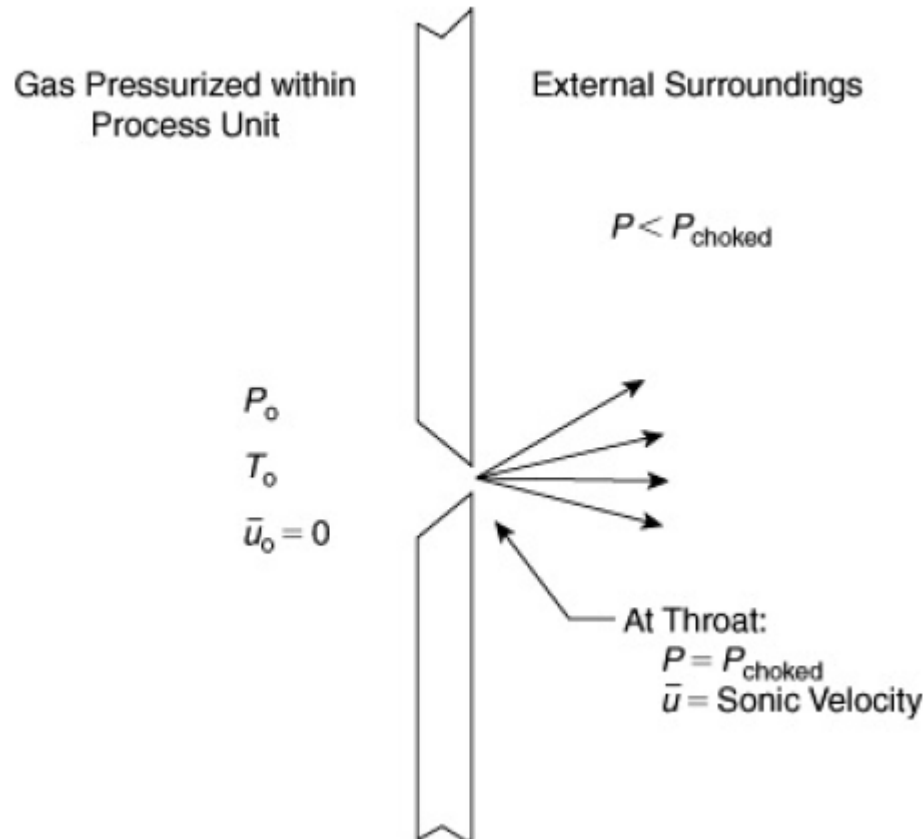
Example: A 0.1-in hole forms in a tank containing nitrogen at 200 psig and 80°F. Determine the mass flow rate through this leak. (nitrogen $\gamma = 1.41$)

$$\frac{P_{\text{choked}}}{P_o} = \left(\frac{2}{\gamma + 1}\right)^{\gamma/(\gamma-1)} = \left(\frac{2}{2.41}\right)^{1.41/0.41} = 0.527.$$

$$P_{\text{choked}} = 0.527(200 + 14.7) \text{ psia} = 113.1 \text{ psia}.$$

Choked flow of gas through a hole

The gas velocity is sonic at the throat.
The mass flow rate is independent of the downstream pressure.



- An external pressure less than 113.1 psia will result in choked flow through the leak.
- Because the external pressure is atmospheric in this case, choked flow is expected.
- The area of the hole is

$$A = \frac{\pi d^2}{4} = \frac{(3.14)(0.1 \text{ in})^2(1 \text{ ft}^2/144 \text{ in}^2)}{4} = 5.45 \times 10^{-5} \text{ ft}^2.$$
- The discharge coefficient C_o is assumed to be 1.0.

$$P_o = 200 + 14.7 = 214.7 \text{ psia},$$

$$T_o = 80 + 460 = 540^\circ\text{R},$$

$$\left(\frac{2}{\gamma + 1}\right)^{(\gamma+1)/(\gamma-1)} = \left(\frac{2}{2.41}\right)^{2.41/0.41} = 0.829^{5.87} = 0.347.$$

$$\begin{aligned} (Q_m)_{\text{choked}} &= C_o A P_o \sqrt{\frac{\gamma g_c M}{R_g T_o} \left(\frac{2}{\gamma + 1}\right)^{(\gamma+1)/(\gamma-1)}} \\ &= (1.0)(5.45 \times 10^{-5} \text{ ft}^2)(214.7 \text{ lb}_f/\text{in}^2)(144 \text{ in}^2/\text{ft}^2) \\ &\quad \times \sqrt{\frac{(1.4)(32.17 \text{ ft lb}_m/\text{lb}_f \text{ s}^2)(28 \text{ lb}_m/\text{lb-mol})}{(1545 \text{ ft lb}_f/\text{lb-mol}^\circ\text{R})(540^\circ\text{R})}(0.347)} \\ &= 1.685 \text{ lb}_f \sqrt{5.24 \times 10^{-4} \text{ lb}_m^2/\text{lb}_f^2 \text{ s}^2} \end{aligned}$$

Flow of Gases or Vapors through Pipes

- Vapor flow through pipes is modeled using two special cases: adiabatic and isothermal behavior.
- For both the isothermal and adiabatic cases it is convenient to define a Mach (Ma) number
- Mach (Ma) number as the ratio of the gas velocity to the velocity of sound in the gas at the prevailing conditions:

$$\text{Ma} = \frac{\bar{u}}{a},$$

- where 'a' is the velocity of sound. The velocity of sound is determined using the thermodynamic relationship

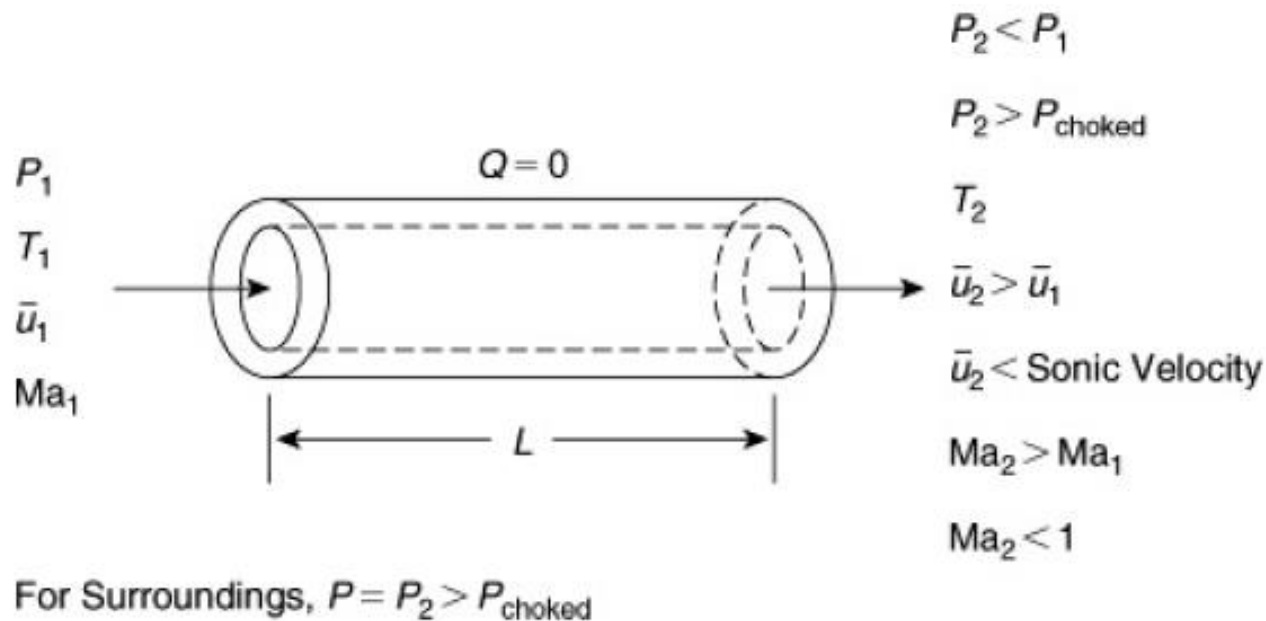
$$a = \sqrt{g_c \left(\frac{\partial P}{\partial \rho} \right)_s},$$

for an ideal gas is equivalent to

$$a = \sqrt{\gamma g_c R_g T / M},$$

which demonstrates that for ideal gases the sonic velocity is a function of temperature only. For air at 20°C the velocity of sound is 344 m/s (1129 ft/s).

Adiabatic Flows



- An adiabatic pipe containing a flowing vapor is shown in Figure.
- For this particular case the outlet velocity is less than the sonic velocity.
- The flow is driven by a pressure gradient across the pipe.
- As the gas flows through the pipe, it expands because of a decrease in pressure.
- This expansion leads to an increase in velocity and an increase in the kinetic energy of the gas.
- The kinetic energy is extracted from the thermal energy of the gas; a decrease in temperature occurs.
- However, frictional forces are present between the gas and the pipe wall.
- These frictional forces increase the temperature of the gas.
- Depending on the magnitude of the kinetic and frictional energy terms, either an increase or a decrease in the gas temperature is possible.

- The mechanical energy balance also applies to adiabatic flows. For this case it is more conveniently written in the form

$$\frac{dP}{\rho} + \frac{\bar{u}d\bar{u}}{\alpha g_c} + \frac{g}{g_c} dz + dF = -\frac{\delta W_s}{m}$$

- The following assumptions are valid for this case: is valid for gases.

$$\frac{g}{g_c} dz \approx 0$$

- Assuming a straight pipe without any valves or fittings, and can be combined and then differentiated to result in

$$dF = \frac{2f\bar{u}^2 dL}{g_c d}$$

Because no mechanical linkages are present,

$$\delta W_s = 0.$$

- An important part of the frictional loss term is the assumption of a constant Fanning friction factor f across the length of the pipe.
- This assumption is valid only at high Reynolds numbers.
- A total energy balance is useful for describing the temperature changes within the flowing gas.
- For this open steady flow process the total energy balance is given by

$$dh + \frac{\bar{u}d\bar{u}}{\alpha g_c} + \frac{g}{g_c}dz = \delta q - \frac{\delta W_s}{m},$$

where h is the enthalpy of the gas and q is the heat.

The following assumptions are invoked:

$dh = C_p dT$ for an ideal gas,

$g/g_c dz \approx 0$ is valid for gases,

$\delta q = 0$ because the pipe is adiabatic,

$\delta W_s = 0$ because no mechanical linkages are present.

- These assumptions are applied to Equations The equations are combined, integrated (between the initial point denoted by subscript “o” and any arbitrary final
- point), and manipulated to yield, after considerable effort,

$$\frac{T_2}{T_1} = \frac{Y_1}{Y_2}, \quad \text{where } Y_i = 1 + \frac{\gamma - 1}{2} \text{Ma}_i^2,$$

$$\frac{P_2}{P_1} = \frac{\text{Ma}_1}{\text{Ma}_2} \sqrt{\frac{Y_1}{Y_2}},$$

$$\frac{\rho_2}{\rho_1} = \frac{\text{Ma}_1}{\text{Ma}_2} \sqrt{\frac{Y_2}{Y_1}},$$

$$G = \rho \bar{u} = \text{Ma}_1 P_1 \sqrt{\frac{\gamma g_c M}{R_g T_1}} = \text{Ma}_2 P_2 \sqrt{\frac{\gamma g_c M}{R_g T_2}},$$

where G is the mass flux with units of mass/(area-time)

$$\frac{\gamma + 1}{2} \ln\left(\frac{\text{Ma}_2^2 Y_1}{\text{Ma}_1^2 Y_2}\right) - \left(\frac{1}{\text{Ma}_1^2} - \frac{1}{\text{Ma}_2^2}\right) + \gamma \left(\frac{4fL}{d}\right) = 0.$$

kinetic energy
compressibility
pipe friction

Relates the Mach numbers to the frictional losses in the pipe.

The various energy contributions are identified.

The compressibility term accounts for the change in velocity resulting from the expansion of the gas.

Equations are converted to a more convenient and useful form by replacing

the Mach numbers with temperatures and pressures,

$$\frac{\gamma + 1}{\gamma} \ln \frac{P_1 T_2}{P_2 T_1} - \frac{\gamma - 1}{2\gamma} \left(\frac{P_1^2 T_2^2 - P_2^2 T_1^2}{T_2 - T_1} \right) \left(\frac{1}{P_1^2 T_2} - \frac{1}{P_2^2 T_1} \right) + \frac{4fL}{d} = 0,$$

$$G = \sqrt{\frac{2g_c M}{R_g} \frac{\gamma}{\gamma - 1} \frac{T_2 - T_1}{(T_1/P_1)^2 - (T_2/P_2)^2}}$$

For most problems the pipe length (L), inside diameter (d), upstream temperature (T_1) and pressure (P_1), and downstream pressure (P_2) are known.

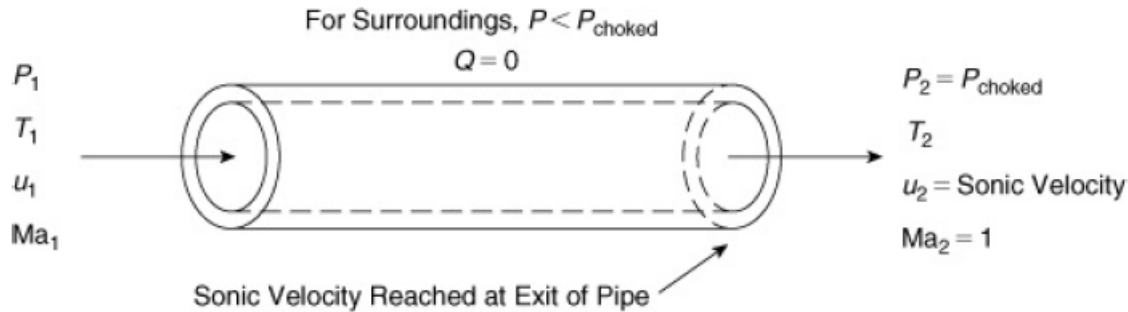
To compute the mass flux G ,

The procedure is as follows:

1. Determine pipe roughness ε from Table Compute ε/d .
2. Determine the Fanning friction factor f from Equation This assumes fully developed turbulent flow at high Reynolds numbers. This assumption can be checked later but is normally valid.
3. Determine T_2 from Equation
4. Compute the total mass flux G from Equation
 - For long pipes or for large pressure differences across the pipe the velocity of the gas can approach the sonic velocity.
 - When the sonic velocity is reached, the gas flow is called choked. The gas reaches the sonic velocity at the end of the pipe.
 - If the upstream pressure is increased or if the downstream pressure is decreased, the gas velocity at the end of the pipe remains constant at the sonic velocity.
 - If the downstream pressure is decreased below the choked pressure P_{choked} , the flow through the pipe remains choked and constant, independent of the downstream pressure.
 - The pressure at the end of the pipe will remain at P_{choked} even if this pressure is greater than the ambient pressure. The gas exiting the pipe makes an abrupt change from P_{choked} to the ambient pressure. For choked flow Equations are simplified by setting $\text{Ma}_2 = 1.0$.

The results are

Adiabatic choked flow of gas through a pipe. The maximum velocity is reached at the end of the pipe.



$$\frac{T_{\text{choked}}}{T_1} = \frac{2Y_1}{\gamma + 1}, \quad (4-63)$$

$$\frac{P_{\text{choked}}}{P_1} = \text{Ma}_1 \sqrt{\frac{2Y_1}{\gamma + 1}}, \quad (4-64)$$

$$\frac{\rho_{\text{choked}}}{\rho_1} = \text{Ma}_1 \sqrt{\frac{\gamma + 1}{2Y_1}}, \quad (4-65)$$

$$G_{\text{choked}} = \rho \bar{u} = \text{Ma}_1 P_1 \sqrt{\frac{\gamma g_c M}{R_g T_1}} = P_{\text{choked}} \sqrt{\frac{\gamma g_c M}{R_g T_{\text{choked}}}}, \quad (4-66)$$

$$\frac{\gamma + 1}{2} \ln \left[\frac{2Y_1}{(\gamma + 1)\text{Ma}_1^2} \right] - \left(\frac{1}{\text{Ma}_1^2} - 1 \right) + \gamma \left(\frac{4fL}{d} \right) = 0. \quad (4-67)$$

Choked flow occurs if the downstream pressure is less than P_{choked} . This is checked using Equation 4-64.

- For most problems involving choked adiabatic flows the pipe length (L), inside diameter (d), and upstream pressure (P_1) and temperature (T_1) are known. To compute the mass flux G , the procedure is as follows:
 1. Determine the Fanning friction factor f using Equation 4-34. This assumes fully developed turbulent flow at high Reynolds numbers. This assumption can be checked later but is normally valid.
 2. Determine Ma_1 from Equation 4-67.
 3. Determine the mass flux G_{choked} from Equation 4-66.
 4. Determine P_{choked} from Equation 4-64 to confirm operation at choked conditions.

Equations 4-63 through 4-67 for adiabatic pipe flow can be modified to use the 2-K method discussed previously by substituting $\sum K_f$ for $4fL/d$.

The procedure can be simplified by defining a gas expansion factor Y_g . For ideal gas flow the mass flow for both sonic and nonsonic conditions is represented by the Darcy formula

Darcy formula

$$G = \frac{\dot{m}}{A} = Y_g \sqrt{\frac{2g_c \rho_1 (P_1 - P_2)}{\sum K_f}},$$

where

G is the mass flux (mass/area-time), is the mass flow rate of gas (mass/time),

A is the area of the discharge (length²),

Y_g is a gas expansion factor (unit less),

g_c is the gravitational constant (force/mass-acceleration),

ρ_1 is the upstream gas density (mass/volume),

P_1 is the upstream gas pressure (force/area),

P_2 is the downstream gas pressure (force/area), and

$\sum K_f$ are the excess head loss terms, including pipe entrances and exits, pipe lengths, and fittings (unit less).

The excess head loss terms $\sum K_f$ are found using the 2-K method presented earlier

For most accidental discharges of gases the flow is fully developed turbulent flow.

This means that for pipes the friction factor is independent of the Reynolds number and that for fittings $K_f = K_\infty$ and the solution is direct.

- The procedure to determine the gas expansion factor is as follows.
- First, the upstream Mach number Ma_1 is determined using Equation 4-67.

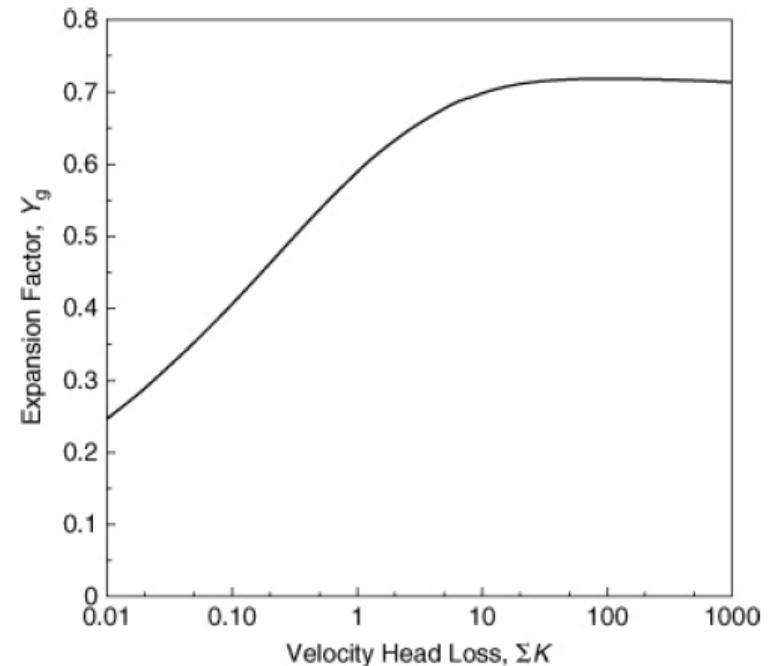
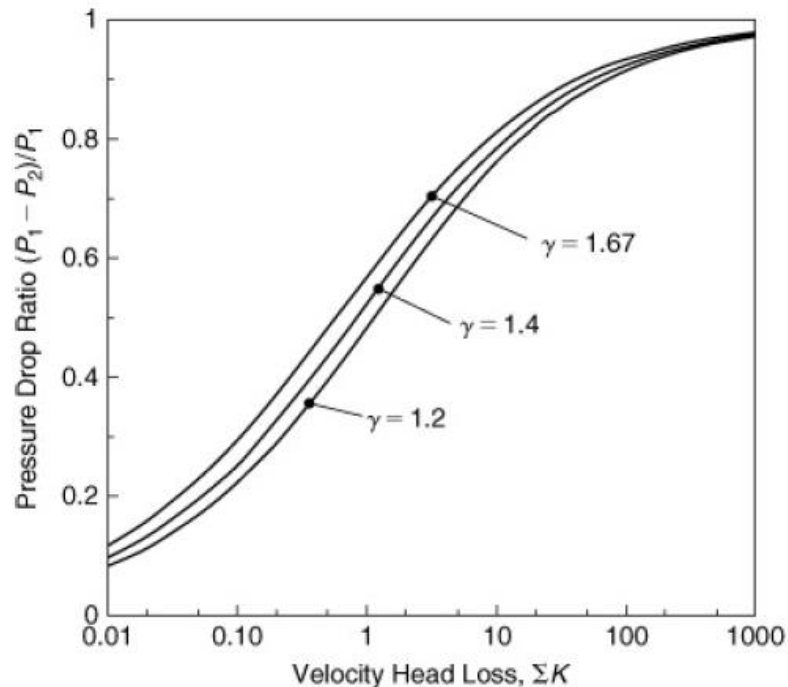
$$\frac{\gamma + 1}{2} \ln \left[\frac{2Y_1}{(\gamma + 1)Ma_1^2} \right] - \left(\frac{1}{Ma_1^2} - 1 \right) + \gamma \left(\frac{4fL}{d} \right) = 0. \quad (4-67)$$

- ΣK_f must be substituted for $4fL/d$ to include the effects of pipes and fittings.
- The solution is obtained by trial and error, by guessing values of the upstream Mach number and determining whether the guessed value meets the equation objectives.
- This can be easily done using a spreadsheet.
- The next step in the procedure is to determine the sonic pressure ratio. This is found from Equation 4-64

$$\frac{P_{\text{choked}}}{P_1} = Ma_1 \sqrt{\frac{2Y_1}{\gamma + 1}}, \quad (4-64)$$

- If the actual ratio is greater than the ratio from Equation 4-64, then the flow is sonic or choked and the pressure drop predicted by Equation 4-64 is used to continue the calculation.
- If less than the ratio from Equation 4-64, then the flow is not sonic and the actual pressure drop ratio is used.
- Finally, the expansion factor Y_g is calculated from Equation 4-69.

$$Y_g = Ma_1 \sqrt{\frac{\gamma \Sigma K_f}{2} \left(\frac{P_1}{P_1 - P_2} \right)},$$



- The calculation to determine the expansion factor can be completed once γ and the frictional loss terms ΣK_f are specified.
- This computation can be done once and for all with the results shown in Figures
- As shown in Figure, the pressure ratio $(P_1 - P_2)/P_1$ is a weak function of the heat capacity ratio γ .
- The expansion factor Y_g has little dependence on γ , with the value of Y_g varying by less than 1% from the value at $\gamma = 1.4$ over the range from $\gamma = 1.2$ to $\gamma = 1.67$.
- The functional results of Figures can be fitted using an equation of the form $\ln Y_g = A(\ln K_f)^3 + B(\ln K_f)^2 + C(\ln K_f) + D$, where A , B , C , and D are constants.
- The results are shown in Table and are valid for the K_f ranges indicated, within 1%.

| Function value ^b | A | B | C | D | Range of validity, K |
|---|---------|---------|-------|--------|------------------------|
| Expansion factor Y_g | 0.00129 | -0.0216 | 0.116 | -0.528 | 0.2-1000 |
| Sonic pressure drop ratio $\gamma = 1.2$ | 0.943 | 0.00727 | 1.12 | - | 0.01-1000 |
| Sonic pressure drop ratio $\gamma = 1.4$ | 0.965 | 0.00461 | 0.944 | - | 0.2-1000 |
| Sonic pressure drop ratio $\gamma = 1.67$ | 0.989 | 0.00178 | 0.767 | - | 0.01-1000 |

- The gas expansion factor Y_g in Equation 4-68 depends only on the heat capacity ratio of the gas γ and the frictional elements in the flow path $\sum K_f$.

$$G = \frac{\dot{m}}{A} = Y_g \sqrt{\frac{2g_c\rho_1(P_1 - P_2)}{\sum K_f}}$$

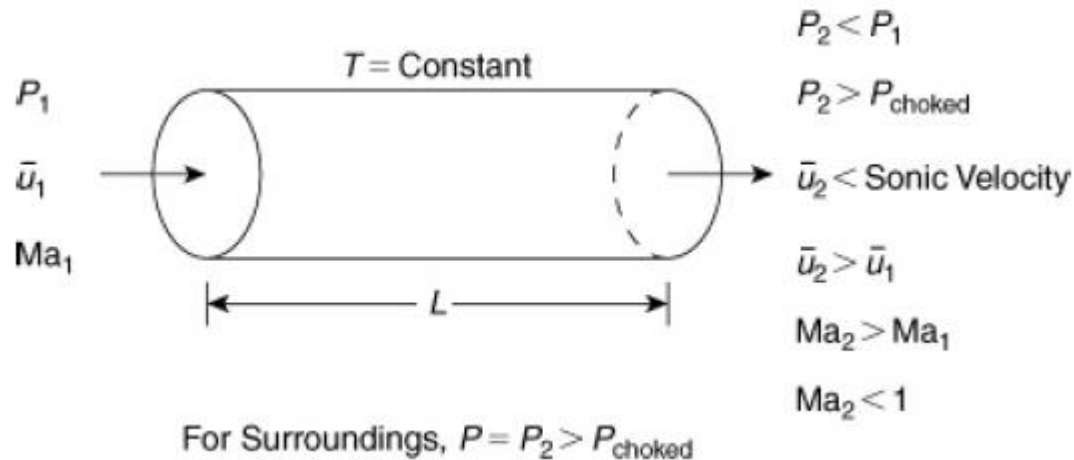
- An equation for the gas expansion factor for choked flow is obtained by equating Equation 4-68 to Equation 4-59 and solving for Y_g .

$$G = \rho\bar{u} = Ma_1P_1\sqrt{\frac{\gamma g_c M}{R_g T_1}} = Ma_2P_2\sqrt{\frac{\gamma g_c M}{R_g T_2}} \quad | \quad (4-59)$$

- The result is

$$Y_g = Ma_1\sqrt{\frac{\gamma\sum K_f}{2}\left(\frac{P_1}{P_1 - P_2}\right)},$$

Isothermal Flows



- Isothermal flow of gas in a pipe with friction is shown in Figure.
- For this case the gas velocity is assumed to be well below the sonic velocity of the gas.
- A pressure gradient across the pipe provides the driving force for the gas transport.
- As the gas expands through the pressure gradient, the velocity must increase to maintain the same mass flow rate.
- The pressure at the end of the pipe is equal to the pressure of the surroundings. The temperature is constant across the entire pipe length.

- Isothermal flow is represented by the mechanical energy balance in the form shown in Equation.

- The following assumptions are valid for this case: $\frac{g}{g_c} dz \approx 0$

- valid for gases, and, by combining Equations 4-29 and 4-30 and differentiating

$$dF = \frac{2f\bar{u}^2 dL}{g_c d},$$

- constant f , $\delta W_s = 0$
- because no mechanical linkages are present. A total energy balance is not required because the temperature is constant.
- By applying the assumptions to Equation and manipulating them considerably, we obtain $T_2 = T_1$,

$$\frac{P_2}{P_1} = \frac{\text{Ma}_1}{\text{Ma}_2},$$

$$\frac{\rho_2}{\rho_1} = \frac{\text{Ma}_1}{\text{Ma}_2},$$

$$G = \rho\bar{u} = \text{Ma}_1 P_1 \sqrt{\frac{\gamma g_c M}{R_g T}},$$

- where G is the mass flux with units of mass/(area-time), and

$$2 \ln \frac{\text{Ma}_2}{\text{Ma}_1} - \frac{1}{\gamma} \left(\frac{1}{\text{Ma}_1^2} - \frac{1}{\text{Ma}_2^2} \right) + \frac{4fL}{d} = 0.$$

kinetic energy
compressibility
pipe friction

A more convenient form of Equation is in terms of pressure instead of Mach numbers.

$$2 \ln \frac{P_1}{P_2} - \frac{g_c M}{G^2 R_g T} (P_1^2 - P_2^2) + \frac{4fL}{d} = 0.$$

A typical problem is to determine the mass flux G given the pipe length (L), inside diameter (d), and upstream and downstream pressures (P_1 and P_2). The procedure is as follows:

1. Determine the Fanning friction factor f using Equation. $\frac{1}{\sqrt{f}} = 4 \log \left(3.7 \frac{d}{\epsilon} \right)$

This assumes fully developed turbulent flow at high Reynolds numbers. This assumption can be checked later but is usually valid.

2. Compute the mass flux G from

$$2 \ln \frac{P_1}{P_2} - \frac{g_c M}{G^2 R_g T} (P_1^2 - P_2^2) + \frac{4fL}{d} = 0.$$

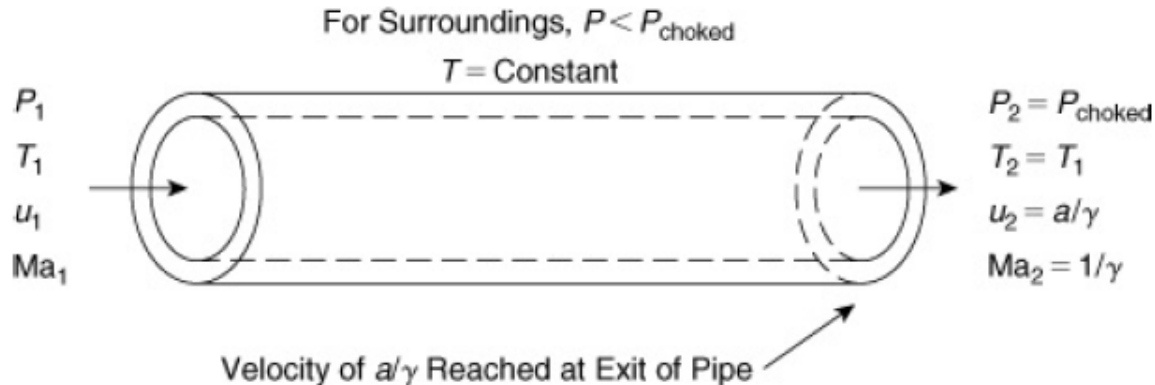
- Levenspiel showed that the maximum velocity possible during the isothermal flow of gas in a pipe is not the sonic velocity, as in the adiabatic case. In terms of the Mach number the maximum velocity is

$$\text{Ma}_{\text{choked}} = \frac{1}{\sqrt{\gamma}}$$

- This result is shown by starting with the mechanical energy balance and rearranging it into the following form:

$$-\frac{dP}{dL} = \frac{2fG^2}{g_c \rho d} \left[\frac{1}{1 - (\bar{u}^2 \rho / g_c P)} \right] = \frac{2fG^2}{g_c \rho d} \left(\frac{1}{1 - \gamma \text{Ma}^2} \right)$$

- The quantity $-(dP/dL) \rightarrow \infty$ when. $\text{Ma} \rightarrow 1/\sqrt{\gamma}$.
- Thus for choked flow in an isothermal pipe, as shown in Figure the following equations apply:



$$T_{\text{choked}} = T_1,$$

$$\frac{P_{\text{choked}}}{P_1} = \text{Ma}_1 \sqrt{\gamma},$$

$$\frac{\rho_{\text{choked}}}{\rho_1} = \text{Ma}_1 \sqrt{\gamma},$$

$$\frac{\bar{u}_{\text{choked}}}{\bar{u}_1} = \frac{1}{\text{Ma}_1 \sqrt{\gamma}},$$

$$G_{\text{choked}} = \rho \bar{u} = \rho_1 \bar{u}_1 = \text{Ma}_1 P_1 \sqrt{\frac{\gamma g_c M}{R_g T}} = P_{\text{choked}} \sqrt{\frac{g_c M}{R_g T}},$$

where G_{choked} is the mass flux with units of mass/(area-time), and

$$\ln\left(\frac{1}{\gamma \text{Ma}_1^2}\right) - \left(\frac{1}{\gamma \text{Ma}_1^2} - 1\right) + \frac{4fL}{d} = 0.$$

For most typical problems the pipe length (L), inside diameter (d), upstream pressure (P_1), and temperature (T) are known.

The mass flux G is determined using the following procedure:

1. Determine the Fanning friction factor using Equation as above.
2. Determine Ma_1 from Equation.

$$\ln\left(\frac{1}{\gamma \text{Ma}_1^2}\right) - \left(\frac{1}{\gamma \text{Ma}_1^2} - 1\right) + \frac{4fL}{d} = 0.$$

3. Determine the mass flux G from Equation.

$$G_{\text{choked}} = \rho \bar{u} = \rho_1 \bar{u}_1 = \text{Ma}_1 P_1 \sqrt{\frac{\gamma g_c M}{R_g T}} = P_{\text{choked}} \sqrt{\frac{g_c M}{R_g T}},$$

The direct method using Equations can also be applied to isothermal flows.

$$G = \frac{\dot{m}}{A} = Y_g \sqrt{\frac{2g_c \rho_1 (P_1 - P_2)}{\sum K_f}}, \quad Y_g = \text{Ma}_1 \sqrt{\frac{\gamma \sum K_f}{2} \left(\frac{P_1}{P_1 - P_2} \right)},$$

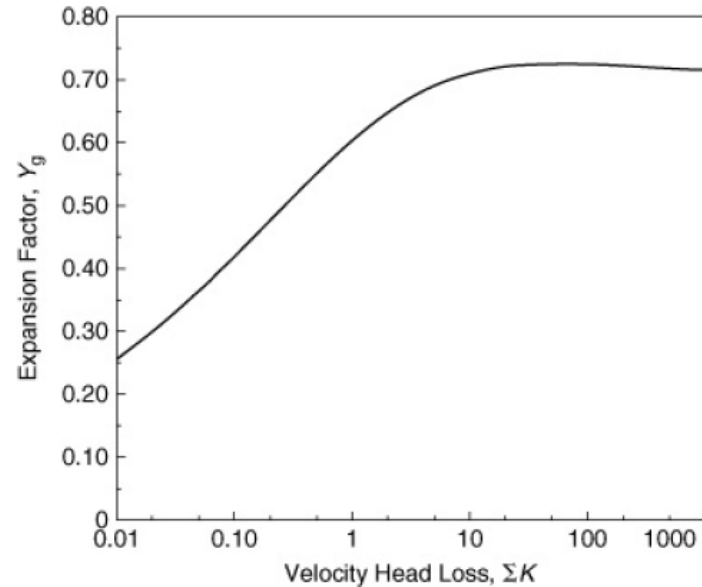
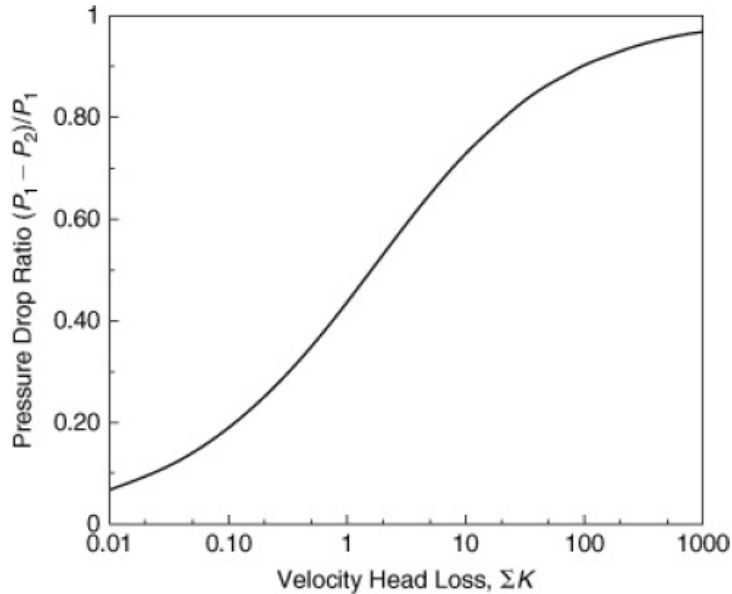
The procedure is identical to the procedure for adiabatic flows. Table provides the equations for the expansion factor and the pressure drop ratio.

Correlations for the Expansion Factor Y_g and the Sonic Pressure Drop Ratio $(P_1 - P_2)/P_1$ as a Function of the Pipe Loss $\sum K$ for Isothermal Flow Conditions

equations used to fit the functions are of the form $\ln Y_g = A(\ln K)^3 + B(\ln K)^2 + C(\ln K) + D$ for the expansion factor and $\{(P_1 - P_2)/P_1\}^{-1} = A + B(\ln K)^2 + C/K^{0.5}$ for the pressure drop ratio.

| Function value ^b | A | B | C | D | Range of validity, K |
|---|---------|---------|-------|--------|----------------------|
| Expansion factor Y_g | 0.00130 | -0.0216 | 0.111 | -0.502 | 0.2-1000 |
| Sonic pressure drop ratio, all γ | 0.911 | 0.0118 | 1.38 | - | 0.01-1000 |

Figures are plots of these functions.



The results are independent of the heat capacity ratio.

Keith and Crowl found that for both the adiabatic and isothermal cases the expansion factor Y_g exhibited a maximum value.

- For isothermal flows this maximum was the same for all values of the heat capacity ratio γ and occurred at a velocity head loss of 56.3 with a maximum expansion factor of 0.7248.
- For adiabatic flows the maximum value of the expansion factor is a function of the heat capacity ratio γ .
- For $\gamma = 1.4$ the expansion factor has a maximum value of 0.7182 at a velocity head loss of 90.0.

- For both the adiabatic and isothermal flow cases the expansion factor approaches an asymptote as the velocity head loss becomes large—the asymptote is the same for both cases.
- This asymptote is for both the adiabatic and isothermal flow cases.
- Comparison of detailed calculations with the asymptotic solution show that for velocity head loss values of 100 and 500 the difference between the detailed and asymptotic solution is 2.2% and 0.2%, respectively.
- The asymptotic solution can be inserted into Equation to result in the following simplified equation for the mass flow:

$$G = \frac{\dot{m}}{A} = Y_g \sqrt{\frac{2g_c \rho_1 (P_1 - P_2)}{\sum K_f}}$$

- For gas releases through pipes the issue of whether the release occurs adiabatically or isothermally is important.
- For both cases the velocity of the gas increases because of the expansion of the gas as the pressure decreases.

- For adiabatic flows the temperature of the gas may increase or decrease, depending on the relative magnitude of the frictional and kinetic energy terms.
- For choked flows the adiabatic choking pressure is less than the isothermal choking pressure.
- For real pipe flows from a source at a fixed pressure and temperature, the actual flow rate is less than the adiabatic prediction and greater than the isothermal prediction.

Example

The vapor space above liquid ethylene oxide (EO) in storage tanks must be purged of oxygen and then padded with 81 psig nitrogen to prevent explosion. The nitrogen in a particular facility is supplied from a 200 psig source. It is regulated to 81 psig and supplied to the storage vessel through 33 ft of new commercial steel pipe with an internal diameter of 1.049 in.

In the event of a failure of the nitrogen regulator, the vessel will be exposed to the full 200-psig pressure from the nitrogen source. This will exceed the pressure rating of the storage vessel. To prevent rupture of the storage vessel, it must be equipped with a relief device to vent this nitrogen. Determine the required minimum mass flow rate of nitrogen through the relief device to prevent the pressure from rising within the tank in the event of a regulator failure.

Determine the mass flow rate assuming

- (a) an orifice with a throat diameter equal to the pipe diameter,
- (b) an adiabatic pipe, and
- (c) an isothermal pipe.

Decide which result most closely corresponds to the real situation. Which mass flow rate should be used?

- **Solution**

a. The maximum flow rate through the orifice occurs under choked conditions.

The area of the pipe is

$$A = \frac{\pi d^2}{4} = \frac{(3.14)(1.049 \text{ in})^2(1 \text{ ft}^2/144 \text{ in}^2)}{4}$$

$$= 6.00 \times 10^{-3} \text{ ft}^2.$$

The absolute pressure of the nitrogen source is

$$P_o = 200 + 14.7 = 214.7 \text{ psia} = 3.09 \times 10^4 \text{ lbf/ft}^2.$$

The choked pressure from Equation is, for a diatomic gas,

$$P_{\text{choked}} = (0.528)(214.7 \text{ psia}) = 113.4 \text{ psia}$$

$$= 1.63 \times 10^4 \text{ lbf/ft}^2.$$

- Choked flow can be expected because the system is venting to atmospheric conditions. Equation provides the maximum mass flow rate. For nitrogen, $\gamma = 1.4$ and

$$(Q_m)_{\text{choked}} = C_o A P_o \sqrt{\frac{\gamma g_c M}{R_g T_o} \left(\frac{2}{\gamma + 1} \right)^{(\gamma + 1)/(\gamma - 1)}},$$

The molecular weight of nitrogen is 28 lbm/lb-mol. Without any additional

- information, assume a unit discharge coefficient $C_o = 1.0$. Thus

$$\left(\frac{2}{\gamma + 1}\right)^{(\gamma+1)/(\gamma-1)} = \left(\frac{2}{2.4}\right)^{2.4/0.4} = 0.335.$$

$$Q_m = (1.0)(6.00 \times 10^{-3} \text{ ft}^2)(3.09 \times 10^4 \text{ lb}_f/\text{ft}^2) \times \sqrt{\frac{(1.4)(32.17 \text{ ft lb}_m/\text{lb}_f \text{ s}^2)(28 \text{ lb}_m/\text{lb-mol})}{(1545 \text{ ft lb}_f/\text{lb-mol}^\circ\text{R})(540^\circ\text{R})}} (0.335)$$

$$= (185 \text{ lb}_f) \sqrt{5.06 \times 10^{-4} \text{ lb}_m^2/\text{lb}_f^2 \text{ s}^2}$$

$Q_m = 4.16 \text{ lb}_m/\text{s}.$

b. Assume adiabatic choked flow conditions. For commercial steel pipe, from Table 4-1, $\epsilon = 0.046 \text{ mm}$. The diameter of the pipe in millimeters is $(1.049 \text{ in}) (25.4 \text{ mm/in}) = 26.6 \text{ mm}$.

| Pipe material | Condition | Typical ϵ | |
|--------------------------------|--------------|--------------------|---------|
| | | mm | inch |
| Drawn brass, copper, stainless | New | 0.002 | 0.00008 |
| Commercial steel | New | 0.046 | 0.0018 |
| | Light rust | 0.3 | 0.015 |
| | General rust | 2.0 | 0.08 |

- Thus

$$\frac{\varepsilon}{d} = \frac{0.046 \text{ mm}}{26.6 \text{ mm}} = 0.00173.$$

$$\begin{aligned}\frac{1}{\sqrt{f}} &= 4 \log\left(3.7 \frac{d}{\varepsilon}\right) \\ &= 4 \log(3.7/0.00173) = 13.32, \\ \sqrt{f} &= 0.0751, \\ f &= 0.00564.\end{aligned}$$

For nitrogen, $\gamma = 1.4$. The upstream Mach number is determined from

$$\frac{\gamma + 1}{2} \ln\left[\frac{2Y_1}{(\gamma + 1)\text{Ma}_1^2}\right] - \left(\frac{1}{\text{Ma}_1^2} - 1\right) + \gamma\left(\frac{4fL}{d}\right) = 0,$$

with Y_1 given by Equation. Substituting the numbers provided gives

$$\frac{T_2}{T_1} = \frac{Y_1}{Y_2}, \quad \text{where } Y_i = 1 + \frac{\gamma - 1}{2} \text{Ma}_i^2,$$

$$\frac{1.4 + 1}{2} \ln \left[\frac{2 + (1.4 - 1)\text{Ma}^2}{(1.4 + 1)\text{Ma}^2} \right] - \left(\frac{1}{\text{Ma}^2} - 1 \right) + 1.4 \left[\frac{(4)(0.00564)(33 \text{ ft})}{(1.049 \text{ in})(1 \text{ ft}/12 \text{ in})} \right] = 0,$$

$$1.2 \ln \left(\frac{2 + 0.4\text{Ma}^2}{2.4\text{Ma}^2} \right) - \left(\frac{1}{\text{Ma}^2} - 1 \right) + 11.92 = 0.$$

This equation is solved by trial and error or a solver program or spreadsheet for the value of Ma. The results are tabulated as follows:

| Guessed Ma | Value of left-hand side of equation |
|-------------------|--|
| 0.20 | -8.43 |
| 0.25 | 0.043 |

This last guessed Mach number gives a result close to zero.

Then from

$$Y_1 = 1 + \frac{\gamma - 1}{2} \text{Ma}^2 = 1 + \frac{1.4 - 1}{2} (0.25)^2 = 1.012,$$

$$\frac{T_{\text{choked}}}{T_1} = \frac{2Y_1}{\gamma + 1} = \frac{2(1.012)}{1.4 + 1} = 0.843,$$

$$T_{\text{choked}} = (0.843)(80 + 460)^\circ\text{R} = 455^\circ\text{R},$$

$$\frac{P_{\text{choked}}}{P_1} = \text{Ma} \sqrt{\frac{2Y_1}{\gamma + 1}} = (0.25) \sqrt{0.843} = 0.230,$$

$$P_{\text{choked}} = (0.230)(214.7 \text{ psia}) = 49.4 \text{ psia} = 7.11 \times 10^3 \text{ lb}_f/\text{ft}^2.$$

- The pipe outlet pressure must be less than 49.4 psia to ensure choked flow.
- The mass flux is computed using

$$\begin{aligned}
 G_{\text{choked}} &= P_{\text{choked}} \sqrt{\frac{\gamma g_c M}{R_g T_{\text{choked}}}} \\
 &= (7.11 \times 10^3 \text{ lb}_f/\text{ft}^2) \sqrt{\frac{(1.4)(32.17 \text{ ft lb}_m/\text{lb}_f \text{ s}^2)(28 \text{ lb}_m/\text{lb-mol})}{(1545 \text{ ft lb}_f/\text{lb-mol}^\circ\text{R})(455^\circ\text{R})}} \\
 &= 7.11 \times 10^3 \text{ lb}_f/\text{ft}^2 \sqrt{1.79 \times 10^{-3} \text{ lb}_m^2/\text{lb}_f^2 \text{ s}^2} = 301 \text{ lb}_m/\text{ft}^2 \text{ s}, \\
 Q_m &= GA = (301 \text{ lb}_m/\text{ft}^2 \text{ s})(6.00 \times 10^{-3} \text{ ft}^2) \\
 &= 1.81 \text{ lb}_m/\text{s}.
 \end{aligned}$$

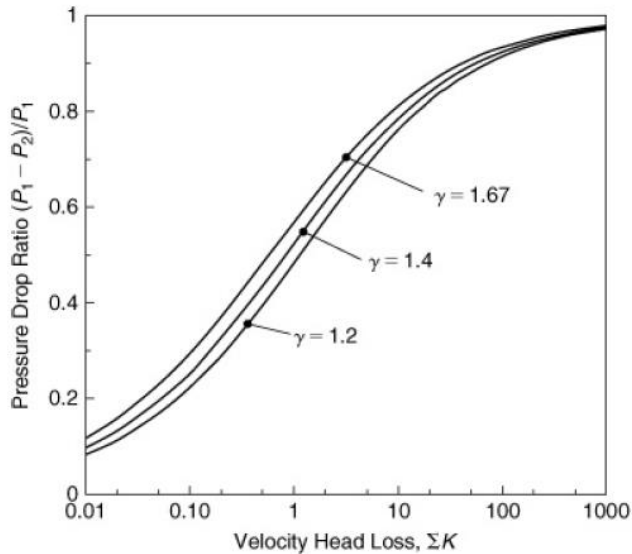
The simplified procedure with a direct solution can also be used.

The excess head loss resulting from the pipe length is given by Equation.

$$K_f = \frac{4fL}{d} = \frac{(4)(0.00564)(10.1 \text{ m})}{(1.049 \text{ in})(0.0254 \text{ m/in})} = 8.56.$$

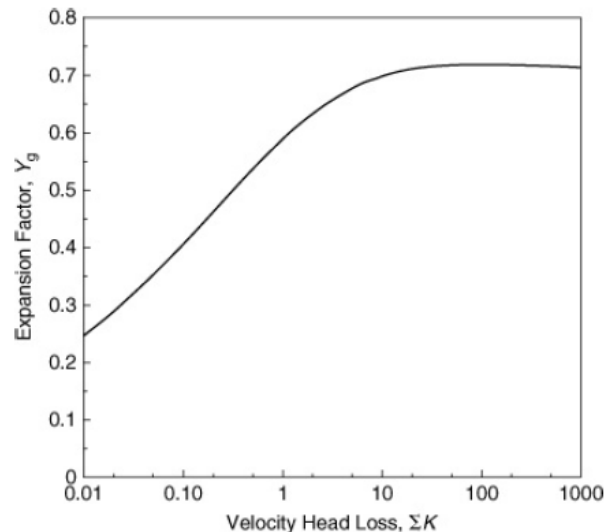
:

- For this solution only the pipe friction will be considered and the exit effects will be ignored.
- The first consideration is whether the flow is sonic.
- The sonic pressure ratio is given in Figure (or the equations in Table). For $\gamma = 1.4$ and $K_f = 8.56$



$$\frac{P_1 - P_2}{P_1} = 0.770 \Rightarrow P_2 = 49.4 \text{ psia}$$

It follows that the flow is sonic because the downstream pressure is less than 49.4 psia



From Figure (or Table) the gas expansion factor $Y_g = 0.69$.

- The gas density under the upstream conditions is

$$\rho_1 = \frac{P_1 M}{R_g T} = \frac{(214.7 \text{ psia})(28 \text{ lb}_m/\text{lb-mol})}{(10.731 \text{ psia ft}^3/\text{lb-mol}^\circ\text{R})(540^\circ\text{R})} = 1.037 \text{ lb}_m/\text{ft}^3.$$

- By substituting this value into Equation and using the choking pressure determined for P_2 , we obtain

$$\begin{aligned} \dot{m} &= Y_g A \sqrt{\frac{2g_c \rho_1 (P_1 - P_2)}{\sum K_f}}, \\ &= (0.69)(6.00 \times 10^{-3} \text{ ft}^2) \sqrt{\frac{(2) \left(32.17 \frac{\text{ft lb}_m}{\text{lb}_f \text{ s}^2}\right) \left(1.037 \frac{\text{lb}_m}{\text{ft}^3}\right) (214.7 - 49.4) \left(\frac{\text{lb}_f}{\text{in}^2}\right) \left(144 \frac{\text{in}^2}{\text{ft}^2}\right)}{8.56}} \\ &= 1.78 \text{ lb}_m/\text{s}. \end{aligned}$$

This result is essentially identical to the previous result, although with a lot less effort.

- For the **isothermal case** the upstream Mach number is given by Equation.

$$\ln\left(\frac{1}{\gamma Ma_1^2}\right) - \left(\frac{1}{\gamma Ma_1^2} - 1\right) + \frac{4fL}{d} = 0.$$

- Substituting the numbers provided, we obtain

$$\ln\left(\frac{1}{1.4Ma^2}\right) - \left(\frac{1}{1.4Ma^2} - 1\right) + 8.52 = 0.$$

- The solution is found by trial and error:

| Gussed Ma | Value of left-hand side of equation |
|-----------|-------------------------------------|
| 0.25 | 0.526 |
| 0.24 | -0.362 |
| 0.245 | 0.097 |
| 0.244 | 0.005 ← Final result |

The choked pressure is

$$P_{\text{choked}} = P_1 Ma_1 \sqrt{\gamma} = (214.7 \text{ lb}_f/\text{in}^2)(0.244) \sqrt{1.4} = 62.0 \text{ psia} = 8.93 \times 10^3 \text{ lb}_f/\text{ft}^2.$$

The mass flow rate is computed using

$$G_{\text{choked}} = P_{\text{choked}} \sqrt{\frac{g_c M}{R_g T}} = 8.93 \times 10^3 \text{ lb}_f/\text{ft}^2 \times \sqrt{\frac{(32.17 \text{ ft lb}_m/\text{lb}_f \text{ s}^2)(28 \text{ lb}_m/\text{lb-mol})}{(1545 \text{ ft lb}_f/\text{lb-mol}^\circ\text{R})(540^\circ\text{R})}}$$

$$= 8.93 \times 10^3 \text{ lb}_f/\text{ft}^2 \sqrt{1.08 \times 10^{-3} \text{ lb}_m^2/\text{lb}_f^2 \text{ s}^2} = 293 \text{ lb}_m/\text{ft}^2 \text{ s},$$

$$Q_m = G_{\text{choked}} A = (293 \text{ lb}_m/\text{ft}^2 \text{ s})(6.00 \times 10^{-3} \text{ ft}^2)$$

$$= 1.76 \text{ lb}_m/\text{s}.$$

Using the simplified, direct solution, from Table

| Function value ^b | A | B | C | D | Range of validity, K |
|---|---------|---------|-------|--------|----------------------|
| Expansion factor Y_g | 0.00130 | -0.0216 | 0.111 | -0.502 | 0.2-1000 |
| Sonic pressure drop ratio, all γ | 0.911 | 0.0118 | 1.38 | - | 0.01-1000 |

$$\frac{P_1 - P_2}{P_1} = 0.70 \Rightarrow P_2 = 64.4 \text{ psia}.$$

And it follows that the flow is sonic. $Y_g = 0.70$.

Substituting into Equation, remembering to use the choking pressure above, gives = 1.74 lbm/sec.

This is close to the more detailed method.

The results are summarized in the following table:

| Case | P_{choked} (psia) | Q_m (lb_m/s) |
|-----------------|--|--|
| Orifice | 113.4 | 4.16 |
| Adiabatic pipe | 49.4 | 1.81 |
| Isothermal pipe | 62.0 | 1.76 |

- A standard procedure for these types of problems is to represent the discharge through the pipe as an orifice.
- The results show that this approach results in a large result for this case.
- The orifice method always produces a larger value than the adiabatic pipe method, ensuring a conservative safety design.
- The orifice calculation, however, is easier to apply, requiring only the pipe diameter and the upstream supply pressure and temperature.
- Also note that the computed choked pressures differ for each case, with a substantial difference between the orifice and the adiabatic/isothermal cases.
- A choking design based on an orifice calculation might not be choked in reality because of high downstream pressures.
- Finally, note that the adiabatic and isothermal pipe methods produce results that are reasonably close.
- For most real situations the heat transfer characteristics cannot be easily determined. Thus the adiabatic pipe method is the method of choice; it will always produce the larger number for a conservative safety design.

Flashing Liquids

- Liquids stored under pressure above their normal boiling point temperature present substantial problems because of flashing.
- If the tank, pipe, or other containment device develops a leak, the liquid will partially flash into vapor, sometimes explosively.
- Flashing occurs so rapidly that the process is assumed to be **adiabatic**.
- The excess energy contained in the superheated liquid vaporizes the liquid and lowers the temperature to the new boiling point.
- If m is the mass of original liquid, C_p the heat capacity of the liquid (energy/mass deg), T_o the temperature of the liquid before depressurization, and T_b the depressurized boiling point of the liquid,
- then the excess energy contained in the superheated liquid is given by

$$Q = mC_p(T_o - T_b).$$

- This energy vaporizes the liquid. If ΔH_v is the heat of vaporization of the liquid, the mass of liquid vaporized m_v is given by

$$m_v = \frac{Q}{\Delta H_v} = \frac{mC_p(T_o - T_b)}{\Delta H_v}$$

The fraction of the liquid vaporized is

$$f_v = \frac{m_v}{m} = \frac{C_p(T_o - T_b)}{\Delta H_v}$$

The change in liquid mass m resulting from a change in temperature T is given by

$$dm = \frac{mC_p}{\Delta H_v} dT$$

integrate between the initial temperature T_o (with liquid mass m) and the final boiling point temperature T_b (with liquid mass $m - m_v$):

$$\int_m^{m-m_v} \frac{dm}{m} = \int_{T_o}^{T_b} \frac{C_p}{\Delta H_v} dT \qquad \ln \left(\frac{m - m_v}{m} \right) = - \frac{\overline{C_p}(T_o - T_b)}{\Delta H_v}$$

where $\overline{C_p}$ and $\overline{\Delta H_v}$ are the mean heat capacity and the mean latent heat of vaporization, respectively, over the temperature range T_o to T_b . Solving for the fraction of the liquid vaporized, $f_v = m_v/m$, we obtain

For flashing liquids composed of many miscible substances, the flash calculation is complicated considerably, because the more volatile components flash preferentially.

Flashing liquids escaping through holes and pipes require special consideration because two-phase flow conditions may be present.

Several special cases need consideration.

If the fluid path length of the release is short (through a hole in a thin-walled container), non equilibrium conditions exist, and the liquid does not have time to flash within the hole; the fluid flashes external to the hole.

The equations describing incompressible fluid flow through holes apply .

- If the fluid path length through the release is greater than 10 cm (through a pipe or thick walled container), equilibrium flashing conditions are achieved and the flow is choked.
- A good approximation is to assume a choked pressure equal to the saturation vapor pressure of the flashing liquid.
- The result will be valid only for liquids stored at a pressure higher than the saturation vapor pressure.
- With this assumption the mass flow rate is given by

$$Q_m = AC_o \sqrt{2\rho_l g_c (P - P^{\text{sat}})},$$

For liquids stored at their saturation vapor pressure, $P = P_{\text{sat}}$, above Equation is no longer valid.

A much more detailed approach is required.

Consider a fluid that is initially quiescent and is accelerated through the leak.

Assume that kinetic energy is dominant and that potential energy effects are negligible.

- Then, from a mechanical energy balance Equation and realizing that the specific volume (with units of volume/mass) $v = 1/\rho$, we can write

$$-\int_1^2 v dP = \frac{\bar{u}_2^2}{2g_c}$$

$$G = \rho \bar{u} = \frac{\bar{u}}{v}$$

Combining the equation $-\int_1^2 v dP = \frac{\bar{u}_2^2}{2g_c} = \frac{G^2 v_2^2}{2g_c}$.

$$G = \frac{\sqrt{-2g_c \int v dP}}{v}$$

Equation contains a maximum, at which choked flow occurs. Under choked flow conditions, $dG/dP = 0$.

Differentiating Equation and setting the result equal to zero gives

$$\frac{dG}{dP} = 0 = -\frac{(dv/dP)}{v^2} \sqrt{-2g_c \int v dP} - \frac{g_c}{\sqrt{-2g_c \int v dP}}$$

$$0 = -\frac{G(dv/dP)}{v} - \frac{g_c}{vG}$$

$$G = \frac{Q_m}{A} = \sqrt{\frac{g_c}{(dv/dP)}}$$

The two-phase specific volume is given by

$$v = v_{fg}f_v + v_f,$$

v_{fg} is the difference in specific volume between vapor and liquid,

v_f is the liquid specific volume, and

f_v is the mass fraction of vapor.

Differentiating Equation with respect to pressure gives

$$\frac{dv}{dP} = v_{fg} \frac{df_v}{dP}.$$

But, from Equation,

$$df_v = -\frac{C_p}{\Delta H_v} dT,$$

from the Clausius-Clapyron equation, at saturation

$$\frac{dP}{dT} = \frac{\Delta H_v}{Tv_{fg}}$$

- Substituting last two Equations into above Equation yields

$$\frac{dv}{dP} = -\frac{v_{fg}^2}{\Delta H_v^2} TC_p$$

The mass flow rate is determined by combining Equation

$$G = \frac{Q_m}{A} = \sqrt{-\frac{g_c}{(dv/dP)}} \quad \longrightarrow \quad Q_m = \frac{\Delta H_v A}{v_{fg}} \sqrt{\frac{g_c}{TC_p}}$$

Liquid Pool Evaporation or Boiling

- The total mass flow rate from the evaporating pool is given by

$$Q_m = \frac{MKAP^{\text{sat}}}{R_g T_L}$$

Q_m is the mass vaporization rate (mass/time),

M is the molecular weight of the pure material,

K is the mass transfer coefficient (length/time),

A is the area of exposure,

P^{sat} is the saturation vapor pressure of the liquid,

R_g is the ideal gas constant, and

T_L is the temperature of the liquid.

For liquids boiling from a pool the boiling rate is limited by the heat transfer from the surroundings to the liquid in the pool.

Heat is transferred

- (1) from the ground by conduction,
- (2) from the air by conduction and convection, and
- (3) by radiation from the sun and/or adjacent sources such as a fire.

The initial stage of boiling is usually controlled by the heat transfer from the ground.

This is especially true for a spill of liquid with a normal boiling point below ambient temperature or ground temperature.

- The heat transfer from the ground is modeled with a simple one-dimensional heat conduction equation, given by

$$q_g = \frac{k_s(T_g - T)}{(\pi\alpha_s t)^{1/2}}$$

q_g is the heat flux from the ground (energy/area-time),

k_s is the thermal conductivity of the soil (energy/length-time-degree),

T_g is the temperature of the soil (degree),

T is the temperature of the liquid pool (degree),

α_s is the thermal diffusivity of the soil (area/time), and

t is the time after spill (time).

The rate of boiling is determined by assuming that all the heat is used to boil the liquid. Thus

$$Q_m = \frac{q_g A}{\Delta H_v}$$

Q_m is the mass boiling rate (mass/time),

q_g is the heat transfer for the pool from the ground, (energy/area-time),

A is the area of the pool (area), and

ΔH_v is the heat of vaporization of the liquid in the pool (energy/mass).

At later times, solar heat fluxes and convective heat transfer from the atmosphere become important.

This model also neglects possible water freezing effects in the ground, which can significantly alter the heat transfer behavior.

Realistic and Worst-Case Releases

- The realistic releases represent the incident outcomes with a high probability of occurring.
- Thus, rather than assuming that an entire storage vessel fails catastrophically, it is more realistic to assume that a high probability exists that the release will occur from the disconnection of the largest pipe connected to the tank.

Guidelines for Selection of Process Incidents

| Incident characteristic | Guideline |
|--|--|
| Realistic release incidents ^a | |
| Process pipes | Rupture of the largest diameter process pipe as follows: For diameters smaller than 2 in, assume a full bore rupture. For diameters 2–4 in, assume rupture equal to that of a 2-inch-diameter pipe. For diameters greater than 4 in, assume rupture area equal to 20% of the pipe cross-sectional area. |
| Hoses | Assume full bore rupture. |

| | |
|--|---|
| Hoses | Assume full bore rupture. |
| Pressure relief devices relieving directly to the atmosphere | Use calculated total release rate at set pressure. Refer to pressure relief calculation. All material released is assumed to be airborne. |
| Vessels | Assume a rupture based on the largest diameter process pipe attached to the vessel. Use the pipe criteria. |
| Other | Incidents can be established based on the plant's experience, or the incidents can be developed from the outcome of a review or derived from hazard analysis studies. |
| Worst-case incidents ^b | |
| Quantity | Assume release of the largest quantity of substance handled on-site in a single process vessel at any time. To estimate the release rate, assume the entire quantity is released within 10 min. |
| Wind speed / stability | Assume F stability, 1.5 m/s wind speed, unless meteorological data indicate otherwise. |
| Ambient temperature / humidity | Assume the highest daily maximum temperature and average humidity. |
| Height of release | Assume that the release occurs at ground level. |

| | |
|----------------------------------|--|
| Topography | Assume urban or rural topography, as appropriate. |
| Temperature of release substance | Consider liquids to be released at the highest daily maximum temperature, based on data for the previous three years, or at process temperature, whichever is higher. Assume that gases liquefied by refrigeration at atmospheric pressure are released at their boiling points. |

The worst-case releases are those that assume almost catastrophic failure of the process, resulting in near instantaneous release of the entire process inventory or release over a short period of time.

The selection of the release case depends on the requirements of the consequence study.

If an internal company study is being completed to determine the actual consequences of plant releases, then the realistic cases would be selected.

However, if a study is being completed to meet the requirements of the EPA Risk Management Plan, then the worst case releases must be used.

Conservative Analysis

- All models, including consequence models, have uncertainties.
- These uncertainties arise because of
 - (1) an incomplete understanding of the geometry of the release (that is, the hole size),
 - (2) unknown or poorly characterized physical properties,
 - (3) a poor understanding of the chemical or release process, and
 - (4) unknown or poorly understood mixture behavior, to name a few.

Thanks

