LEAKS AND VENTING FROM PRESSURE VESSELS:
SIMULATIONS WITH RIGOROUS EVALUATIONS OF THE
THERMODYNAMIC PROPERTIES

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Abstract. This paper introduces a simulator for leaks and venting from pressure vessels. The simulator accounts for deviations from ideal gas behavior in all the required thermodynamic properties and individually considers all the chemical components present. Its development is based on the assumption that phase equilibrium is achieved instantaneously inside the vessel and, thus, the dynamics of the fluid in the vessel comprises a sequence of equilibrium states. The underlying mathematical problem is a system of differential-algebraic equations (DAE) in which the component mass balances and the energy balance are ordinary differential equations. The algebraic equations account for the phase equilibrium conditions inside the vessel and at the discharge point. Due to the size and complexity of the model, numerical solution is necessary. The simulator allows detailed predictions of the conditions inside the vessel and at the discharge point as a function of time, including the flow rate and composition of the discharge. These outputs are crucial pieces of information when planning for emergencies and studying containment alternatives. The paper shows conceptual applications of the simulator to predict the effect of leaks from vessels containing mixtures of light gases and/or hydrocarbons.

Keywords: Leaks, venting, pressure vessels.
1. Introduction

Discharges of hazardous chemicals can bring about serious consequences to populations living close to industrial units, in addition to financial losses. In some cases, the discharges are accidental, as in the case of leaks. In others, as in operations for pressure relief, they are intentional and aim to prevent further damage, such as the explosion of pressure vessels. In both cases, it is important to predict the flow and composition of the material discharged to the environment in order to plan measures of containment and remediation.

Due to the growing importance of this practical problem, there are various programs for the simulation of leaks and venting from pressure vessels (e.g., Woodward and Mudan (1990), Bendiksen et al. (1991), Richardson and Saville (1996), Mahgerefteh and Wong (1999), Cumber (2001), Witlox and Bowen (2002)). However, in order to simplify the formulation and shorten their execution time, many of them use approximations that increase the uncertainty of their predictions. Two of these approximations are that the fluid behaves as an ideal gas and that its chemical components can be lumped into a single pseudo-component.

This paper introduces a simulator for leaks and venting from pressure vessels that accounts for deviations from ideal gas behavior in all the required thermodynamic properties and individually considers all the chemical components present. The basis for its development is the assumption that phase equilibrium is achieved instantaneously inside the vessel and, thus, the dynamics of the fluid in the vessel comprises a sequence of equilibrium states. The underlying mathematical problem is a system of differential-algebraic equations (DAE) in which the component mass balances and the energy balance are ordinary differential equations. The algebraic equations account for the phase equilibrium conditions inside the vessel and at the discharge point. Due to the size and complexity of the model, numerical solution is necessary.

At each time step during the integration of the ordinary differential equations of the model, the values of the internal energy and component amounts inside the vessel become known. Since the vessel volume is known and fixed, the state of the fluid can be found by maximizing the fluid’s entropy. To compute the discharge conditions, the assumption is that the region inside the vessel close to the discharge point acts as an
adiabatic converging nozzle whose operation is isentropic. This leads to an unusual equilibrium problem with specification of fluid entropy and stagnation enthalpy (enthalpy plus kinetic energy). The model also accounts for the possibility of choked flow at the discharge point, in which case the fluid speed is equal to the local thermodynamic sound speed. Therefore, a procedure to compute the thermodynamic sound speed in systems with multiple phases is also part of the formulation.

The simulator allows detailed predictions of the conditions inside the vessel and at the discharge point as function of time, including the flow rate and composition of the discharge, which are crucial pieces of information when planning for emergencies and studying containment alternatives. The paper shows applications of the simulator to predict the effect of leaks from vessels containing hydrocarbon mixtures.

2. Assumptions

A set of assumptions underlies the development of the mathematical model of leak and vent operations from pressure vessels. A central one is that the fluid inside the vessel is in thermodynamic equilibrium at all times, and that properties such as temperature, pressure, and chemical potential of each component are the same everywhere within the vessel. In the absence of chemical reactions, as is the case considered here, this means that determining the state of the fluid within the vessel requires a phase equilibrium computation.

Another key assumption is related to finding the leak or vent flow rate, for which it is necessary to model the region in the vessel near the orifice. As usual in similar simulations, the assumption is that this region is a hypothetical converging nozzle that operates adiabatically and reversibly. As such, the flow in the converging nozzle is taken as isentropic. During leaks from vessels that contain condensed phases, the violent boiling caused by depressurization can swell the liquid phase, i.e., its level may rise because of bubble formation within the liquid. This effect is neglected under the assumption that there is instantaneous disengagement of the phases present.

With these assumptions, the mathematical model consists of a set of differential-algebraic equations (DAE). The mass and energy balances are ordinary differential
equations. However, to find the fluid properties inside the vessel, it is necessary to solve algebraic equations that represent the phase equilibrium conditions.

Furthermore, to determine the leak or vent flow rate, it is necessary to find several fluid properties at the fluid’s exit point from the vessel, namely, its temperature, pressure, number of phases with their amounts and compositions, and thermodynamic sound speed. The sound speed is relevant because it is the maximum achievable fluid speed at the exit of a converging nozzle. Flows at sonic speed are referred to as choked and the pressure at the exit point is larger than the backpressure, which is the environmental pressure away from the vessel. Flows below sonic speed are referred to as non-choked and the exit pressure is equal to the backpressure. An additional assumption is that the vessel’s construction material has negligible heat capacity.

3. Formulation

We consider storage vessels with no material input during the simulated time. The number of output streams is arbitrary and user-defined. The possibility of simulating the simultaneous discharge from more than one output stream is useful in situations such as the aperture of a relief valve followed by the opening of a bust disk. We consider vertical cylindrical vessels; if the phase volumes are known, it is simple to compute the level of the interfaces. By knowing these levels and the shape and position of the orifices, it is possible to determine the leaking phase at any given moment. This may change during the simulation. For example, at the beginning of a simulation, the liquid phase may leak but, as its level decreases, vapor may leave the vessel through the same orifice in later stages of the process. In this paper, we assume that the orifices are rectangular and their sizes remain constant during the simulated time. The differential mass balance of each component, written on a molar basis, is:

$$\frac{dn}{dt} = -\sum_{n=1}^{n_{out}} \dot{n}_{im}$$  

(1)
In Eq. (1), \( t \) represents time, \( n_i \) is the number of moles of component \( i \) in the vessel, and \( \dot{n}_{im}^{\text{out}} \) is the molar flow rate of component \( i \) in stream \( m \), which is one of the \( n_{s_{out}} \) streams that exit the vessel. The energy balance takes the form:

\[
\frac{dU}{dt} = -\sum_{m=1}^{n_{s_{out}}} \dot{n}_{m}^{\text{out}} \left( h_{m}^{\text{out}} + M_{m}^{\text{out}} \frac{u_{m}^{\text{out}}}{2} \right) + \dot{Q} \tag{2}
\]

In Eq. (2), \( U \) is the internal energy of the fluid in the vessel, \( \dot{Q} \) is the heat transfer to the fluid in the vessel, and \( h_{m}^{\text{out}} \), \( M_{m}^{\text{out}} \), and \( u_{m}^{\text{out}} \) are the molar enthalpy, molar mass, and speed at exit point \( m \). Because of the complexity of the algebraic computations to determine the state of the fluid in the vessel and at the exit point, the differential set comprised by Eqs. (1) and (2) does not have, in general, analytical solution. Therefore, it is necessary to employ a procedure for the numerical solution of ordinary differential equations and, in this work, the Bulirsch-Stoer method (Press et al., 1992) is used.

The numerical integration of Eqs. (1) and (2) provides the values of the number of moles of each component and of the internal energy of the fluid in the vessel, whose total volume is known. The knowledge of internal energy, volume, and component amounts is tantamount to the specification of a flash problem whose solution maximizes the entropy of the fluid. The flash algorithm proposed by Castier (2009) for this set of specifications is used. This algorithm is the first important algebraic element of the solution procedure.

The second important algebraic element of the solution procedure is the determination of the state of fluid exiting the vessel. With the assumption of steady-state and isentropic operation of a hypothetical converging nozzle, the mass balance around the nozzle is trivial. The energy balance equates the stagnation enthalpy (enthalpy plus kinetic energy) of the fluid at the entrance of the hypothetical nozzle and at its exit, which coincides with the fluid’s exit point from the vessel. In addition, the entropies at these two locations are equal. Hence, determining the state of the fluid at the exit point of the hypothetical nozzle involves finding the solution of a phase
equilibrium problem whose specifications are the component amounts, entropy, and stagnation enthalpy. An algorithm proposed recently by Castier et al. (2015) to that end is used. An important feature of this algorithm is that it begins with the assumption that the pressure at the exit point is equal to the specified value of the backpressure. If it turns out that the flow is supersonic under these considerations, the solution is invalid because the sound speed is the upper limit for flow speed at the exit of an adiabatic converging nozzle. When this happens, the problem is solved again relaxing the pressure specification and considering that the flow is sonic. It is therefore clear that the sound speed calculations play an important role on the overall computation path and they are the third major algebraic element of the simulator. Very importantly, they are occasionally necessary for systems with more than one phase if flashing conditions occur at the exit point. Few algorithms exist to this end. The procedure proposed by Castier (2011) for the calculation of thermodynamic sound speed in systems with any number of fluid phases is used in this work.

In summary, the formulation leads to DAE systems whose differential equations are the mass and energy balances in the leaking vessel. Three important sets of algebraic equations complete the problem formulation: (1) an entropy-maximization flash problem to determine the state of the fluid in the vessel; (2) a flash problem with specification of entropy and stagnation enthalpy, which is responsible for determining the exit conditions when paired with the third algebraic component, which is the (3) calculation of thermodynamic sound speed in multiphase systems.

The Peng-Robinson equation of state (Peng and Robinson, 1976) with binary interaction coefficients equal to zero is used to compute the thermodynamic properties, including the fugacity coefficients, residual internal energy, residual enthalpy, residual entropy, and thermodynamic sound speed, as well as their derivatives, as required by the phase equilibrium calculations. In this sense, the same thermodynamic model is used to evaluate all the thermodynamic properties of the fluid. This is different from most work in the field of process safety, which usually simplifies the evaluation of physical properties. The critical properties, acentric factor, and coefficients of a 3rd degree polynomial correlation in temperature for the molar ideal gas heat capacities are taken from Reid et al. (1987).
4. Results

This section shows simulation results of cases in which light gases or hydrocarbons are vented from vertical cylindrical vessels. The possible occurrence of chemical reactions is neglected in all cases.

4.1 Discharge of nitrogen or methane

This case illustrates the discharge of a nearly pure component, in the presence of a small amount of another, because the computational code is set-up to run for mixtures. The components used were nitrogen and methane. The vessel is adiabatic and has a volume of 1.0000 m$^3$, with height of 2.0000 m and diameter of 0.7979 m. A square-shaped orifice is used with edge sizes equal to 5.0x10$^{-3}$ m and a center located 1 m above the bottom of the vessel. The initial temperature of the fluid in its interior is 400 K. The vessel load consists of 79.99 moles of nitrogen and 0.01 moles of methane or vice-versa, hereafter referred to as pure nitrogen case and pure methane case, respectively. Figure 1 shows how the pressure inside the vessel drops as function of time until it becomes equal to the backpressure, which is specified to be equal to 0.10132 MPa. It is noticeable that the discharge of nitrogen takes longer, which is an outcome associated to the fluid speed at the exit point.

![Figure 1. Pressure in vessels loaded with either pure nitrogen or pure methane.](image)

Methane has larger molar heat capacity than nitrogen and its temperature drop is accordingly smaller.
**Fig. 2.** Temperature in vessels loaded with either pure nitrogen of pure methane.

Figure 3 shows the fluid and sound speeds at the point of discharge. For each compound, these speeds overlap in the beginning of the simulated time, until 38.7 s for methane and 40.5 s for nitrogen, meaning that the exit flow is sonic, i.e., choked. The plot also shows that the discharge speed of pure methane is faster than that of pure nitrogen, justifying the fact that the pressure in the methane vessel becomes equal to the backpressure before this happens in the nitrogen vessel (Fig. 1).

**Fig. 3.** Fluid and sound speed in vessels loaded with either pure nitrogen of pure methane.
Therefore, these results illustrate how two pure light compounds behave differently during a leak, even though there is only one phase inside the vessel and at the exit point for both of them throughout the simulated period.

Figure 4 shows the effect of increasing the orifice size to $1.0 \times 10^{-2}$ m by $1.0 \times 10^{-2}$ m, i.e., quadrupling its area compared to the previous situations. As expected, the times needed to equalize the vessel pressure and the backpressure are one-fourth of the times reported in Fig. 1.

![Graph showing pressure vs. time for pure nitrogen and pure methane](image)

**Fig. 4.** Pressure in vessels loaded with either pure nitrogen or pure methane: effect of larger orifice.

### 4.2 Discharge of nitrogen+methane mixture from heated vessel

This case considers the discharge of an equimolar mixture of nitrogen and methane from a vessel of the same size and shape as that of case 4.1. The vessel initially contains 40 moles of each compound at the temperature of 400 K. There is heat transfer to the fluid in the vessel at a rate of 1000 J/s. The vessel is initially closed and a relief valve ($5.0 \times 10^{-3}$ m by $5.0 \times 10^{-3}$ m, located 1.0 m above the bottom) opens when the pressure reaches 0.35 MPa. A second relief valve ($1.0 \times 10^{-2}$ m by $1.0 \times 10^{-2}$ m, located 1.5 m above the bottom) opens when the pressure reaches 0.40 MPa.

Figure 5 displays the pressure as function of time. It initially increases because the vessel is closed and there is heat transfer to the fluid. When the pressure reaches 0.35 MPa, the first of the relief valve opens. The effect appears as a change of slope in this pressure-time diagram. However, because of the small cross sectional area of the first
relief valve, the pressure keeps increasing after its opening. When the pressure reaches 0.40 MPa, the second relief valve opens. With a much larger cross sectional area, its opening causes a sharp pressure drop bringing the vessel pressure quickly down to the backpressure value.

![Pressure graph](image1)

**Fig. 5.** Pressure in vessel loaded with equimolar nitrogen+methane mixture: effect of two relief valves.

Figure 6 shows the fluid temperature during the simulated period. The opening of the first relief valve has little effect on the temperature but, when the second valve opens, it drops sharply.

![Temperature graph](image2)

**Fig. 6.** Temperature in vessel loaded with equimolar nitrogen+methane mixture: effect of two relief valves.
Figure 7 is a plot of the total molar amount within the vessel as function of time. The amount is initially constant and equal to 80 moles because the vessel is closed; it then undergoes a small decrease while the first valve relief is open but the second is closed, and finally decreases rapidly when both valves are open.

![Plot of total molar amount within the vessel](image)

**Fig. 7.** Amount within vessel loaded with equimolar nitrogen+methane mixture: effect of two relief valves.

Figure 8 shows the fluid and sound speeds in the relief valves. The first relief valve opens at about 293 s of simulated time. Between this time and the time the second valve opens, at about 795 s, the flow is sonic and of increasing velocity. Shortly after the opening of the second valve, at about 815 s, the flow becomes subsonic. It should be noted that the flow and sound speeds in the two valves, when both are open, is identical. This happens because there is only one phase within the vessel at all times and, therefore, the properties of the fluid vented through both valves are equal.
Fig. 8. Fluid and sound speed in vessel loaded with equimolar nitrogen+methane mixture: effect of two relief valves.

4.3 Discharge of nitrogen: comparison with experimental data

Véchot (2006) measured temperature and pressure during the discharge of nitrogen from a 0.0107 m³ vessel initially at 0.3612 MPa and 293.67 K through an orifice whose area is equal to 1.1310x10⁻⁶ m². To match these specifications, the initial amount of nitrogen in the simulation is equal to 1.585 moles of nitrogen (and 0.001 moles of methane because the computational code is designed to run for mixtures).

For an adiabatic vessel, the fluid temperature would decrease from the beginning until the end of the experiment. The experimental data show that there is a minimum in temperature equal to 274.73 K at 58 s. The nitrogen temperature increases after that, indicating that there is heat transfer to the fluid in the vessel. Correlations for the prediction of heat transfer coefficients are unavailable in the existing version of the simulator and, therefore, it is currently unfeasible to use it for a detailed simulation of this venting process. Instead, the discharge was simulated with a constant heat transfer rate to the fluid (equal to 41 J/s) so that the simulated temperature exhibits the same minimum value, which occurs at 28.9 s of simulated time. The ratio of the simulated and experimental times for the minimum in temperature, equal to 0.50, was interpreted as a practical coefficient of discharge for this venting process. While this value is somewhat smaller than typical coefficients of discharge for orifices, it is acceptable given the approximate nature of the comparison done here.
Figures 9 and 10 display the pressure and temperature profiles. The experimental data are plotted against the measured time. The calculated data are plotted against a rescaled time equal to the simulated time divided by the coefficient of discharge of 0.50. The plots end at 58 s, when the minimum in temperature occurs. The experimental and calculated results are in acceptable agreement during this period. Beyond it, the disagreement between the two results increases, especially for temperature, because of the crude approximation adopted for the heat transfer rate.

**Fig. 9.** Pressure in vessel loaded with nitrogen: comparison of experimental and calculated values.

**Fig. 10.** Temperature in vessel loaded with nitrogen: comparison of experimental and calculated values.
4.4 Discharge of a two-phase n-hexane+n-octane mixture

This case simulates the discharge of an equimolar mixture of n-hexane+n-octane from an adiabatic vessel whose volume is 0.7894 m$^3$, with height of 1.0000 m and diameter of 1.0000 m. The orifice is 3.545x10^{-3}m by 3.545x10^{-3}m, centered 0.5 m above the vessel’s bottom. The initial temperature of the fluid in its interior is 400 K. The load consists of 100 moles of each component. This section presents results of two cases with different initial fluid temperatures, equal to 450 K and 460 K. In both of them, the fluid has two phases inside the vessel at the beginning of the simulated period. However, the liquid level is low and the leak is from the vapor phase at all times.

Figures 11 and 12 show the evolution of pressure and temperature in the vessel as function of the simulated time. For the initial temperature of 450 K, the fluid in the vessel has two phases throughout the simulated period. However, for the initial temperature of 460 K, the fluid has two phases up to only about 670 s, when the liquid phase disappears from the vessel. In Fig. 12, the liquid phase disappearance coincides with the change in slope of that occurs at about 670 s in the curve that represents the system evolution from the initial temperature of 460 K.

![Fig. 11. Pressure in vessel loaded with equimolar n-hexane+n-octane mixture: effect of initial vessel temperature.](image)
**Fig. 12.** Temperature in vessel loaded with equimolar n-hexane+n-octane mixture: effect of initial vessel temperature.

Figure 13 shows the temperature at the exit point for the two simulated cases. Comparing Figs. 11 and 13, it is clear that the temperature at the exit point is smaller than in the vessel at any given time. For example, at the beginning of the simulation, the temperature at the exit point is about 10 K smaller than the temperature inside the vessel. The curve for the initial vessel temperature of 450 K (solid line in Fig. 13) has a change of slope at about 960 s, which coincides with the transition from sonic to subsonic flow at the exit point. The curve for the initial vessel temperature of 460 K (dotted line in Fig. 13) exhibits two changes of slope. The first of them occurs at about 670 s and is a consequence of the liquid phase disappearance from the vessel. The second one occurs at about 980 s, when the exit flow becomes subsonic.

Figure 14 displays the instantaneous leak flow rates of n-hexane and n-octane as function of time for the initial fluid temperature of 450 K. Because the leak is from the vapor phase, the exit flow rate of n-hexane is larger than that of n-octane at the beginning of the simulation, thus n-hexane depletes faster. At about 940 s, the flow rates of the two components become equal. After that, until the end of the simulated time, the flow rate of n-octane is larger.

This case illustrates the simulator’s ability of dealing with the change to the number of phases present in the vessel and its effect on the properties of the exiting stream.
5. Conclusions

This work presented the results of a simulator for leaks and venting from pressure vessels that contain non-reactive mixtures. The particular feature of this simulator is that it evaluates all the thermodynamic properties using the same equation of state, including phase equilibrium conditions, calorimetric properties, and derivative properties, such as the sound speed.
The conceptual and sensitivity analyses reported here demonstrate that the simulator predicts meaningful trends for the complex phenomena that take place during a leak or venting operation. The comparison with the experimental data for the discharge of nitrogen from an adiabatic vessel points out the need for the use of a coefficient of discharge. Once this is incorporated, the calculated and experimental results exhibit good agreement. Work is in progress to compare the results of the simulator to additional experimental data for vessel venting at controlled conditions.

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