EQUATIONS FOR GAS RELEASING PROCESS FROM PRESSURIZED VESSELS IN ODH EVALUATION

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ABSTRACT

The evaluation of Oxygen Deficiency Hazard (ODH) is a critical part in the design of any cryogenic system. The high-pressure gas tank or low-temperature liquid container that contain asphyxiated fluid could be the sources to bring about the oxygen deficiency hazard. In the evaluation of ODH, the calculation of the spill rate from the pressurized vessel is the central task. The accuracy of the engineering estimation becomes one of the safety design issues. This paper summarizes the equations for the oxygen concentration calculation in different cases, and discusses the equations for the gas release process calculation both for the high-pressure gas tank and the low-temperature liquid container. Some simplified formulas for engineering estimation are presented along with the theoretical background that involves the process analyses under variable mass, variable pressure and variable temperature.

INTRODUCTION

The use of compressed gases, liquefied gases, and volatile liquids is commonplace in cryogenic plants. Introduction of these gases to the atmosphere can present an oxygen deficiency hazard. Air normally contains about 21% oxygen with the remainder consisting mostly of nitrogen. Individuals exposed to reduced-oxygen atmosphere may suffer a variety of harmful effects, including unconsciousness or death. Therefore, the calculation of ODH classification is required for any building enclosing equipment that may release cryogenic or pressurized gases. The lowest possible oxygen concentration in these enclosures must be estimated. The gas release process at high pressure and low temperature is a thermodynamic process that involves transient fluid flows with heat and mass transfer. Computational simulations can provide detailed information to reveal the mechanism of the process, which have been used in the design of the cryogenic plants at Brookhaven National Laboratory. However, in the engineering practices of the field and in the safety design codes and standards, the simplified equations to evaluate the gas release process are
still the measure of the scale of the ODH [1-3]. These equations are simple and easy to apply and can provide a quick answer in the first order for most cases. Furthermore, they have been adopted in some safety design manuals of the cryogenic systems even though some of the equations are not defined in the technical standards of the engineering societies. The establishment of the accepted safety design codes requires a legislative process. As a technical point of view, the following sections collect the equations in the field and discuss the physical implications as well as their limitations. The engineering examples are given at the end of the paper.

EQUATIONS FOR OXYGEN CONCENTRATION

Some equations for oxygen concentration, based on volume fraction in the confined space during an inert gas release from the pressurized vessel, have been widely cited in the safety design manuals in the national laboratories. These equations may be summarized in the following different cases to follow the conventional format. For each case, the differential equation and its integration at certain condition are given, which is based on the oxygen mass balance in the control volume. The assumptions are

1. Complete and instantaneous mixing takes place in the confined space.
2. Pressure in the confined space remains constant and is near atmospheric pressure through the louvers or natural leakage.
3. Gas entering the confined space from outside is air.

In the following equations, \( C \) is the oxygen concentration in the confined space by volume fraction; \( C_{air} \) is the oxygen concentration in air by volume fraction (21%); \( V \) is confined volume, m\(^3\); \( Q \) is the ventilation volume rate of fans, m\(^3\)/sec; \( \dot{R} \) is gas spill rate, m\(^3\)/sec; and \( t \) is time, sec.

**Case I** For \( \dot{Q} > \dot{R} \) and \( \dot{Q} - \dot{R} > 0 \),

\[
\begin{align*}
\dot{R} &\quad \frac{dC}{dt} = (\dot{Q} - \dot{R})C_{air} - \dot{Q}C \\
\dot{Q} &\quad = \dot{R} > 0
\end{align*}
\]

if \( \dot{R} = \text{const.} \) and \( \dot{Q} = \text{const.} \), then

\[ C(t) = C_{air} \left( 1 - \frac{\dot{R}}{\dot{Q}} \right) + \left[ C_{in0} - C_{air} \left( 1 - \frac{\dot{R}}{\dot{Q}} \right) \right] \left( \frac{\dot{Q}}{\dot{V}} \right) e^{-\frac{\dot{Q} t}{\dot{V}}} \]  

**Case II** For \( \dot{Q} < \dot{R} \) and \( \dot{Q} - \dot{R} < 0 \),

\[
\begin{align*}
\dot{R} &\quad \frac{dC}{dt} = (\dot{R} - \dot{Q})C - \dot{Q}C = -\dot{R}C \\
\dot{Q} &\quad = \dot{R} < 0
\end{align*}
\]

if \( \dot{R} = \text{const.} \) and \( \dot{Q} = \text{const.} \), then

\[ C(t) = C_{in0} e^{-\frac{\dot{R} t}{\dot{V}}} \]  

**Case III** For \( \dot{Q} = \dot{R} \) and \( \dot{Q} - \dot{R} = 0 \),

\[
\begin{align*}
\dot{R} &\quad \frac{dC}{dt} = \dot{Q}C \\
\dot{Q} &\quad = \dot{R} = \text{const.}
\end{align*}
\]

if \( \dot{Q} = \dot{R} = \text{const.} \), then

\[ C(t) = C_{in0} e^{\frac{\dot{Q} t}{\dot{V}}} \]
Case IV  For $\dot{R} = 0$ and $\dot{Q} > 0$

\[
C(t) = C_{l=0} e^{\left(\frac{\dot{Q}}{\nu}\right)t}
\]  \hfill (6)

Case V  For $\dot{R} > 0$ and $\dot{Q} = 0$

\[
\dot{R} \frac{dC}{dt} = -\dot{R} C
\]  \hfill (9)

Case VI  For $\dot{R} > 0$ and $\dot{Q} > 0$

\[
\dot{R} \frac{dC}{dt} = \dot{Q} C_{air} - (\dot{R} + \dot{Q}) C
\]  \hfill (11)

\[
C(t) = C_{l=0} - \frac{\dot{Q}}{\dot{R} + \dot{Q}} \left[ C_{l=0} e^{\left(\frac{\dot{Q}}{\nu}\right)t} - C_{air} \right] e^{\left(\frac{\dot{Q}}{\nu}\right)t}
\]  \hfill (12)

FIGURE 1. Numerical examples for the cases defined by the equations 2, 4, 6, 8, 10, and 12.
FIGURE 1 provides the numerical examples for each case. In the calculation, the volume of the confined space is 10 m³. The gas spill rate and the fan ventilation rate are indicated in each figure. It must be noticed that, the direction of the fan blowing makes some difference that is shown by comparing the figures for Case I and Case VI.

ESTIMATION OF GAS RELEASING RATE

To calculate the oxygen concentration by using the above equations, one must determine the releasing rate from a gas or liquid container. There are some conventional methods to model the gas discharge process from rigid pressurized vessels. In general, there are two kinds of situations, one is the gas discharge process through an accidental puncture or a leak in the vessel, and the other is the controlled process through the pressure relief devices, such as spring-loaded relief valves or burst discs. The gas release process is a transient phenomenon and the mass flow rate varies with the changes in temperature and pressure of the fluid flows. However, in certain cases, the process may be simplified into the classical models that are well established in the Gas Dynamics. One can model the opening of a leak or the pressure relief device as converging flow passage with a minimum discharge flow area. The flow can be identified as the critical (choked) or sub-critical (non-choked) flow by comparing the ratio of ambient pressure to the internal pressure of the container with the critical pressure ratio,

\[
\frac{P^*}{P_0} = \left( \frac{2}{\gamma + 1} \right)^{\gamma/(\gamma - 1)}
\]

where \(P^*\) is the critical pressure at which the flow at nozzle exist is sonic. \(P_0\) is the stagnation pressure and equal to the internal pressure of the container if the flow is modeled as isentropic one. \(\gamma\) is the specific heat ratio of fluid. For example, for helium, \(\gamma = 1.659\) and \(P^*/P_0 = 0.488\). The corresponding minimum internal pressure for a choking flow is 2.05 atm for helium. For the choked isentropic flow the mass flow rate through an opening is fixed.

Mass Flow Rate In Sub-Critical Isentropic Discharge

Assuming the one-dimensional steady flow of a perfect gas, for a sub-critical isentropic flow at constant ambient pressure, the mass flow rate, \(\dot{m}_s\), during the discharge process may be given as follows [4],

\[
\dot{m}_s = \frac{P_0 A_t}{\sqrt{\gamma R T_0}} \left\{ \frac{2\gamma^2}{\gamma - 1} \left( \frac{P_1}{P_0} \right)^{\frac{\gamma}{\gamma - 1}} \left[ 1 - \left( \frac{P_1}{P_0} \right)^{\frac{\gamma - 1}{\gamma}} \right] \right\}^{\frac{1}{2}} = \frac{\rho P_0 A_t}{\sqrt{\gamma R T_0}}
\]

where, \(P_0\) and \(T_0\) are the stagnation pressure and stagnation temperature, respectively; \(A_t\) is the minimum flow area; \(P_1\) is the static pressure of gas at the opening; \(R\) is the gas constant.

Mass Flow Rate In Critical Isentropic Discharge
For a choked isentropic discharge, assuming the one-dimensional steady flow of a perfect gas, the critical mass flow rate through an opening of the leak or the relief device may be given as follows,

$$m_c = \frac{\Gamma P_0 A}{\sqrt{\gamma RT_0}}, \quad \Gamma = \gamma \left( \frac{2}{\gamma + 1} \right)^{\frac{\gamma + 1}{2(\gamma - 1)}}, \quad \frac{P_\infty}{P_0} \leq \left( \frac{2}{\gamma + 1} \right)^{\frac{\gamma}{\gamma - 1}}$$  \hspace{1cm} (15)

where $P_\infty$ is ambient pressure. The choking flow condition is determined by pressure ratio.

The equation 15 shows in a different form as given by the national standards and codes for sizing the relief valves [5-6]. It must be noticed that the stagnation parameters in the equations 14 and 15 may not be the same as the stagnation parameters of the gas in the container. The releasing process through a long pipe may cause the stagnation pressure drop, even though the flow can be modeled as the adiabatic flow in a pipe installed in the vacuum insulated space. The discharge coefficient of 0.8-0.9 is commonly used in the calculations for the pressure loses. The cryogenic systems often involves violent heat transfer, the heating to the pipe that has a relief valve at the exiting end will reduce stagnation pressure and increase the stagnation temperature of the fluid. This requires a larger cross section area of a relief valve. The worst-case scenario assumption must be applied for sizing the safety relief device in a cryogenic system, for example, the ambient temperature is used in the calculation.

In order to size the relief valve for a cryogenic system, to determine the minimum cross section area using the above equations, the mass flow rate, $m_c$, must be provided. In some cases, the mass flow rate may be correlated with heat flux to the dewar, as $m_c = \dot{q}/h_f$, where $\dot{q}$ is the heat load, and $h_f$ is the latent heat of the cryogen. The heat load could vary under different circumstances, including the loss of vacuum by air or other gases in the cryogenic system, the fire adjacent to the cryogenic system, and the quench heating in the superconducting magnet system. For a helium dewar, the equation for the diameter of the opening in a relief valve, $D_t$, is given as,

$$D_t = \left( \frac{4\dot{q}(\gamma RT_0)^{0.5}}{\pi h_f \Gamma P_0} \right)^{0.5}$$ \hspace{1cm} (16)

FIGURE 2 shows the examples for sizing the diameter of an opening with respect to the stagnation temperature and the heat load in a helium system by equation 15 and 16. The mass flow rate of 1.0 g/s and the stagnation pressure of 3.0 atm are used in FIGURE 2a.

![FIGURE 2a. Size of opening vs. stagnation temperature for helium by equation (15).](image)

![FIGURE 2b. Size of opening vs. heat load for helium system, by equation (16).](image)
The stagnation temperature of 300 K and the stagnation pressure of 3.0 atm are used in the FIGURE 2b.

**Transient Mass Flow Rate In Critical Isentropic Discharge**

The change of stagnation temperature and pressure in the pressurized gas container during the gas releasing process leads to the variable spill rate. For a critical isentropic releasing flow, the time-dependent functions of the pressure, temperature and mass flow rate could be obtained for the process through an opening of puncture or a relief device of a pressurized vessel [4].

For mass conservation, the rate of mass flowing out of the opening is equal to the rate of decrease of mass in the vessel. For a choked isentropic flow, equation 15 yields

\[ \dot{m}_r(t) = \frac{\Gamma P_0(t) A_i}{\sqrt{\gamma R T_i}} \left( \frac{P_i}{P_0(t)} \right)^{(\gamma-1)/\gamma} \text{, where } \frac{P_0(t)}{P_i} = \left( \frac{T_0(t)}{T_i} \right)^{\gamma/(\gamma-1)} \]  

(17)

\[ \dot{m}_e(t) = \frac{d}{dt} \left( \frac{P_0(t) V}{R T_i(t)} \right) = \frac{V P_i^{(\gamma-1)/\gamma} P_0(t)^{(\gamma-1)/\gamma}}{\gamma R T_i} \frac{dP_0}{dt} \]  

(18)

Combining equation 17 and 18 and integrating between the limits \( P = P_i \) when time \( t = 0 \), the result is

\[ P_0(t) = \frac{P_i}{\left[ 1 + \left( \frac{\gamma-1}{2\gamma} \right) \left( \frac{RT_i}{P_i} \right)^{1/2} \left( \frac{A_i}{V} \right)^{1/2} \right]^{2\gamma/(\gamma-1)}} \]  

(19)

\[ T_0(t) = T_i \left( \frac{P_0(t)}{P_i} \right)^{(\gamma-1)/\gamma} \]  

(20)

\[ \dot{m}_r(t) = \frac{\Gamma A_i P_0(t)}{\sqrt{\gamma R T_0(t)}} \]  

(21)

\[ M_e(t) = \frac{V P_i^{(\gamma-1)/\gamma} P_0(t)^{\gamma} \gamma}{RT_i} \]  

(22)

**FIGURE 3** shows the example plots for a leak in helium gas tank, which has a leak opening diameter of 10 mm, tank volume of 10 m³, initial internal pressure of 10 atm, and initial temperature of 300 K.

![FIGURE 3a. Pressure ratio by equation (19).](image1)

![FIGURE 3b. Temperature ratio by equation (20).](image2)
CONCLUSION

Analyses on gas releasing process for the ODH evaluation require the computational simulation. However, this will take extensive effort to model the complicated events such as those in the cryogenic systems even using the commercial software packages. Therefore, the simple equations such as that discussed in this paper are still used by many engineers in the field. Some of the equations have been adopted in the safety manuals by the national laboratories. These equations have been evaluated at BNL for different cases in the design practice of the cryogenic plants. The results from these equations provided the first order estimation and helped to get reasonable understanding in some complicated cases. The examples given in much simplified cases presented in the paper are attempted for the engineer’s tastes.

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REFERENCES

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