STORAGE AND DISCHARGE CHARACTERISTICS OF HALON ALTERNATIVES

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ABSTRACT

Three important issues regarding the use of halon alternatives for in-flight fire protection applications were studied as part of the current halon alternative research program at the National Institute of Standards and Technology (NIST): (1) the conditions inside the vessel at different ambient temperatures before discharge, (2) the discharge of the contents into a confined space, and (3) the distribution of the agent/nitrogen mixture in piping systems. The first issue addresses the resultant pressure inside the vessel before discharge. Such information dictates the vessel structural integrity and subsequent discharge behavior of the agent/nitrogen mixture. The second deals specifically with military aircraft dry bay fire protection, and the third concerns general (commercial and military) aircraft engine nacelle fire protection applications. To establish the internal vessel conditions, the effects of fill density, initial nitrogen pressure, and ambient temperature were studied. For the discharge of agent/nitrogen mixture into a confined space, the effects of vessel geometry, initial nitrogen pressure, fill density, initial vessel temperature, discharge mechanism, discharge orientation, and orifice size were examined. For the distribution of agent/nitrogen mixture in piping systems, the effects of initial nitrogen pressure, fill density, initial bottle temperature, and piping geometries (sudden pipe expansion and contraction, different piping diameters, tees, and elbows) on the two-phase flow behavior were explored. Experimental results and model predictions will be presented and discussed for each issue.

INTRODUCTION

Current aircraft fire suppression bottles for dry bay and engine nacelle applications, which are designed to meet Military Specification MIL-C-22284A (proof pressure of 9.62 MPa and minimum burst pressure of 12.37 MPa), are normally filled with liquid halon 1301 (CF_3Br) to about half of the bottle volume, and the bottle is then pressurized with nitrogen to a specified equilibrium pressure (typically 4.1 MPa) at room temperature. The purpose of using the pressurization gas is to expedite the discharge of the agent and to facilitate the dispersion of the agent. Without nitrogen pressurization, the bottle pressure, which is simply the vapor pressure of the agent, can be very low at extremely cold conditions so that there is virtually no driving force to expel the agent from the bottle in case of a fire, thus hindering a rapid release of the mixture. Due to pressurization, nitrogen is dissolved in the liquid agent, and the presence of dissolved nitrogen complicates the discharge process in that the fluid leaving the vessel is not pure halon but a mixture of halon and nitrogen mixture. The degassing of the dissolved nitrogen, *i.e.*, the dissolved nitrogen will come out of the liquid in the form of bubbles, will occur inside the vessel during discharge (depressurization).

In this paper, the issues which are pertinent to agent storage and its subsequent discharge will be addressed in detail. This paper focuses on the four selected agents (HFC-125, FC-218, CF_3I, and HFC-227ea) for the two applications (dry bays and engine nacelles).

STORAGE CHARACTERISTICS

The total pressure in the bottle is a complex function of ambient temperature because of the temperature dependence of the agent vapor pressure, the partial pressure of nitrogen in the gas ullage, and the solubility of nitrogen in the liquid agent. For halon 1301, the bottle pressure-temperature relationship and the solubility of nitrogen in halon 1301 have been well characterized. By contrast, such a relationship and solubility data are scarce or do not exist for some of the halon alternatives.

The storage characteristics herein refer to the initial and final thermodynamic states of the vessel. In order to establish the initial conditions of the vessel, the following pieces of information need to be known or determined: (1) the amount of nitrogen required to pressurize the vessel to the equilibrium pressure, (2) the initial temperature of the vessel, (3) the amount of agent in the vessel, and (4) the vessel volume. The final thermodynamic state of the vessel corresponds to the conditions (more specifically, pressure) inside the vessel when the vessel is exposed to different ambient temperatures.

The major objectives of this study were to determine the initial and final conditions of the vessel, given certain initial constraints (*e.g.*, fixed amount of agent and initial temperature being room temperature). Specifically, the objectives were to measure the amount of nitrogen that was needed to pressurize the bottle to a specified equilibrium pressure and to determine the final pressure of the bottle when the bottle, filled with either a pre-determined amount of pure agent or with agent pressurized with nitrogen, was exposed to two extreme temperatures (− 60 °C and 150 °C). Experiments on pure agents were also performed in order to obtain pressure-temperature relationships for some of the agents (especially CF_3I) where documented data were not readily available.

The experimental apparatus basically consists of: a pressure vessel; means to evacuate the vessel, to dispense the liquid agent, and to pressurize the vessel with nitrogen; a pressure transducer; a thermocouple; and a constant cold temperature bath to chill the vessel or a temperature-controlled oven to heat the vessel to the desired final temperature. Details of the experimental set-up and procedure can be found in Yang *et al.* (1995).

In order to assimilate the experimental results into useful engineering correlations that could be easily used by the bottle designers, a computer code that could facilitate such calculations was developed. The thermodynamic properties of agent/nitrogen mixtures are modeled using a computer program PROFISSY (acronym for Properties Of Fire Suppression Systems). The program incorporates a model known as "extended corresponding states" (ECS) (*e.g.*, see Huber and Ely, 1994). The ECS model is a powerful tool, applicable to the entire range of fluid states, from dense liquid to dilute gas, as well as to the supercritical fluid regime. It may be used with only minimal information on a fluid: the critical point, the normal boiling point, and the molecular weight. Additional information on a fluid, such as vapor pressures, saturated liquid densities, and liquid viscosities can be used to refine the model predictions.

The central idea of extended corresponding states is that all points on the *PVT* surface of any fluid may be represented by scaling the *PVT* surface of a reference substance. These "scale factors" involve the critical properties of the fluid of interest and the reference fluid and may also be functions of temperature and density.

The computer code PROFISSY was developed for the primary purpose of helping fire suppression bottle designers or users to obtain temperature-pressure characteristics of bottle contents. In other words, given a vessel charged with agent and nitrogen at room temperature, one would like to know what the final vessel pressure will be when the vessel is exposed to a different temperature. Only four pieces of information are required to run the program: (1) agent mass, (2) vessel volume, (3) fill temperature, and

(4) either nitrogen mass needed to pressurize the vessel, or the fill pressure of the vessel. Only the information which is pertinent to the problem is provided in the output although the computer program can perform other thermodynamic property calculations.

Experimental data have been obtained to validate and compare to the model predictions. The measured amount of nitrogen required to pressurize the vessel to a specified equilibrium pressure at room temperature with a specified amount of agent in the vessel compares favorably with the predictions and differs from the predicted value by 10 % or less. The measured final pressures of the vessel when exposed to the two extreme temperatures (− 60 °C and 150 °C) were also found to be within 10 % or less of the predicted values. However, the model tends to underestimate the final pressures at 150 °C in some cases.

In addition, the experimental data show that the resulting vessel pressures, when used with the selected four agents (under initially half or two-thirds filled volume) and exposed to 150 °C, are greater than the design pressure stipulated in the current Military Specification MIL-C-22284A (proof pressure of 9.62 MPa and minimum burst pressure of 12.37 MPa).

DISCHARGE CHARACTERISTICS

(a) Dry Bay Applications

The main objective of this task was to study the discharge characteristics of the three selected agents, HFC-125, FC-218, and CF_3I (CF_3Br was also included as a reference), in an unconfined space to simulate a dry bay (without airflow and obstacles) under various experimental conditions.

The simulated dry bay was essentially a room with dimensions of 3 m (width) x 3 m (length) x 3.4 m (height). No clutter or obstacles were placed in the flow path of the flashing spray. Figure 1 shows a schematic of the experimental apparatus. Three pressure vessels (a cylindrical, a spherical, and a cylindrical with sight gages) were used in this study. The temporal variations of the pressure inside the vessel were monitored during discharges. Four types of release mechanisms were also used: two solenoid valves, a pyrotechnic piston-actuated valve, and a squib. The five lasers and photodiode detectors shown in the figure were used to measure the average dispersion velocities of the leading edge of the evaporating spray propagating downstream from the vessel exit. The measurement technique was based on the principle of laser attenuation, details of which can be found in Grosshandler *et al.* (1994). A piezoelectric dynamic pressure transducer oriented normal to the flow direction was placed along the centerline of the valve outlet at a downstream position of approximately 1.4 m and was used to measure the impact pressure and to obtain some qualitative two-phase behavior of the flashing spray. A high-speed movie camera operating at 2000 frames per second was used to document the flashing behavior of agent/nitrogen mixtures at the exit of the vessel and the events occurring inside the vessel during discharge when the cylindrical vessel with sight gages was used. The experimental sequence was controlled by a timing circuit.

The effects of several experimental parameters on the discharge characteristics were examined. These parameters included the following: (1) discharge orifice size, (2) initial amount of agent, (3) nitrogen charge pressure, (4) initial temperature of agent, (5) discharge orientation, and (6) degree of nitrogen saturation in the liquid agent.

The visual observations made in this study by using the cylindrical vessel with sight gages and high-speed photography revealed the following phenomena. For CF_3Br, HFC-125, and FC-218, the liquid agent/nitrogen mixture remained clear for a short duration (~ 5 ms) after the initiation of the discharge. This duration was found to be agent dependent, with CF_3Br the shortest and FC-218 the longest. During this period, the receding liquid/vapor interface was clearly visible. The interior of the vessel as seen through the sight gages then became completely foggy, and the liquid/vapor interface was no longer visible. It was not possible to determine from the movies whether the fogginess prevented the observation of the liquid/vapor interface or the degassing of the dissolved nitrogen induced frothing of the liquid mixture throughout the vessel, thus causing the liquid/vapor interface to disappear. The fogginess was sustained for a period of time during which the liquid mixture was assumed to be completely discharged. The sight gages on the vessel then became clear once again. This fogginess is *conjectured* to be due both to vapor condensation as a result of cooling by the adiabatic expansion of the ullage vapor, and the evolution of the dissolved nitrogen as bubbles in the liquid mixture. The existence of the nitrogen bubbles could not be visually confirmed from the high speed movies due to the limited spatial resolution of the pictures. For CF_3I, the receding liquid/vapor interface and the liquid mixture remained clear for a relatively long time (for at least half of the liquid discharge period) after the initiation of the discharge. The fogginess then appeared throughout the vessel, and the liquid/vapor interface vanished. The interior of the vessel became clear again after a period of fogginess. It was postulated that nitrogen degassing did not occur in the CF_3I/nitrogen mixture.

The flashing behavior of the spray at the vessel exit was noted for all the agents during discharges. Regardless of the release mechanism, the general appearances of the flashing sprays (other than the spray angles) were also observed to be very similar.

A complete set of the experimental results and detailed discussion can be found in Yang *et al.* (1995). Only some of the important observations will be discussed in the following. Figure 2 shows a comparison of the pressure decay curves (non-dimensionalized using the initial pressure P_i) for all the agents inside the vessel during discharges at room temperature. Several sequential events occurring inside the vessel were postulated by these pressure traces. In the case of CF_3Br, HFC-125, and FC-218 discharges, when the release valve was activated, there was a short duration during which the pressure continuously decreased, and the liquid agent/dissolved nitrogen mixture was discharged as a superheated liquid. Nitrogen remained dissolved in the liquid agent as a non-equilibrium supersaturated solution, and the liquid/nitrogen mixture remained a clear solution. As the pressure inside the vessel decreased further, degassing of dissolved nitrogen in the solution occurred. Once the bubbles nucleated, the dissolved nitrogen quickly came out of the solution into the bubbles causing the bubbles to grow. Due to rapid bubble expansion, the liquid level swelled, and the rising bubbles disengaged from the vapor-liquid interphase thus releasing nitrogen into the ullage. As a result, the ullage was compressed to a higher pressure noted as a short transient pressure recovery in the pressure decay history. The pressure then began to decrease again until an inflection point in the pressure decay curve was reached. A low quality (defined as the fraction of the mass flow rate which is gas) bubbly two-phase agent/nitrogen mixture was assumed to be discharged from the vessel during this time interval. The inflection point indicated the depletion of the low quality two-phase mixture and the initiation of the discharge of the ullage gas mixture (agent vapor and nitrogen) from the vessel. In Figure 2, the pressure recovery near the end of the CF_3I discharge is an artifact caused by the dynamic pressure transducer. In addition, the initial pressure recovery, an indication of nitrogen degassing, in the pressure decay curve of CF_3I is absent. It is clear that different agents exhibit different discharge rates and degassing characteristics. The pressure decay curves reflect how fast these agents are discharged. CF_3I discharges the fastest, and CF_3Br the slowest. These observations were also confirmed qualitatively by the high-speed movies.

Figure 3 summarizes the average dispersion velocities of the spray obtained by the laser attenuation technique. The dispersion of CF_3I has the slowest average downstream velocities. All other agents have similar but higher spray dispersion velocities than CF_3I.

Based on the experimental observations, a model that predicts the discharge times of an agent under various experimental conditions is proposed. The model, under certain assumptions, can predict the occurrence or the non-occurrence of degassing. Detailed formulation of the model is given in Yang *et al.* (1995). Only a qualitative description of the model and the underlying assumptions are presented here.

The discharge configuration of the vessel is assumed to be vertically downward, *i.e.*, the liquid mixture will be discharged first, followed by the ullage vapor mixture. During discharge, no heat and mass transfer between the liquid and the vapor phases is assumed to occur. The liquid is assumed to undergo an isothermal depressurization during discharge, and the degassing of dissolved nitrogen is modeled by homogeneous nucleation theory, as described in Forest and Ward (1977). The occurrence of degassing is determined by comparing the ullage pressure to the calculated homogeneous bubble nucleation pressure during the liquid discharge period. If the ullage pressure at some instant in this time interval is equal to or less than the homogeneous nucleation pressure, degassing is assumed to occur. When no degassing is predicted by the homogeneous nucleation theory, *i.e.*, during the liquid discharge period the ullage pressure never goes below the homogeneous nucleation pressure, the discharge is modeled as a two-step process, a superheated liquid discharge followed by an emptying of ullage vapor. When degassing occurs, the model is formulated as a four-step process, a superheated liquid discharge followed by swelling of the liquid level due to degassing, discharge of an incompressible, homogeneous, frozen two-phase mixture, and finally a vapor discharge. The control volume under consideration is the ullage above the liquid and is assumed to be an adiabatic closed system. Furthermore, due to the rapidity of the discharge, the ullage expansion or momentary compression (caused by degassing) is assumed to be *isentropic*.

Consistent with the experimental observations, the model predicts the non-occurrence of nitrogen degassing under certain experimental conditions and during CF_3I/nitrogen discharges. Despite all the simplified assumptions used and the uncertainties associated with the estimation of the thermophysical properties in the homogeneous nucleation pressure calculations, the model can still estimate the discharge times within a factor of four (usually better) when compared to the experimental data. Further refinement of the model is needed in order to improve the predictability of the model.

(b) Engine Nacelle Applications

Three potential near-term halon alternatives for engine nacelle fire protection applications have been identified by the Technology Transition Team (Grosshandler *et al.*, 1994): HFC-227ea, CF_3I, and HFC-125. In engine nacelle applications, the fire suppression agent is located remotely from the nacelle and a piping system delivers the agent to the nacelle injection location(s). It is crucial to deliver the proper amount of agent in a timely manner to achieve the desired agent concentration in the nacelle for the required time interval. The flow regime in the piping is characteristically a two-phase, two-component gas/liquid system. Since no universally accepted flow prediction method is available for two-phase flows, an experimental study was undertaken to investigate the effects of selected parameters on the flow of alternative agents.

In this study, the effects of the following design parameters were examined: bottle fill condition and temperature, pipe diameter, length, elbows, tees, contractions, and expansions. From these experiments, mass flow rate and pipe pressure drop as functions of fixed bottle pressure were obtained.

An actual bottle discharge exhibits highly transient flow. At first, as the pipe is filling up with agent, the pipe pressure at any point is rising rapidly while the bottle pressure is falling rapidly. The pipe pressure achieves a maximum when the pipe just fills, then starts to fall along with the bottle pressure. As the bottle pressure drops, the dissolved nitrogen in the liquid phase may not come out of solution immediately, resulting in a metastable, supersaturated solution. After some time delay, degassing of the dissolved nitrogen can produce a net pressure rise inside the bottle due to the expansion of a bubbly two-phase fluid. The bottle pressure may reach a local maximum then start to drop again as this two-phase fluid continues to empty. At the point where the last of the two-phase mixture is being expelled from the bottle, a pressure rise is observed in the piping for a short period of time. The fluid in the piping is changing from a low quality (mostly liquid) fluid to a high quality (mostly gaseous) fluid, which exhibits a different pressure drop in the piping. At that point, most of the agent has been discharged from the bottle and piping. The pressure in the piping starts dropping again as the ullage contents discharge.

A range of test conditions was examined to better understand the nature of the alternative agent flows under conditions that may be encountered in suppression system piping. Both transient and quasi-steady flow cases were investigated. The quasi-steady flow experiments were performed to obtain the mass flow rate and steady pipe pressure drop for a fixed discharge pressure. The transient flow experiments were conducted to simulate the actual transient discharge events.

The experimental apparatus was designed so that different configurations and conditions could be studied. A schematic diagram of the experimental apparatus is shown in Figure 4. The major components are: a pressure vessel, a piping system, agent recovery system, and nitrogen make-up tank. System constraints, specific to engine nacelle applications, limited the range of conditions investigated. Pipe diameters and lengths were selected based on a review of military aircraft specifications. Also the fill condition and nitrogen pressurization were selected based on knowledge of typical halon 1301 engine nacelle systems. A transparent acrylic tube test section was installed in the piping system in order to observe the two-phase behavior of agent/nitrogen mixture in the pipe. A high speed movie camera operating at 500 frames per second was used to record the flow through the transparent section.

Two sets of experiments were performed: (1) constant-head discharges and (2) transient discharges. In the constant-head tests, the total pressure above the depleting liquid inside the pressure vessel was maintained constant using the nitrogen make-up tank. For the transient discharges, the nitrogen make-up tank was not used.

Figure 5 is a typical constant-head pressure trace. As indicted, the pressure inside the storage vessel remained relatively constant until the flow of the make-up nitrogen was terminated. Initially, the pipe pressures rose sharply and remained nearly constant until the liquid ran out of the vessel. As the liquid depleted from the vessel, the pressure started to rise in the pipe, then fell as the pipe emptied its two-phase fluid contents. After the make-up tank valve was closed, the bottle and pipe pressures continued to drop until the pressure equilibrated.

Figure 6 is a typical transient discharge result. As soon as the discharge valve was opened, the vessel pressure started to drop while the pressures in the pipe and recovery tanks started to rise. The pipe pressures peaked, then started to fall with the vessel pressure. The vessel and pipe pressures achieve a momentary local maximum before continuing the drop in pressure. This pressure recovery is thought to be due to degassing of nitrogen in the storage bottle. At about 1800 ms the vessel pressure started to decrease at a faster rate, which is attributed to the discharge of the ullage vapor. At the same time, pipe pressures increased, peaked, and then decreased at a much faster rate which is indicative of the two-phase mixture leaving the piping followed by discharge of the ullage vapor. Eventually, all pressure traces equilibrate.

The most important observation from the high-speed movies for all of these tests was that a cloudy two-phase fluid was observed immediately after the vessel valve was opened and it persisted until essentially all of the liquid contents of the vessel had emptied. This implies that two-phase flow is always present during the liquid discharge period. The time interval between the initial cloudy flow and until it started to clear is indicative of the liquid discharge time and roughly corresponds to the time from the initial pipe pressure rise to the end of the hump in the pipe pressure traces.

Based on the experimental results, the effects of piping configuration, and initial fill conditions were shown to have significant impact on the flow characteristics. Even though a number of tests were performed, only a very limited range of conditions and piping configurations were explored. Modeling the pipe flow would allow other configurations and conditions to be examined. With this in mind, a computer model was developed that predicts the transient discharge of an alternative agent superpressurized with nitrogen from a storage bottle through piping.

The model assumes homogeneous, equilibrium two-phase compressible flow. The homogeneous assumption specifies that the gas and liquid phase are well mixed and traveling at the same velocity. This is a good assumption for bubbly flow at low void fractions (Whalley, 1990). The fluid is assumed to be in thermodynamic equilibrium at all locations. Adiabatic, isenthalpic flow is assumed, greatly simplifying the analysis. The change in entropy is attributed to lost work due to frictional losses. The agent flow in the piping is always assumed to be two-phase flow for initially nitrogen-saturated bottle conditions. If the liquid agent is not saturated with nitrogen, the flowing agent is a single-phase liquid until the pipe pressure drops to the equilibrium nitrogen saturation pressure, and at that point degassing occurs. The liquid in the bottle can either follow the isenthalpic pressure/density path, or be frozen (constant density, single-phase liquid) until a critical pressure is reached. There is no mass transfer across the initial liquid-gas boundary in the bottle; bubbles that form in the liquid phase are assumed to stay in the liquid phase. The ullage gas expands adiabatically and isentropically, and is treated as an ideal gas.

The foundation for the flow prediction is an application of the steady-state mechanical energy balance and continuity equation for pipe flow. An important assumption is that the process is quasi-steady, *i.e.*, the upstream stagnation properties (the bottle conditions) are fixed over a time increment, and a steady mass flow rate is calculated. The small out-flow of mass changes the bottle conditions for the next time increment. Pressure drops across bends, valves, and other piping elements were treated in terms of effective pipe lengths (Perry *et al.*, 1984). The constant-head tests were simulated by fixing the upstream conditions and calculating the steady mass flow rate and the pipe pressures at the tap locations. Details of the model and the solution technique can be found in Yang *et al.* (1995).

Figure 7 is a plot of experimentally determined flow rates versus the calculated flow rates for all the tests under constant-head conditions. The dashed lines represent ± 10 % deviation of predictions. Estimated measurement errors are indicated by error bars. The calculated results for the small pipe diameter tests are within 10 % of the mean experimental value. For the large pipe diameter tests, the experimental values are higher than the predicted values. Given the scatter in the experimental values, the results compare favorably. In addition, calculated pipe pressures show good agreement with the experimental pressures.

Figure 8 show the experimental liquid discharge times (discharge time of the original liquid contents) versus the calculated discharge times for the transient discharge tests of HFC-125. In the figure, the dashed lines represent ± 10 % deviation from the experimental discharge times, and the error bars indicate 2σ uncertainty in the experimental values. The calculations based on equilibrium bottle conditions tend to be shorter than those based on a fixed degassing pressure or no bottle degassing. For most cases, the calculated liquid discharge time is less than 90 % of the experimental discharge time.

CONCLUDING REMARKS

Several important aspects related to agent storage and discharge characteristics have been studied in detail. A computer program (PROFISSY) has been developed to facilitate predictions of pressure-temperature characteristics of the selected agent/nitrogen mixtures. The nitrogen initially dissolved in the liquid agent was found to play a very important role in dry bay and engine nacelle applications. A discharge model which incorporates nitrogen degassing has been formulated and was used to predict agent discharge times without any *a priori* information other than the initial conditions of the vessel. A homogeneous two-phase pipe flow model has also been developed to facilitate transient calculations for engine nacelle applications.

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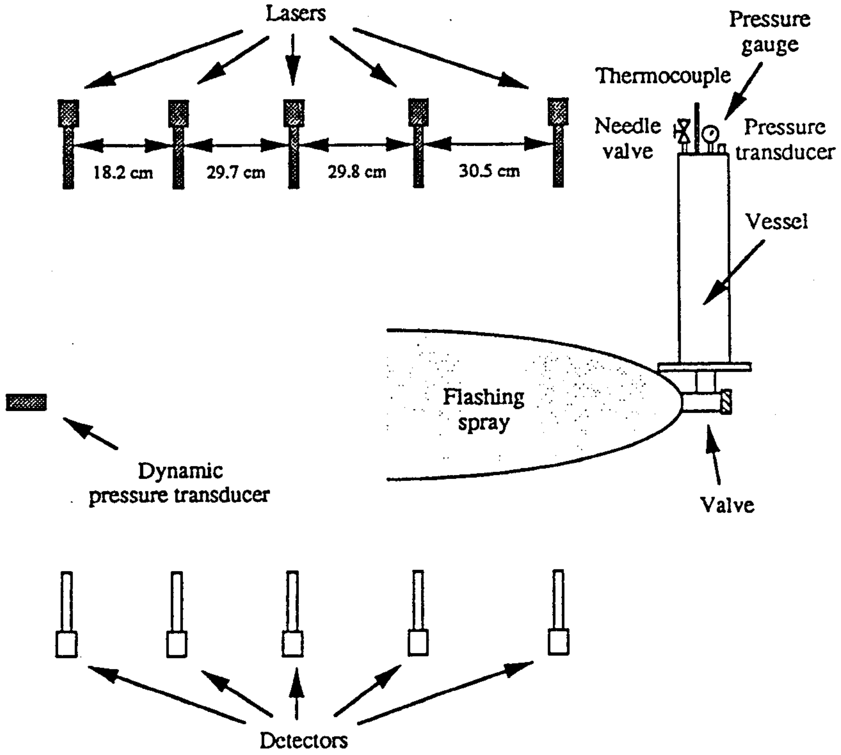

Figure 1. A schematic of the simulated dry bay discharge apparatus.

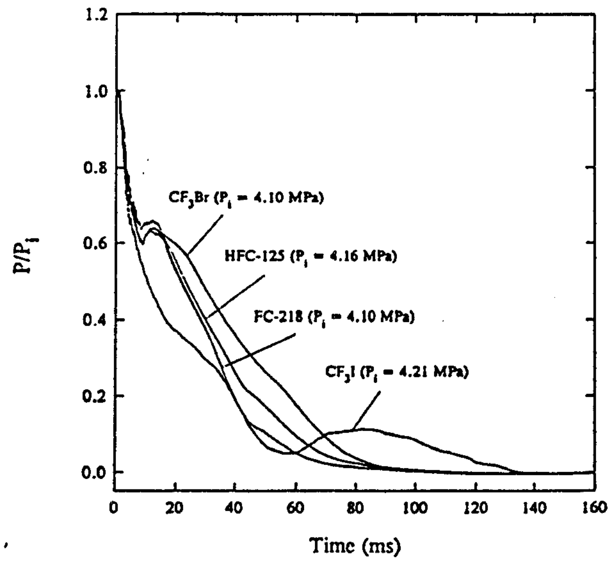

Figure 2. Comparison of pressure decay curves during discharges at room temperature using a solenoid valve.

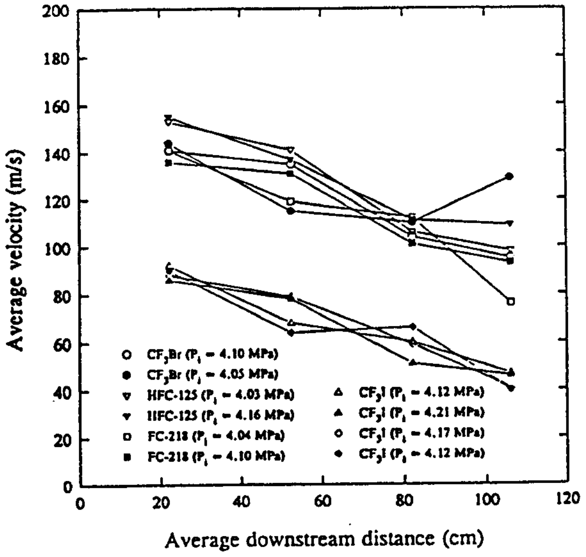

Figure 3. Average downstream velocities during discharges at room temperature using a solenoid valve.

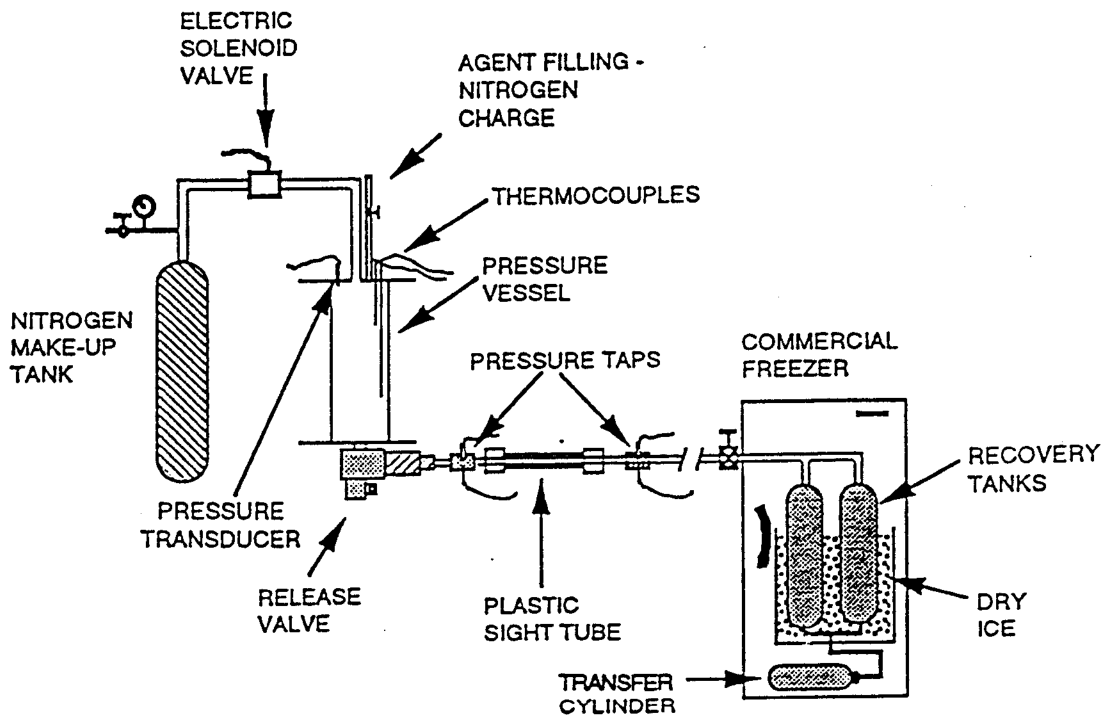

Figure 4. A schematic of the two-phase pipe flow apparatus.

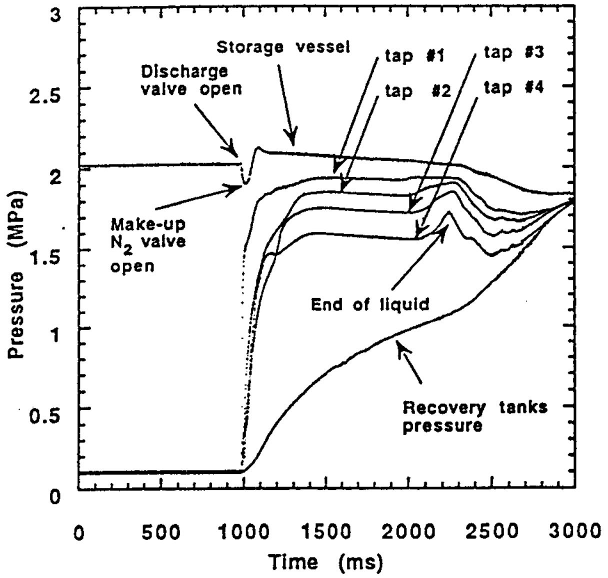

Figure 5. A constant-head CF_3Br discharge.

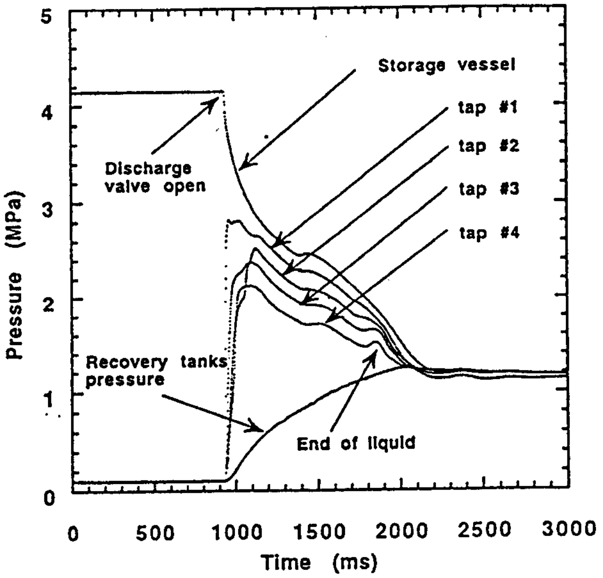

Figure 6. A transient HFC-125 discharge.

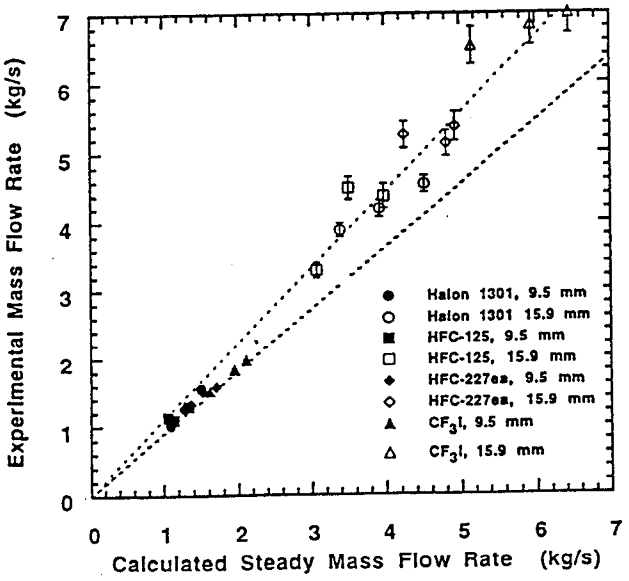

Figure 7. Experimental and predicted constant-head mass flow rate.

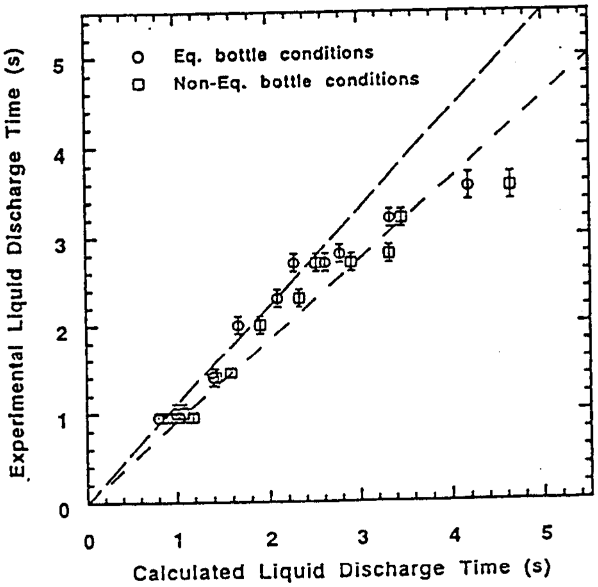

Figure 8. Experimental and calculated liquid discharge times for HFC-125.