



Relief System Sizing for Runaway Chemical Reactions: A Simple Comprehensive Approach

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Abstract

When conducting relief sizing calculations for reactive systems, experimental data is of paramount importance. Experimental techniques for gathering the necessary kinetic data highlighting VSP2 (Vent Sizing Package 2) and ARSST (Advanced Reactive System Screening Tool) testing will be outlined. In addition, the principles behind the system classifications (vapor, gassy and hybrid) will be outlined with example experimental data sets. Relief sizing calculations and source term considerations for each system will be discussed. Two-phase flow and experimental techniques for determining flow regime (vapor, churn, bubbly or homogeneous flow) will be presented with the goal of providing the audience with a simple comprehensive experimental approach to designing relief systems.

Upset Scenario Selection

Evaluation of reactive chemistries for relief system design requires consideration of plausible upset scenarios. What exactly goes wrong (and when it goes wrong) in a chemical process can have a great affect on the rates at which a reaction runs away. This in turn affects relief requirements and whether or not a particular relief system design is adequate to handle the worst potential scenario. Common upset scenarios include, but are not limited to, loss-of-cooling during normal process conditions, inadvertent heating, wrong reagent addition, and addition at wrong temperature. Upset scenario selection is typically done in a process hazard analysis (PHA) that includes process engineers, chemists, reactive hazards experts, operators, and maintenance workers.

Experimental Techniques

Once plausible upset scenarios have been determined, it is critical that adiabatic calorimetry experiments be performed to characterize the reactive chemistry in question. The VSP2 and ARSST adiabatic calorimeters provide a means to directly simulate a specific upset scenario on the bench scale and do so in a safe manner. Due to the low phi-factor, the measured reaction rates are directly applicable to the process scale.

Source Term Considerations

During a reactive upset scenario, overpressurization of a process vessel can be caused by an increase in vapor pressure, generation of non-condensable gas, or a combination of the two. These overpressure sources are classified as vapor, gassy, or hybrid. Adiabatic calorimetry experiments provide a means for determining the source of overpressure.

Reactive systems in which the increase in pressure is due solely to an increase in vapor pressure are commonly referred to as vapor systems. Vapor systems have the advantage that the latent heat from boiling prevents the temperature from increasing (or tempers the system). As a result, the temperature rise due to the runaway reaction can be controlled by venting. In these cases, the relief system must be designed to accommodate the vapor generated during venting. As such, the relief requirement is based on the temperature rise rate. Adiabatic calorimetry experiments for these types of systems are typically run as closed cell tests. This allows for vapor pressure data to be collected in addition to reaction rate data.

Reactive systems in which the increase in pressure is due solely to the generation of non-condensable gas are commonly referred to as gassy systems. When dealing with gassy reactive systems, it is important to recognize that the reaction temperature rise cannot be controlled by venting. Because the temperature cannot be controlled in these cases, the relief system must be designed to accommodate the peak rate of non-condensable gas generation. Because obtaining the peak pressure rise rate is important, adiabatic calorimetry experiments for these types of systems are commonly run as open cell tests to allow for a large volume of non-condensable gas formation.

Reactive systems in which the increase in pressure is due to vapor and non-condensable gas generation are commonly referred to as hybrid systems. Latent heat is available to remove reaction heat. Due to the generation of both vapor and non-condensable gas, it is important to consider both temperature and pressure rise rates for relief design. Similar to gassy systems, adiabatic calorimetry experiments for these types of systems are often times run as open cell tests. This not only provides a large volume for non-condensable gas formation but also allows for confirmation of tempering.

Flow Regime Considerations

After the determinations of system classification and reaction rates, it is also important to consider vessel flow regime. The flow regime determines the amount of two-phase flow that will occur during venting. This in turn affects the size of the required emergency relief vent. Predictions of the flow regime based on material properties of the vessel contents are not reliable. Prior industrial experience with the chemistry in question or experimental data are required.

Either adiabatic calorimeter previously mentioned can be used for flow regime determination. The ARSST utilizes a Flow Regime Detector (FRED) for distinction between foamy or non-foamy venting. The FRED uses a heater and thermocouple combination in the headspace of the test cell. The heater is programmed to heat the headspace above the test cell to a temperature

hotter than the sample temperature. Foamy conditions are detected when the thermocouple in the headspace is quenched by the sample. Specially designed tests for flow regime determination in the VSP2 are called blowdown tests. A blowdown test involves depressurizing the test cell and determining the quantity of material remaining afterwards. The small scale VSP2 test is designed to mimic the dimensionless superficial velocity that would be seen on the large scale during venting. This way, one can make the distinction between churn-turbulent (non-foamy) or bubbly and homogeneous (foamy) flow regimes.

Fauske's Simple Relief Sizing Equation

Fauske has worked to develop a simplified relief sizing methodology for reactive systems that can be used with low phi-factor adiabatic calorimetry data and limited knowledge of material properties. This methodology bases the required vent size on the all vapor or gas vent area by allowing for a modest overpressure. While the vent area is calculated on this basis, it does not imply that two-phase flow will not occur. The following equation can be applied to all classifications of reactive systems venting at or above the critical pressure ratio.

$$A = \frac{1}{0.61 \cdot C_D} \left[\frac{m \cdot c_p \cdot \dot{T}}{\lambda \cdot P} \left(\frac{R \cdot T}{MW_v} \right)^{1/2} + \frac{m \cdot v \cdot \dot{P}}{m_t \cdot P} \left(\frac{MW_g}{R \cdot T} \right)^{1/2} \right]$$

where A	=	required vent area (m ²)
C _D	=	discharge coefficient (-)
m	=	mass of vessel contents (kg)
c _p	=	heat capacity of vessel contents (J/kg·K)
\dot{T}	=	temperature rise rate from calorimetry test (K/s)
λ	=	latent heat of vessel contents (J/kg)
P	=	venting pressure (Pa)
R	=	universal gas constant (8314.47 J/kmol·K)
T	=	venting temperature (K)
MW _v	=	molecular weight of vapor (kg/kmol)
v	=	freeboard volume of test (m ³)
\dot{P}	=	pressure rise rate from calorimetry test (Pa/s)
m _t	=	mass of test sample (kg)
MW _g	=	molecular weight of gas (kg/kmol)

In order to use the aforementioned equation for vapor systems, the overpressure available during venting is required to be at least 40% on an absolute basis. The temperature, pressure, temperature rise rate, and material properties for vapor systems are evaluated at the set pressure of the relief device. It is also important to note that the equation is applicable to non-foamy systems. If a foamy flow regime is expected to prevail, the calculated vent area should be increased by a factor of 2.

For gassy systems, the temperature, pressure, and material properties are evaluated at the maximum allowable accumulation pressure (MAAP). Applicable code permits an overpressure

of 10% above the maximum allowable working pressure (MAWP) of the vessel on a gauge basis. The pressure rise rate is the maximum measured during the adiabatic calorimetry test.

For tempered hybrid systems, the temperature, pressure, temperature rise rate, pressure rise rate, and material properties are evaluated at the set pressure of the relief device.

Vapor System Example

3500 kg of a phenol-formaldehyde resin is produced in a reactor with a volume of 5 m³ and a maximum allowable working pressure of 30 psig. The reaction is run at a temperature of 50°C with a sodium hydroxide catalyst being metered to a mixture of phenol, water, and formaldehyde. The total batch has a final composition as follows:

Component	Concentration (wt.%)
Phenol	31.25
Water	20.50
50% Formaldehyde	44.25
50% Sodium Hydroxide	4.00

Results from a PHA indicate an abnormally fast addition of the catalyst charge would overwhelm the cooling system of the reactor leading to a runaway reaction. It is desired to size a rupture disk with a set pressure of 10 psig based on this upset scenario.

Phenol-formaldehyde systems such as this are known to be foamy vapor systems, making the VSP2 an excellent choice for obtaining runaway reaction data. A closed-cell VSP2 test was run to simulate this upset scenario. The phenol, water, and formaldehyde were loaded to the test cell (in the appropriate ratios) and heated to a temperature of 50°C. The sodium hydroxide catalyst was then injected to the test cell and the reactants were allowed to run away adiabatically. The data from this test that are pertinent to the vent sizing evaluation are provided in Figures 1 and 2.

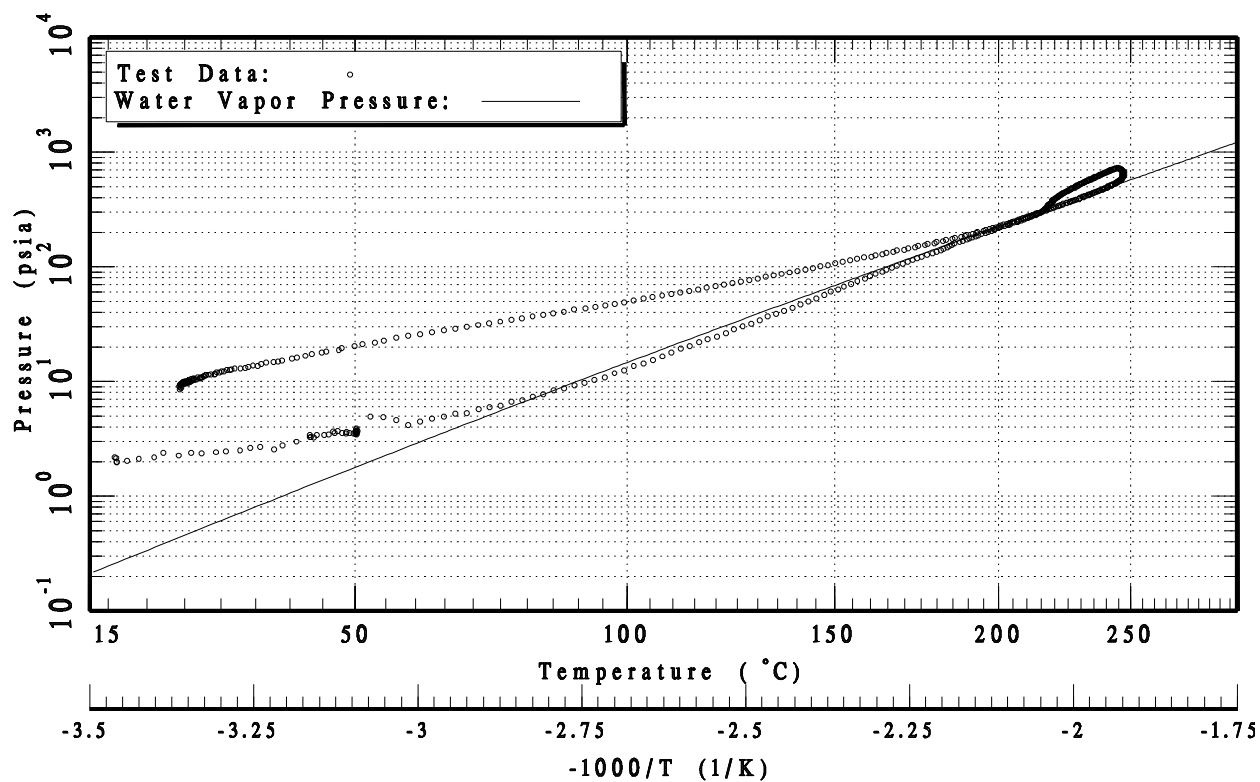


Figure 1 Pressure vs. Temperature for Phenol-Formaldehyde

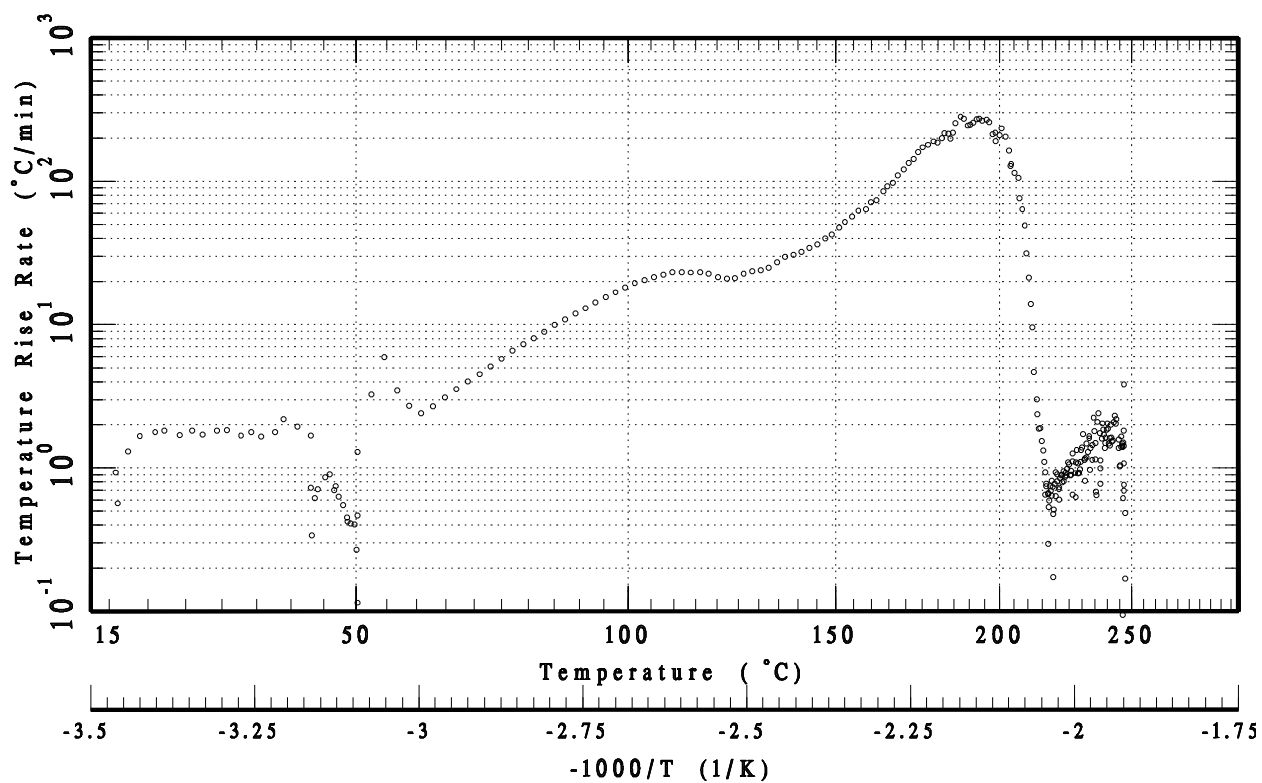


Figure 2 Temperature Rise Rate vs. Temperature for Phenol-Formaldehyde

In this case, the pressure within the test cell closely matches the vapor pressure of water at conditions where relief is expected to occur. Since there is an abundance of water in the batch, this reactive system is expected to be a vapor system during venting. Based on Figure 1, the desired relief set pressure of 10 psig corresponds to a temperature of 115°C. The corresponding temperature rise rate of 23.1°C/min is shown in Figure 2. The vent sizing calculation for this particular upset scenario is shown below. A factor of 2 has been used to account for the expected foamy behavior of the phenol-formaldehyde system. In addition, a discharge coefficient of 0.5 has been chosen to represent reasonably designed outlet piping from the rupture disk.

$$A = \frac{2}{0.61 \cdot C_D} \left[\frac{m \cdot c_p \cdot \dot{T}}{\lambda \cdot P} \left(\frac{R \cdot T}{MW_v} \right)^{1/2} \right]$$
$$A = \frac{2}{0.61 \cdot 0.5} \frac{(3500 \text{ kg})(3380 \text{ J/kg} \cdot \text{K})(0.385 \text{ K/s})}{(2.2 \times 10^6 \text{ J/kg})(170300 \text{ Pa})} \left[\frac{(8314.47 \text{ J/kmol} \cdot \text{K})(388 \text{ K})}{(18.015 \text{ kg/kmol})} \right]^{1/2}$$
$$A = 3.37 \times 10^{-2} \text{ m}^2 \text{ or } 52.3 \text{ in}^2$$

Gassy System Example

210 kg of 40% dicumyl peroxide in 2,2,4-trimethyl-1,3-pentanediol diisobutyrate is stored in a 340 L tank. The maximum allowable working pressure of the tank is 80 psig.

Results from a PHA indicate a fire in the surrounding area would elevate the temperature of the tank to cause decomposition of the dicumyl peroxide. The external fire exposure rate was determined to be 0.5°C/min. It is desired to size a rupture disk with a set pressure of 50 psig based on this upset scenario.

Because non-condensable gas is expected to be generated due to decomposition of the dicumyl peroxide, the ARSST is an excellent choice for obtaining runaway reaction data. An open-cell ARSST test was run to simulate this upset scenario. The dicumyl peroxide and diisobutyrate were loaded to the test cell (in the appropriate ratios) and heated at an external rate of 0.5°C/min. In accordance with open cell methodology, the test was performed with an initial nitrogen backpressure equal to the storage tank MAAP of 88 psig. This ensures sufficient reaction rate data are obtained for vent sizing purposes. The data from this test that are pertinent to the vent sizing evaluation are provided in Figures 3 and 4.

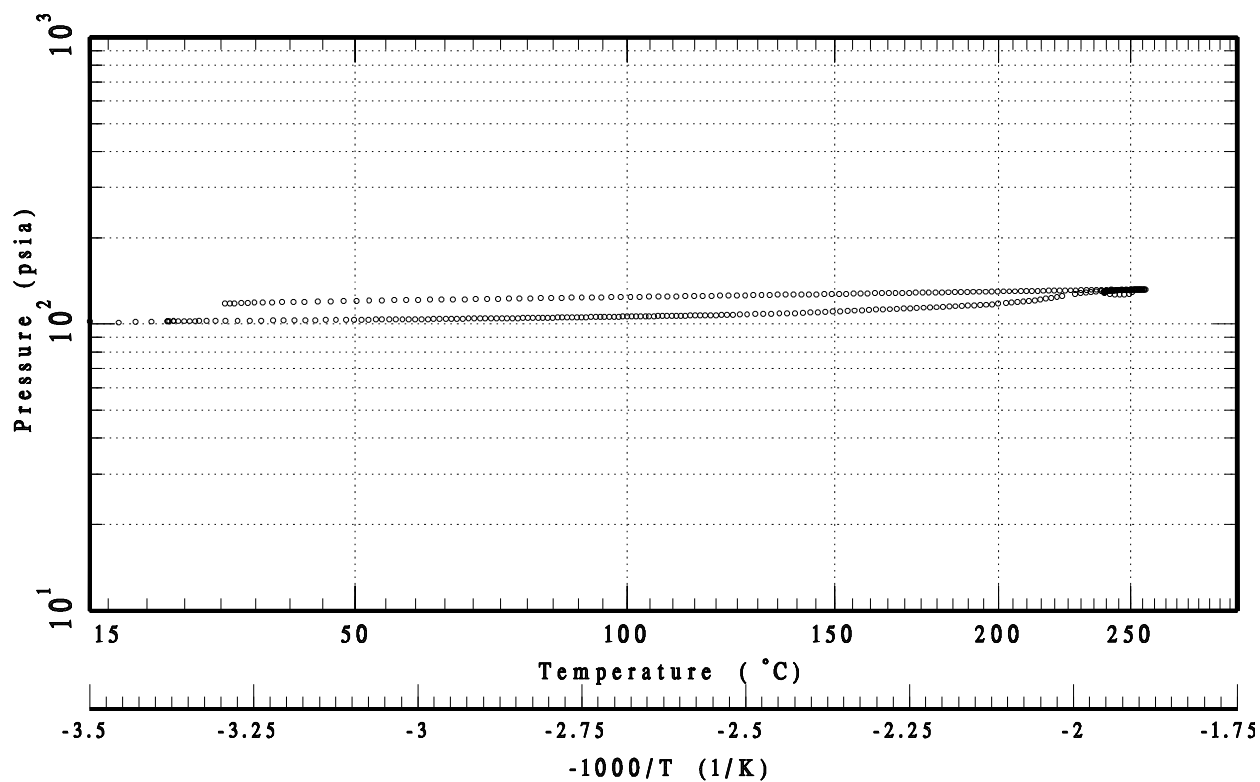


Figure 3 Pressure vs. Temperature for 40% Dicumyl Peroxide in Diisobutyrate

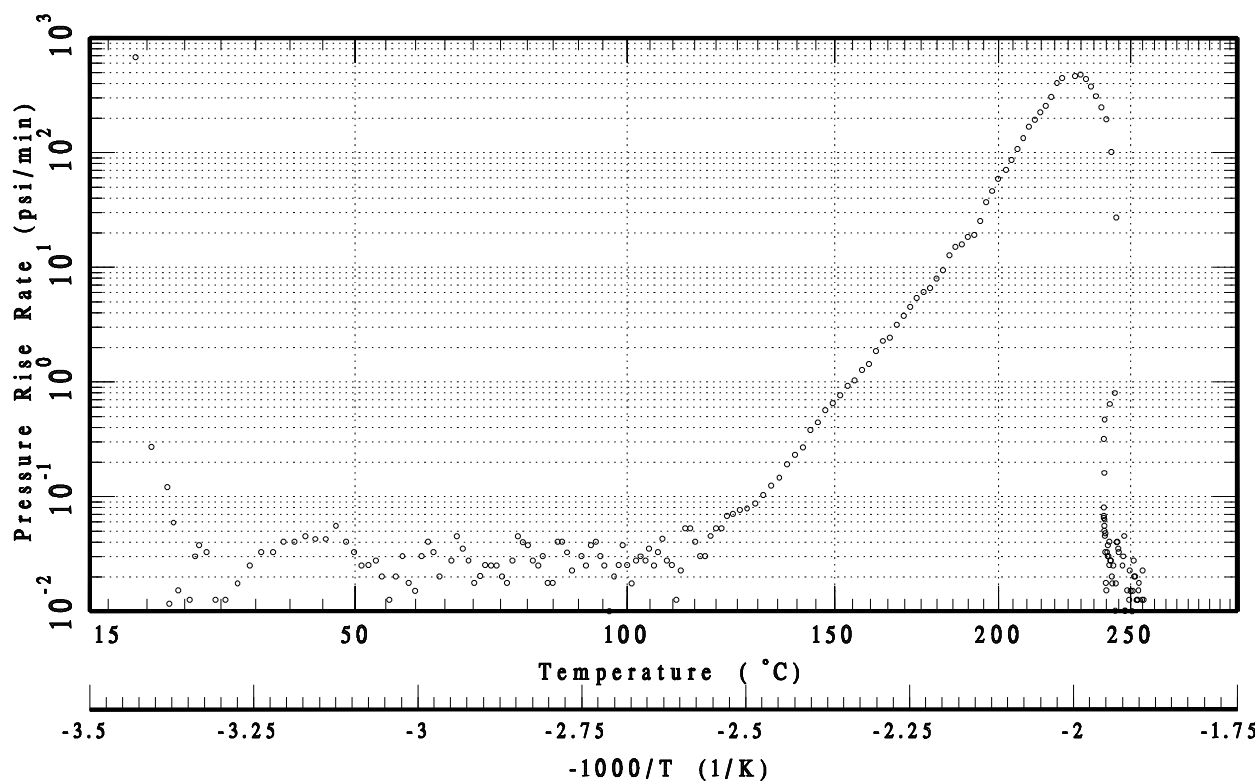


Figure 4 Pressure Rise Rate vs. Temperature for 40% Dicumyl Peroxide in Diisobutyrate

In this case, a significant amount of non-condensable gas was generated as evidenced by the cool down pressure of 103 psig. The peak reaction temperature from the runaway reaction was 250°C. Since the diisobutyrates does not boil until a temperature of 280°C, significant vapor generation will not occur. This reactive system is expected to be a gassy system during venting. Based on Figure 4, the maximum pressure rise rate is 477 psi/min and occurs at a temperature of 230°C. The vent sizing calculation for this particular upset scenario is shown below and based on all gas venting. A discharge coefficient of 0.5 has been chosen to represent reasonably designed outlet piping from the rupture disk.

$$A = \frac{1}{0.61 \cdot C_D} \left[\frac{m \cdot v \cdot \dot{P}}{m_t \cdot P} \left(\frac{MW_g}{R \cdot T} \right)^{1/2} \right]$$

$$A = \frac{1}{0.61 \cdot 0.5} \frac{(210 \text{ kg})(3.5 \times 10^{-4} \text{ m}^3)(54800 \text{ Pa/s})}{(8 \times 10^{-3} \text{ kg})(708090 \text{ Pa})} \left[\frac{(44.01 \text{ kg/kmol})}{(8314.47 \text{ J/kmol} \cdot \text{K})(503 \text{ K})} \right]^{1/2}$$

$$A = 7.56 \times 10^{-3} \text{ m}^2 \text{ or } 11.7 \text{ in}^2$$

Hybrid System Example

2000 kg of 25% hydrogen peroxide is stored in a 700 gallon tank. The maximum allowable working pressure of the tank is 100 psig.

Results from a PHA indicate iron contamination could cause a runaway reaction due to accelerated decomposition rates of the hydrogen peroxide. It is desired to size a rupture disk with a set pressure of 20 psig based on this upset scenario.

Because non-condensable gas is expected to be generated due to decomposition of the hydrogen peroxide, open cell VSP2 testing is an excellent choice for obtaining runaway reaction data. The hydrogen peroxide and iron contaminant were loaded to the test cell (in the appropriate ratios) and subjected to heat-wait-search methodology. In accordance with open cell methodology, the test was performed with an initial nitrogen backpressure equal to the storage tank MAAP of 110 psig. This ensures sufficient reaction rate data are obtained for vent sizing purposes. The data from this test that are pertinent to the vent sizing evaluation are provided in Figures 5 through 7.

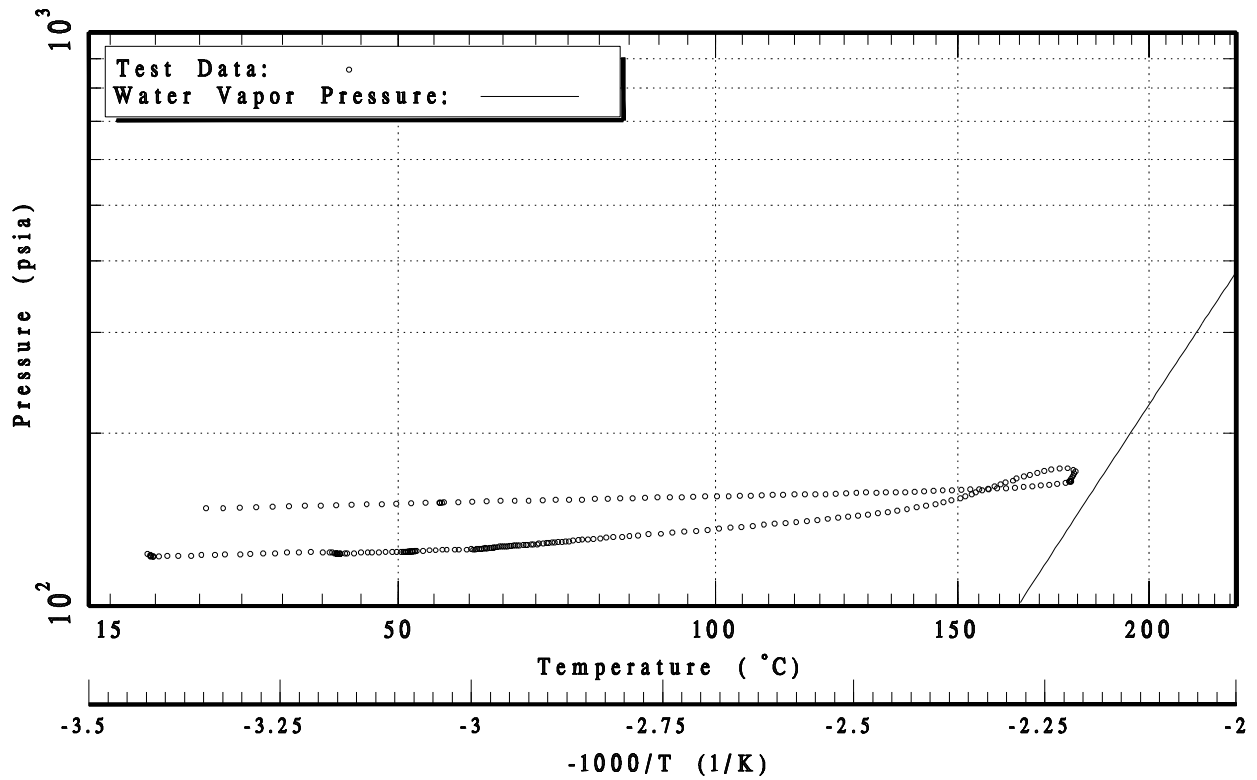


Figure 5 Pressure vs. Temperature for 25% Hydrogen Peroxide System

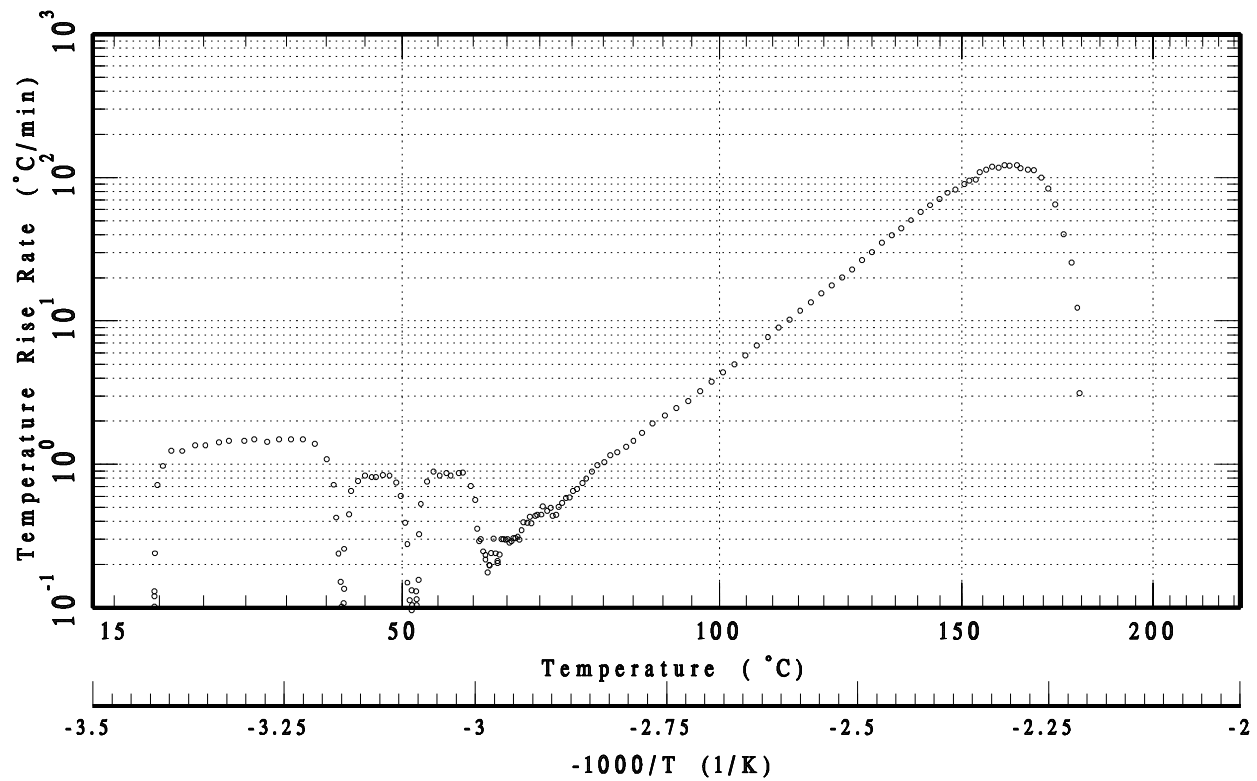


Figure 6 Temperature Rise Rate vs. Temperature for 25% Hydrogen Peroxide System

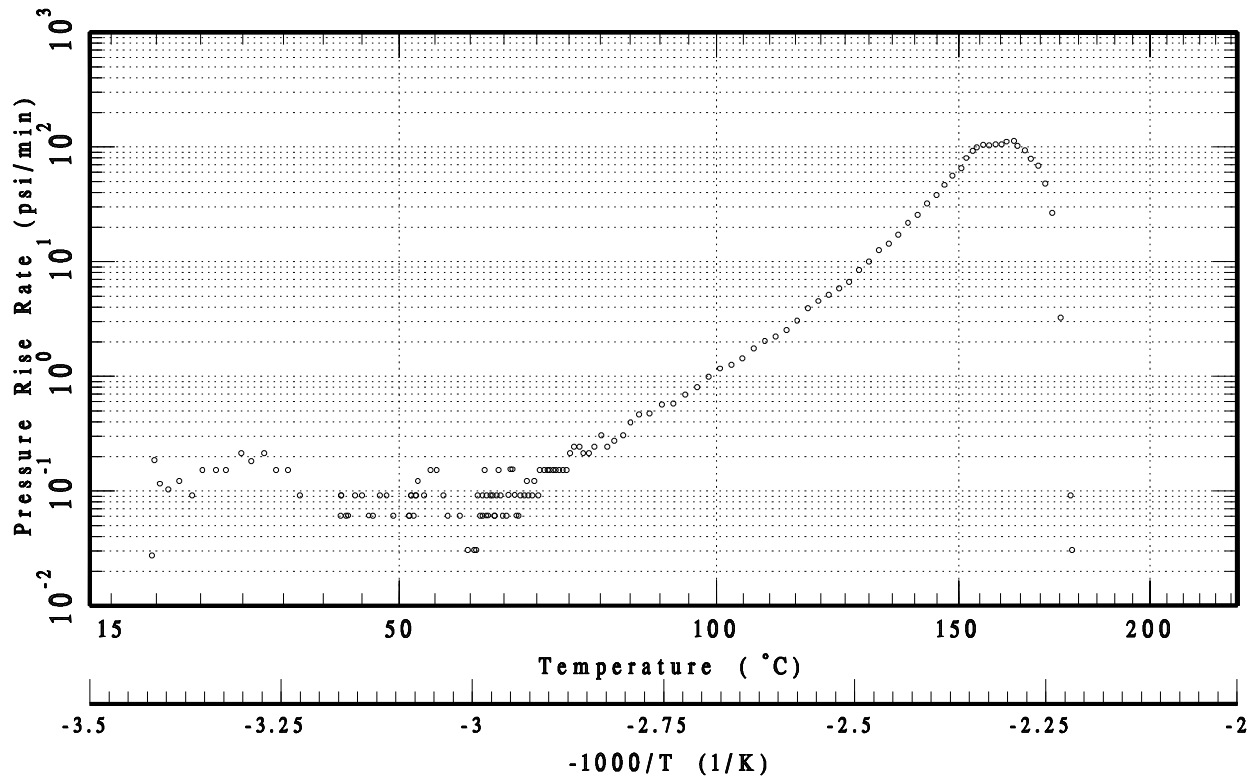


Figure 7 Pressure Rise Rate vs. Temperature for 25% Hydrogen Peroxide System

In this case, a significant amount of non-condensable gas was generated as evidenced by the cool down pressure of 133 psig. The peak temperature during this test was 179°C. This implies that the water will boil during a venting scenario and tempering of the reaction is possible. In order to verify this assumption and determine at what temperature tempering may occur, an open-cell test was run at 20 psig. The data from this test that are pertinent to the vent sizing evaluation are provided in Figure 8.

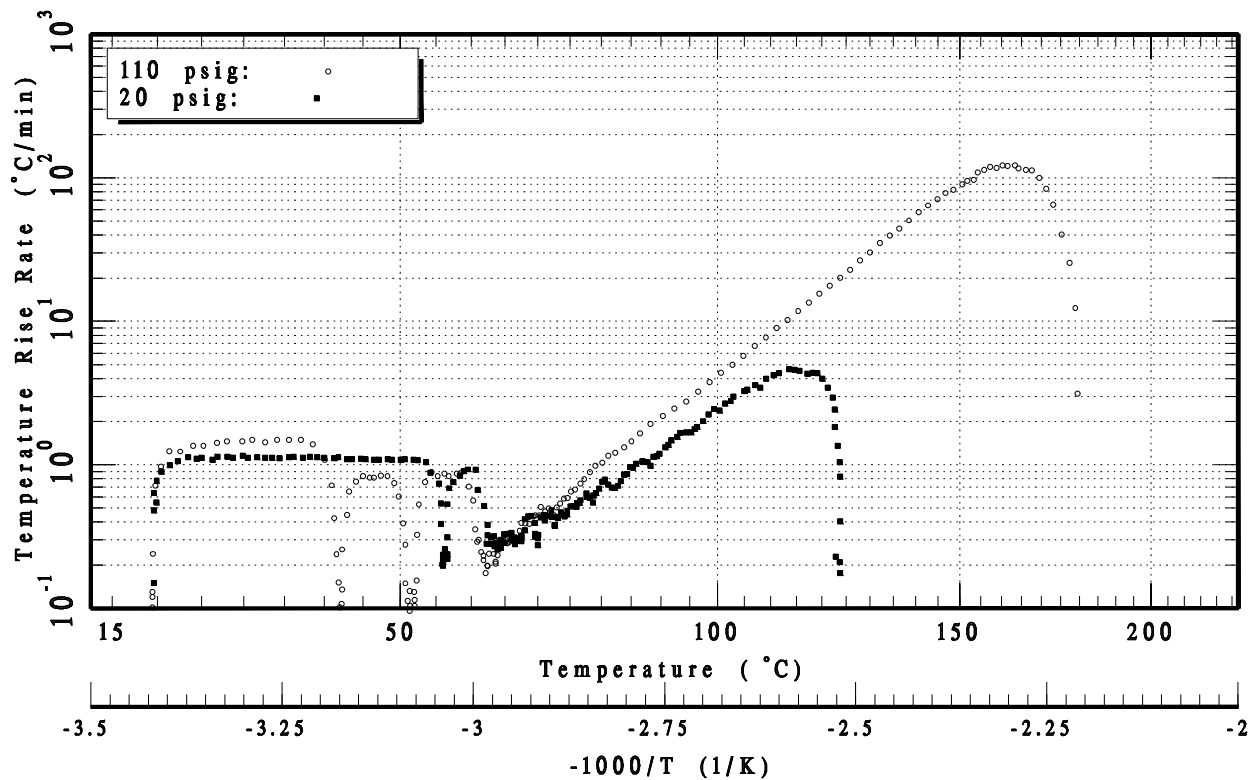


Figure 8 Comparison Temperature Rise Rates for 25% Hydrogen Peroxide System

As evidenced in Figure 8, the low backpressure test exhibited tempering at a temperature of 124°C. This reactive system is thus expected to be a hybrid system during venting. Based on Figures 6 and 7, the reaction rates corresponding to the tempering point are 21°C/min and 6 psi/min. The vent sizing calculation is shown below and based on all gas and vapor venting. A discharge coefficient of 0.5 has been chosen to represent reasonably designed outlet piping from the rupture disk.

$$\begin{aligned}
 A &= \frac{1}{0.61 \cdot C_D} \left[\frac{m \cdot c_p \cdot \dot{T}}{\lambda \cdot P} \left(\frac{R \cdot T}{MW_v} \right)^{1/2} + \frac{m \cdot v \cdot \dot{P}}{m_t \cdot P} \left(\frac{MW_g}{R \cdot T} \right)^{1/2} \right] \\
 A &= \frac{1}{0.61 \cdot 0.5} \frac{(2000 \text{ kg})(3900 \text{ J/kg} \cdot \text{K})(0.35 \text{ K/s})}{(2.2 \times 10^6 \text{ J/kg})(239248 \text{ Pa})} \left[\frac{(8314.47 \text{ J/kmol} \cdot \text{K})(397 \text{ K})}{(18.015 \text{ kg/kmol})} \right]^{1/2} \\
 &\quad + \frac{1}{0.61 \cdot 0.5} \frac{(2000 \text{ kg})(3.8 \times 10^{-3} \text{ m}^3)(689 \text{ Pa/s})}{(8.0 \times 10^{-2} \text{ kg})(239248 \text{ Pa})} \left[\frac{(32.0 \text{ kg/kmol})}{(8314.47 \text{ J/kmol} \cdot \text{K})(397 \text{ K})} \right]^{1/2} \\
 A &= 1.01 \times 10^{-2} \text{ m}^2 \text{ or } 15.6 \text{ in}^2
 \end{aligned}$$

Summary

A simple comprehensive experimental approach has been provided to size emergency relief devices in reactive service. Once credible reactive upset scenarios have been determined, low phi factor calorimeters can be used to directly simulate the upset conditions and obtain data regarding system classification, reaction rates, and flow regime. Using the simplified vent sizing equation provided by Fauske, required vent sizes can then be determined from these data. The applied methodology is consistent with available experimental data for all three types of reactive systems.

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