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Methodology for Assessing a Boiling Liquid Expanding Vapor Explosion (BLEVE) Blast Potential

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Introduction

- Composite Vessels are now used to store a variety of fluids or gases including cryogenic fluids under pressure

- Sudden failure of these vessels under certain conditions can lead to a potentially catastrophic vapor expansion if thermal control is not maintained prior to failure

- This can lead to a "Boiling Liquid Expanding Vapor Explosion" or BLEVE

Scope

- BLEVEs
  - Definition
  - "Superheat Energy" and "Superheat Limit"
  - Thermodynamics of BLEVEs
  - Work Available for Blast
    - Reversible Adiabatic
    - Irreversible Isentropic
  - Step-by-step methodology for estimation
- Cryogenic BLEVES
  - Nitrogen Example (Comparison of Blast Potentials)
    - Hydrostatic
    - Pneumatic
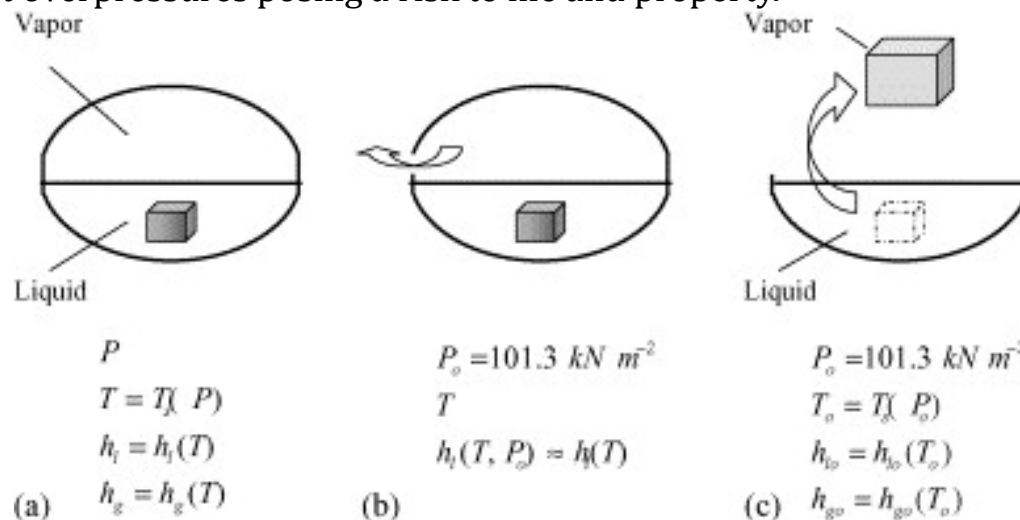   - BLEVE
  - Other Cryogens, Current Work, and Safety

BLEVE

- Boiling Liquid Expanding Vapor Explosion (BLEVE)
  - Any heated fluid under sufficient pressure that is suddenly exposed to lower pressures (ex. ambient) can 'flash' to vapor if the fluid temperature is above a certain value known as the 'superheat limit' temperature (T_{sl})
  - The mechanism at or above T_{sl} is a homogeneous nucleation process throughout the entire liquid mass and vaporization proceeds in the millisecond timeframe. This process is similar to rapid combustion in solids that convert solids to gas in the sub-millisecond domain (i.e. explosives).
  - The process creates a co-volume of liquid and a gas near the density of the original liquid acting like a highly pressurized gas volume within the vessel at a pressure typically well in excess of the original design burst pressure.
  - The end result is a blast that is very similar to a non-ideal gas pneumatic burst event and can create significant overpressures posing a risk to life and property.

Typically the T_{sl} for a wide range of compounds has been found to be:

$T_{sl} \sim 0.89 T_c$ to $0.90 T_c$

T_c = Critical Temperature of Fluid

(a)

Vapor

Liquid

P

$T = T_i(P)$

$h_i = h_i(T)$

$h_g = h_g(T)$

(b)

$P_o = 101.3 \ kN \ m^{-2}$

T

$h_i(T, P_o) \approx h_i(T)$

(c)

Vapor

Liquid

$P_o = 101.3 \ kN \ m^{-2}$

$T_o = T_i(P_o)$

$h_{io} = h_{io}(T_o)$

$h_{go} = h_{go}(T_o)$

Properties of Interest

- ## State Variables
  - T = Temperature (K)
  - P = Pressure (N/m^2)
  - M = Mass (kg)
  - U, u = Internal energy (kJ), Specific internal energy (kJ/kg)
  - H, h = Enthalpy (kJ), Specific enthalpy (kJ/kg)
  - V, v = volume (m^3). Specific volume (m^3/kg)
  - S, s = entropy (kJ/K), specific entropy (kJ/kg·K)

- ## States Subscripts
  - Subscript 1 refers to the initial state
  - Subscript 2 refers to the expanded state (ambient)
  - Subscript g refers to state of saturated vapor at ambient conditions (state 2)
  - Subscript f refers to state of saturated liquid at ambient pressure (state 2)

Thermodynamics

- State calculations can be used to estimate the available energy (work) available to generate a blast wave
- Two bounding values bracket the range of available work
  - Maximum : Reversible Adiabatic Expansion (isentropic work) = $W_i = U_1 - U_2$
  - Minimum: Irreversible Expansion work against atmospheric pressure $(W_o = P_o \Delta V)$
- Typically the maximum isentropic work value is used to bound the 'worse' case scenario for hazard assessment $(W_i = \Delta U)$
- The liquid's initial internal energy, U_1, can be found for the initial state using tables or graphs. Since most tables or graphs only supply h, ν, and s the value of U_1 can be found from $u = h - p\nu$ and the system mass
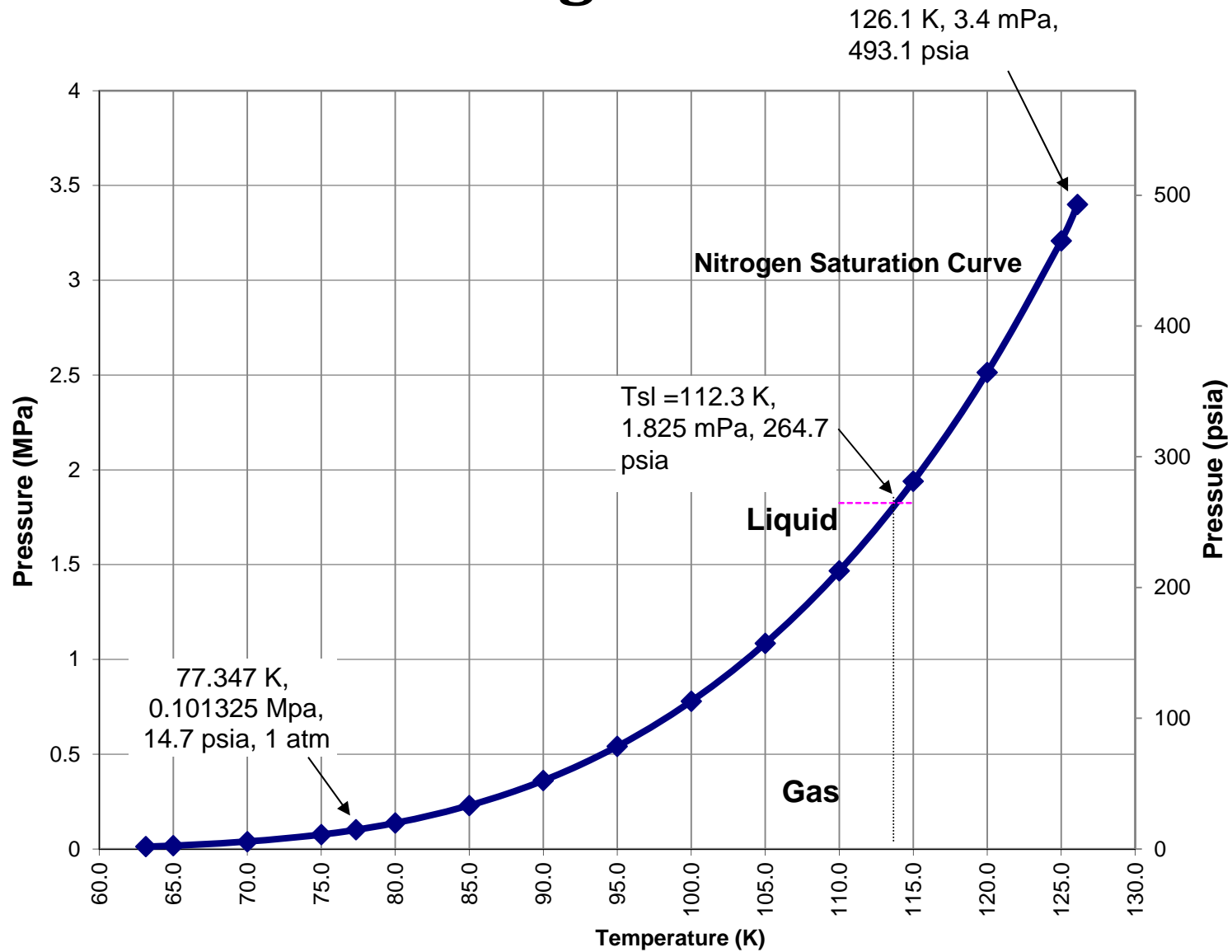
Step-by-Step Methodology

- First determine the initial state
  - Ideally the exact temperature of the fluid is desirable
  - Alternatively the pressure just prior to BLEVE can be use to determine the maximum temperature of the fluid by assuming saturated conditions

  Example: Liquid Nitrogen
  - Find Initial state
  - Determine if at or above T_{sl}
  - Solve for initial and final states

Nitrogen Curve

126.1 K, 3.4 mPa, 493.1 psia

Nitrogen Saturation Curve

Tsl =112.3 K, 1.825 mPa, 264.7 psia

Liquid

77.347 K, 0.101325 Mpa, 14.7 psia, 1 atm

Gas

Pressure (MPa)

Pressue (psia)

Temperature (K)

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Primary Method

Reversible Adiabatic Expansion (Isentropic)

(Isentropic Work, Δu) (Subscript 1 indicates initial state)

- Find u_1 (find h_1 and v_1 at P_1 and T_1)
  Where
  $$u_1 = h_1 - p_1 v_1 \qquad \text{(eq. 1)}$$

- Find u_2 based on:

  $$u_2 = (1-X)h_f + Xh_g - (1-X)p_2 v_f - Xp_2 v_g \qquad \text{(eq. 2)}$$
  where
  $$X = \text{Vapor Ratio} = (s_1 - s_f)/(s_g - s_f) \qquad \text{(eq. 3)}$$
  - Subscript 1 refers to the initial state
  - Subscript 2 refers to the expanded state (ambient)
  - Subscript g refers to state of saturated vapor at ambient conditions (state 2)
  - Subscript f refers to state of saturated liquid at ambient pressure (state 2)

Isentropic Work

Calculated Values are readily available for various compounds

(Table Right)
Table 6.12 Guidelines for Evaluating the Characteristics of Vapor Cloud Explosions, Flash Fires, and BLEVES, Center for Chemical Process and Safety, American Institute of Chemical Engineers, 1994
Shows values of isentropic work W_i expressed as E_{ex} (Energy of Explosion) for a range of temperatures

(Table below)
Table 1: Casal, J. and Salla B., "Using Liquid Superheating Energy for the a Quick Estimation of Overpressure in BLEVEs and Similar Explosions", Journal of Hazardous Materials, Vol. 137, Issue 3, 10-2006, pg 1321-1327
SE = Total Superheat Energy of System

TABLE 6.12. Expansion Work of NH_3, CO_2, N_2, O_2

Fluid	T_1(K)	p_1 (10^5 Pa)	Liquid e_{ex} (kJ/kg)	e_{ex}/v_1 (MJ/m^3)
Ammonia, T_{sl} = 361.0 K				
	324.8	21.2	82.5	46.2
	360.0	48.0	152.5	74.7
	400.0	102.8	278.5	95.7
Carbon dioxide, T_{sl} = 270.8 K				
	244.3	14.8	54.4	58.2
	255.4	21.1	60.9	62.1
	266.5	29.1	68.1	65.6
Nitrogen, T_{sl} = 112.3 K				
	104.0	10.0	13.2	8.78
	110.0	14.5	18.2	11.3
	120.0	24.8	28.6	15.0
Oxygen, T_{sl} = 137.7 K				
	120.0	10.1	12.8	12.5
	130.0	17.3	18.7	16.8
	140.0	27.5	27.2	22.1

	$T_{sl\text{-}E}$ (K)	$P_{T_{sl\text{-}E}}$ (kPa)	$\rho_{l,T_{sl\text{-}E}}$ (kg m^{-3})	$SE_{m,T_{sl\text{-}E}}$ (kJ kg^{-1})	$SE_{V,T_{sl\text{-}E}}$ (MJ m^{-3})	W_i (kJ kg^{-1})	W_o (kJ kg^{-1})
Water	606.4	13357.0	632.5	1131.0	715.4	319.9	83.0
Nitrogen	118.6	2389.0	533.3	97.0	51.7	28.4	10.6
Ammonia	375.2	6507.0	450.9	684.1	308.4	187.0	55.7
Methane	174.7	2696.0	297.8	258.3	76.9	72.3	26.4

Comparison of Various Fluids
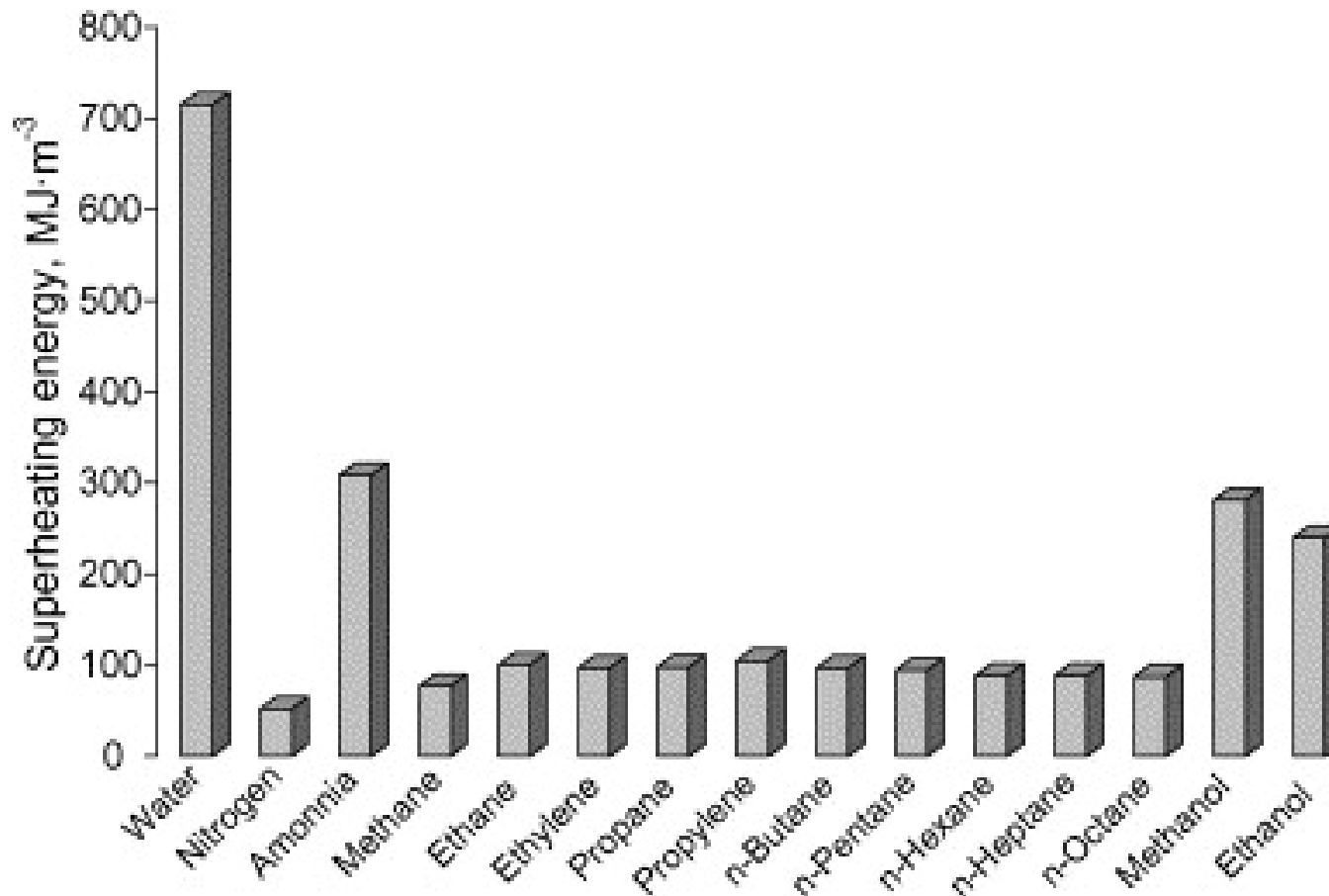
Casal, J. and Salla B., Using Liquid Superheating Energy for the a Quick Estimation of Overpressure in BLEVEs and Similar Explosions, Journal of Hazardous Materials, Vol. 137, Issue 3, 10-2006, pg 1321-1327

Comparison of relative isentropic work (W_i) potential for various fluids near T_{sl}

Blast Characterization
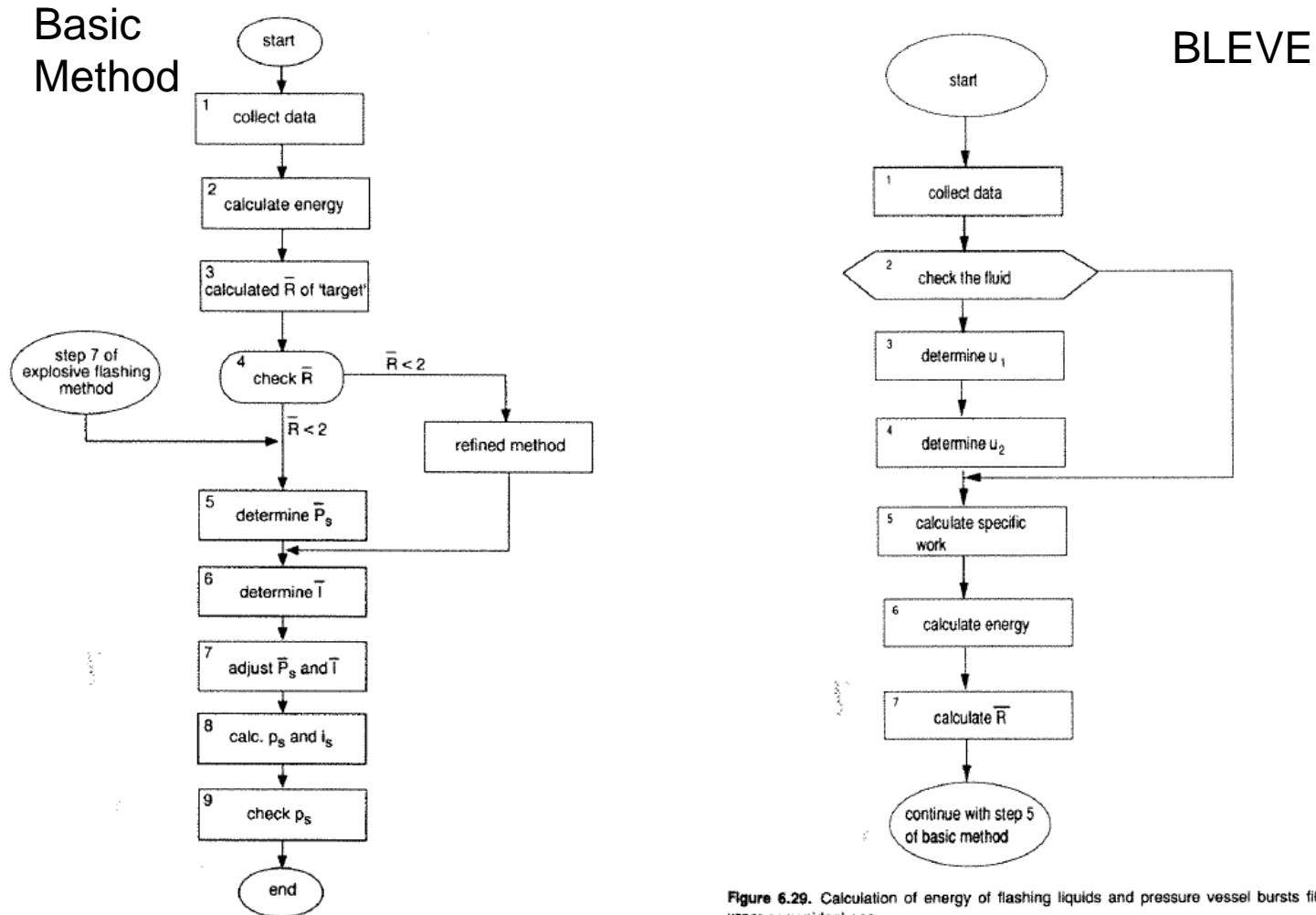
Basic Method

BLEVE

Figure 6.20. Basic method.

Figure 6.29. Calculation of energy of flashing liquids and pressure vessel bursts filled with vapor or nonideal gas.

Guidelines for Evaluating the Characteristics of Vapor Cloud Explosions, Flash Fires, and BLEVES, Center for Chemical Process and Safety, American Institute of Chemical Engineers, 1994

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Comparison of Blast Potential (Nitrogen)

- Example: 1 liter (0.001 m^3) of Nitrogen, P_1 = 500 psi (3.45 MPa)
- Stored Energy Comparison
  - Hydrostatic: The approximate stored energy in pressurized liquids is relatively small, (based on a bulk modulus of liquid nitrogen of ~13 Gpa) 1 liter of nitrogen at 500 psi stores
    - ~0.5 J
  - Pneumatic: Nitrogen gas (assumed ideal) at 500 psi and 1 liter can store
    - ~5.5 kJ

  $$U = \frac{P_1 \cdot V_1}{\gamma - 1}\left[1 - \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}\right], \gamma = 1.4, P_1 = 3.45 MPa, P_2 = 0.1014 MPa$$

  - BLEVE: 1 liter Superheated Liquid Nitrogen at 500 psi (T= 126 K) can store up to
    - ~30 kJ

Equivalent Pneumatic System

- The previous calculations showed the 'work' available to a BLEVE can be several times that of relatively low pressure (500 psi) gaseous pressure vessel or hydrostatic case
  - BLEVE vs. Pneumatic up to ~6 times greater (in this case)
  - BLEVE vs. Hydrostatic up to ~60,000 times greater (in this case)
- To 'match' pneumatic and BLEVE potentials a pneumatically charged nitrogen vessel would be at ~2,250 psi
- Finally it should be noted that nitrogen BLEVEs (or pneumatic releases) generate a local asphyxiation hazard

Other Cryogens

- Liquid Oxygen (LOX) is very similar to liquid nitrogen (LN2) in its BLEVE behavior but has the added hazard of an oxidizer and promoted combustion risks
- Liquid Hydrogen (LH2)
  - Examination of Characteristics
  - Boiling Point (1 atm) = 20.37 K
  - Critical Point = 32.97 K
  - T_{sl} (estimate Redlich-Kwong equation of state) = 29.51 K
  - The final result is LH2 BLEVEs have an estimated blast potential less than LN2 (based on mass) but can still be catastrophic and have an additional vapor cloud explosion hazard in air (combustion, deflagration, or deflagration to detonation)
- Current WSTF efforts include:
  - Verifying BLEVE threshold (T_{sl}) value for Nitrous Oxide (N2O)
  - Determining Blast Potential of Nitrous Oxide BLEVEs

Other Hazards

- Additional Safety Notes
  - Cryogenic systems can condense 'Air' and form a liquid consisting of ~50% liquid oxygen and ~50% liquid nitrogen as it drips off the cold surfaces
  - Liquid oxygen when in contact with hydrocarbons or products containing hydrocarbons (ex. oil, grease, asphalt, leather goods, etc.) can form impact or shock sensitive explosive compounds rivaling the strength of similar solid high explosives