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Thermal Expansion Estimates

Natural Gas Liquids

Report to: The U.S. Chemical Safety Board (CSB)



Date: July 10, 2018

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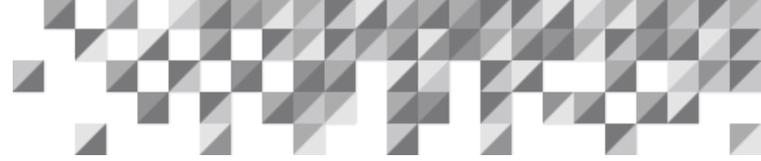
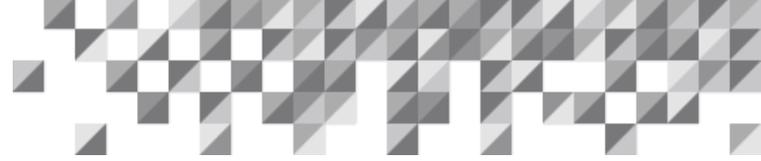


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1 Thermal Expansion of Natural Gas Liquids (NGL)

ioMosaic Corporation was retained by the U.S. Chemical Safety Board (CSB) to perform detailed thermal expansion estimates of two NGL compositions. The molar compositions are shown in Table 1.

1.1 Thermal Expansion Estimates

The thermal expansion estimates were performed using SuperChems Expert™, version 8.3, a component of Process Safety Office®. The starting temperature, pressure, and volume (-42 F, 480 psig, and 0.51ft³) provided by the CSB indicated that these initial conditions are both in the two-phase region as illustrated in Figure 1 and Figure 2.

Heating both compositions to 41 F in a closed volume will lead to an increase in pressure, 647 psig and 705 psig for NGL-1 and NGL-2 respectively. The increase in pressure would have been more significant if the starting conditions were all liquid. The slight compressibility of the liquid is significantly tempered by the presence of compressible vapors for both starting compositions.

**Table 1: NGL compositions (mole fraction)**

Chemical Name	NGL-1	NGL-2
METHANE	0.863036	0.702500
ETHANE	0.059469	0.172100
PROPANE	0.039996	0.076800
n-BUTANE	0.012679	0.041700
ISOBUTANE	0.006091	
n-PENTANE	0.002984	
ISOPENTANE	0.002881	
n-HEXANE	0.001674	
CYCLOHEXANE	0.001674	
CARBON DIOXIDE	0.005542	0.006800
NITROGEN	0.003972	0.000100

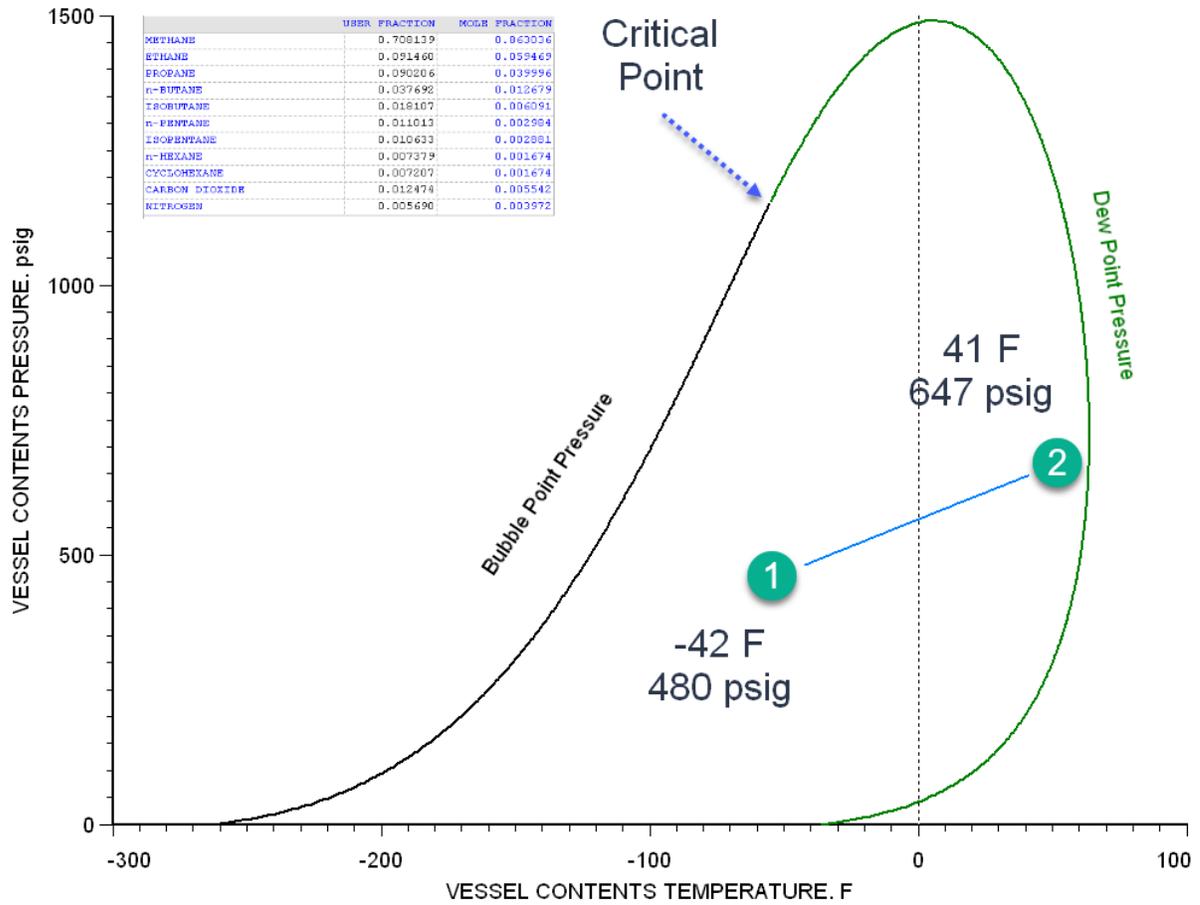
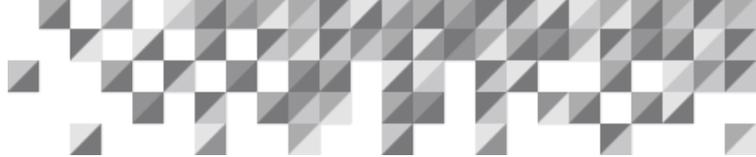


Figure 1: Thermal Expansion Estimates of Mixture NGL-1

Source: ioMosaic Corporation / SuperChems Expert v8.3

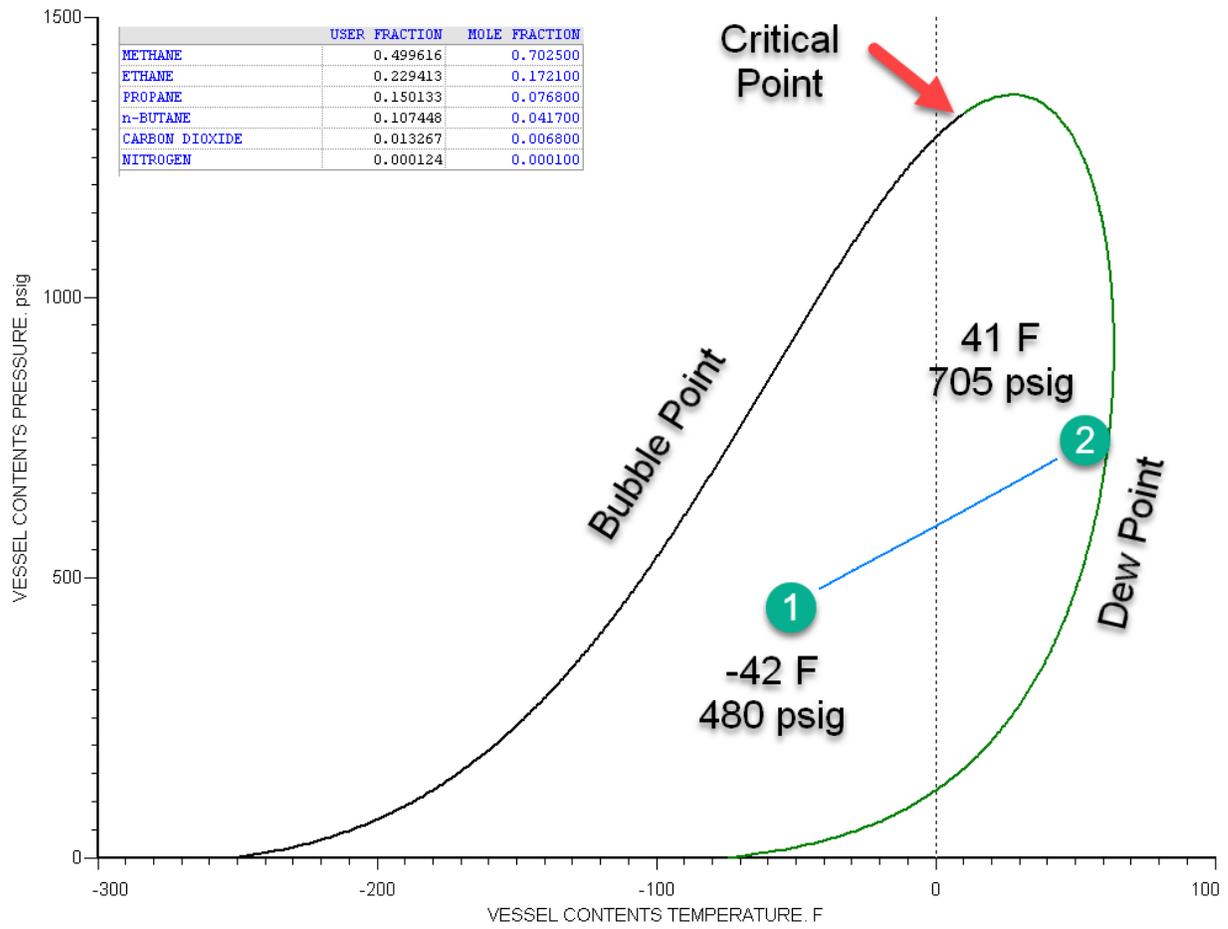
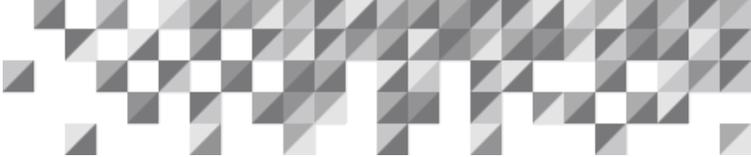
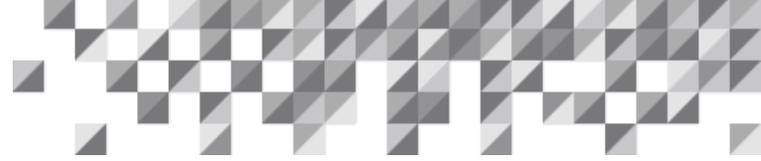
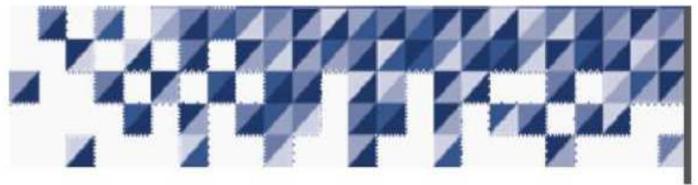


Figure 2: Thermal Expansion Estimates of Mixture NGL-2

Source: ioMosaic Corporation / SuperChems Expert v8.3



Appendix A: “Thermal Expansion Relief Requirements for Liquids, Vapors, and Supercritical Fluids”, An ioMosaic White Paper, January 2018.



Thermal Expansion Relief Requirements for Liquids, Vapors, and Supercritical Fluids



An ioMosaic Corporation White Paper

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IO MOSAIC CORPORATION

Relief and Flare Systems Design and Evaluation Practices

Fluid Flow

*Thermal Expansion Relief Requirements for Liquids, Vapors, and
Supercritical Fluids*

authored by

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January 9, 2018

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1 Introduction

Vessels and pipes filled with fluids require pressure relief in order to protect from loss of containment caused by fluid thermal expansion. Thermal expansion of fluids occurs when the fluid is heated as a result of steam tracing, solar radiation, external fire, etc.

In addition to establishing the required thermal relief requirements, it is also useful to establish the maximum pressure that can be reached during limited heating for either non-vented or partially vented fluid filled systems. In order to obtain better estimates of the maximum pressure reached, the elasticity of the piping/vessel should be considered. For partially vented systems, the excess volumetric expansion (fluid expansion - vessel/piping expansion) rate will govern the relief requirements.

2 Volume Change for Piping and Vessels

The volume of a solid, just like a fluid, expands and contracts due to changes in temperature and pressure. Because the change in volume for solids is smaller than the volume change for liquids and gases, it is normally neglected in most fluid flow applications. There are some practical applications where the volume change of a pipe or vessel can be important when considering scenarios dealing with loss of containment. Thermal expansion of liquid full vessels and/or piping is one such application. The depressuring of long high pressure pipelines is another practical application.

For vessels or piping containing liquids or vapors that are subjected to heating, the overall change of vessel volume due to thermal expansion and increase in internal pressure as a function of time is given by:

$$\frac{dV_s}{dt} = \left[\frac{\partial V_s}{\partial T} \right]_P \frac{dT}{dt} + \left[\frac{\partial V_s}{\partial P} \right]_T \frac{dP}{dt} = 3\alpha_s V_s \frac{dT}{dt} + \left(\frac{D_i}{\delta} \right) \left(\frac{V_s}{E_{s,T}} \right) f(\nu) \frac{dP}{dt} \quad (1)$$

where α_s is the material of construction coefficient of thermal linear expansion, $E_{s,T}$ is the material of construction modulus of elasticity (see Figure 1), D_i is the internal vessel diameter, δ is the vessel wall thickness, ν is Poisson's ratio, and $f(\nu)$ depends on the vessel geometry:

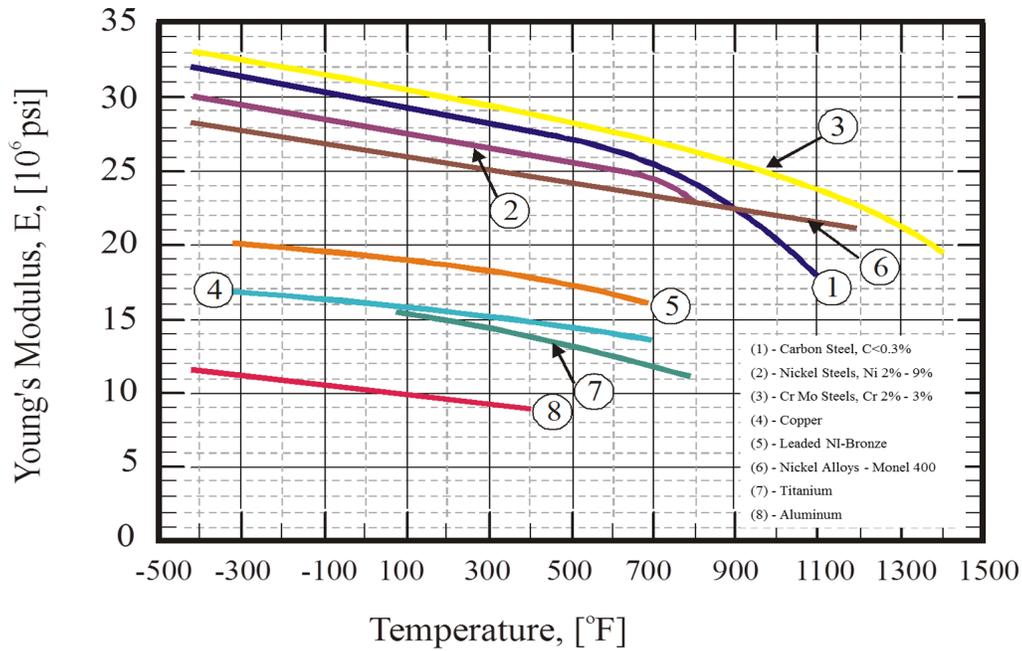
$$f(\nu) = 1.25 - \nu \simeq 0.95 \quad \text{for a cylindrical vessel, and} \quad (2)$$

$$f(\nu) = \frac{3}{4}(1 - \nu) \simeq 0.53 \quad \text{for spherical vessel.} \quad (3)$$

2.1 Change of Volume with Respect to Temperature

Unlike liquids and gases, the change of volume of a solid due to a change in temperature is typically calculated from the solid linear expansion coefficient, α_s :

Figure 1: Temperature dependency of modulus of elasticity for some common materials of construction [1]



$$\frac{\partial L}{\partial T} = \alpha_s(T)L \tag{4}$$

where L is the length of the solid, T is the temperature, and α_s is the coefficient of linear thermal expansion typically expressed in units of $\frac{m}{m.K}$. It can be shown that thermal expansion of a solid in 2D (area) or 3D (volume) can be related to the linear coefficient of thermal expansion ¹:

$$\frac{\partial A_s}{\partial T} = 2\alpha_s(T)A_s \tag{5}$$

$$\frac{\partial V_s}{\partial T} \simeq 3\alpha_s(T)V_s \tag{6}$$

Typical values of α_s are shown in Table 1 for some common metals and materials of construction. As shown by Table 1, liquid thermal expansion is much larger than steel thermal expansion and almost all the liquid thermal expansion will contribute to stressing the liquid full pipe or vessel. α_s is a weak function of temperature.

¹For example, for a cylinder, $V_s = \frac{\pi D^2}{4}L$. Differentiating V_s with respect to temperature yields $\frac{\partial V_s}{\partial T} = \frac{\pi}{4} [D^2\alpha_s L + 2\alpha_s L D^2] = 3\alpha_s \frac{\pi D^2}{4} L = 3\alpha_s V_s$

Table 1: Coefficient of linear thermal expansion for some common metals and materials of construction at 293.15 K

Solid	$\alpha_s \times 10^6, \text{ m/m/K}$	$3\alpha_s \times 10^6, \text{ m/m/K}$
Aluminum	25	75
Brass	19	56
Copper	17	51
Gold	14	42
Steel	12	35
Invar (Nickel-Iron Alloy)	0.9	2.7
Lead	29	87
Silver	18	54
Glass (typical)	9	27
Glass (Pyrex)	3	9
Quartz	0.4	1
Concrete, Brick	$\simeq 12$	$\simeq 36$
Marble (typical)	2.5	7.5
Water		210
Air		3400

2.2 Change of Volume with Respect to Pressure

The change of a solid volume with respect to pressure can be related to the isothermal compressibility of the solid. The isothermal compressibility, κ , is not used for solids. Instead, the bulk modulus of elasticity is typically used:

$$\kappa = -\frac{1}{V} \left[\frac{\partial V}{\partial P} \right]_T = \frac{1}{\rho} \left[\frac{\partial \rho}{\partial P} \right]_T = \frac{1}{E_T} \quad (7)$$

For thin walled ($\frac{D_i}{\delta} > 10$), hollow piping and vessels, the change of volume with respect to pressure is proportional to the isothermal compressibility and diameter to thickness ratio:

$$\frac{\partial V_s}{\partial P} = \left(\frac{D_i}{\delta} \right) \left(\frac{V_s}{E_{s,T}} \right) [1.25 - \nu] \quad \text{Cylinder} \quad (8)$$

$$\frac{\partial V_s}{\partial P} = \left(\frac{D_i}{\delta} \right) \left(\frac{V_s}{E_{s,T}} \right) \left[\frac{3}{4} (1 - \nu) \right] \quad \text{Sphere} \quad (9)$$

where ν is Poisson's ratio² which is approximately equal to 0.3 for steel.

²Ratio of strain in a traverse direction to that in the longitudinal direction, $\nu = \frac{\epsilon_{lateral}}{\epsilon_{axial}} = \frac{\frac{\Delta D}{D}}{\frac{\Delta L}{L}}$ where ϵ is the strain in m/m or in/in.

3 Volume Change for Fluids

The excess volume change of a liquid / gas mixture contained in an elastic vessel/pipe caused by a change in temperature and/or pressure is given by:

$$\frac{dV_{excess}}{dt} = (V_v\beta_v + V_l\beta_l) \frac{dT}{dt} - (V_v\kappa_v + V_l\kappa_l) \frac{dP}{dt} + \sum_i \bar{V}_{v_i} \frac{dN_i}{dt} + \sum_i \bar{V}_{l_i} \frac{dn_i}{dt} - \frac{dV_s}{dt} \quad (10)$$

where κ is the isothermal compressibility and β is the volume expansion coefficient. κ and β are typically calculated from an equation of state.

Excess volumetric change due to thermal expansion would have to be provided by the relief device in order to keep the pressure from exceeding a limiting value. If we assume the piping or vessel containing the fluid mixture is rigid, i.e. $\frac{dV_s}{dt} = 0$ then:

$$\frac{dV_{excess}}{dt} = (V_v\beta_v + V_l\beta_l) \frac{dT}{dt} - (V_v\kappa_v + V_l\kappa_l) \frac{dP}{dt} + \sum_i \bar{V}_{v_i} \frac{dN_i}{dt} + \sum_i \bar{V}_{l_i} \frac{dn_i}{dt} \quad (11)$$

If we also assume the piping and/or vessel is full of a single phase fluid with a negligible partial molar volume we can write:

$$\frac{dV_{excess}}{dt} = (V\beta) \frac{dT}{dt} - (V\kappa) \frac{dP}{dt} \quad (12)$$

4 Pressure Increase Due to Fluid Thermal Expansion

The theoretical rate of pressure rise caused by fluid thermal expansion is a function of isothermal compressibility and volume expansivity as shown by Equation 12:

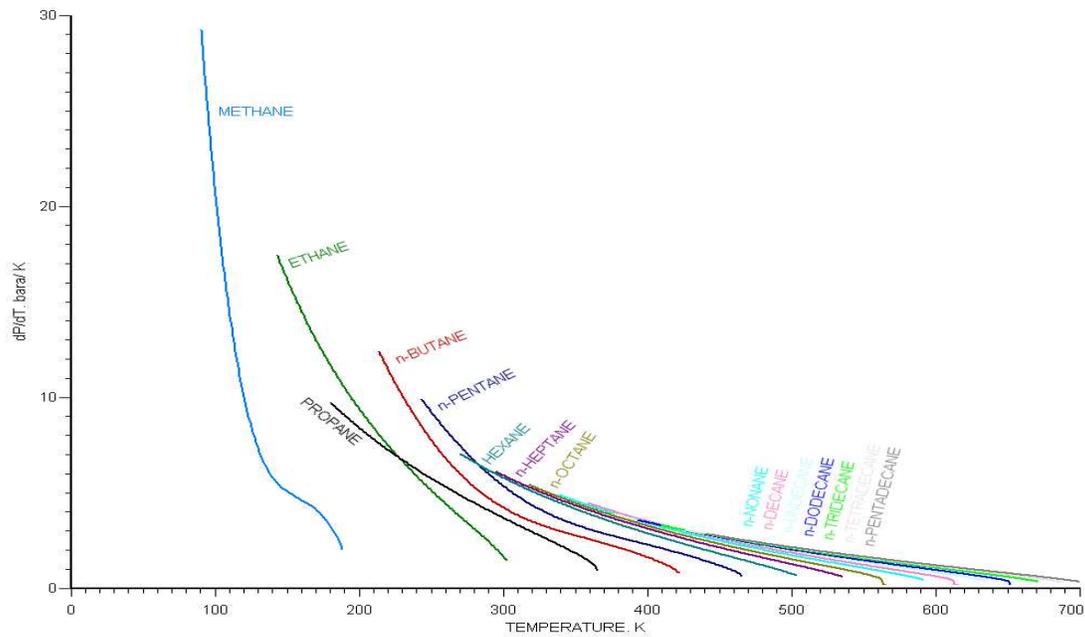
$$\frac{dV_{excess}}{dt} = (V\beta) \frac{dT}{dt} - (V\kappa) \frac{dP}{dt} = 0 \quad \text{or} \quad (13)$$

$$\left[\frac{dP}{dT} \right]_V = \frac{\beta}{\kappa} = \frac{\beta}{\frac{1}{\rho c_s^2} + \frac{T\beta^2}{\rho C_P}} \quad (14)$$

4.1 Isothermal Compressibility, κ

The isothermal compressibility factor κ is the fractional change of density with respect to pressure at constant temperature. κ is typically calculated from an equation of state. The real fluid value is always larger than the ideal gas value.

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \frac{1}{P} - \frac{1}{Z} \left(\frac{\partial Z}{\partial P} \right)_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T \quad (15)$$

Figure 2: $\frac{dP}{dT}$ for liquid alkanes as calculated by SuperChems Expert

Typical values of κ range from 10^{-12} Pa^{-1} to 10^{-5} Pa^{-1} .

Gases $\kappa \simeq 10^{-5} \text{ Pa}^{-1}$

Liquids $10^{-10} < \sim \kappa < \sim 10^{-9} \text{ Pa}^{-1}$

Solids $10^{-12} < \sim \kappa < \sim 10^{-11} \text{ Pa}^{-1}$

The isothermal compressibility factor is always larger than the adiabatic or isentropic compressibility factor. Where measured speed of sound data is available for liquids, the value of the isothermal compressibility can be obtained from such measurements:

$$\kappa = \frac{1}{\rho c_s^2} + \frac{T\beta^2}{\rho C_P} \quad (16)$$

$$\approx \frac{1}{\rho c_s^2} \quad (17)$$

The second term in the above equation, $\frac{T\beta^2}{\rho C_P}$, is approximately 10 % of the total value of κ for most liquids. As a result, the value of κ is not very sensitive to small errors in that term.

4.2 Volume Expansivity, β

The volume expansion factor (volume expansivity) β is equal to the change of density with respect to temperature at constant pressure:

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{T} + \frac{1}{Z} \left(\frac{\partial Z}{\partial T} \right)_P = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P \quad (18)$$

$$(19)$$

4.3 Bulk Modulus of Elasticity, E_T

Another common method of expressing the compressibility of a substance is the bulk modulus of elasticity. The modulus of elasticity, E , has units of pressure. If the compression is isothermal, the modulus of elasticity, E_T , can be expressed as:

$$E_T = \rho \left[\frac{\partial P}{\partial \rho} \right]_T = \frac{1}{\kappa} \quad (20)$$

If the compression is adiabatic, the modulus of elasticity, E_S , can be expressed as:

$$E_S = \rho \left[\frac{\partial P}{\partial \rho} \right]_S = \frac{c_p}{c_v} \frac{1}{\kappa} = \frac{c_p}{c_v} E_T \quad (21)$$

For a solid, the heat capacity ratio is approximately one. As a result, E_S and E_T are approximately equal for a solid:

$$E_{s,S} \simeq E_{s,T} = \frac{1}{\kappa} \quad (22)$$

As a result the speed of sound for solids can be approximated by the following expression:

$$c_s \simeq \sqrt{\frac{E_{s,T}}{\rho}} \quad (23)$$

For a non-ideal fluid, E_S can also be related to the volume expansion coefficient β and the Joule-Thompson coefficient μ_H :

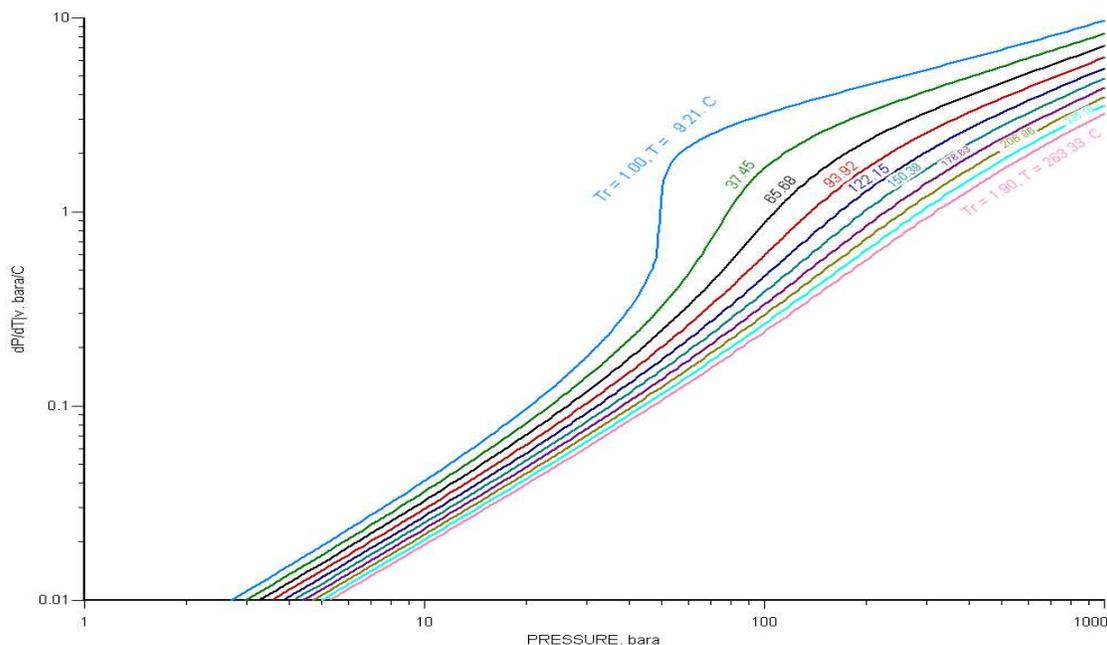
$$E_S = \frac{1}{\kappa - \frac{T\beta^2}{\rho c_p}} = \frac{1}{\kappa - \beta [\mu_H - 1]} = \frac{1}{\kappa - \beta \left[\left(\frac{\partial T}{\partial P} \right)_H - 1 \right]} \quad (24)$$

For an ideal gas, $E_T = P$, and $E_S = \gamma P$.

5 Thermal Expansion for Vapors and Supercritical Fluids

The theoretical pressure rise rate due to thermal expansion of vapors and gases is generally less than that of liquids. While the isothermal compressibility of vapors and gases is around 10^{-5} Pa, the value for liquids typically ranges from 10^{-10} Pa to 10^{-9} Pa. For supercritical vapors, the pressure rise rate due to thermal expansion can become large at high pressures as shown in Figure 3 for ethylene. This is especially true at temperatures close to the critical temperature.

Figure 3: $\frac{dP}{dT}$ for supercritical ethylene as calculated by SuperChems Expert



For an ideal gas, $\kappa = \frac{1}{P}$ and $\beta = \frac{1}{T}$, or:

$$\left[\frac{dP}{dT} \right]_V = \frac{P}{T} \quad (25)$$

6 Thermal Expansion for Incompressible Liquids

Pressure rise rates can be substantial for slightly compressible liquids as shown in Table 2 and infinite for a totally incompressible liquid. Theoretical pressure rise rates for normal alkanes liquids are calculated using SuperChems Expert and are shown in Figure 2.

If we assume a totally incompressible liquid to equation 12:

$$\frac{dV_{excess}}{dt} = (V_l \beta_l) \frac{dT}{dt} = \frac{\beta_l}{\rho_l} \frac{dT}{dt} \quad (26)$$

Table 2: Thermal relief requirement for typical liquids at 363.15 K and 1 bar

Liquid	$\beta_l (K^{-1})$	$\kappa_l (Pa^{-1})$	dP/dT (bar/K)	$\frac{1}{Q} \frac{dV_l}{dt} (m^3/J)$	$C_{pl} (J/kg/K)$
Water	316.5×10^{-6}	2.329×10^{-10}	13.58	7.703×10^{-11}	4207
Toluene	1284×10^{-6}	1.972×10^{-9}	6.51	8.349×10^{-10}	1920
Methanol	1524×10^{-6}	1.279×10^{-9}	11.91	6.863×10^{-10}	3074
Ethanol	1544×10^{-6}	1.431×10^{-9}	10.78	6.773×10^{-10}	3161
Acetone	1922×10^{-6}	3.349×10^{-9}	5.74	1.118×10^{-9}	2440
n-pentane	2287×10^{-6}	8.603×10^{-9}	2.65	1.520×10^{-9}	2742
Aniline	894×10^{-6}	6.912×10^{-10}	12.93	4.240×10^{-10}	2188

Equation 26 is often used to determine the amount of the liquid that needs to be vented in order to keep the pressure in the pipe and/or vessel under allowable limits.

The required thermal relief capacity at constant pressure is given by:

$$\frac{dV_{excess}}{dt} = \frac{\dot{Q} \beta_l}{c_{v,l} \rho_l} \quad (27)$$

where $\frac{dV_{excess}}{dt}$ is in m^3/s , \dot{Q} is in Watts, ρ_l is in kg/m^3 and $c_{v,l}$ is in $J/kg/K$. Typical values for κ_l , β_l and $[\frac{dP}{dT}]_V$ are tabulated in Table 2. As shown in Table 2, pressures developed if thermal relief is not provided can be very large. Values for β_l can be approximated using the following equation, given two close points for density:

$$\beta_l = \frac{(\rho_{l,1} + \rho_{l,2}) \left(\frac{1}{\rho_{l,2}} - \frac{1}{\rho_{l,1}} \right)}{T_2 - T_1} \quad (28)$$

Required relief areas for thermal liquid expansion are typically small. A 3/4 inch x 1 inch relief valve is usually sufficient for most applications. The required thermal expansion relief area can be calculated by equating the volumetric flow rate for a relief valve (calculated from the mechanical energy balance) at the valve's opening pressure with the required flow rate due to thermal expansion as given by Equation 27:

$$\frac{dV_{excess}}{dt} = A_h C_d \sqrt{\frac{2}{\rho_l} [P - P_s]} = \frac{\dot{Q} \beta_l}{c_{v,l} \rho_l} \quad (29)$$

or, we can solve for A_h directly:

$$A_h = \frac{\frac{\dot{Q} \beta_l}{c_{v,l} \rho_l}}{C_d \sqrt{\frac{2}{\rho_l} [P - P_s]}} \quad (30)$$

For equilibrium or liquid flow, P_s is the fluid saturation pressure at the relief temperature or the ambient pressure, whichever is larger. P is the maximum allowable pressure, typically 10 % overpressure over the maximum allowable working pressure of the vessel.

For subcooled liquid flow where non-equilibrium effects dominate during flow, i.e. the flow does not have enough time for flashing to occur, P_s can be lower than the saturation point pressure. This occurs inside the two-phase boundary but without flashing. In extreme conditions of non-equilibrium (where the rate of pressure drop is very high), this pressure can reach the thermodynamic stability limit at which spontaneous generation of vapor has to occur regardless of whether there is enough time for bubbles to form or not. The Bernoulli flow driving pressure in this case becomes larger and more flow is realized. Non-equilibrium flow becomes less important as the initial temperature gets closer to the critical point. The thermodynamic stability pressure limit is equal to the critical pressure at the critical point. The maximum possible driving pressure for Bernoulli flow gets smaller as the initial subcooled liquid temperature gets closer to the critical temperature.

Burnell [2] used a bubble delay factor, C , to approximate the impact of non-equilibrium on mass flux, G , by modifying the standard Bernoulli flow equation:

$$G = \sqrt{2\rho_l [P - (1 - C) P_s]} \quad (31)$$

where C is directly related to the bubble growth delay time and typically ranges from 0.2 to 0.3. The magnitude of C determines the pressure undershoot at the choke point/exit due to the superheating of the liquid. C tends to 0 as the starting initial temperature approaches the critical temperature. Depending on the flow conditions, C can also depend on the length of pipe and initial vapor quality. For pipe flow, it has long been recognized that a pipe flow length of approximately 4 inches [3] is required for equilibrium two-phase flow to develop, $C = 0$. Non-equilibrium is most important for nozzle flow (PRV flow) and for short piping.

The calculation of thermodynamic stability limits for vapor and liquid is complex for mixtures and requires an equation of state. In the case of a pure component, an equation of state is still required. However, the thermodynamic stability limit can be approximated with reasonable accuracy as shown in Figure 5. For a pure component, the stability limit temperature at atmospheric pressure is approximately equal to:

$$T_{sl} \simeq 0.92 T_c \quad (32)$$

where T_c is the critical temperature in Kelvins. If the stagnation temperature of a subcooled liquid pure component is greater or equal to T_{sl} then P_s must be greater or equal to P_{sl} :

$$P_s \geq P_{sl} \geq P_{atm} + (P_c - P_{atm}) \left[\frac{\frac{T}{T_c} - 0.92}{0.08} \right] \quad \text{where } T_{sl} \leq T \leq T_c \quad (33)$$

6.1 Liquid Heat Capacity at Constant Volume

The value of liquid $c_{p,l}$ is often used as $c_{v,l}$. While this may be adequate for certain compounds, actual values of $c_{v,l}$ may be different from $c_{p,l}$ by as much as factor of 1.5 for certain chemicals such as diethyl ether, and ethyl acetate.

Table 3: Liquid heat capacity at constant volume for typical liquids at 363.15 K and 1 bar

Liquid	$\beta_l (K^{-1})$	$\kappa_l (Pa^{-1})$	$\rho_l, \text{kg/m}^3$	$c_{v,l} (\text{J/kg/K})$	$c_{p,l} (\text{J/kg/K})$	$\frac{c_{p,l}}{c_{v,l}}$
Water	316.5×10^{-6}	2.329×10^{-10}	963	4044	4207	1.040
Toluene	1284×10^{-6}	1.972×10^{-9}	801	1541	1920	1.246
Methanol	1524×10^{-6}	1.279×10^{-9}	722	2161	3074	1.422
Ethanol	1544×10^{-6}	1.431×10^{-9}	721	2322	3161	1.361
Acetone	1922×10^{-6}	3.349×10^{-9}	704	1871	2440	1.304
n-pentane	2287×10^{-6}	8.603×10^{-9}	548	2339	2742	1.172
Aniline	894×10^{-6}	6.912×10^{-10}	962	1751	2188	1.249

The value of liquid $c_{v,l}$ should be computed from an equation of state and from the liquid heat capacity at constant pressure, $c_{p,l}$:

$$c_p - c_v = T \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial P}{\partial T} \right)_V \quad (34)$$

or

$$c_v = c_p + \frac{T \left(\frac{\partial P}{\partial T} \right)_V^2}{\left(\frac{\partial P}{\partial V} \right)_T} = c_p - T \frac{\beta^2}{\rho \kappa} \quad (35)$$

$$\frac{c_p}{c_v} = \frac{\kappa}{\kappa_s} = \frac{1}{1 - T \frac{\beta^2}{c_p \rho \kappa}} \quad (36)$$

For some liquids, the heat capacity ratio can be as large as 1.5. The same relationship applies to a real gas as well. For an ideal gas the form reduces to the well known form $c_p - c_v = R_g$:

$$\begin{aligned} \kappa &= \frac{1}{P} \\ \beta &= \frac{1}{T} \\ P &= \rho R_g T \\ c_p - c_v &= T \frac{\beta^2}{\rho \kappa} = R_g \frac{T}{T} = R_g \\ \frac{c_p}{c_v} &= \frac{\kappa}{\kappa_s} = \gamma \end{aligned}$$

The constant volume heat capacity for the liquids shown in Table 2 is shown in Table 3. The heat capacity ratio for methanol is close to 1.5 while that for water is essentially one.

To illustrate the impact of isothermal compressibility of the value of the heat capacity ratio for liquids, we consider the special cases of water and acetone at 20 C and 1 atmosphere.

6.2 Water Liquid Heat Capacity Ratio

$\kappa = 4.591 \times 10^{-10}$ /Pa, $\beta = 0.206 \times 10^{-3}$ /K, $c_p = 4184$ J/kg/K, and $\rho = 1000$ kg/m³.

$$c_p - c_v = \frac{293 \times (0.206 \times 10^{-3})^2}{1000 \times 4.591 \times 10^{-10}} = 27.08 \text{ J/kg/K} \quad (37)$$

and

$$\frac{c_p}{c_v} = \frac{4184}{4184 - 27.08} = 1.0065 \simeq 1 \quad (38)$$

6.3 Acetone Liquid Heat Capacity Ratio

$\kappa = 12.62 \times 10^{-10}$ /Pa, $\beta = 1.46 \times 10^{-3}$ /K, $c_p = 2167$ J/kg/K, and $\rho = 790$ kg/m³.

$$c_p - c_v = \frac{293 \times (1.46 \times 10^{-3})^2}{1000 \times 12.62 \times 10^{-10}} = 626.45 \text{ J/kg/K} \quad (39)$$

and

$$\frac{c_p}{c_v} = \frac{2167}{2167 - 626.45} = 1.4066 \quad (40)$$

6.4 Relief Requirements for Thermal Expansion

Consider 50,000 ft of 4 inch pipe containing n-pentane with a heat input of 50 W/ft (typical of solar radiation in the summer. see [4]), we calculate a required relief area of 0.180 in² for a valve with a set pressure of 150 psig:

$$A_h = \frac{(1.748 \times 10^{-9}) \times 50 \times 50,000}{0.62 \sqrt{\frac{2}{548}(11.204 - 1) \times 10^5}} = \frac{0.0038}{37.83} = 1.155 \times 10^{-4} \text{ m}^2 \text{ or } 0.180 \text{ in}^2 \quad (41)$$

If the heat capacity at constant pressure was used instead, we would calculate a required relief area of 0.155 in², a 15 % smaller value.

7 Dynamics of Thermal Expansion Relief

We consider a vessel full of a single phase fluid that is exposed to a heating rate \dot{Q} . Simplifying the detailed vessel balances derived by Melhem [5] and ignoring the fluid partial molar volumetric change, we can fully describe the temperature and pressure in the fluid full vessel:

Mass Balance:

$$\frac{dm}{dt} = \dot{m}_{in} - \dot{m}_{out} \quad (42)$$

Internal Energy Balance:

$$(m c_v + m_s c_{v,s}) \frac{dT}{dt} + U \frac{dm}{dt} = \dot{Q} - \dot{H}_{out} - \dot{E}_{out} + \dot{H}_{in} + \dot{E}_{in} \quad (43)$$

or

$$\frac{dT}{dt} = \frac{\dot{Q} + \dot{H}_{in} + \dot{E}_{in} - \dot{H}_{out} - \dot{E}_{out} - U \frac{dm}{dt}}{m c_v + m_s c_{v,s}} \quad (44)$$

and

$$c_v = c_p - \frac{T \beta^2}{\rho \kappa} \quad (45)$$

Expressing internal energy and enthalpy in terms of c_p and c_v leads to the following expression for dT/dt :

$$\frac{dT}{dt} = \frac{\dot{Q} + \frac{1}{2} (\dot{m}_{in} u_{in}^2 - \dot{m}_{out} u_{out}^2) + (\dot{m}_{in} - \dot{m}_{out}) q - \dot{m}_{in} q^* + \dot{m}_{in} q'}{\underbrace{\dot{E}_{in} - \dot{E}_{out}}_{m \left[c_p - \frac{T \beta^2}{\rho \kappa} \right] + m_s c_{v,s}}} \quad (46)$$

$$q = \int_{T_0}^T (c_p - c_v) dT = \int_{T_0}^T \left[\frac{T \beta^2}{\rho \kappa} \right] dT$$

$$q^* = \int_{T_0}^T c_p dT \quad (48)$$

$$q' = \int_{T_0}^{T_{in}} c_p dT \quad (49)$$

$$\frac{dq}{dt} = c_p - c_v = \frac{T \beta^2}{\rho \kappa} \quad (50)$$

$$\frac{dq^*}{dt} = c_p \quad (51)$$

The internal energy equation assumes that the vessel material of construction is at the same temperature as the fluid because the heat transfer coefficient between the inner wall of the vessel and the fluid is large enough. This is a reasonable approximation for liquid full vessels. Detailed analysis involving actual heat transfer through the metal shows that for gas filled vessels the metal will heat up much faster than the gas contents [6].

Overall Volume Balance:

$$V = \frac{m}{\rho} \quad (52)$$

$$\frac{dV_{excess}}{dt} = V\beta\frac{dT}{dt} - V\kappa\frac{dP}{dt} - 3\alpha_s V_s\frac{dT}{dt} - \left(\frac{D_i}{\delta}\right) \left(\frac{V_s}{E_{s,T}}\right) f(\nu)\frac{dP}{dt} = 0 \quad (53)$$

or since V_s must equal V at all times:

$$\frac{dP}{dt} = \left[\frac{V\beta - 3\alpha_s V_s}{V\kappa + \left(\frac{D_i}{\delta}\right) \left(\frac{V_s}{E_{s,T}}\right) f(\nu)} \right] \frac{dT}{dt} = \left[\frac{(\beta - 3\alpha_s) E_{s,T}}{E_{s,T}\kappa + \left(\frac{D_i}{\delta}\right) f(\nu)} \right] \frac{dT}{dt} \quad (54)$$

Vessel Metal Volume:

$$\frac{dV_s}{dt} = 3\alpha_s V_s\frac{dT}{dt} + \left(\frac{D_i}{\delta}\right) \left(\frac{V_s}{E_{s,T}}\right) f(\nu)\frac{dP}{dt} \quad (55)$$

PVT:

$$\rho = f(T, P) = \frac{m}{V} = \frac{m}{V_s} \quad (56)$$

For liquid flow:

$$\dot{m}_{out} = \rho_l A_h C_d u_{out} = \rho_l A_h C_d \underbrace{\sqrt{\frac{2}{\rho_l} [P - (1 - C) P_s]}}_{u_{out}} = A_h C_d \sqrt{2\rho_l [P - (1 - C) P_s]} \quad (57)$$

$$(58)$$

$\dot{m}_{out} = 0$ unless the relief device used for thermal relief is open. P_s is the larger of ambient pressure or the bubble point pressure of the liquid at the current temperature.

Burnell [2] used the bubble delay factor, C , to approximate the impact of non-equilibrium on mass flow. C is directly related to the bubble growth delay time and typically ranges from 0.2 to 0.3. The magnitude of C determines the pressure undershoot at the choke point/exit due to the superheating of the liquid. C tends to 0 as the starting initial temperature approaches the critical temperature. Depending on the flow conditions, C can also depend on the length of pipe and initial vapor quality. For pipe flow, it has long been recognized that a pipe flow length of approximately 4 inches [3] is required for equilibrium two-phase flow to develop, $C = 0$. Non-equilibrium is most important for nozzle flow (PRV flow) and for short piping (also see [7]).

The above equations can easily be solved using a differential equations solver for T , P , V_s , and V as a function of time. For liquid full vessels, the solution is valid until the temperature of liquid equals the bubble point temperature at the calculated pressure at which point a two-phase solution

is required. The solution requires temperature dependent values of thermodynamic properties. The values of β and κ are almost always obtained from an equation of state or actual measured data. The constant volume heat capacity of the vessel material of construction is effectively equal to the heat capacity at constant pressure.

For a single phase ideal gas fluid, we can show that gas pressure, temperature, and mass change as a function of time as follows:

$$\frac{dm}{dt} = \dot{m}_{in} - \dot{m}_{out} \quad (59)$$

$$\frac{dT}{dt} = \frac{1}{mc_v + m_s c_{v,s}} \left[\dot{Q} + \frac{(\dot{m}_{in} u_{in}^2 - \dot{m}_{out} u_{out}^2)}{2} + c_v \gamma (\dot{m}_{in} T_{in} - \dot{m}_{out} T) - c_v T \frac{dm}{dt} \right] \quad (60)$$

$$\frac{dP}{dt} = \frac{R_g}{M_w V} \left[T \frac{dm}{dt} + m \frac{dT}{dt} \right] \quad (61)$$

$$\frac{dV}{dt} = \frac{dV_s}{dt} = 3\alpha_s \frac{dT}{dt} + \left(\frac{D_i}{\delta} \right) \left(\frac{1}{E_{s,T}} \right) f(\nu) \frac{dP}{dt} \quad (62)$$

$$\rho = \frac{m}{V} = \frac{PM_w}{R_g T} \quad (63)$$

where $c_v T$ is the specific internal energy of the gas, $c_v \gamma T$ is the specific enthalpy of the gas, \dot{m}_i is the mass flow into the vessel at temperature T_i , \dot{m}_o is the mass flow into the vessel at the gas temperature T , $c_v = \frac{R_g}{M_w(\gamma-1)}$ is the specific heat capacity at constant volume, R_g is the universal gas constant, \dot{Q} is the heat exchange rate between the gas and vessel metal and/or surroundings, γ is the ideal gas heat capacity ratio, m is the gas total mass, ρ is the gas mass density, and V is the vessel volume. The subscript s references the vessel material of construction where α_s is the material of construction coefficient of thermal linear expansion, $E_{s,T}$ is the material of construction modulus of elasticity, D_i is the internal vessel diameter, δ is the vessel wall thickness, ν is Poisson's ratio, and $f(\nu)$ depends on the vessel geometry. If we ignore vessel metal expansion and/or contraction, then:

$$\frac{dV}{dt} = \frac{dV_s}{dt} = 0 \quad (64)$$

These equations can be used to calculate the temperature, pressure, and mass time history during a vessel blowdown, or during charging of a gas vessel. These equations assume that the vessel metal is at the same temperature as the vessel contents. Detailed analysis involving actual heat transfer through the metal shows that for gas filled vessels the metal will heat up much faster than the gas contents [6].

For ideal gas flow, \dot{m}_{out} can be calculated from the following equation assuming that the stagnation fluid velocity is zero:

$$\dot{m}_{out} = C_d A_h \sqrt{2P\rho \left(\frac{\gamma}{\gamma-1} \right) \left[\left(\frac{P_e}{P} \right)^{2/\gamma} - \left(\frac{P_e}{P} \right)^{\frac{\gamma+1}{\gamma}} \right]} \quad (65)$$

where $P_e = P_c$ if P_c is greater than the ambient back pressure, P_s :

$$P_e = P_c = P \left(\frac{2}{\gamma + 1} \right)^{\frac{\gamma}{\gamma - 1}} \geq P_s \quad (66)$$

P_c is the critical flow pressure. Under these conditions the mass flux is not influenced by the ambient back pressure up to P_c and the flow is said to be choked or sonic. Under choked flow conditions, the mass flow rate can be calculated from a simplified form of the above equation which incorporates the critical pressure ratio P_c from Equation 66:

$$\dot{m}_{out} = C_d A_h \sqrt{\gamma P \rho \left(\frac{2}{\gamma + 1} \right)^{\frac{\gamma + 1}{\gamma - 1}}} \quad (67)$$

For subsonic flow, P_e is equal to P_s , and the mass flow is calculated from Equation 65.

7.1 Thermal Expansion Pressure Increase for a Compressible Liquid

If we assume constant fluid and metal properties over a small temperature range without thermal relief, the pressure change can be related to temperature change using equation 54:

$$\frac{dP}{dT} = \frac{(\beta_l - 3\alpha_s) E_{s,T}}{E_{s,T} \kappa_l + \left(\frac{D_i}{\delta} \right) f(\nu)} \quad (68)$$

or

$$P_2 = P_1 + \left[\frac{(\beta_l - 3\alpha_s) E_{s,T}}{E_{s,T} \kappa_l + \left(\frac{D_i}{\delta} \right) f(\nu)} \right] [T_2 - T_1] \quad (69)$$

If we consider a 12 inch diameter steel cylindrical vessel (pipe) with a thickness of 0.5 inch containing water at 363.15 K without pressure relief, we calculate a pressure increase of 8 bar/K:

$$\frac{dP}{dT} = \frac{(316.5 \times 10^{-6} - 3 \times 12 \times 10^{-6}) 200 \times 10^9}{200 \times 10^9 \times 2.329 \times 10^{-10} + \left(\frac{12}{0.5} \right) (1.25 - 0.3)} = 8.09 \text{ bar/K} \quad (70)$$

This is a value that is 60 % of the theoretical value calculated in Table 2. dP/dT decreases as the diameter to thickness ratio increases and vice versa.

8 Catastrophic Vessel Failure Caused by Liquid Thermal Expansion

Pressure relief is required for thermal expansion. This is especially important for liquids and liquid mixtures where the initial conditions are saturated/subcooled and/or where the conditions due to

expansion caused by heating can lead to a superheated liquid or liquid mixture with respect to ambient pressure.

As illustrated in the previous sections, pressure increase for closed/isolated equipment due to thermal expansion for liquids can be substantial even with a small increase in temperature. Equipment without pressure relief can be overpressured to the point where a large enough opening/tear caused by the increasing pressure can cause catastrophic vessel failure due to non-equilibrium effects and explosive boiling of the liquid. This can lead to a superheat limit Boiling Liquid Expanding Vapor Explosion (BLEVE) or a Boiling Liquid Compressed Bubble Explosion, BLCBE. Although the relief requirement for thermal expansion is small, the equipment can still fail catastrophically if the rate of pressure drop is large due to a large enough opening/tear [8].

In a superheat limit explosion, the sudden formation of a large enough opening/tear in the vessel leads to a rapid pressure drop. The liquid becomes metastable and superheated because the rapid pressure drop renders any nucleation sites inactive and flashing does not occur immediately. If the pressure drops below the mechanical stability limit, $\frac{\partial P}{\partial V} = 0$ for a pure component, spontaneous generation of vapor/flashing occurs inside the vessel. This leads to choked flow through the opening/tear and an extreme rise in pressure in the vessel causing failure. The maximum pressure spike can be estimated by isentropically compressing the spontaneously formed vapor and liquid mixture into the vessel volume.

A BLCBE can occur well below the superheat limit. The rapid pressure drop causes the liquid to become metastable and superheated. This is followed by homogeneous bubble formation of the pre-nucleated liquid. Rapid two-phase swell, re-pressurization, and coherent collapse of vapor bubbles containing non-condensable gas (cavitation) produces a shock wave which is radiated through the liquid to cause vessel failure.

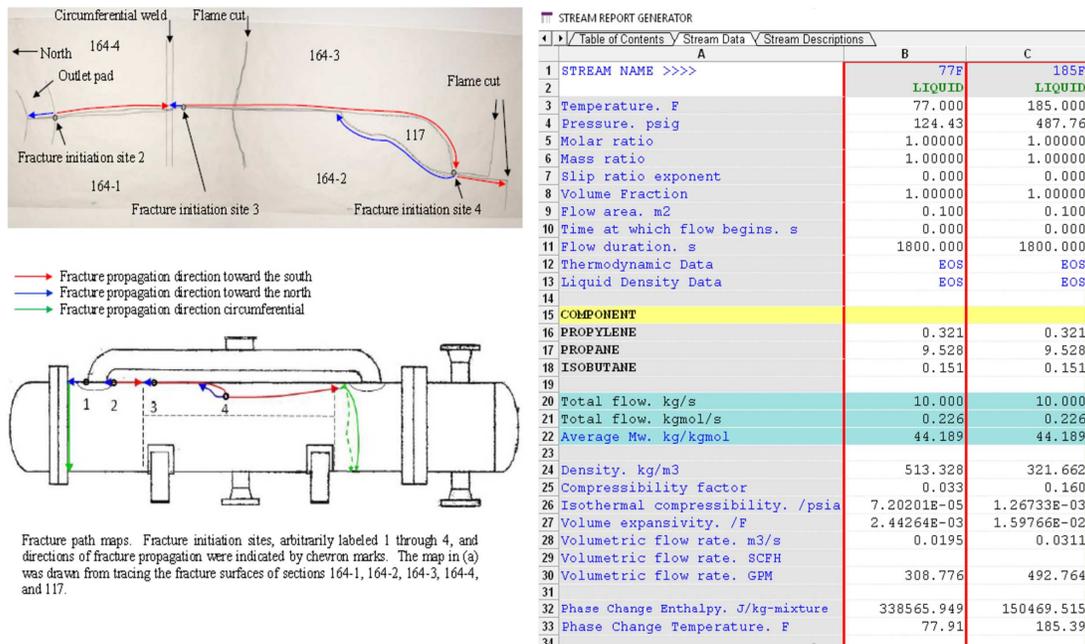
8.1 June 2013 Williams Geismar Olefins Plant Explosion

Thermal liquid expansion of a mixture consisting of mostly propane was recently identified as the cause of a reboiler rupture at the Williams Geismar olefins plant in Louisiana on June 13, 2013. The catastrophic reboiler rupture, explosion, and fire killed two Williams employees.

Propane was mistakenly introduced into a standby reboiler that was isolated from the relief system. Heat was then introduced to the reboiler which was offline, creating an overpressure event while the vessel was isolated from its pressure relief system. The introduced heat increased the temperature of the liquid propane mixture confined within the reboiler shell, resulting in a dramatic pressure rise within the vessel due to liquid thermal expansion. The reboiler shell catastrophically ruptured, causing a BLEVE and fire.

The calculated pressure rise rate due to thermal expansion of the liquid mixture as shown in Figure 4 ranges from 12.8 psi/F at 77 F to 33.95 psi/F at 185 F. This leads to a maximum potential pressure increase of 2,524 psi which is more than enough to cause the large fractures in the shell as shown in Figure 4.

The failure pressure of the shell was estimated to be between 674 and 1,212 psig by the Chemical Safety Board (CSB) [9]. The large flow area of the fractures caused the rapid pressure drop below

Figure 4: $\frac{dP}{dT} = \frac{\beta}{\kappa}$ as calculated by SuperChems Expert for the propane mixture

the superheat limit (shown here for propane only) as shown in Figure 5. As a result, we calculate a maximum pressure spike in the vessel of approximately 7,000 psig (CSB estimated ≈ 5000 psig) and a coincident maximum temperature of 668 F as shown in Figure 6. The magnitude of this pressure spike is consistent with the observations that the reboiler failed catastrophically due to internal pressure despite having sufficient flow area for liquid thermal expansion provided by the large fractures. The calculated maximum temperature of 668 F is below the autoignition temperature of propane and is consistent with the CSB assertion that the resulting vapor cloud found an ignition source elsewhere in the plant.

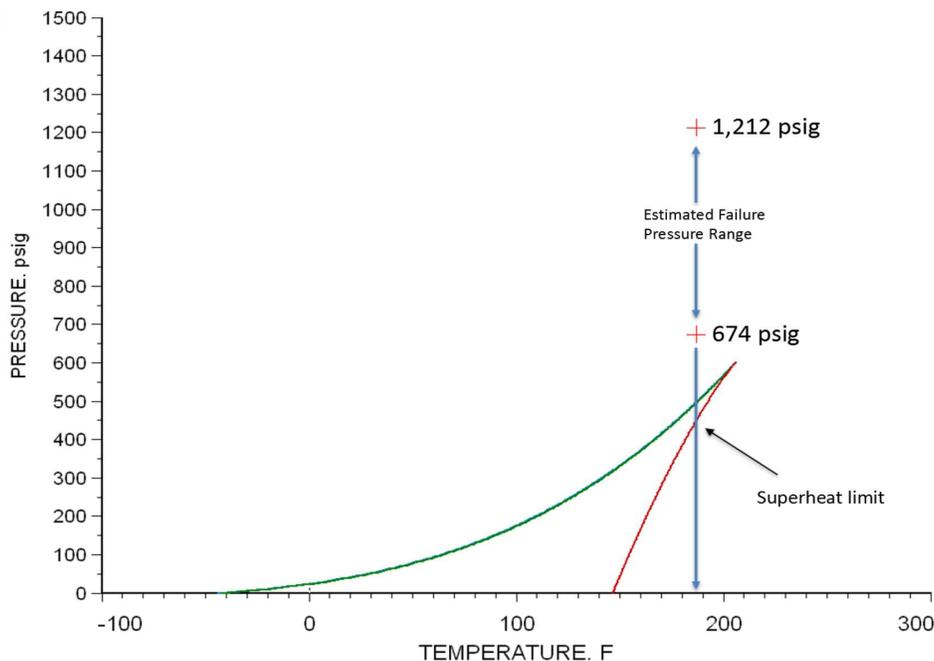
9 Forces Associated with Thermal Expansion

Thermal expansion or contraction of solids can lead to significant stress and has to be compensated for with expansion loops in piping systems to prevent buckling. The stress due to thermal expansion is given by:

$$\sigma_T = \frac{F}{A} = \alpha_s E_{s,T} \Delta T \quad (71)$$

where σ_T is the thermal stress due to expansion in pressure units, F is the thermal expansion force, and A is the cross sectional area of the metal.

Figure 5: Superheat Limit for Propane as calculated by SuperChems Expert



10 Upper Limits for Relief Device Set Pressure

It is desirable to keep the set/opening pressure of non-reseating, fast opening, relief devices below the superheat limits of pressure and temperature as shown in Figure 7. This will ensure, that even in the case of an oversized relief device, the pressure does not drop below the thermodynamic stability limit causing a large pressure spike in the vessel that can lead to catastrophic failure. In addition, pressure relief protection should be provided for equipment that can be blocked in with a set pressure below superheat limit pressure.

Although repressurization is still possible in what is shown as the BLCBE region, very large rates of pressure drop would be required to cause a BLCBE.

11 Conclusions

Fluid thermal expansion can lead to significant pressures that can cause equipment failure. Thermal expansion pressure relief for liquids and supercritical fluids should be considered for equipments that can be isolated and subjected to heating. Vessel metal expansion can reduce the thermal expansion relief requirement but is often neglected since the requirement for thermal expansion relief is typically small. Considerations for thermal expansion relief should take into account the type of fluid or mixture, non-equilibrium flow, and the thermodynamic stability limit. The thermal expansion relief requirement as calculated by Equation 30 is typically oversized.

Figure 6: Calculated Superheat Limit Maximum Pressure Spike by SuperChems Expert

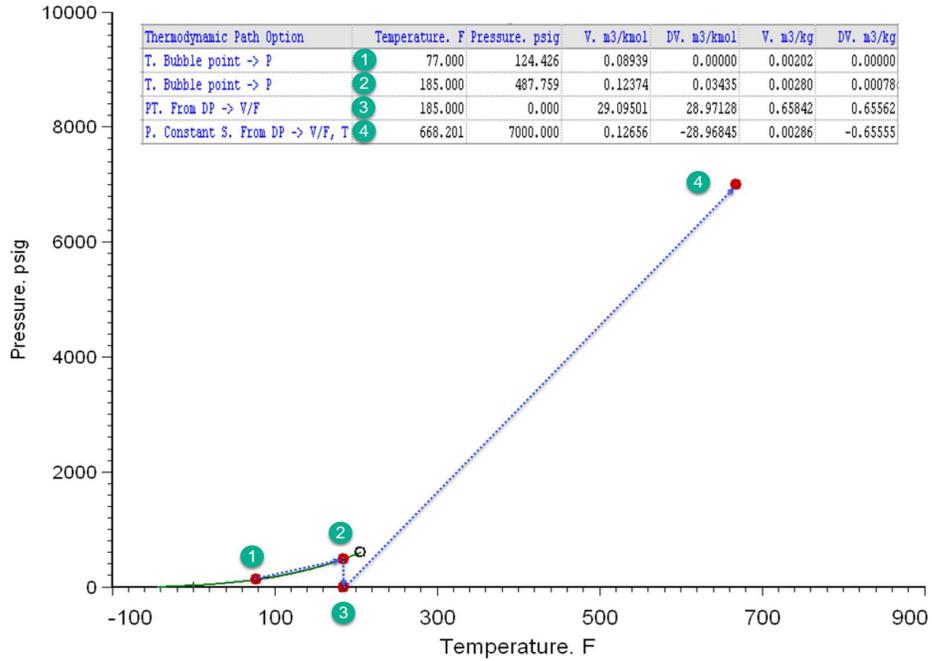
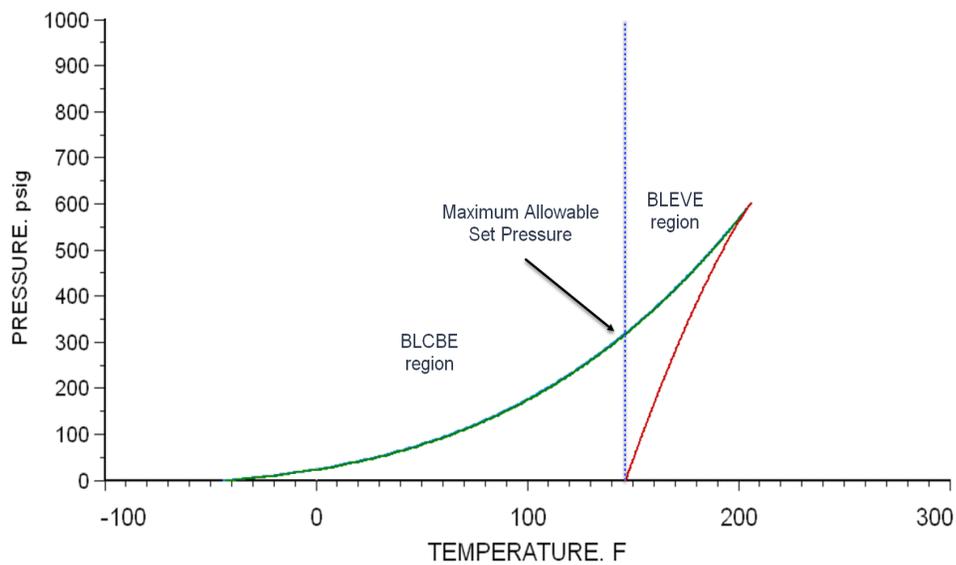


Figure 7: Propane Upper Limit for Relief Device Set Pressure



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About the Author



Dr. Melhem is an internationally known pressure relief and flare systems, chemical reaction systems, process safety, and risk analysis expert. In this regard he has provided consulting, design services, expert testimony, incident investigation, and incident reconstruction for a large number of clients. Since 1988, he has conducted and participated in numerous studies focused on the risks associated with process industries fixed facilities, facility siting, business interruption, and transportation.

Prior to founding ioMosaic Corporation, Dr. Melhem was president of Pyxsys Corporation; a technology subsidiary of Arthur D. Little Inc. Prior to Pyxsys and during his twelve years tenure at Arthur D. Little, Dr. Melhem was a vice president of Arthur D. Little and managing director of its Global Safety and Risk Management Practice and Process Safety and Reaction Engineering Laboratories.

Dr. Melhem holds a Ph.D. and an M.S. in Chemical Engineering, as well as a B.S. in Chemical Engineering with a minor in Industrial Engineering, all from Northeastern University. In addition, he has completed executive training in the areas of Finance and Strategic Sales Management at the Harvard Business School. Dr. Melhem is a Fellow of the American Institute of Chemical Engineers (AIChE) and Vice Chair of the AIChE Design Institute for Emergency Relief Systems (DiERS).

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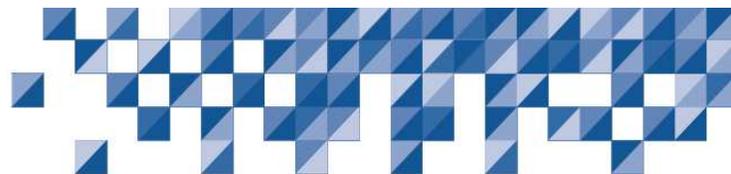
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