



Heat of Vaporization Considerations for Relief Systems Applications

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Heat of Vaporization Considerations for Relief Systems Applications

Process Safety and Risk Management Practices

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1 Introduction

A common scenario that is encountered in pressure relief systems design centers around the calculation of vapor generation rates from liquids under external heating, internal heating, or fire exposure.

Pressure relief design is all about a volume balance. As the heating increases the liquid temperature and generates more vapor (volume) in a vessel, the pressure increases to fit the additional vapor generation (volume created) within the confines of the vessel. Relieving the vapor at a specific pressure, removes the additional vapor volume and keeps the pressure in the vessel in check.

This relief design scenario shares some commonalities with batch distillation when the liquid being heated is a chemical mixture. Similar to batch distillation, mixture light ends are preferentially depleted first. The resulting volumetric vapor generation rate depends on the vapor composition. Initially the vapor composition will be rich in light components.

As the light components are preferentially depleted, the vapor composition will become rich in heavier components. Thermodynamic, physical, and transport properties change as the mixture is fractionated for both the liquid and the vapor. The maximum relief requirement may occur anywhere along the fractionation curve.

For reactive mixtures where all vapor venting occurs, special care must be taken to ensure that materials that are preferentially concentrated do not spontaneously decompose or deflagrate.

2 Prevailing Practices

Simple design equations, such as those provided by API [1], continue to be widely used. However, these simple equations require a value of the latent heat of vaporization which varies with composition for a liquid mixture as venting is occurring.

Limited guidance provided in API-521 [1] includes the following statements: (a) "*The latent heat and relative molecular mass values used in calculating the rate of vaporization should pertain to the conditions that are capable of generating the maximum vapor rate*" and (b) "*The vapor to be relieved is the vapor that is in equilibrium with the liquid under conditions that exist when the PRD is relieving at its accumulated pressure*".

Dynamic software tools such as Process Safety Office[®] SuperChems ExpertTM can automatically identify the mixture conditions leading the the maximum vapor generation rate under equilibrium conditions and can also calculate the vessel wall temperatures and expected time to failure or time to yield as heavies are concentrated. A reclosing pressure relief device can only protect from overpressure and not overtemperature [2, 3].

Several operating companies have also resorted to rules of thumb on how to calculate a representative latent heat of vaporization value. While it is relatively simple to establish relief requirements for vessels containing a single liquid component, there are many pitfalls associated with vessels containing multicomponent liquid mixtures. The value of the heat of vaporization for mixtures (enthalpy or internal energy) is not straight forward to calculate. The vapor composition is only equal to the bubble point liquid composition at the dew point.

Some companies exclude sensible heat when calculating the vapor generation rate while others remove dissolved and non-condensible gases as well as water in hydrocarbon systems. Normally, the latent heat, relieving temperature, and vapor composition are calculated at some percentage (5 or 10 %) by mass vaporized based on the normal liquid composition at relief conditions. Methods for performing a pseudo-dynamic estimate are also used where the required vent area is calculated at 5 % intervals over the entire fractionation range. The largest calculated vent area is then selected. A floor value (typically ranging from 50 to 100 BTU/lb vaporized) is placed on the latent heat of vaporization during relief as critical conditions are approached or as heavies become predominant in the mixture and can decompose endothermically during relief.

3 Thermodynamics of Vapor Generation

For pressure relief evaluation and design, we are interested in the rate of vapor generation and not just the overall amount of vapor generated. Let's consider a vessel that contains a mixture of vapor and liquid that is exposed to either internal or external heating. If we confine the thermodynamic system to the overall contents of the vessel, liquid and vapor, and assume only heat exchange with the contents, we can write an overall energy balance for the contents based on the first law of thermodynamics:

$$\frac{d}{dt}\left[m_v e_v + m_l e_l\right] = \frac{dQ}{dt} \tag{1}$$

where m is mass, e is internal energy, Q is heat exchange, t is time, v indicates the vapor phase, l indicates the liquid phase, and vl indicates a mixture property or a phase change.

Equation 1 can be expressed in differential form in terms of vapor generation, assuming no mass exchange with the surroundings:

$$\frac{dm_v}{dt} = \frac{\frac{dQ}{dt} - m_v \frac{de_v}{dt} - m_l \frac{de_l}{dt}}{e_v - e_l} = \frac{\frac{dQ}{dt} - m_v \frac{de_v}{dt} - m_l \frac{de_l}{dt}}{\Delta e_{vl}}$$
(2)

where Δe_{vl} is the internal energy heat of vaporization. The internal energy for a real fluid changes with temperature, pressure, and composition. When the composition effects are minimal:

$$\frac{de}{dt} = \frac{\partial e}{\partial T}\frac{dT}{dt} + \frac{\partial e}{\partial P}\frac{dP}{dt} = c\frac{dT}{dt} + \frac{\partial e}{\partial P}\frac{dP}{dt}$$
(3)

where c is the specific heat capacity at constant volume. Therefore, Equation 2 can be written as:

$$\frac{dm_v}{dt} = \frac{\frac{dQ}{dt} - \overbrace{(m_v c_v + m_l c_l)}^{\text{Sensible heat}} \underbrace{\frac{dT}{dt} - \overbrace{(m_v \frac{\partial e_v}{\partial P} + m_l \frac{\partial e_l}{\partial P})}^{\text{Pv or pressure energy}}}_{\Delta e_{vl}}$$
(4)

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Equation 4 provides an expression for the vapor generation rate. This vapor generation rate is what needs to be removed by a relief system in order to keep the pressure from exceeding a maximum allowable accumulation limit. We note that that a portion of the heating rate goes to increase the temperature (sensible heat), and a portion of the heating rate also goes to increase pressure (Pv or pressure energy).

If the relief system is sized properly to remove the vapor generation rate, then the rate of pressure change should go to zero. However, the temperature rise rate does not necessarily go to zero:

$$\frac{dm_v}{dt} = \frac{\frac{dQ}{dt} - \overbrace{(m_v c_v + m_l c_l)}^{\text{Sensible heat}} \frac{dT}{dt}}{\Delta e_{vl}}$$
(5)

For a single component, i.e. where fractionation is not occurring due to heating, the rate of temperature change also goes to zero. As a result, there are no sensible heat effects at the maximum allowable accumulation as long as the relief device is properly sized:

$$\frac{dm_v}{dt} = \frac{dQ}{dt} \frac{1}{\Delta e_{vl}} \tag{6}$$

However, for a multicomponent mixture, the rate of temperature rise can continue to increase due to ongoing heating as the light components of the mixture are preferentially depleted. This preferential depletion will lead to increasingly higher temperatures until the mixture finally consists of the heaviest component. For a multicomponent mixture the sensible heat contribution needs to be accounted for and removed from the heating rate as the mixture is fractionated (see Equation 5). This is yet another reason for why dynamic software tools such as SuperChems Expert should be used to determine the optimal relief requirements.

4 Single Component Vapor Relief Requirements

This is the simplest of the vapor relief sizing methods. We note that for a single component, a vapor and liquid mixture can exist at the same saturation conditions with different vapor to liquid ratios. The dew point is equal to the bubble point and the equilibrium composition is the same at both conditions.

Equation 6 is often used for developing the vapor relief requirements for single components and mixtures, but instead of the internal energy heat of vaporization, Δe_{vl} , the enthalpy of vaporization, Δh_{vl} , is commonly used instead. This is thermodynamically incorrect and can lead to reduced venting requirements.

While for many systems the values of Δe_{vl} and Δh_{vl} are approximately the same, there are some systems where the values can differ significantly, especially near the critical point. The use of the generic term latent heat of vaporization can refer to either "enthalpy" or "internal energy" heat of vaporization.

For a constant volume system, the enthalpy of vaporization is related to the internal energy of vaporization as follows:

$$\frac{dm_v}{dt} = \frac{dQ}{dt}\frac{1}{\Delta h_{vl}} = \frac{dQ}{dt}\frac{1}{\Delta e_{vl} + \Delta(Pv)_{vl}}$$
(7)

where h is the specific enthalpy. As a result Δe_{vl} is always smaller than Δh_{vl} , typically between 85 to 90 % of of Δh_{vl} .

CCPS [4] recommends the use of a density correction factor to determine the vapor generation rate (relief requirement) for a single component:

$$\frac{dm_v}{dt} = \underbrace{\left(1 - \frac{\rho_v}{\rho_l}\right)}_{\ell l} \quad \frac{dQ}{dt} \frac{1}{\Delta h_{vl}}$$
(8)

where ρ is a specific volume correction factor. Note that both ρ and Δh_{vl} will go to zero as critical conditions are approached. Equation 8 does not apply directly to mixtures. However, CCPS published guidance on how to identify the mixture component that will determine the relief requirement in order to size the relief device. A physical property factor, PPF, is introduced to determine which mixture component will set the relief requirement:

$$PPF = \frac{ZT_s}{\Delta h_{vl} M_w k^{0.35}}$$
(9)

where Z is the compressibility factor, T_s is the absolute saturation temperature at the maximum allowable relief pressure, Δh_{vl} is the specific latent heat of vaporization, M_w is the molecular weight, and k is the isentropic expansion coefficient. Equation 9 has to be applied with consistent units and should only be used for components that can boil at the relief pressure. Furthermore, CCPS [4] recommends that components less the 1 mole % in the mixture should be eliminated from consideration.

While Equation 9 can result in a proper selection of a relief device size, the actual (not calculated) relief temperature, volumetric flow rate, composition, and other important properties are clearly mixture dependent properties. These properties would not be truly representative of the actual relief properties by just using the calculated relief properties for the component with the largest PPF.

5 Single Component Heat of Vaporization

The heat of vaporization for a single component is simply the amount of energy required to transform a saturated liquid unit mass to a saturated vapor unit mass. For a single component, the composition of the saturated liquid is the same as the composition of the saturated vapor, i.e. 1. The latent heat of vaporization can be related to the vapor pressure of a single component using the Clapeyron relationship:

$$\Delta h_{vl} = T \frac{(V_v - V_l)}{M_w} \frac{dP}{dT}$$
(10)

where V is the molar volume at saturation conditions. The same relationship can be expressed as a function of the compressibility factor Z:

$$\Delta h_{vl} = \frac{R_g T^2}{M_w} \left(Z_v - Z_l \right) \frac{1}{P} \frac{dP}{dT} = \frac{R_g T}{M_w} \left(Z_v - Z_l \right) \frac{d\ln P}{d\ln T} = -\frac{R_g}{M_w} \left(Z_v - Z_l \right) \frac{d\ln P}{d\frac{1}{T}}$$
(11)

When the vapor pressure is expressed as a function of 1/T, $\ln(P) = A + B/T$, then it can be shown that the latent heat of vaporization is equal to:

$$\Delta h_{vl} = -\frac{R_g}{M_w} \left(Z_v - Z_l \right) B \simeq -Z_v \frac{R_g}{M_w} B \simeq -Z_v \frac{8314}{M_w} B \tag{12}$$

where Δh_{vl} is in J/kg, P is in Pa, T in in K, and R_g is in J/kmol/K. Using a simple expression for water vapor pressure ($\ln P = 25.0921 - \frac{5143.37}{T}$), we can calculate the latent heat of vaporization of water assuming ideal gas behavior:

$$\Delta h_{vl} = \frac{5143.37 \times 8314}{18.016} = 2.375 \times 10^6 \text{ J/kg or } 1022 \text{ BTU/lb}$$
(14)

6 The Four Multicomponent Heats of Vaporization

Mixtures heat of vaporization is an important thermodynamic property that is required for the proper design of heat exchange equipment and for relief and flare systems evaluation and design. For vessels containing liquid mixtures, the relief requirement is driven by the rate of vapor generation which depends on the "differential" heat of vaporization of the mixture. Most existing simple steady-state methods utilize an "integral" value of the heat of vaporization to establish relief requirements. We can show that using the "integral" value of the heat of vaporization can often lead to an over-estimate of relief requirements and in some cases can lead to an under-estimate of the relief requirements.

As mentioned earlier, for a single component, a vapor and liquid mixture can exist at the same saturation conditions with different vapor to liquid ratios. The dew point is equal to the bubble point and the equilibrium composition is the same at both conditions. This is not the case for a mixture. For a mixture, the bubble point and dew points are different (see Figure 1) and the vapor composition is only equal to the bubble point liquid composition at the dew point.

Depending on the composition of the mixture and the difference in boiling points of the mixture constituents, the phase envelope can either be narrow or wide. The phase envelope shown in





Figure 1 was produced using SuperChems Expert (also see [5] and [6]) for a 50/50 molar mixture of ethane-heptane with a binary interaction parameter $k_{ij} = 0.0102$. There are four different values of the heat of vaporization as shown in Figure 1:

- 1. Integral isobaric heat of vaporization,
- 2. Differential isobaric heat of vaporization,
- 3. Integral isothermal heat of vaporization, and
- 4. Differential isothermal heat of vaporization.

Point 1 represents a liquid mixture at its bubble point, i.e. the point at which the first bubble of vapor forms. The composition of the vapor phase is not equal to the composition of the liquid phase and will contain higher fractions of the lighter mixture constituents. The differential amount of energy required to produce a small differential amount of vapor at a small temperature increase over any temperature in the twophase region starting with the bubble point is called the "differential" heat of vaporization.

Point 2, represents the dew point of the mixture. The dew point is the point at which the first drop of liquid forms. Note that the vapor composition at the dew point is equal to the liquid composition at the bubble point. The difference between the enthalpies (or internal energies) between points 2

and 1 is called the "integral" isobaric heat of vaporization. This is the amount of energy required to completely vaporize the liquid and convert it to vapor.

The differential heat of vaporization is not equal to the integral heat of vaporization because it involves a vapor of a different composition from the liquid.

Point 4 also represents a dew point of the mixture. The difference between the enthalpies (or internal energies) between point 4 and point 1 is called the "integral" isothermal heat of vaporization. The "integral" isothermal heat of vaporization is easily related to the "integral" isobaric latent heat of vaporization since enthalpy and internal energy are state functions.

The same discussion can be applied to heat of condensation. The heat of condensation can be defined similarly to the heat of vaporization. The heat of condensation, differential or integral, is equal to the heat of vaporization but opposite in sign, i.e. negative. The heat of vaporization is positive to represent heat added to the system while the heat of condensation is negative to represent heat liberated by the system.

7 The Differential Heat of Vaporization

Calculation of differential isobaric heat of vaporization is simple if a suitable PVT relation (equation of state) is available with adequate mixing and combining rules. Let w be defined as the molar vapor to feed ratio, a common quantity used in vapor/liquid equilibrium estimation methods:

$$w = \frac{V}{F} = \frac{z_i - x_i}{y_i - x_i} \tag{15}$$

where V is the total number of vapor moles, F is the total number of liquid and vapor moles (feed), i indicates the i_{th} component, x is the equilibrium liquid mole fraction, y is the equilibrium vapor mole fraction, and z is the feed mole fraction.

It can be shown that the differential and integral isobaric heats of vaporization can be easily calculated from the following relations (use either H or U):

$$d\lambda_P = \frac{1}{w_{T_2} - w_{T_1}} \int_{w_{T_1}}^{w_{T_2}} \left(\frac{\partial H}{\partial w}\right)_{P, z_i} dw = \frac{H(P, w_{T_2}) - H(P, w_{T_1})}{w_{T_2} - w_{T_1}}$$
(16)

where λ is the heat of vaporization, H is the molar enthalpy and U is the molar internal energy. For example, $d\lambda_P$ at the bubble point (w = 0) can be calculated by first establishing the bubble point temperature at the system pressure. Then a constant V/F flash calculation is performed at a small differential value of w, say w = 0.005. The differential heat of vaporization is then calculated using the above equation:

$$d\lambda_P = \frac{H(P, w_{T_2}) - H(P, w_{T_1})}{w_{T_2} - w_{T_1}} = \frac{H(P, 0.005) - H(P, 0)}{0.005}$$
(17)

 $d\lambda_P$ at w = 0.5 can be calculated similarly:

$$d\lambda_P = \frac{H(P, w_{T_2}) - H(P, w_{T_1})}{w_{T_2} - w_{T_1}} = \frac{H(P, 0.5 + 0.005) - H(P, 0.5)}{0.005}$$
(18)

The integral isobaric heat of vaporization is also calculated similarly from the bubble point to the dew point:

$$d\lambda_P = \frac{H(P, w_{T_2}) - H(P, w_{T_1})}{w_{T_2} - w_{T_1}} = \frac{H(P, 1.0) - H(P, 0.0)}{1.0 - 0.0} = H(P, 1.0) - H(P, 0.0)$$
(19)

It should be obvious from the equations above that the differential heat of vaporization is a strong function of composition. Calculation of the differential and integral isothermal heat of vaporization can be performed in a similar fashion. First establish the bubble point pressure at the temperature of interest (point 1 in Figure 1). Next establish the dew point pressure at the temperature point of interest (point 4 in Figure 1). Starting at the bubble point pressure, select a small pressure drop, say $\Delta P = 0.01$ bar, and perform an isothermal flash calculation at $T, P - \Delta P$ (use for either H or U).

$$d\lambda_T = \frac{1}{w_{P_1} - w_{P_1 - \Delta P}} \int_{w_{P_1 - \Delta P}}^{w_{P_1}} \left(\frac{\partial H}{\partial w}\right)_{T, z_i} dw = \frac{H(T, w_{P_1}) - H(T, w_{P_1 - \Delta P})}{w_{P_1} - w_{P_1 - \Delta P}}$$
(20)

The isothermal heat of vaporization can also be calculated using entropy instead of enthalpy.

8 Differential Latent Heat of Vaporization Example

We consider a hydrocarbon mixture of methane (10 % mass fraction), propane (20 % mass fraction), n-hexane (40 % mass fraction), and n-dodecane (30 % mass fraction) to illustrate the various concepts of heat of vaporization for mixtures. The isobaric heat of vaporization at was calculated at the maximum relief pressure of 10 bara using SuperChems Expert and is summarized in Figure 2.

Figure 2 illustrates the impact of composition on differential heat of vaporization. Both the enthalpy heat of vaporization and internal heat of vaporization are shown with the lower value being that of the internal energy heat of vaporization. The differential heat of vaporization is calculated by performing a flash and a phase split at a specified vapor mass quality or vapor to liquid ratio. The differential heat of vaporization represents the change in energy that is required to generate a change in vapor quality divided by the weight change of the vapor.

The integral heat of vaporization is also shown in Figure 2 using a vaporized material basis and also the initial liquid mass basis. The integral value represents the the overall change in heat of vaporization starting from a vapor quality of zero divided by the mass of vaporized material or starting mass of the overall liquid. Therefore, the integral value at a vapor quality of one represent the overall isobaric heat of vaporization and is equal for both vaporized and liquid basis.

Figure 3 shows the dependence of vapor quality on temperature at constant pressure starting with the bubble point and ending with the dew point. The same behavior can be illustrated for a wide

Figure 2: Calculated isobaric heat of vaporization for Methane-Propane-Hexane-Dodecane mixture at 10.0 bara using SuperChems Expert



variety of mixtures. The nonlinear dependence of vapor quality on temperature also shows that the molecular weights of both vapor and liquid phases are increasing with temperature as heavier components are fractionated at higher temperatures. An optimal relief device size can only be obtained using a dynamic simulation of the vessel balances.

9 Case Study

We consider a 10 m³ spherical vessel containing 8,000 lbs of the hydrocarbon mixture described earlier. The starting temperature and pressure conditions in the vessel are -120 °C and 8.44 bara. The vessel is exposed to a fire leading to a heating rate of 780,000 W ($2.67 \times 10^6 \text{ BTU/hr}$). The maximum allowable accumulated pressure is 10 bara. The vessel is equipped with a pressure relief valve that discharges directly to atmosphere.

We use all four methods to determine the required vent size and compare and contrast the calculated values and exit conditions.

The CCPS method designates n-Dodecane as the component that requires the largest vent size as shown by Table 1. Using a 10 % vaporized mass basis shows a similar volumetric flow rate but significantly different values for relief temperature, mass flow rate, and heat of vaporization. Varying the interval of vaporized mass in 5 % increments (pseudo dynamic method) results is the peak required vent area between the bubble point temperature and the first 5 % as shown in Figure 4.

Figure 3: Calculated vapor quality vs. temperature at 10 bara for Methane-Propane-Hexane-Dodecane mixture using SuperChems Expert



Figure 4: calculated pseudo dynamic vaporization interval method results for required vent area



Quantity	Methane	Propane	n-Hexane	n-Dodecane
Molecular weight, kg/kmol	16.04	44.09	86.17	170.33
Saturation temperature, K	149.12	300.00	439.50	615.80
Heat of vaporization, J/kg	413,463	331,998	236,296	148,413
Liquid density, kg/m^3	361.64	490.32	496.55	436.46
Vapor density, $\rm kg/m^3$	12.94	17.68	23.59	33.28
Heat capacity ratio	1.35	1.12	1.04	1.01
$PPF \times 10^{12}$	48.90	59.21	89.97	163.14
Mass flux, $kg/m^2/s$	2,374	2,598	2,919	3,434

The relief requirements were also calculated using SuperChems Expert which includes the impact of fire heating on wall temperatures. We used the recommended API default flame parameters assuming a surface average fire heat flux.

This assumption is the right assumption to develop the relief requirement. Surface peak fire heat flux values should be used in an additional simulation to determine the expected time to failure or time to yield for walls under heating and where reclosing pressure relief devices are used. Figure 5 illustrates the calculated pressure profile in the vessel as a function time. We note that the contents of the vessel become all vapor at approximately 90 min during the fire exposure.



Figure 5: Calculated pressure profile in the vessel using SuperChems Expert



9 CASE STUDY

Quantity		10 %	Pseudo	
	CCPS	Method	Dynamic	Dynamic
Required relief area, $\times 10^4$, m ²	11.50	2.33	3.33	2.95
Heat of vaporization, BTU/lb-vaporized	63.85	708.23	450.07	Variable
Temperature at maximum relief pressure, °C	342.65	-32.03	-82.22	-96 to 570
Mass flow rate, lb/s	10.71	1.03	1.618	1.43 to 2.48
Volumetric flow rate, SCFH	51,755	78,139	136,146	16,012 to 120,429
Reaction force, N	1,427	267	385	689 to 756

Table 2: Compa	rison of relief re	quirements and	l conditions us	sing different met	hods
ruore 2. Compu		qui cincinto una		sing anterent met	nous

preferentially depleted first and the heavier components get concentrated. We note that the contents of the vessel became all vapor at approximately 90 min. The maximum pressure in the vessel is reached at approximately the same time as the heavies becomes more concentrated and the phase change occurs to all vapor in the vessel.



Figure 6: Calculated composition profile in the vessel using SuperChems Expert

Table 2 illustrates how the selection of a representative heat of vaporization leads to significantly different relief requirements and relief conditions. The relief exit conditions are needed for materials selection, structural support, safe discharge location calculation for thermal radiation and flammable or toxic dispersion, sound power levels for vibration risk, and noise.

10 Overtemperature Considerations

An additional simulation was conducted using SuperChems Expert to determine the expected time to failure or time to yield. The API recommended flame properties and peak surface heat flux values were used with the previously calculated relief area using surface average fire flux values. The peak surface heat flux values represent luminous portions of the flame surface that lead localized higher level of heating of the vessel walls. The localized heating cause the heated metal to stretch and thin and eventually tear or fail due to the reduce metal thickness and elevated internal pressure. Most metal failures are expected to occur in the vapor space or around the vapor/liquid interface.

Figure 7 shows the estimated time to failure based on the steel properties of the vessel walls. Failure is expected when the internal stress reaches 2/3 the ultimate tensile strength of any of the wall segments. Because the vessel was divided in ten segments, we can see from Figure 7 when specific wall segments close to the bottom became dry as the liquid level decreased due to boiling of the liquid and venting of the vapor. Failure is expected to occur in 20 min at segment (9-10) at the vessel top.



Figure 7: Calculated time to failure using SuperChems Expert

11 Conclusions

The most practical and appropriate method for determining the relief requirement for vapor venting for a multicomponent mixture of liquid is the dynamic method. This is illustrated using SuperChems Expert . While the other methods can establish a reasonable vent size, they fall short in providing reasonable estimates for relief exit conditions. Credible relief exit conditions are necessary for pipe materials selection, structural support calculations, piping vibration risk and noise considerations, as well as safe discharge location considerations involving thermal radiation and flammable dispersion. In addition, for reclosing pressure relief devices, the estimated time to failure or time to yield should be calculated and stated in the design basis documentation because it is critical for emergency response and preparedness.

References

- [1] API. API Standard 521 Pressure Relieving and Depressuring Systems. American Petroleum Institute, 7th edition, 2020.
- [2] G. A. Melhem and D. Gaydos. Properly calculate vessel and piping wall temepratures during depressuring and relief. *Process Safety Progress*, 34(1):64–71, 2015.
- [3] G. A. Melhem. RAGAGEP considerations for overtemperature protection in relief systems. *ioMosaic Corporation White Paper*, December 2021.
- [4] CCPS/AIChE H. G. Fisher and G. A. Melhem (Editors). *Guidelines for Pressure Relief and Effluent Handling Systems*. Wiley, New York, 2nd edition, 2016.
- [5] G. A. Melhem, R. Saini, and B. M. Goodwin. A modified Peng-Robinson equation of state. *Fluid Phase Equilibria*, 47:189–237, 1989.
- [6] G. A. Melhem, R. Saini, and C. F. Leibovici. On the application of concentration dependent mixing rules to systems containing large numbers of compounds. In *2nd International Symposium of SuperCritical Fluids*, pages 475–477, May 1991.

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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.

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Process Safety Enterprise®

Centralize the process safety management lifecycle to accelerate business goals

Process Safety Office®

Identify, evaluate, and control process hazards with tools used by process safety consultants



Process Safety Learning®

Build your process safety competencies incrementally with online training



Process Safety tv®

View, share, and discuss PSM worldwide on a secure platform

Contact Us

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About ioMosaic Corporation

Through innovation and dedication to continual improvement, ioMosaic has become a leading provider of integrated process safety and risk management solutions. ioMosaic has expertise in a wide variety of areas, including pressure relief systems design, process safety management, expert litigation support, laboratory services, training and software development.

As a certified ISO 9001:2015 Quality Management System (QMS) company, ioMosaic offers integrated process safety and risk management services to help you manage and reduce episodic risk. Because when safety, efficiency, and compliance are improved, you can sleep better at night. Our extensive expertise allows us the flexibility, resources, and capabilities to determine what you need to reduce and manage episodic risk, maintain compliance, and prevent injuries and catastrophic incidents.

Our mission is to help you protect your people, plant, stakeholder value, and our planet.

Consulting Services

- Asset Integrity
- Auditing and Due Diligence
- Combustible Dust Hazard
 Analysis and Testing
- Facility Siting
- Fault Tree/SIL/SIS Analysis
- Fire and Explosion Dynamics
- Incident Investigation, Litigation
 Support and Expert Testimony
- Liquefied Natural Gas Safety
- Pipeline Safety
- Process Engineering Design and Support

- Process Hazards Analysis (PHA)
- Process Safety Management (PSM)
- Reactive Chemicals Evaluation
 and Testing
- Relief and Flare Systems Design and Evaluations
- Risk Management Program
 Development
- Quantitative Risk Assessments
 (QRA)
- Software Solutions
- Structural Dynamics
- Training

Laboratory Testing Services (ISO accredited)

- Chemical Reactivity
- Combustible Dust
- Battery Safety
- Specialized Testing