

Retrograde and Phase Change (RPC) Flow Considerations for Relief and Flare Systems



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Relief and Flare Systems Design and Evaluation Practices

Fluid Flow

*Retrograde and Phase Change (RPC) Flow Considerations for
Relief and Flare Systems*

authored by

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1 Introduction

Retrograde and phase change (RPC) flow considerations are important for relief and flare systems design and evaluations. RPC flow can occur in high pressure systems, including subcooled and/or supercritical flow, or at lower pressures where the starting relief conditions are close to a phase boundary. RPC flow is also encountered in other flow systems applications such as gas transmission pipelines for example.

This type of flow can present technical challenges in relief and flare systems design and evaluations for pure components and mixtures alike. Proper consideration of RPC flow is essential for the evaluation of:

- Proper relief device sizing, selection, and installation,
- Pressure Relief Valve (PRV) stability,
- Depressuring systems,
- Piping vibration risk,
- Temperature estimates in downstream piping, i.e. metallurgy considerations, and
- Effluent handling and flare systems design.

This paper discusses best practices for the identification of RPC flow and for the numeric evaluation of associated choking pressures, temperatures, flow rates, and compositions. Two examples dealing with pure ethylene and an ethylene-butyl acrylate mixture are used to illustrate a variety of concepts dealing with RPC flow.

2 RPC Flow Scenarios

We divide scenarios dealing with RPC flow into three general categories where the initial starting conditions of the mixture or pure component can be classified as:

Liquid Saturated (L1), subcooled (L2), and supercritical liquid (L3),

Vapor Saturated, (V1), superheated (V2), and supercritical vapor (V3), and

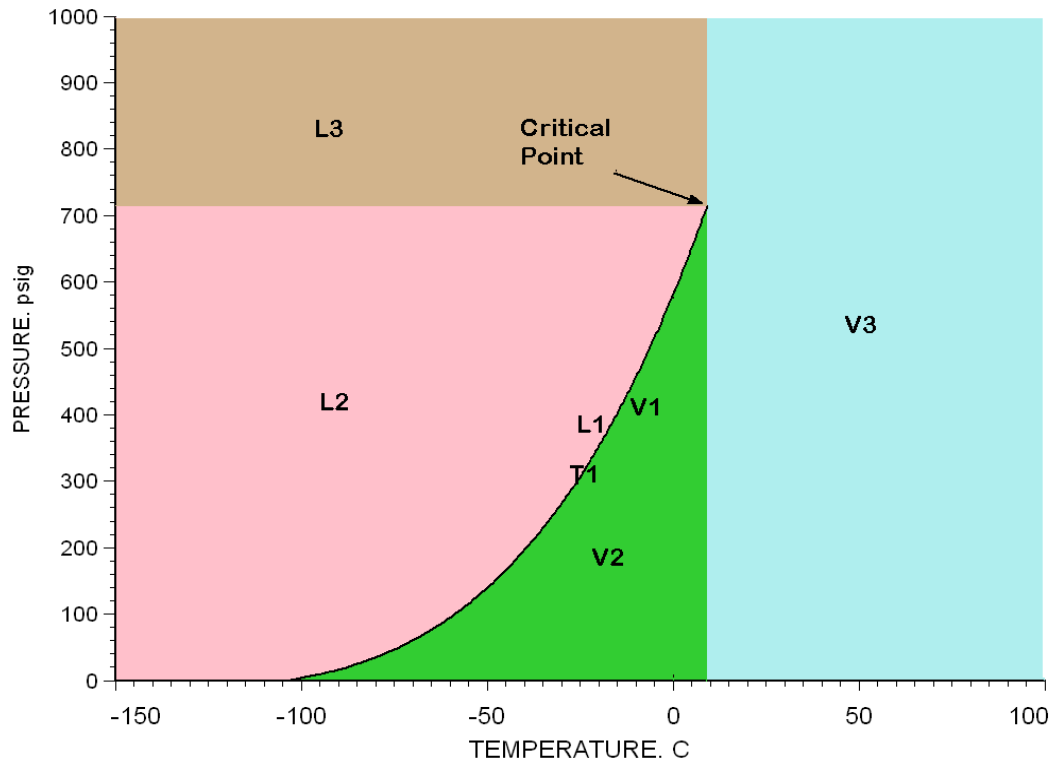
Two-phase Saturated (T1) and/or retrograde two-phase vapor/liquid (T2).

This is illustrated for pure ethylene in Figure 1 and for a mixture of ethylene (94 weight %) and butyl acrylate (6 weight %) in Figure 2. For a pure component, the phase envelope is the saturation or vapor pressure curve.

A pure component can exist as either saturated vapor (V1), saturated liquid (L1), or a saturated two-phase mixture (T1) at the same temperature and pressure. At temperatures greater than the critical

temperature, the vapor (V3) is a supercritical vapor at all pressures of interest. At temperatures below the critical temperature, the vapor (V2) is a superheated vapor because the temperature is greater than the saturation temperature. A liquid is a subcooled liquid (L2) at temperatures below the saturation temperature and pressures below the critical pressure. A liquid is a supercritical liquid (L3) at pressures in excess of the critical pressure and temperatures less than the critical temperature.

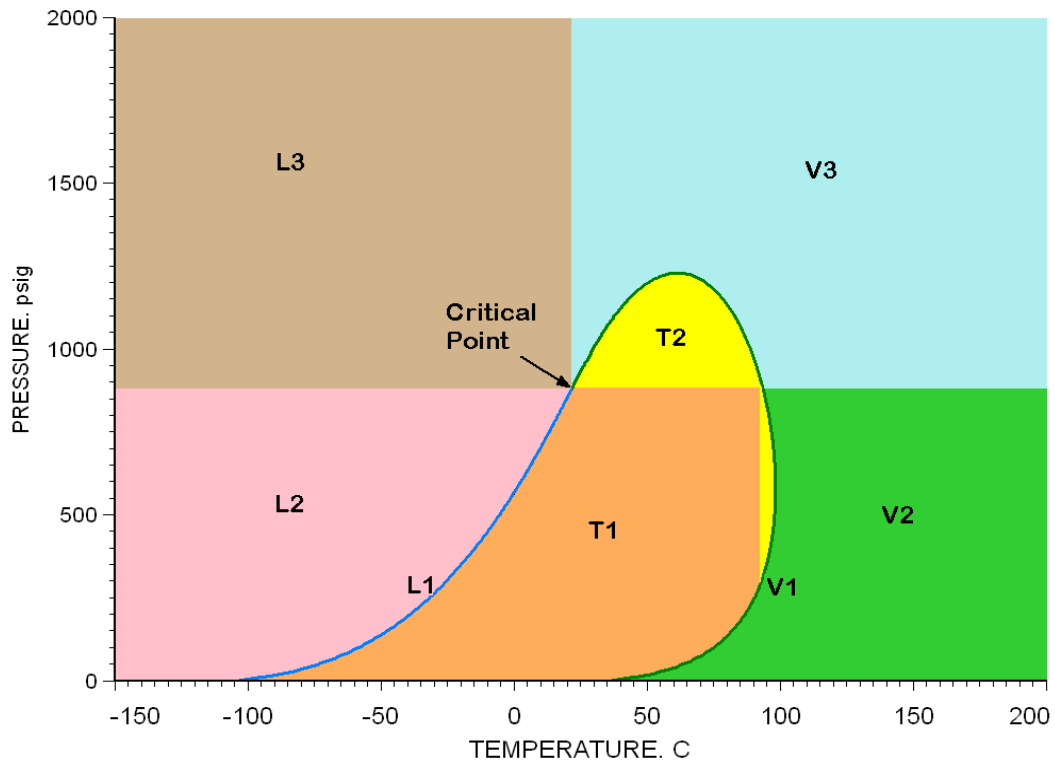
Figure 1: RPC Flow Categories for pure Ethylene



Unlike a pure component, a mixture cannot exist as a saturated liquid (bubble point), saturated vapor (dew point), and as a two-phase mixture at the same temperature and pressure as shown in Figure 1. The critical point of a mixture is not always less than the temperature at the point of maximum pressure (cricondonbar) and mixtures can sometimes have multiple critical states. For this particular example of ethylene-butyl acrylate, the critical temperature is below the temperature at the cricondonbar. It is always important to construct a phase envelope of the mixture of interest before any flow calculations are attempted.

Depending on the starting conditions, a multitude of possible RPC flow scenarios are possible. If the starting pressure is high enough, choking conditions can be reached at the same phase as the starting phase. This is even possible for liquids at extremely high pressures since liquids are slightly compressible. For these scenarios, phase change almost always occurs following the expansion discontinuity after the first choke point leading to very cold temperatures. If discharge piping is present with expansions, multiple choke points can be possible. At extreme pressures above the inversion curve limit (Joule Thompson coefficient equals 0), the resulting choke temperatures may

Figure 2: RPC Flow Categories for Ethylene-Butyl acrylate mixture



not be as cold due to JT expansion heating as shown later for the mixture of ethylene-butyl acrylate at starting pressures of 30,000 psig.

As the starting pressure is decreased, choking will occur at the phase boundary, i.e. at the bubble point for L2 and L3 flows, and at the dew point for V2 and V3 flows (if the starting vapor temperature is low enough and the starting liquid temperature is high enough). Further reduction in pressure can result in choking inside the two-phase region, T1.

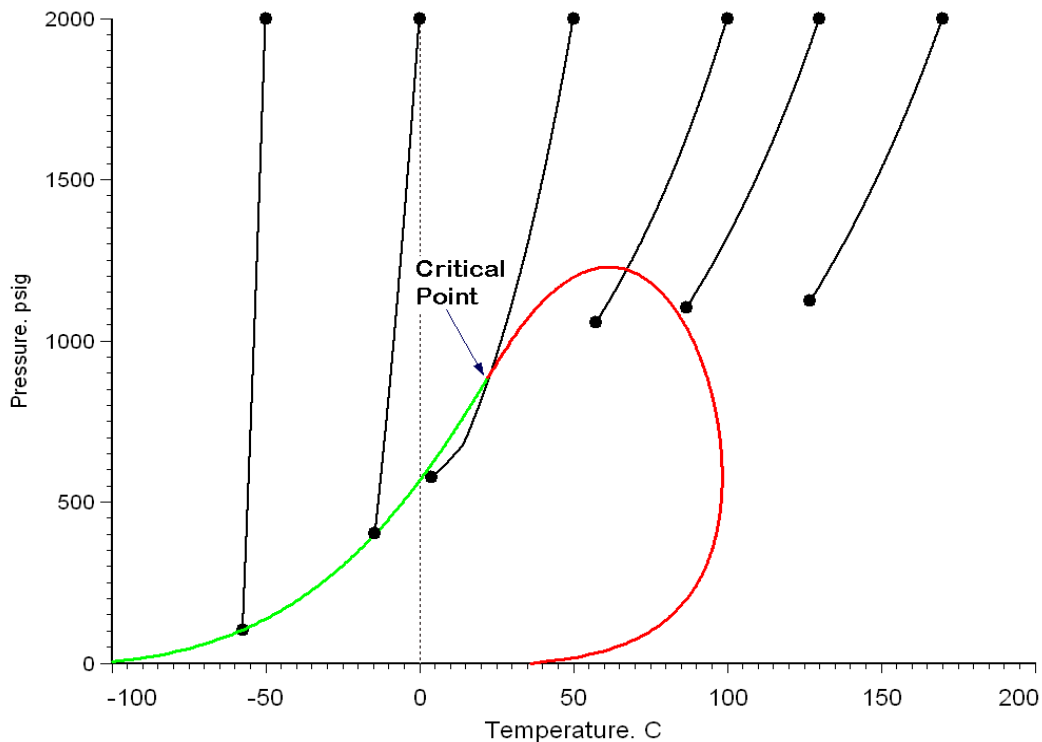
For saturated vapor flow or vapor flow near the phase boundary, it is possible the phase change will occur at the throat or nozzle of the flow limiting element, and then the two-phase mixture will disappear after the expansion discontinuity.

Starting conditions in region T2 are particularly challenging for RPC flow since we now have a two-phase mixture at conditions in excess of the critical temperature and pressure. Initial conditions near the cricondonbar or critical point can result in choking inside the retrograde region T2. RPC flow estimates require robust flow and VLE solvers to figure out the ending state of the flowing fluid as the pressure is decreased due to flow in a nozzle or a pipe.

3 Nozzle Flow

The final conditions for nozzle flow are determined using an isentropic thermodynamic flow path. The final pressure, temperature, phase, and composition are those at which mass flow is maximized [1, 2]. Figure 3 illustrates the nozzle isentropic thermodynamic flow path for the mixture of ethylene and butyl acrylate at different starting temperatures and 2000 psig. As the starting temperature is decreased the choke point phase of maximum flow shifts from vapor, to two phase, and then to saturated liquid. Note that at the 50 C starting condition the flow path goes through the critical point and ends up close to the bubble point boundary in the two phase region. We also note that the final choking temperature for highly subcooled liquid flow is very close to the value of the starting temperature since the liquid is only slightly compressible. As the flow expands from the choke point to lower pressures, it is possible to cross the phase boundaries if the pressure is low enough. If the flow is expanding into a pipe with a larger flow area, it is possible to cross the phase boundaries and to have multiple chokes downstream of the first choke. For choked (sonic) flow, the flow is always regulated by the first choke. However, subsequent chokes typically occurring at area changes such as sudden expansions in the discharge piping, can reduce the capacity of a pressure relief valve due to the increase of backpressure.

Figure 3: Isentropic nozzle flow for ethylene-butyl acrylate mixture at 2000 psig



If we increase the starting pressure to 30,000 psig for the ethylene-butyl acrylate mixture we notice that these starting conditions are well above the inversion curve for the mixture. An inversion curve represents the zero limit of the Joule-Thompson (JT) coefficient. At points above the inversion curve, a negative JT coefficient indicates that as the pressure is decreased the temperature should

increase, while a positive JT coefficient indicates the opposite. It is a very good practice to establish an inversion curve for high pressure systems before attempting flow estimates.

This JT coefficient is expressed in terms of the change of temperature with respect to pressure at constant enthalpy, μ_H . At high pressures, negative values of μ_H indicate an increase in temperature for a constant enthalpy pressure drop. At low pressures, positive values of μ_H indicate a decrease in temperature for a constant enthalpy pressure drop.

$$\mu_H = \left(\frac{\partial T}{\partial P} \right)_H = -\frac{1}{C_p} \left(\frac{\partial H}{\partial P} \right)_T = \frac{RT^2}{PC_p} \left(\frac{\partial Z}{\partial T} \right)_P = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] \quad (1)$$

$$= \frac{1}{\rho C_p} (\beta T - 1) \quad (2)$$

where C_p is the real fluid heat capacity at constant pressure. Equation 2 can be used to construct a complete inversion curve, a curve that represents the locus of all the zero values of the Joule-Thompson coefficient. Figure 4 displays an inversion curve calculated by SuperChems using the Melhem modification of the Peng-Robinson equation of state for hydrogen. Hydrogen is depressured using both an isenthalpic and an isentropic thermodynamics paths from 1500 psig and 100 C to the flow choke point. As shown in Figure 4, the isenthalpic path heats up to 100.6 C while the isentropic path cools down to 34.7 C. For an ideal gas, $\beta = 1/T$ and the Joule-Thompson coefficient is equal to 0. At critical conditions, it can be shown that μ_H will approach:

$$\mu_H \rightarrow \left(\frac{\partial T}{\partial P} \right)_\rho = \frac{\kappa_T}{\beta} \quad (3)$$

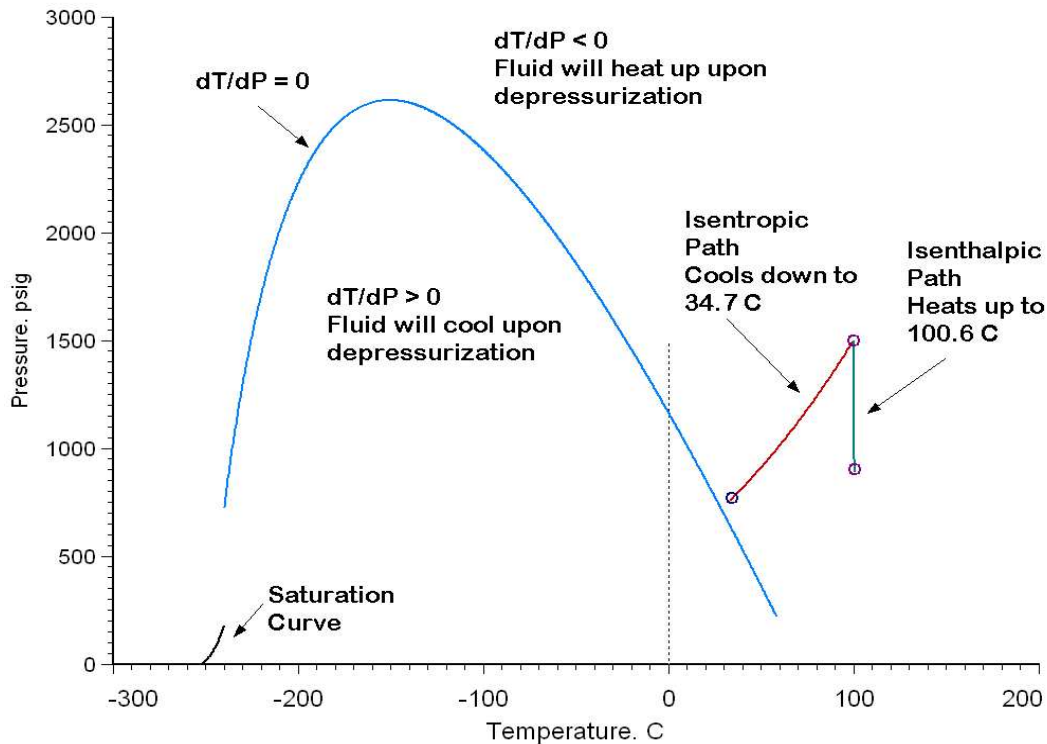
The inversion curve represents a severe test of the performance of an equation of state. Figure 5 illustrates the impact of JT on the final temperature reached at choking conditions. For example, the temperature only drops from 200 C to approximately 140 C despite a pressure drop from 30000 psig to 9300 psig. This is attributed to the selected thermodynamic path for flow illustrated in Figure 5 which is isentropic for an ideal nozzle and not isenthalpic.

4 Pipe Flow

Unlike nozzle flow, the final conditions for pipe flow are determined by conserving stagnation enthalpy. The final pressure, temperature, phase, and composition are those at which the maximum possible flow can traverse the entire pipe and still reach the choke point at exactly the end of the pipe and/or the flow limiting element. In relief systems applications, choking typically occurs at the nozzle of a pressure relief valve, a control valve, or at a change of flow area in the piping system. Multiple chokes are possible if the starting pressure is high enough. For many applications, phase change will occur after the pressure expansion following the choke location.

For relief systems piping consisting of pipe segments and a pressure relief valve and/or a control valve, the flow through these devices is still established using isentropic flow because choking typically will occur at the valve. However, the approach velocity to the nozzle has to be accounted

Figure 4: Calculated inversion curve for Hydrogen



for when calculating stagnation enthalpy via an isentropic flow path. The piping flow solvers will try to push as much mass flow as possible through the relief systems piping. If the flow is choked at the relief device or control valve, the choke point is established iteratively until the maximum mass flow rate requested by the pipe solvers matches the one established by the nozzle solvers.

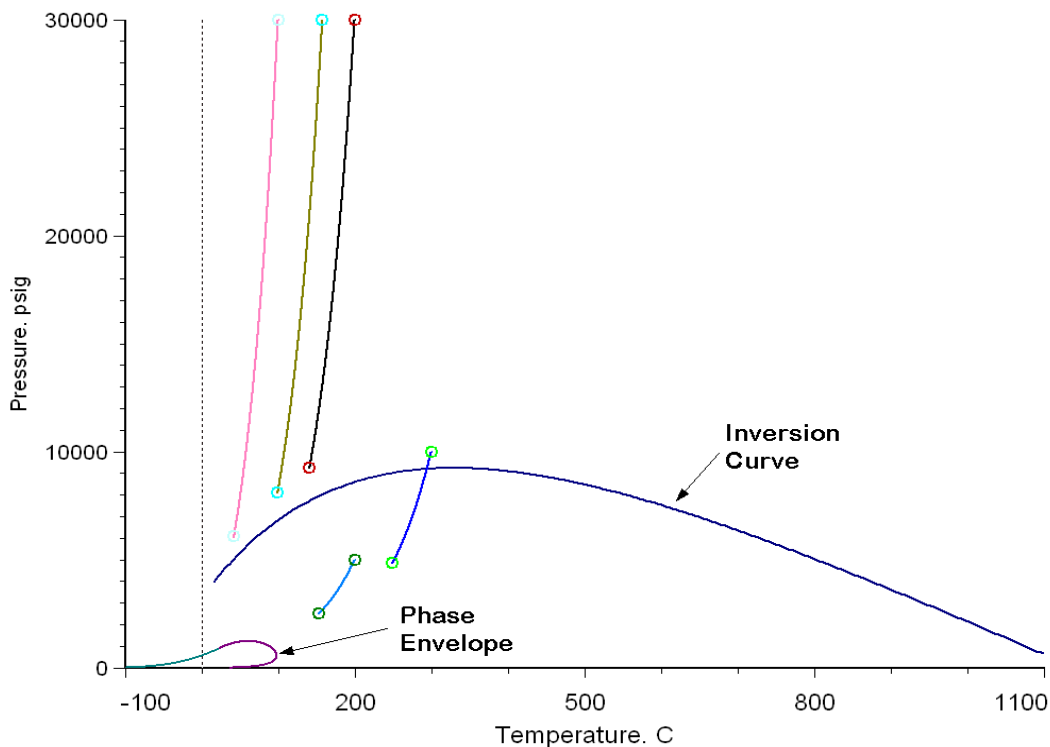
We consider the flow of pure ethylene from a relief line with a short 1 m inlet line (3 inch) and a 10 m discharge line (4 inch) and a 3K4 pressure relief valve. The starting conditions are 100 barg and 10 C. As illustrated in Figure 6 the flow chokes at the two phase boundary since the starting temperature was slightly above the critical temperature of ethylene. We notice the small pressure drop in the inlet line, followed by choking at the phase boundary, and then flashing after the choke discontinuity. We note that this flow is choked at the nozzle and the exit of the discharge line.

Also shown in Figure 6 is the vapor quality as a function of piping axial distance. All vapor flow is present in the inlet line, followed by liquid at the choke point, and a two-phase mixture in the discharge line. The final exit conditions at the end of the discharge are choked at -32 C, 17.25 barg, and a mass vapor quality of 37 %.

5 Why Consider RPC Flow

Improper calculation of RPC flow, especially for subcooled liquid flows near the liquid phase boundary, can result in undersized pressure relief devices. This is because the actual RPC mass

Figure 5: Isentropic nozzle flow for ethylene-butyl acrylate mixture at 5000, 10000, and 30000 psig



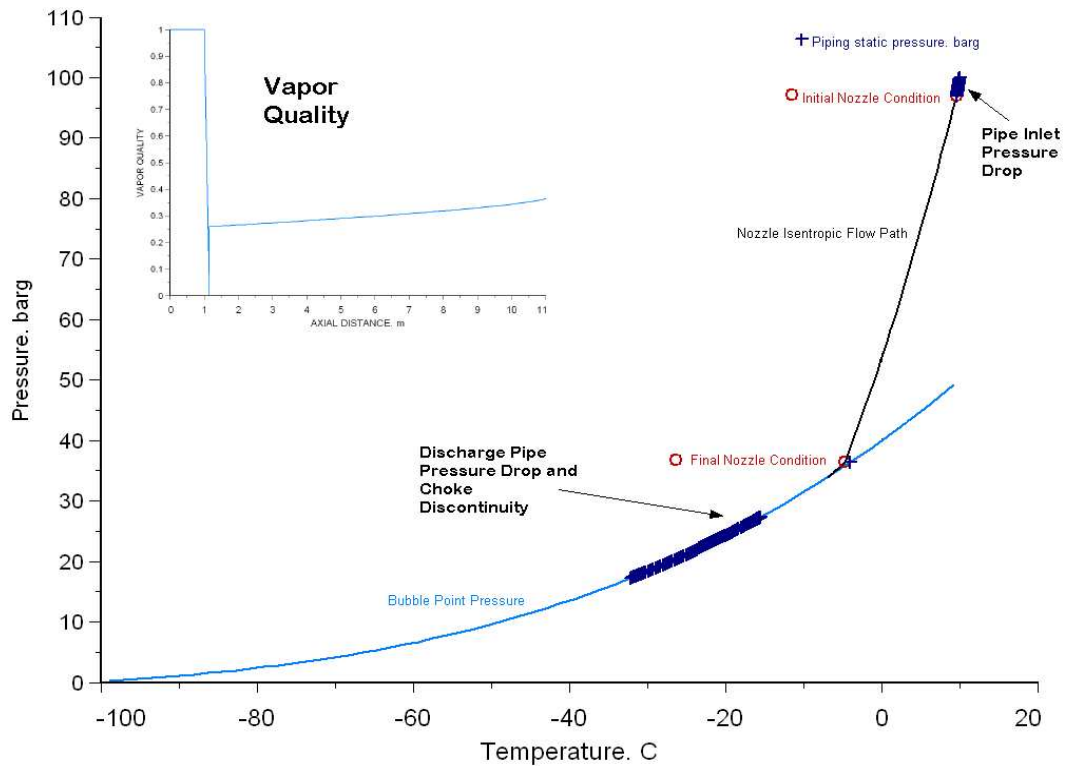
flow rate can be substantially less than the single phase (all liquid) mass flow rate due to choking at the phase boundary which leads to less pressure differential to drive the flow across the nozzle. Conversely, for all vapor initial conditions, condensation in the valve can also reduce the valve capacity.

In addition to undersizing of the relief devices, RPC choking conditions also influence the final temperatures reached in the flow limiting element and discharge piping. This can lead to designs that are not safe because of poor piping materials selections for a temperature service that can be well below the embrittlement temperature of carbon steel depending on the chemical(s) used and relief conditions. Other important design considerations for relief systems include vibration risk and effluent handling.

6 Non-Equilibrium Flow

We illustrate important non-equilibrium concepts using a mixture of C2 (ethane, 30 % by weight) and C7 (heptane, 70 % by weight). A subcooled liquid mixture of C2/C7 flows through an ideal nozzle from a reservoir with stagnation conditions of 40 C and 60 barg. If flow occurs such that thermal and mechanical equilibrium conditions are achieved, i.e. where there is enough time for flashing to take place, choking conditions will occur at the phase boundary as shown in Figure 7.

Figure 6: Pressure profile for relief systems piping with starting ethylene conditions at 100 barg and 10 C



As a result, the liquid mass flux can be accurately calculated using Bernoulli flow:

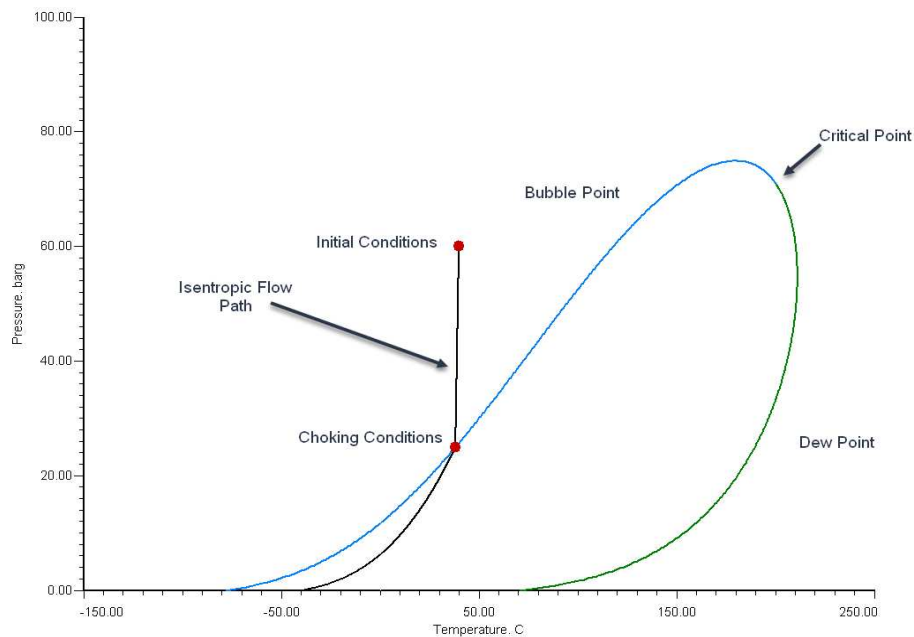
$$G = \sqrt{2\rho_o (P_o - P_b)} \quad (4)$$

where P_o is the initial stagnation pressure, T_o is the initial stagnation temperature, and P_b is the bubble point pressure or saturation pressure at the isentropic flow temperature T_b . We note that for liquids, the value of T_b will be approximately equal to T_o , even where the pressure difference between P_o and P_b is large.

The mass flux is calculated for ideal nozzle flow by selecting isentropic end conditions (pressure, temperature, and quality) that maximize flow. This is illustrated graphically in Figure 8. We note the clear change in slope of the mass flux vs. backpressure curve associated with the choke conditions at the phase boundary.

If non-equilibrium effects dominate, i.e. the flow does not have enough time for flashing to occur, the choke point can occur at a lower pressure than the bubble 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

Figure 7: Initially subcooled C2/C7 flow



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.

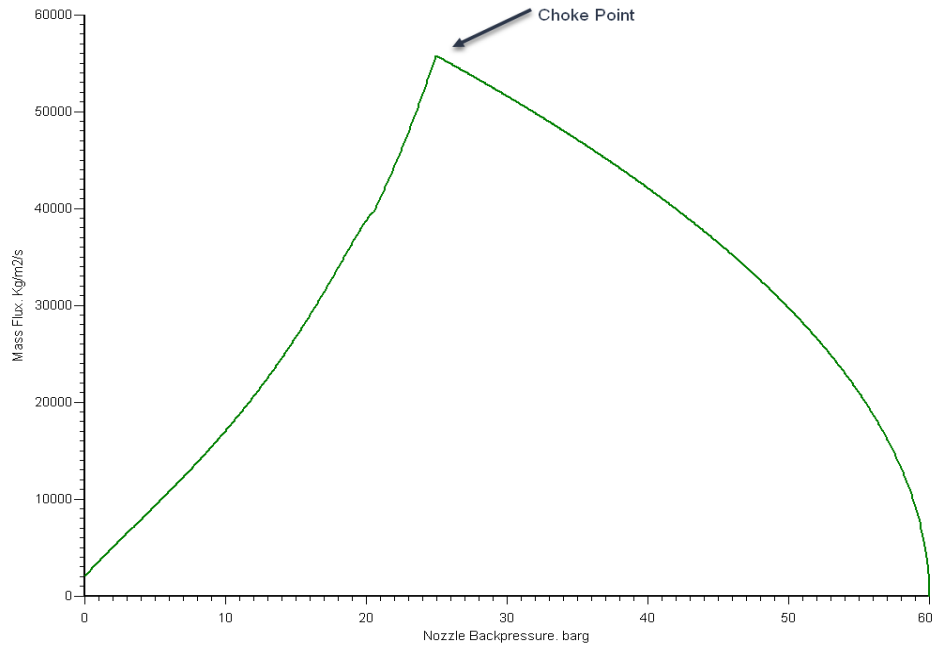
Burnell [3] used a bubble delay factor, C , to approximate the impact of non-equilibrium on mass flux by modifying the standard Bernoulli flow equation:

$$G = \sqrt{2\rho_o [P_o - (1 - C) P_b]} \quad (5)$$

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 [4] 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.

If we use a non-equilibrium correction factor of $C = 0.27$ for the C2/C7 example and allow non-equilibrium effects for the ideal nozzle mass flux calculation, we obtain the results shown in Figure 9. Figure 9 also shows an all liquid solution starting at -80 C, an all vapor solution starting at 250 C, and a two-phase solution starting at 160 C and 21 % vapor mass fraction in order to contrast and compare typical shapes of mass flux vs. backpressure for liquid, vapor, two-phase, and subcooled liquid flows. For all vapor and two-phase flashing flow, the correct values of choke pressure and choke temperature are strongly dependent on the numerical accuracy of the calculations and vapor quality. Small deviations in mass flux at the maximum point can lead to

Figure 8: Initially subcooled C2/C7 flow mass flux vs. backpressure



large deviations in choke pressure.

The isentropic flow path is shown in Figure 10 along with the thermodynamic stability limit. 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 11. For a pure component, the stability limit temperature at atmospheric pressure is approximately equal to:

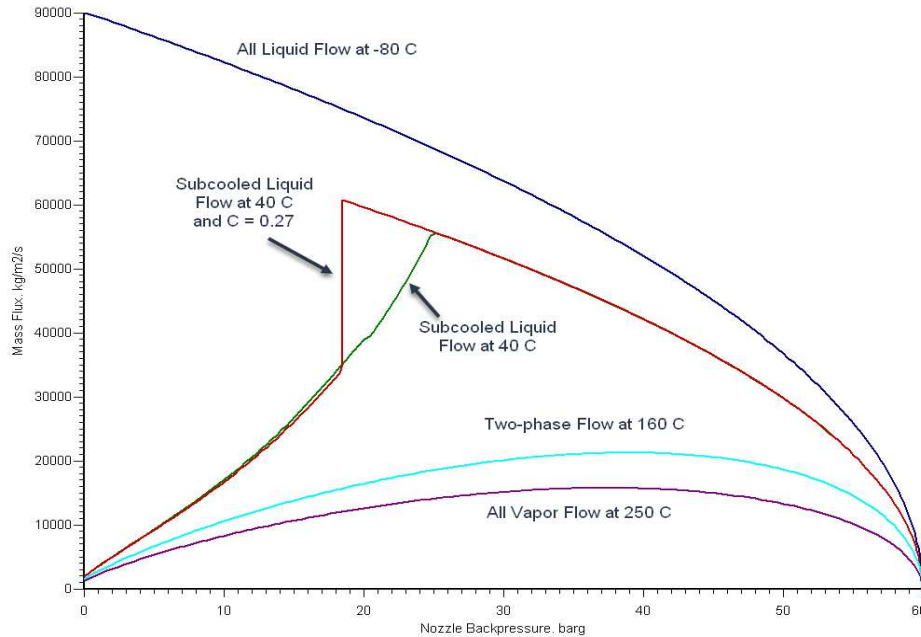
$$T_{sl} \simeq 0.92 T_c \quad (6)$$

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

$$P_b \geq P_{sl} \geq P_{atm} + (P_c - P_{atm}) \left[\frac{\frac{T}{T_c} - 0.92}{0.08} \right] \quad \text{where } T_{sl} \leq T \leq T_c \quad (7)$$

6.1 Typical Values of C

Numerous publications report values of C for water flow. Reference [5] recommends a value of C as a function of water saturation pressure as shown in Figure 12. The value of C decreases as the the saturation pressure of water increases, i.e. at higher initial stagnation temperatures for the

Figure 9: Initially subcooled C2/C7 flow mass flux vs. backpressure, $C = 0.27$ 

subcooled liquid water. The entire data set is well below the thermodynamic stability limit shown in Figure 11.

More recently, reference [6] recommended similar values for C for water as a function of a dimensionless subcooled temperature number as shown in Table 1.

Sallet [7] correlated C for water with surface tension as a function of temperature as originally suggested by Burnell [3]. Burnell considered a vapor bubble of radius r at the throat of the nozzle ($P = P_b$) where the pressure is $P_{sat}(T_o)$ inside the bubble because the flow is so rapid that the liquid is still at T_o when the liquid reached the throat:

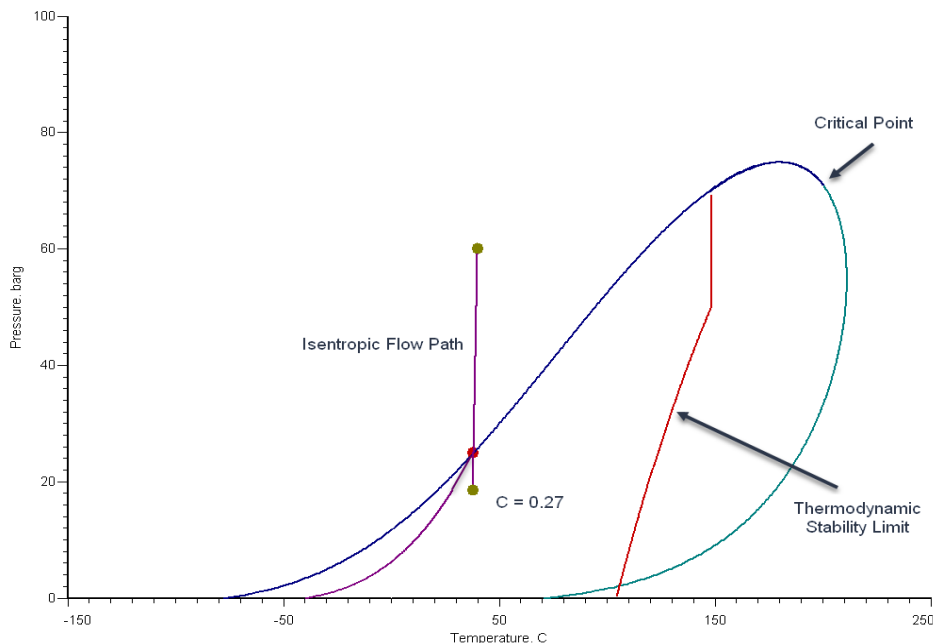
$$P_{sat}(T_o) - P_b = \frac{2\sigma}{r} \quad (8)$$

or

$$C = 1 - \frac{P_b}{P_{sat}(T_o)} = \frac{2\sigma}{rP_{sat}(T_o)} \quad (9)$$

where σ is the surface tension of water. Burnell [3] notes that the product $rP_{sat}(T_o)$ is constant over a large pressure range. As a result, if an actual value of C exists for water at one temperature, one can estimate the C value at a different temperature by using the ratio of the surface tension at those different temperatures:

$$C_o = C_{ref} \frac{\sigma(T_o)}{\sigma(T_{ref})} \quad (10)$$

Figure 10: Initially subcooled C2/C7 flow using $C = 0.27$ 

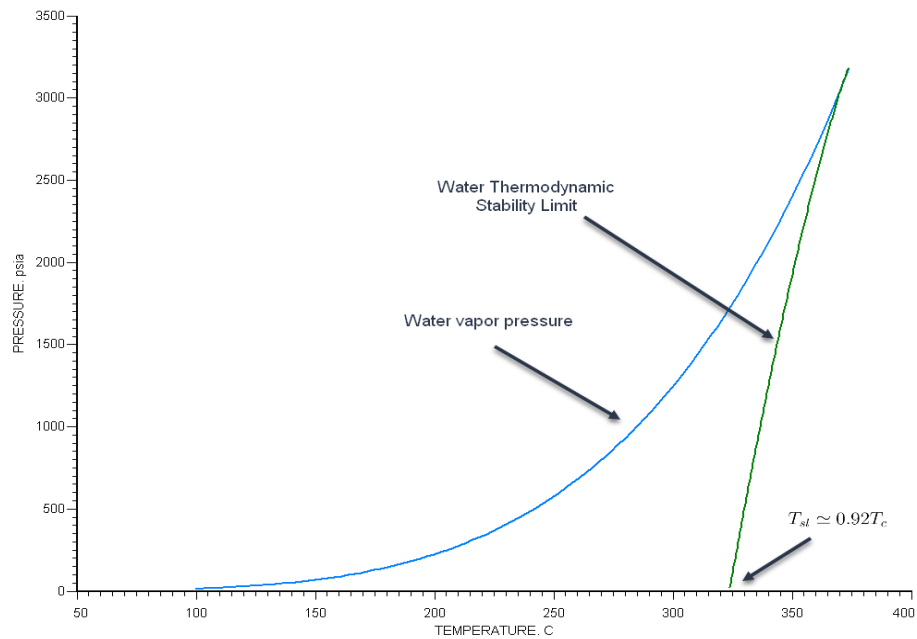
In theory, we should be able to apply this equation to any fluid where one C value is measured and where surface tension data is available as a function of temperature.

7 Guidance for Using SuperChems Expert

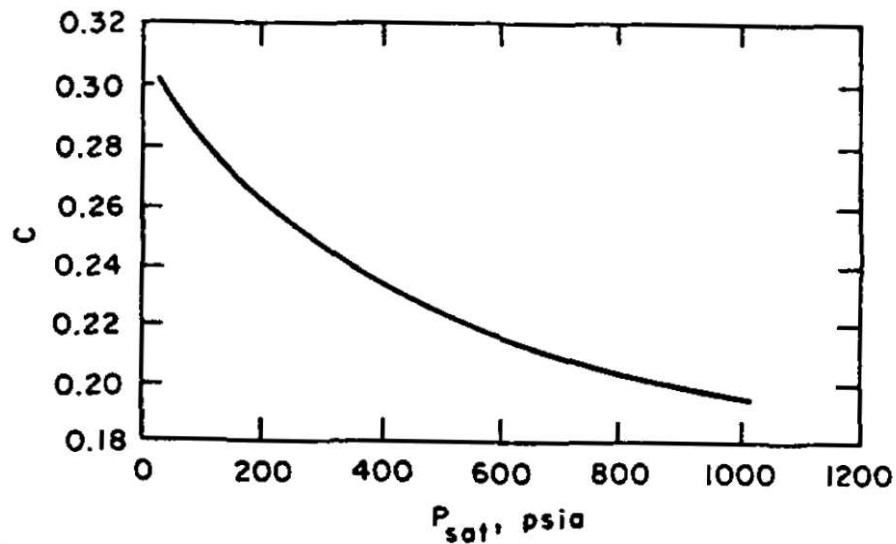
Versions 8.20 and higher of SuperChems include options for solving flow applications where RPC flow is possible. The "Globals Calculations Limits" option includes choices for checking the phase boundaries during flow and for the selection of nozzle flow integration methods. This option is most effective in conjunction with the selection of VdP integration for nozzle flow. The option for checking phase boundaries should not be enabled when flow maps are being used for flare systems calculations with the ideal gas behavior option.

The user should always establish a phase envelope or a saturation curve before attempting any flow calculations. Inversion curves can be associated with streams in SuperChems and are very useful for high pressure applications. Although the SuperChems pipe flow and nozzle flow modules allow the user to specify the starting phase of flow, it is highly recommended to allow the module to determine the starting phase by selecting the "Determine Flow Phase" option. Care must be exercised when dealing with pure components where the starting temperature is very close to the saturation point due to small deviations of the vapor pressure equations used. In these cases, a better approach is to specify the pressure and starting vapor fraction and to let the code select the coincident temperature. Use of the ideal nozzle or stream flow options in conjunction with flashing of the choke point (by conserving stagnation enthalpy) to ambient or user imposed back pressure will help the user select the appropriate pipe flow module.

Figure 11: Thermodynamic Stability Limit for Water



When the phase boundary check options are enabled, the single phase piping flow modules will detect phase change and issue an error or warning message to the user recommending the use of the two-phase pipe flow module.

Figure 12: Recommended Burnell C value for water [5]Table 1: Recommended C values for water [6]

Upstream state	Condition	P_0 (MPa)	C_f	Remark
Subcooled and saturated water	$0.0 \leq \Delta T_{sub}^* < 0.15$	0.5	0.87	10% error
		1.0	0.85	
		2.0, 3.0	0.83	
		4.0–6.0	0.82	
		7.0–20.0	0.81	
Two-phase mixture	$0.15 \leq \Delta T_{sub}^* \leq 1.0$	0.5–20.0	1.0	5% error
		$0.0 < x \leq 1.0$		
	$0.0 < x \leq 1.0$	0.5	0.81	10% error
		1.0	0.80	
		2.0–11.0	0.79	
		12.0, 13.0	0.78	
		14.0–17.0	0.77	
		18.0	0.76	
19.0, 20.0	0.75			

$$C_f = 1 - C$$

$\Delta T_{sub}^* = \frac{T_{sat}(P_0) - T_o}{T_{sat}(P_0) - 20}$ where T is in degrees C, P_0 is the stagnation pressure, and T_o is the stagnation temperature.

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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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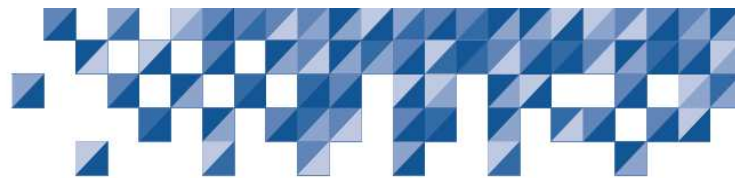
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