

BLEVE and its Importance in Enhanced Gas Recovery and Carbon Capture and Storage

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BLEVEs are very violent explosions, which can occur when a vessel containing a fluid under pressure ruptures for some reason. For a particular substance or mixture they can occur only under certain conditions of pressure and temperature, according to theory. Because of the recent increased interest in the use of carbon dioxide in enhanced gas recovery and carbon capture and storage, it is important to calculate these conditions for relevant fluids and fluid mixtures.

BLEVEs are extremely violent explosions that occur very infrequently. They can occur with liquids and high-density fluids under pressure when there is a failure in the containing vessel. The acronym stands for Boiling Liquid Expanding Vapour Explosion, which is probably a misnomer in view of the explanation below. The explosions are orders of magnitude more violent than most explosions. Strong steel containers are highly distorted, flattened, broken into pieces and fragments propelled hundreds of metres. The premises in which the tanks were located are completely destroyed. Fire or other forms of heating may be involved, but not necessarily. An example at low temperature was the explosion of a tank of carbon dioxide at a plant in Worms, Germany [1]. A tank of 30 tonne capacity was shattered into a number of pieces and only 20% of the tank was present in the original premises after the explosion. Most of the tank was propelled 300 metres into the Rhine. There were three fatalities and a further eight casualties.

Because of the recent increased interest in the use of carbon dioxide in enhanced gas recovery and carbon capture and storage, it is important to consider whether to conditions of pressure and temperature used in these processes could give rise to BLEVEs. This involves calculations for mixtures of carbon dioxide and natural gas, which are described below, following an explanation of the theory of the phenomenon.

Why do BLEVEs occur? There does not yet appear to be universal agreement on the answer to this question. However, a theory developed by Professor Reid and colleagues at MIT [2] shows that a very dramatic physical event must occur under certain thermodynamic conditions, and this is likely to be the explanation (or at least one of the explanations) of BLEVEs.

A brief account of this theory can be given with the aid of Figure 1, which is a diagram of the relationship between the pressure in a substance and the volume it occupies as a liquid, gas or fluid at various constant temperatures. The continuous thick black line **ABCD** shows the behaviour of the substance at a lower constant temperature and at thermodynamic equilibrium. In the section **AB**, the substance is a liquid and as the volume it occupies is expanded the pressure falls dramatically. Eventually the pressure falls to the vapour pressure of the liquid at the particular temperature at **B**. The liquid then starts to evaporate to become a liquid-gas mixture, and the pressure stays constant at the vapour pressure. Eventually it reaches **C**, where the liquid has been completely converted to gas. The pressure then drops as

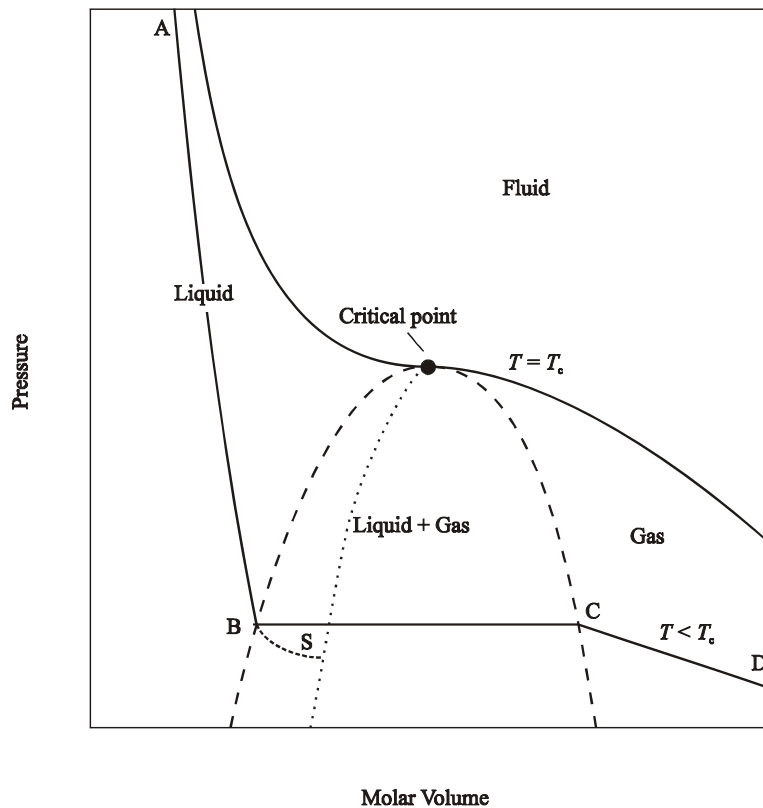


Figure 1. Variation of pressure with volume occupied at constant temperature and equilibrium shown as solid lines: the higher at the critical temperature and the lower at a temperature below critical. The metastable situation is shown as the dashed line BS and the spinodal curve as the dotted line.

BC. This can be achieved by, for example, by attaching a tube to the outlet of a bursting disc to slow the rate of exit of gas.

However, in the unlikely event that the point **S** is reached a special and catastrophic situation arises. **S** is known as a *spinodal* point and the slope of the line at this point is zero (i.e. $(\partial p / \partial V)_T = 0$). The dotted line connects these points at different temperatures and is known as the *spinodal curve*, which ends at the critical point. The special nature of situations represented by points along this curve are that large density fluctuations can occur because of the insensitivity of pressure to volume ($(\partial p / \partial V)_T = 0$). This is because random molecular motion causes molecules to move excessively into some regions and sparsely into others. These densities are normally smoothed out by pressure differences between the high- and low-density regions. However, because $(\partial p / \partial V)_T = 0$ there is no pressure force to do this. These density fluctuations cannot easily be observed for obvious practical reasons except near the critical point, where the phenomenon is known as *critical opalescence*.

Once the spinodal curve is reached separation into liquid and gas **must** occur and rapidly. The density variations develop spontaneously into liquid and gas regions. This occurs homogeneously throughout the whole liquid. The rise in pressure on to the vapour pressure

it is expanded further. However, if the pressure falls suddenly, perhaps due to a failure in the container, the substance can become an unstable liquid along the dashed path **BS**. Along the path **BS** the substance is metastable and can at any time boil to return to the equilibrium horizontal line **BC**. Although such an event can be very violent it is not thought to be a BLEVE and is described as 'bumping'. Typically violent boiling will occur before the point **S** is reached.

One way of making it less probable that point **S** is reached is to arrange for the drop in pressure following failure to be slower, which can be done in some situations. If the fall in pressure is slower this gives more time for the system to move from the metastable curve **BS** on to the equilibrium curve

line **BC** is not large but it happens at great speed, homogeneously and at the time-scale of molecular motion. The shock to the containing vessel is huge and a disastrous BLEVE happens.

For a BLEVE to occur, the substance has therefore to find itself on the spinodal curve. As practical conditions do not normally allow pressures below atmospheric, the system must hit the spinodal curve between 1 bar or thereabouts and the critical point where the curve ends. When a catastrophic failure occurs there is not time for heat to pass into the system and so the path during failure is adiabatic. We must then assume that a smooth pressure drop occurs the rupture and therefore the pressure drop will be reversible, and thus not only adiabatic but also isentropic. Thus for a BLEVE to occur the entropy of the system before failure must be below the entropy at the critical point but above the entropy on the spinodal curve at 1 bar.

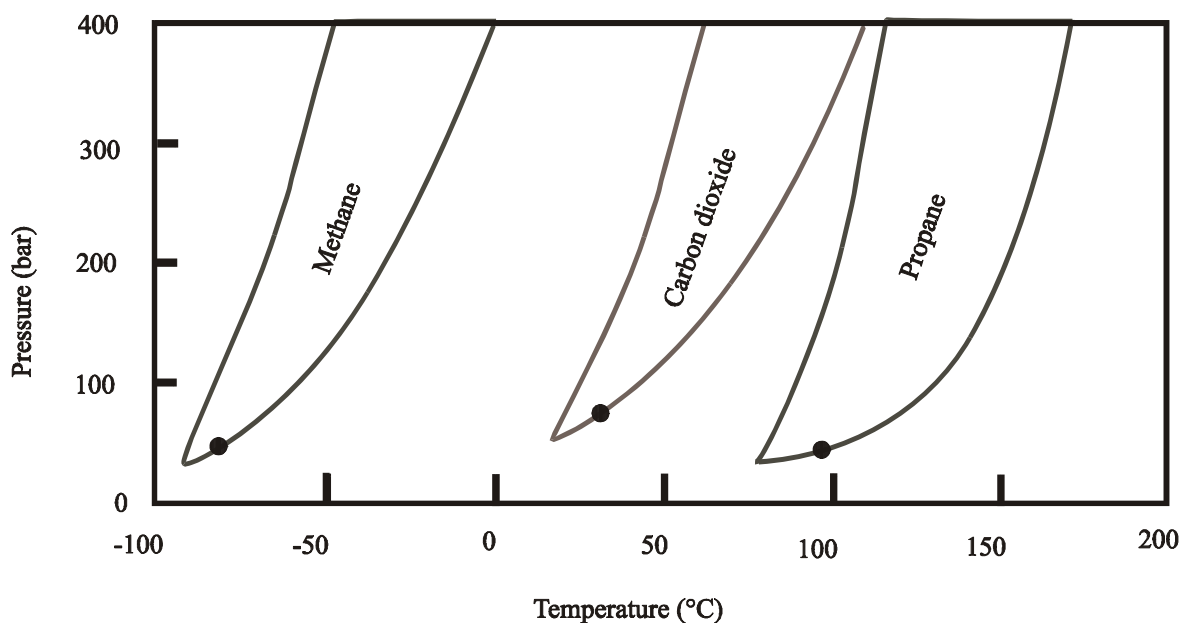


Figure 2: The BLEVE envelopes for methane, carbon dioxide and propane, showing the critical point as filled circles.

Using standard thermodynamic methods, it is possible to calculate, using an equation of state, the range of temperatures and pressures in which the entropy will be in the required range. For each fluid or fluid mixture this will take the form of an envelope, as shown for methane carbon dioxide and propane in Figure 2. Within the envelope BLEVE can occur, but outside it cannot. The right hand curve of each envelope delineates pair of tempature and pressure where the entropy is equal to the entropy at the critical point. The critical point will lie on this boundary. To the right of this boundary the entropy will be above the critical entropy and therefore not subject to BLEVE. The left-hand (lower temperature) boundary of this envelope represents temperature-pressure conditions where the entropy equals the entropy on the spinodal curve at 1 bar. To the left of this boundary the entropy will be below the spinodal entropy at 1 bar and therefore not subject to BLEVE.

Figure 2 compares the BLEVE envelopes for methane, carbon dioxide and propane. As the critical point is on the BLEVE envelope, the curves follow the critical temperatures. Thus for propane higher temperatures are reached and that is believed to be the reason that

propane BLEVEs occur in fires. For methane the BLEVE envelope is at lower temperatures, removed from normal ambient conditions. However, natural gas is transported at atmospheric pressure as a cooled liquid to avoid BLEVE. The natural gas boils to keep the liquid cool and the vaporising gas is collected, cooled and returned to the vessel Figure 3 shows the BLEVE envelopes for mixtures of carbon dioxide and methane, which lie between those of the pure gases. Curves like these must be considered when designing processes for the recovery of natural gas using carbon dioxide. Also, as the BLEVE envelopes are predicted to be wider for mixtures [3], the curves overlap.

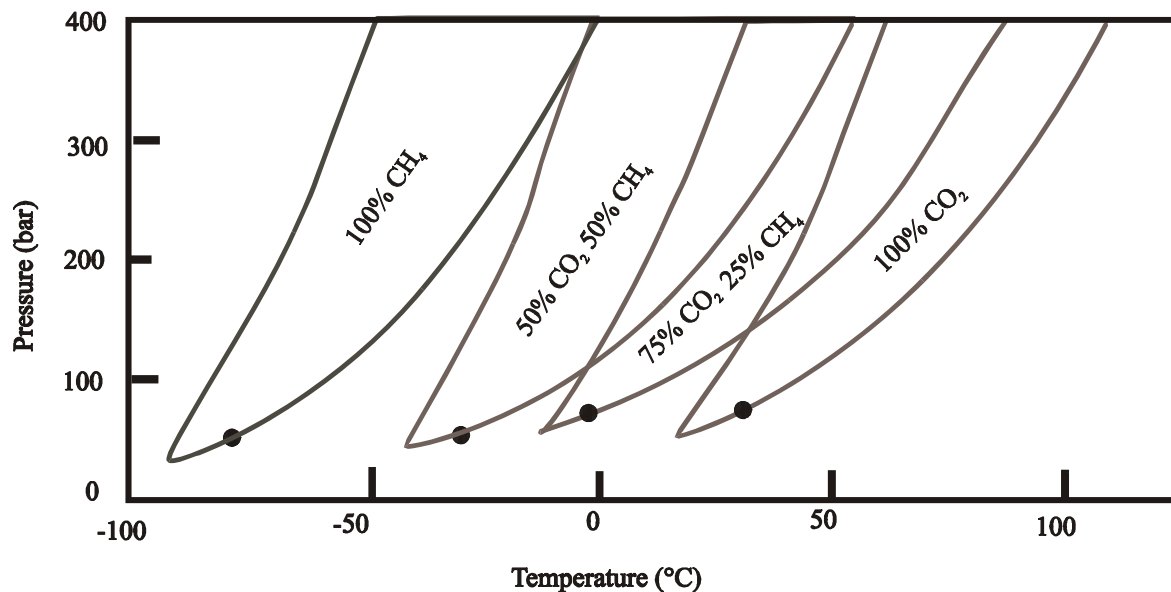


Figure 3: The BLEVE envelopes for methane, carbon dioxide and two mixtures.

To summarise, we have a situation where very catastrophic explosions occasionally occur, which are orders of magnitude more violent than most explosions. At the same time we have a theory based on physical principles, which predicts that in some circumstances a phenomenon may occur to produce these huge explosions. However, what we don't have is an experimental study showing that the theory and the physical manifestations are definitely related. Experiments on carbon dioxide did not result in BLEVEs [2,4] and the study for propane did not seem to accord with the theory. Nevertheless, it is very likely that the Reid theory does explain at least some BLEVEs, although other theories may be valid in some cases.

In conclusion for companies operating processes involving gases under pressure, BLEVE calculations should be carried out and the BLEVE envelope avoided during operations. If this is not done, the chances of a BLEVE event are still small but, if it does happen, the consequences would be catastrophic.

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