It can't hold anymore – heat

The relationship between heat and pressure, how they relate to the 'saturation' of cryogenic liquids

By Keith Hall, of Applied Cryogenic Technologies

Saturation is an important, yet often misunderstood concept in the cryogenic industry. A basic understanding of the term "saturation" is necessary to harness and exploit the benefits of using cryogenic liquids in our specific industries and end-use applications.

In the cryogenic realm, the word 'saturation' is a thermodynamic term defining the condition of a liquid whose temperature and pressure are such that any increase in temperature, without a corresponding increase in pressure, causes it to boil and turn to vapor. Alternately, any decrease in pressure, without a corresponding decrease in temperature, also causes the liquid to boil.

In laymen's terms, a cryogenic liquid (at a given pressure) becomes 'saturated' with all the heat it can hold if the addition of anymore heat immediately causes the liquid to begin to boil. In turn, if the pressure in the tank is lowered, by even a fraction, the liquid will also begin to boil. Imagine water slowly dripping into a sponge. The sponge becomes saturated when one more drop of water is added to the sponge, causing one drop to drip from the bottom of the sponge. Similarly, a cryogen becomes saturated with heat, at a given pressure, when the addition of even one more BTU of heat causes the liquid to boil and change phase into vapor.

The higher the pressure in a cryogenic tank, the more heat the cryogen can hold. If the pressure is reduced, the liquid, saturated at the higher initial pressure, will begin to boil and turn to vapor. The liquid will continue to boil-away heat until the temperature comes back into equilibrium with the new lower pressure.

A British Thermal Unit (BTU) is a small unit of measurement of heat. One BTU is approximately the amount of heat generated when you strike a wooden kitchen match and let it burn down

Boiling water without burning it

At sea level atmospheric pressure, if a thermometer is placed in a teapot filled with water and placed on a hot stove burner, the water becomes saturated with all the heat it can hold and begins to boil at 212^{0}F (100^{0}C). Even if you apply additional heat from a blow torch to the bottom of the teapot, the temperature will never rise above 212^{0}F; the water will only boil harder, with the liquid water changing phase into steam, and the teapot will boil dry more quickly. However, if you place the lid on a pressure cooker (or a cap on the radiator of an automobile), as the water boils inside, both the temperature and the pressure increase. This is due to the pressure pushing back down on the surface of the water. It now takes more heat (increased temperature) for the water to continue to boil as the water molecules need more energy to break-free of the water's surface to turn into steam. If the stove burner is left on high, both the temperature and the pressure in the pressure cooker will continue to increase until the petcock safety relief device rattles and bleeds out excess pressure.

Temperature and pressure are directly related. If the pressure of a cryogenic liquid stored in a pressure vessel increases, you can be certain that the temperature of the liquid has also increased; and vice-versa. Likewise, if the pressure in a vessel decreases you can assuredly know that the temperature will correspondingly decrease.

Let's dive into this topic a little deeper – but before we do, let's define some common terms.

Heat is a form of energy. The flow of energy from a warm object to a colder object is measured in BTUs, Joules, or Calories.

Temperature – We use comparative temperature scales when referencing the intensity or degree of heat (enthalpy) in a substance, particle, or object, when measured using a thermometer. Even on a cold wintry day, a thermometer does not inform you how cold it is outside. It expresses the degree of ambient heat or warmth. Temperature measurements are a scaled reference of the degree of 'hotness' of something.

Enthalpy of vaporization is an important property of any liquid, which states that when heat (enthalpy) is transferred to any liquid substance at a certain pressure and temperature, the liquid will change into its gaseous form. A transformation from one state or phase to another occurs. Enthalpy of vaporization is also known as 'latent heat of vaporization'.

Pressure is measured as force on a given unit of area. Pressure in cryogenic tanks is generated by the weight of the liquid and the vapor molecules contained in the tank, as well as by the resulting force against the tank walls generated by the kinetic energy of the molecules contained therein. The warmer the molecules are inside the tank, the more kinetic energy they possess, which causes them to move faster and farther apart from each other and impact the walls of the tank with greater force.

Ullage pressure – The term 'ullage' refers to the 'head space' or 'vapor space' above the liquid in the top of a cryogenic tank. Ullage pressure is the pressure of the vapor in the head space that pushes down on the surface of the liquid in a tank.

Head pressure – Head is a combination of the vapor pressure in the ullage, or head space, and the pressure at the bottom of a vessel created by the weight of the liquid and vapor product. The taller the column of liquid (the higher the liquid level), the higher the pressure produced at the bottom of a vessel. The ullage pressure and the weight of the liquid serve to 'push' the liquid out of a vessel when pressure decant dispensing – transferring product into a lower pressure vessel. Head pressure is also used to push the cryogen to its final point of use, or to push it into a vaporizer if the gaseous phase of the product is needed. Head pressure additionally is used to "push" the liquid into a pump so that the pump can catch and maintain prime (See *Who likes a low-down, lousy, leaking pump seal?* in the December 2019 and January 2020 issues of **gas**world).

"A liquid is 'saturated' with heat when, at a given pressure, the addition of even one more BTU of heat causes the liquid to boil"

Artificial pressure – Over time, if the product in a cryogenic vessel is not used, ambient heat leaking into the tank causes the liquid to boil and the pressure in the tank to rise. This pressure rise is considered naturally generated head pressure. Artificial pressure is pressure that is intentionally created to increase the pressure in the ullage space of a closed vessel. In the cryogenic industry, the most common method used to create artificial pressure is to divert liquid from the bottom of a vessel and pass it through a pressure building unit (PBU) to convert the liquid into gaseous vapor. A PBU is a heat exchanger and is commonly made of extruded aluminum finned tubes. The aluminum fins serve to transfer heat, from the relatively warm ambient air, into the liquid, causing it to boil and vaporize. The warm vapor is then routed into the head space of the vessel to increase the pressure in the ullage space. Typical cryogenic liquids expand 600 to 700 times in volume when they change phase from liquid to vapor! The expansion factor for liquid nitrogen, for example, is almost 697! One gallon of liquid nitrogen produces 93.11 standard cubic feet (SCF) of nitrogen vapor.

In summary, the intentional pressure increase in the head space of a tank is termed 'artificial pressure' because it is not generated by natural heat-leak into the tank. However, if the artificial pressure remains in the tank over time, for example if the artificial pressure is not blown down (vented) after completing a pump delivery operation, the added heat in the artificially created vapor will eventually be conducted into the colder liquid. The temperature of the vapor will decrease, and temperature of the liquid will increase until they come to equilibrium.

Temperature and pressure

Temperature and pressure are directly related to each other. As heat leaks into a cryogenic tank and the temperature of a cryogen increases, so does the pressure in the tank in which it is contained. And heat escapes from a cryogenic tank when the pressure is reduced. Controlling heat and pressure are perhaps the most important, yet common things we do in the cryogenic industry. We try to limit the transfer of heat into the cryogen when we need to store or transport it. We try to maintain cold, low pressure liquid to feed a pump. Conversely, we intentionally add heat to a liquid cryogen when we want to vaporize it, or to create artificial pressure in the head space of a storage tank to withdraw product. Pressure is often increased for end-use applications such as laser cutting. Understanding such basic principles of physics as temperature and pressure allows us to harness and use them to our benefit in the cryogenic world.

Backpacking in the Utah mountains

If we carry a cooking thermometer while backpacking in the beautiful Uinta Mountains of Utah, we will discover that when we build a campfire at 13,000 feet and boil our dinner, the temperature of the water does not reach 212°F (100°C). Instead, the water begins to boil at only ▸

188°F (86.6°C)! The column of air from the mountain top to the edge of space is not as tall as the column of air at sea level. The weight of the air at 13,000 feet does not press down as hard on the surface of the water as at sea level. At this elevation, the H_2O molecules have enough energy at 188°F to burst free of the surface of the water and change phase into steam. Since the water boils at a lower temperature as the elevation increases, the food takes longer to cook than at sea level.

In contrast, a pressure cooker decreases cooking time by increasing the pressure on the surface of the water, and thus temperature. The steam in the 'ullage' space of the pressure cooker pushes down on the surface of the liquid like a firm invisible hand. The additional pressure created in the pressure cooker as steam builds temporarily prevents the liquid from boiling. It is only after additional heat has been added to the liquid in the pressure cooker that it finally becomes saturated with enough heat energy to begin boiling again. Eventually the petcock (relief valve) begins to rattle. Both the liquid and the vapor are saturated at approximately the same temperature, around 260°F. With the additional energy, the temperature of the liquid is higher than it would have been had the pot been left open (unpressurized); so, the food cooks faster.

Saturation of cryogenic liquids

Due to heat leak, the pressure in a cryogenic vessel will rise overtime if the product is left unused. Cryogenic vessels are designed to minimize heat-leak; however, some heat still manages to migrate inside and eventually saturates the liquid. Once saturated, the liquid boils and some of the liquid is converted into vapor. This vapor, added to the ullage space above the liquid in the closed vessel, causes the pressure in the tank to increase; pressing down harder on the surface of the liquid. This in turn causes the liquid to stop boiling. But as heat constantly leaks into the vessel, this natural pressure building process continues. Eventually the primary safety relief valve will open to relive the pressure, and the liquid will remain saturated at or near the relief valve pressure setting.

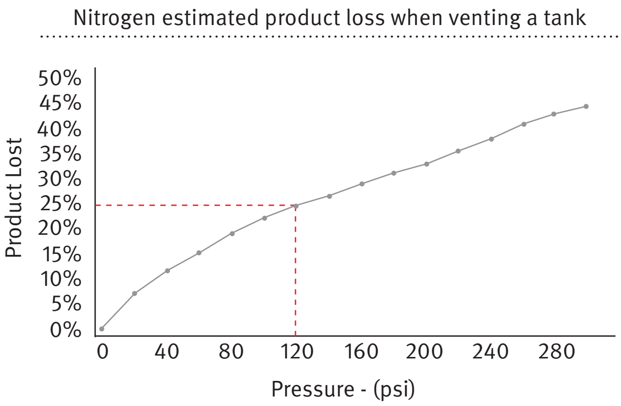
How is saturation expressed?

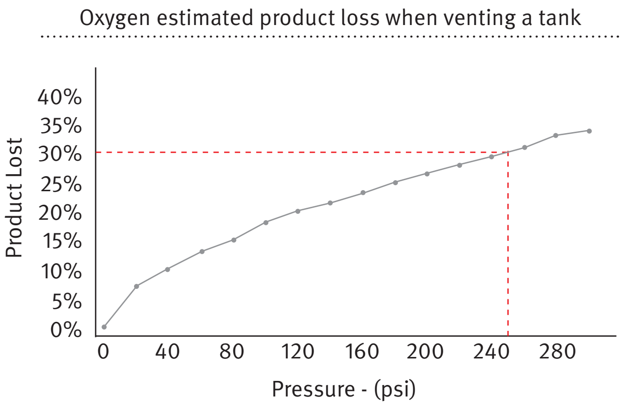
Since pressure and temperature are directly related, the saturation point of a liquid can be expressed as either a pressure or a temperature value. In the cryogenic industry, saturation is generally expressed in terms of pressure, not temperature. This is because most cryogenic vessels are equipped with pressure gauges, not thermometers. It is challenging to pass a temperature measurement device through the annular vacuum space. However, since we know that pressure and temperature are directly related, we simply express saturation as a pressure value.

For example, if someone observes that a cryogenic vessel at 100 psi has been sitting unused for some time (and without the pressure building unit coming on), he or she can accurately state that the cryogen contained therein is saturated at 100 psi. This means that if even one more BTU of heat leaks into the tank, the liquid will begin to boil, and the pressure and temperature will both rise. If the tank is vented, both the pressure and the temperature will drop as heat is boiled away as some of the liquid boil and turns into escaping vapor.

Desaturation product loss

The dangerous and unsafe act of removing the cap from a hot automobile radiator is a common example of what happens when pressure is suddenly released from a vessel saturated at a pressure higher than atmospheric. Scalding hot coolant and steam forcefully spew out from uncapped radiator, potentially causing serious burns. Not only is coolant lost due to the sudden pressure release, but additional coolant is lost as the liquid continues to vigorously boil for the next few minutes, turning





'Rule of Thumb' charts, different for each gas species, are used to estimate product loss when venting down a vessel. Percentages shown are based on the volume of product (liquid level) in the tank immediately prior to venting (Charts use data provided courtesy of Taylor-Wharton)

additional coolant into steam. The boiling continues until the coolant has released enough heat energy (turning liquid into steam) so that atmospheric pressure is able to suppress the boiling and the temperature and pressure once again achieve equilibrium.

In the cryogenic industry it is important to remember that, if you vent a tank down (like removing the cap on a hot car radiator), the product it contains is going to boil. This boiling-away of heat results in a phase change of some of the liquid product turning into vapor.

It is a common misconception to believe that if you vent, or blow, a tank down, the only product that will be lost is the vapor in the head space above the liquid. As we have learned, not only is the vapor above the liquid lost, but additionally a significant quantity of liquid also turns into vapor as it boils-off heat and de-saturates to come into equilibrium with the lower pressure. “The invisible hand” of pressure that was pressing down on the surface of the liquid preventing it from boiling, was removed.

Rules of thumb

Included below are useful ‘rule-of-thumb’charts for liquid nitrogen, liquid argon, liquid oxygen, and carbon dioxide. With the liquid saturated at any given pressure, these charts permit you to estimate the desaturation product release or loss percentage you can expect when blowing down a tank.

As pressure is released, the liquid boils away heat until the energy in the liquid can no longer overcome the reacting pressure exerted on the surface of the liquid. If a tank is vented to completely down (0 psig), the pressure on the surface of the liquid is only the weight of air molecules from the edge of space to the surface of the liquid (atmospheric pressure). Otherwise it is the remaining pressure in the tank.

Using the chart for liquid nitrogen, and assuming a 15,000-gallon liquid nitrogen tank saturated at 120 psig, as an example, we can estimate that a tank vented completely down to atmospheric pressure (0 psig) would result in a product loss of approximately 24 percent (reference the pink-dotted lines) or 3,060 gallons (0.24 X 15,000 = 3600)!

If a 9,000-gallon oxygen tank, saturated at 250 psi, is vented completely down, the estimated product loss is 30% (reference the blue dotted lines) or 2,700 gallons (0.30 * 9,000 = 2,700)!

If the same 9,000 gallon oxygen tank, only half full, and saturated at 250 psi, is vented completely down, the estimated product loss is expected to be approximately 30% of the 50% full tank or 1,350 gallons (0.30 * (0.50 * 9000) = 1,350).

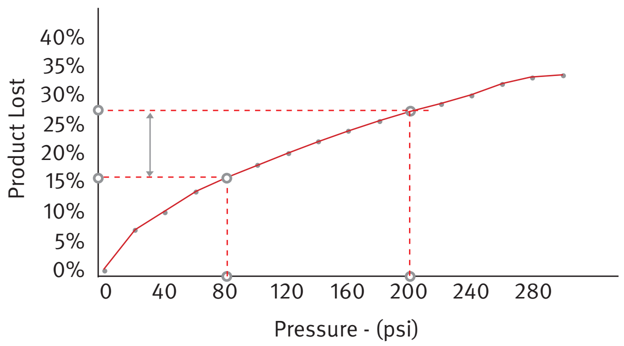
If a 1500-gallon argon tank, ¾ full (0.75 * 1,500 = 1,125 gallon in the tank before venting), and saturated at 200 psig, is vented down to only 80 psig, an approximate, yet expensive, 12-percent of the liquid level is lost back to the atmosphere! [27% - 15% = 12%). That equates to 135 gallons of lost argon (0.12 * 1,125 = 135). The percentage quantity of product lost is seen in the argon chart in the area between the two-red dotted-horizontal lines (reference the area indicated by the green arrowheads).

As we have discussed in this article, the amount of product lost due to venting is not simply the initial quantity of vapor in the ullage space above the liquid, rather as a tank is vented and the pressure therein drops, the liquid in the tank begins to boil as it desaturates, turning into additional vapor which also escapes and is lost. gw

ABOUT THE AUTHOR

Keith Hall is a member of the gasworld editorial board and Vice-President of Product Development and LNG Equipment Sales at Applied Cryogenic Technologies in Houston, Texas. ACT designs and manufactures cryogenic transport trailers and other cryogenic transportation and vaporization equipment. The views expressed in this article are those of the author and do not necessarily express the views of his employer. Keith also thanks John Wimberley of Taylor-Wharton for his input to this article and for sharing the desaturation product loss charts.

Argon estimated product loss when venting a tank



CO_2 estimated product loss when venting a tank