

On the thermodynamic boundaries of cryogenic liquid storage in closed containers

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Abstract. The self-pressurisation of a cryogenic liquid due to heat inleak into a closed cryogenic system is essential for the design of storage vessels. The resurgence of liquid hydrogen as a fuel for sustainable transportation and logistics sparked new interest in this topic. The cryogenic fuel tank represents the core of these applications. It is the goal to store as much hydrogen mass loss-free for as long as possible. Key design parameters of such a tank are the dormancy time and the pressure increase rate. It is already known that the geometry and the heat inleak distribution significantly influence the self-pressurisation of a closed cryogenic system. We want to expand on this idea and study the underlying thermodynamic changes of state resulting in two theoretical boundary cases: Processes that give the minimum/maximum pressure increase rate in case of identical heat inleak. We want to capture the notion of non-uniformly distributed heat being the most significant influencing factor of the self-pressurisation behaviour of such vessels. These boundary cases allow to assess actual cryogenic storage vessels and to consider the maldistribution of heat on an abstract level. This theoretical analysis could support future design choices of cryogenic liquid storage systems.

1. Introduction

The current development from a fossil-fuel-based transportation and logistics infrastructure towards a more sustainable one requires the usage of alternative on-board fuels. Due to its relatively high volumetric energy density, cryogenic liquid hydrogen (LH₂) is considered a promising candidate for the decarbonisation of future mobility. In this context, the on-board LH₂ fuel tank will most probably be realised in the form of a closed container to ensure loss-free LH₂ storage. During vehicle downtimes, the inevitable heat inleak from the ambient surroundings into the cryogenic system leads to the self-pressurisation of the closed fuel tank. After a certain period of time, the tank's maximum allowable working pressure is reached and a relief valve starts to vent boil-off gas to the environment as a pressure control measure. This period of time is defined as the dormancy time of the cryogenic storage container and constitutes a key design parameter of such a system. The second key design parameter is the pressure increase rate of the vessel. Both parameters are interconnected: A short dormancy time implies a high pressure increase rate whereas a long dormancy time implies a low pressure increase rate. From this, the following obvious design question arises: In case of identical heat inleak, what thermodynamic process results in the minimum/maximum pressure increase rate and therefore the maximum/minimum



dormancy time possible? It is already known that the heat inleak distribution into a cryogenic system plays an important role in its self-pressurisation behaviour [1-3]. In the following, we investigate this aspect on a thermodynamic level and define absolute limits within which closed cryogenic liquid storage containers can be operated. If those thermodynamic boundary cases are known, any actual storage container can be assessed on a more abstract level and can therefore be characterised in comparison to those absolute limits. This allows for differentiating between thermally poorly and thermally well designed vessels. Furthermore, considering those absolute limits helps to explain, why non-uniformly distributed heat inleak is the most significant influencing factor on the self-pressurisation process of such a vessel and additionally allows for conclusions concerning the vessel's thermal stratification behaviour.

2. Theory

2.1 Self-pressurisation via restricted volume expansion

A closed cryogenic liquid storage container can be seen as a globally isochoric system due to the overall system density being constant throughout all changes of state. Accordingly, volume expansion of the fluid is restricted and cannot help compensating heat input as would be the case in an isobaric storage container. Instead, heat input into the closed system results in pressure increase. To derive which thermodynamic processes result in the aforementioned boundary cases for minimum/maximum pressure increase rates in isochoric systems, we look into which isobaric processes lead to the minimum/maximum volume expansion of fluid upon heat input. For this, the vaporisation of saturated liquid and the superheating of saturated vapour in isobaric conditions are discussed. In the following, pure parahydrogen is chosen as the example fluid.

Figure 1 shows the two-phase diagram of the independent variables specific internal energy u and specific volume v . At first, the isobaric vaporisation of saturated liquid parahydrogen at a pressure of 1 bar is considered. We see that if the saturated liquid is converted into saturated vapour, the specific volume increases by $0.386 \text{ m}^3\cdot\text{kg}^{-1}$. For this increase in specific volume, the specific energy of vaporisation of $352 \text{ kJ}\cdot\text{kg}^{-1}$ is necessary. If this exact amount of energy was not to be converted into the vaporisation of liquid but instead into the uniform superheating of saturated vapour at 1 bar, the specific volume of the vapour would increase by $1.144 \text{ m}^3\cdot\text{kg}^{-1}$. Thus, the superheating of vapour results in an increase in specific volume that is roughly three times higher than the increase during liquid vaporisation alone. It can be concluded that as soon as some amount of heat input into a two-phase cryogenic system is converted into the superheating of gas, the resulting increase in specific volume would be higher than if the heat was purely converted into the vaporisation of liquid. Hence, vaporisation of liquid at constant equilibrium conditions throughout the whole container results in the least amount of volume expansion possible.

As already stated, a closed isochoric system does not allow for volume expansion. Instead, the restricted expansion leads to self-pressurisation. As we were able to deduce, the minimum pressure increase rate can be achieved when all heat inleak into the closed cryogenic system is converted into the vaporisation of liquid at constant equilibrium conditions without any superheating of gas. Vice versa, the conversion of heat inleak exclusively into the superheating of gas leads to the maximum pressure increase rate possible.

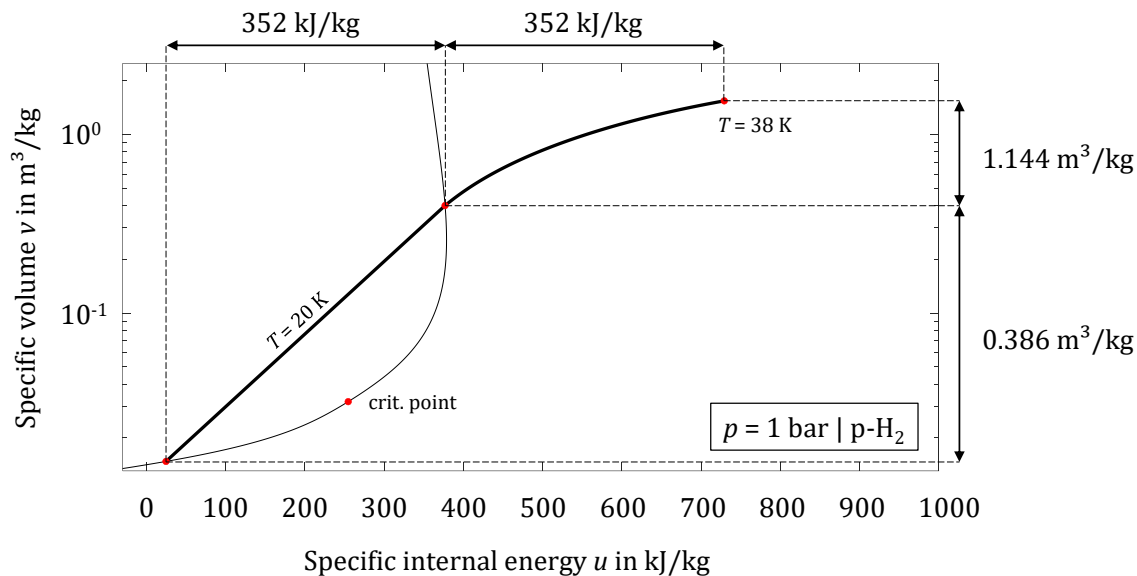


Figure 1. ($\lg v-u$) diagram of parahydrogen. Shown are the vaporisation of saturated liquid and the uniform superheating of saturated vapour at constant 1 bar pressure. The superheating leads to an about three times higher increase in specific volume than the vaporisation of saturated liquid.

2.2 Thermodynamic boundary #1 – minimum pressure increase rate

Following the considerations in section 2.1, the minimum pressure increase rate in a closed cryogenic liquid storage container can be achieved when all heat inleak into the cryogenic system is converted into the vaporisation of liquid. To prevent superheating of gas, a constant thermal equilibrium throughout the entire fluid must be assumed. This implies that no temperature gradients exist and that all liquid and gas are always at saturation condition according to the momentary pressure level during the entire self-pressurisation process.

Figure 2 shows the two-phase diagram of the independent variables specific internal energy u and pressure p for pure parahydrogen. Let us consider the self-pressurisation process with the minimum pressure increase rate from 2 to 10 bar, starting with a closed container in thermal equilibrium, in which both phases are saturated. At all times during the self-pressurisation process, the state points of the liquid and the gas phase strictly follow the saturation curve. Accordingly, the initial liquid fill level cannot be an influencing factor for this thermodynamic boundary case. This theoretical model process can be approximated quite well with heat inleak exclusively into the liquid phase, as was experimentally shown by [4].

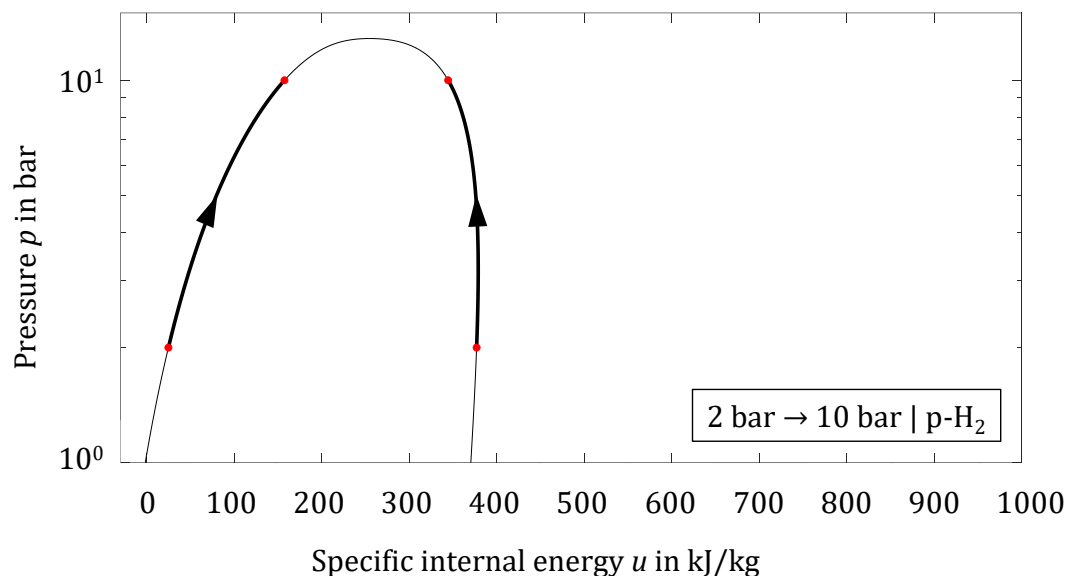


Figure 2. ($\lg p$ - u) diagram of parahydrogen. Shown are the thermodynamic changes of state of the liquid and the gas phase during the self-pressurisation process from 2 to 10 bar of a closed cryogenic liquid storage container with minimum pressure increase rate. Both phases are saturated during the entire change of state.

2.3 Thermodynamic boundary #2 – maximum pressure increase rate

Following the considerations in section 2.1, the maximum pressure increase rate in a closed cryogenic liquid storage container can be achieved when all heat inleak into the cryogenic system is exclusively converted into the superheating of gas. A uniform superheating of gas is chosen to construct a meaningful thermodynamic boundary case. It is fact that in reality, a thermal stratification in the gas phase will establish, leading to higher gas temperatures at the top of the container than near the liquid-vapour interface. However, when we consider the volumetric thermal expansivity of parahydrogen, which rapidly decreases with increasing temperature, we see that above a temperature of about 50 K, the volume expansion falls below 2 vol.-%·K⁻¹. The most significant amount of volume expansion would therefore happen below 50 K. Hence, a uniform superheating of gas reflects this critical behaviour quite well. Additionally, any heat and mass transfer between the two phases must be prohibited.

Figure 3 shows the two-phase diagram of the independent variables specific internal energy u and pressure p for pure parahydrogen. Let us consider the self-pressurisation process with the maximum pressure increase rate from 2 to 10 bar, starting with a closed container in thermal equilibrium, in which both phases are saturated. As per the assumptions, the liquid phase undergoes a so-called isoenergetic change of state, meaning that the specific internal energy of the liquid stays constant at all times during the self-pressurisation process. At the same time, the initially saturated vapour superheats.

In this boundary case, the thermodynamic change of state of the gas phase is influenced by the initial liquid fill level. The liquid density increases during the self-pressurisation process. Throughout this process, it is always well-defined by the constant specific internal energy and the pressure and therefore independent of the initial fill level. According to the liquid density's increase, the gas density decreases. The percent decrease of the gas density is dependent on the

initial fill level. This percent decrease is higher, with a higher initial fill level. Hence, there exist different changes of state of the gas phase for processes with the same pressure increase rate depending on the initial fill level. Figure 3 shows the changes of state for the two initial liquid fill levels 10 and 90 vol.-% as an example.

The above described theoretical model process can be approximated quite well within cryogenic storage containers, in which the stored liquid mass is much higher than the gas mass and thermal stratification of the liquid phase is considered significant. In these vessels, the thermal stratification of the liquid phase leads to high amounts of subcooled cryogenic liquid. Any heat inleak into such a liquid decreases the amount of subcooling by raising its specific internal energy. However, because of the comparatively high liquid mass, the increase in specific internal energy of the liquid is small, such that its thermodynamic change of state tends towards an isoenergetic one. Hence, the pressure increase rate of the overall system is dominated by the thermal state of the gas phase.

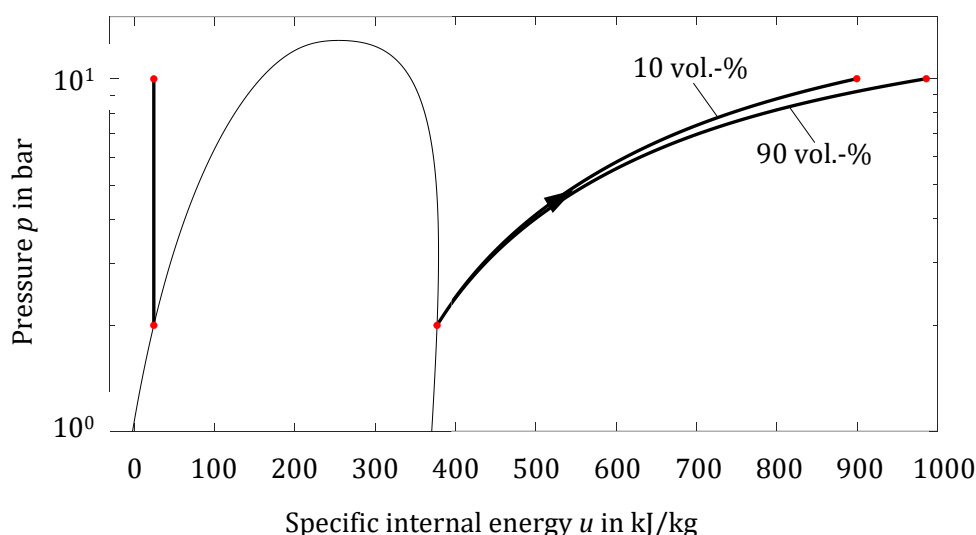


Figure 3. ($\lg p-u$) diagram of parahydrogen. Shown are the thermodynamic changes of state of the liquid and the gas phase during the self-pressurisation process from 2 to 10 bar of a closed cryogenic liquid storage container with maximum pressure increase rate. Both phases are initially saturated; initial liquid fill levels are set at 10 and 90 vol.-%.

2.4 Actual thermodynamic changes of state during cryogenic liquid storage in closed containers

The sections 2.2 and 2.3 define absolute thermodynamic limits between which any actual self-pressurisation process of a closed cryogenic liquid storage container must take place. Figure 4 shows both those limits for the aforementioned example process of a self-pressurisation of parahydrogen from 2 to 10 bar in a ($\lg p-u$) diagram with 50 vol.-% initial liquid fill level. Following the considerations in the sections 2.2 and 2.3, it becomes apparent that all possible thermodynamic changes of state of the liquid phase must be located in the blue region and all possible thermodynamic changes of state of the gas phase must be located in the red region of figure 4. To determine the exact change of state inside these limits for an actual self-pressurisation process of a closed cryogenic liquid storage container, three parameters need to be measured precisely at any time during the process: the pressure of the vessel, the volumetric fill level and the temperature distribution within the liquid and the gas phase.

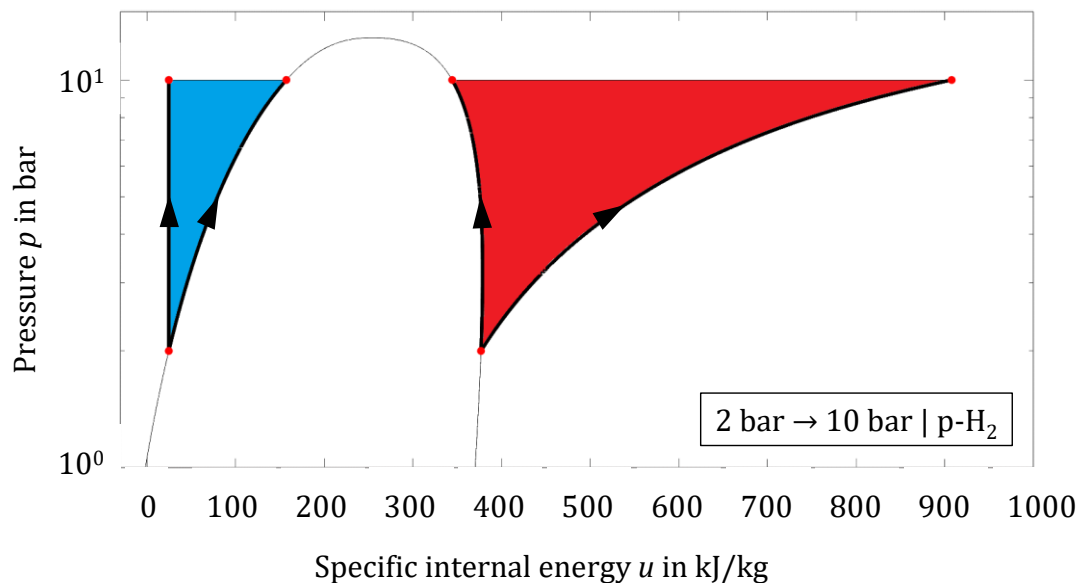


Figure 4. ($\lg p$ - u) diagram of parahydrogen. Shown are the thermodynamic boundaries of cryogenic liquid storage in closed containers for the self-pressurisation process from 2 to 10 bar. All possible thermodynamic changes of state must be located in the coloured regions. The initial liquid fill level is set at 50 vol.-%.

3. (p - u) analysis – example and potentials

As stated in section 2.4, to plot the exact change of state of an actual self-pressurisation process, precise knowledge of the three parameters pressure, volumetric fill level and temperature is required. But experimental literature data on LH₂ self-pressurisation is scarce, especially concerning an exact measurement of the temperature distribution over time. The only source of knowledge to us, reporting such an experiment with all three parameters measured sufficiently, is Schmidt et al. 1961 [5]. In their experiment, the authors investigated the self-pressurisation of a 2366 litre LH₂ vessel from 0.9 to 10 bar(a). The self-pressurisation took 72 hours and was started with an initial volumetric liquid fill level of 68 vol.-%. From the geometric and experimental data given in [5], the changes of state of the liquid and the gas phase can approximately be reconstructed after 0, 24, 48 and 72 hours after the start of the experiment. These reconstructed thermodynamic state points are shown in figure 6 below. The experimental data used to reconstruct the state points is shown in figure 5 [5]. It shows the temperature distribution in the liquid and the gas phase plotted against the height of the vessel at 0, 24, 48 and 72 hours after the start of the experiment.

Figure 6 shows that the pressure increase rate during the first 24 hours of self-pressurisation is 0.09 bar·h⁻¹. After that, it increases by a factor of about 1.5 up to 0.14 bar·h⁻¹. This initial, low pressure increase rate can be explained by an initially high level of liquid vaporisation, as the liquid is saturated across the entire phase at the start of the experiment (see figure 5). Hence, any amount of heat entering the liquid in the beginning of the experiment leads to liquid vaporisation. Because of the liquid's thermal inertia, however, the gradual self-pressurisation of the vessel creates a significant amount of liquid subcooling during the first 24 hours and the liquid phase becomes thermally stratified (see figure 5). From there on, the heat entering the liquid mostly

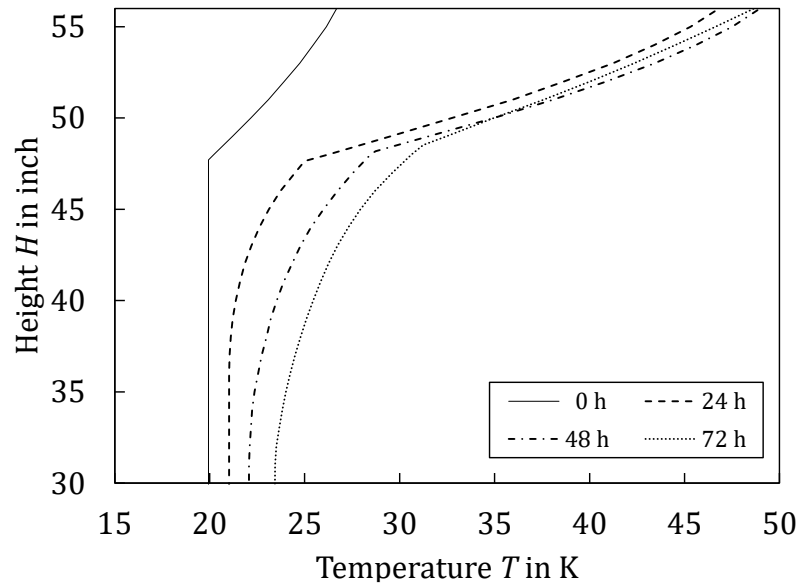


Figure 5. Experimental data of Schmidt et al. 1961 [5]: Temperature distribution over the height of the LH₂ vessel at 0, 24, 48 and 72 hours after the start of the self-pressurisation process.

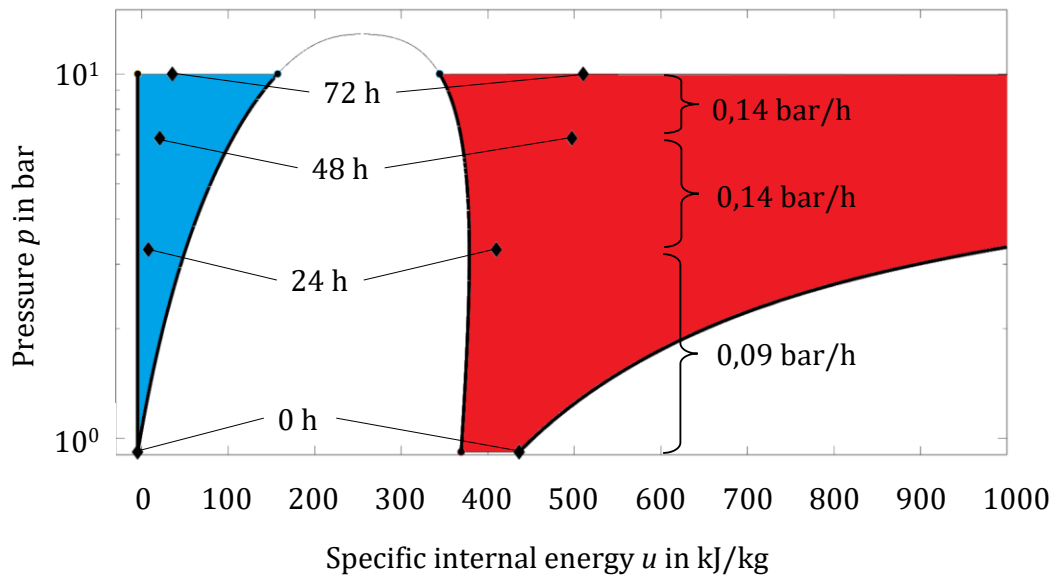


Figure 6. ($\lg p$ - u) diagram of parahydrogen. Shown are the thermodynamic boundaries of cryogenic liquid storage in closed containers for the self-pressurisation process from 0.9 to 10 bar(a). The initial liquid fill level is set at 68 vol.-%. The approximate reconstruction of the (p - u) relation of the geometric and experimental data according to Schmidt et al. 1961 [5] is given at 0, 24, 48 and 72 hours after the start of the self-pressurisation.

decreases the amount of liquid subcooling as can be seen from the according liquid state points after 48 and 72 hours (see figure 6). This initially high level of liquid vaporisation also dominates the thermal state of the gas phase during the first 24 hours. The newly formed saturated vapour entering the gas phase and relatively high convective currents caused by the vaporisation process

suppress the effect of gas superheating. All of this leads to the overall specific internal energy of the gas phase to decrease during this period. The according state point of the gas phase tends towards the saturation curve (see figure 6). During the next 48 hours of the experiment, this is no longer the case. With less liquid vaporisation and heat input to the liquid mostly resulting in the decrease of subcooling, the superheating of gas dominates the self-pressurisation process. The according state points of the gas phase tend away from the saturation curve (see figure 6). All of the described observations are in accordance with the presented theory in section 2. The thermal behaviour during the first 24 hours can be approximated by the first thermodynamic boundary case (see section 2.2), the second 48 hours by the second one (see section 2.3). The presented example shows quite well that a rather complex thermal behaviour of a cryogenic liquid storage container can be made apparent by such a ($p-u$) analysis.

This ($p-u$) analysis of the self-pressurisation behaviour of a closed cryogenic liquid storage container is an abstract view on the thermodynamic changes of state involved, as it disregards the size and shape of the storage vessel and the amount of parasitic heat inleak. Hence, it allows for assessment and characterisation of any cryogenic storage vessel and provides comparability between them. Thermally poorly and thermally well designed vessels can be distinguished from one another; the impact of different vessel geometries and design configurations can be identified. Furthermore, it is a tool to analyse the heat inleak distribution and the thermal stratification behaviour of a cryogenic vessel. Optimisation measures and potential remedies can directly be assessed with regards to their effectiveness.

4. Conclusion and outlook

A new method of analysing the thermal behaviour of closed cryogenic liquid storage containers on an abstract thermodynamic level is presented. Therefore, two thermodynamic boundary cases, resulting in minimum and maximum pressure increase rates, are derived. Any actual self-pressurisation behaviour must therefore be in between those limits. The introduced ($p-u$) analysis is demonstrated by an example from the literature [5] where its potential is highlighted. In the future, the authors of this paper plan to use an LH₂ fuel tank test rig [6] to further investigate the self-pressurisation and thermal stratification behaviour of closed cryogenic liquid storage containers. The presented analysis and these further investigations could support future design choices for such containers.

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