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The isentropic expansion energy of compressed and cryogenic hydrogen

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ABSTRACT

Pressure is often perceived as the single most important parameter when considering the safety of a storage system, for example when calculating the pneumatic energy that could be released in the event of a sudden accidental failure (or burst energy). In this paper, we investigate the role of temperature as another degree of freedom for minimizing the burst energy. Results are first presented for ideal gases, for which the relationship between burst energy as a function of initial and final volumes, temperature and pressures can be expressed analytically. Similar analysis is then derived for the specific case of H₂ using real gas equations of state. Assuming the expansion is isentropic, which holds for an adiabatic and sudden release as in a burst, it is shown that the energy released during a sudden burst is a weak function of pressure, revealing that the effect of increasing pressure is negligible beyond a certain value (~100 bar); whereas the burst energy is a linear function of temperature. This suggests that temperature controls the burst energy in a much greater way. This analysis is carried out in the frame of onboard H₂ storage systems, for which it is shown that the use of cryogenic temperature for hydrogen vehicles, where risks of collision and impact on the surroundings are high, appears as a safety feature since burst energy is up to 18 times less than room temperature, high pressure storage.

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Introduction

The very low density of hydrogen (H₂) at atmospheric conditions makes it difficult to store onboard a vehicle. Different technologies such as materials-based (adsorption or absorption) [1], room temperature high pressure (350–700 bar [1]), or cryogenic storage at low (6 bar [2]) or high (350 bar [3]) pressure have been developed in order to store enough hydrogen within a reasonable weight and volume. These storage modes are characterized by thermodynamic states far away from equilibrium (i.e. from atmospheric conditions) and are thus

prone to release energy when hydrogen escapes the storage system.

We here investigate how both pressure and temperature affect the released expansion energy in case of sudden failure of a high pressure storage system. In such a case, hydrogen is released to the atmosphere within a short time (seconds to minutes [4]), so that its expansion is assumed to be isentropic. Only calculations of total sudden released energy to atmospheric pressure are presented here (thermal equilibrium would take much longer to take place). More detailed calculations on how expansion happens as a function of time for a

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cryogenic high pressure storage system can be found in Ref. [4].

Expansion energy calculations are shown first for ideal then for real gases, with an emphasis on the role of temperature.

Expansion energy of an ideal gas with a constant specific heat

The expansion of an ideal gas with a constant specific heats is described in this section. The ideal gas assumption becomes less and less valid as the initial conditions approach high pressures (and low temperatures) but is used here to simplify the analysis. Next section will conduct similar analysis using real gas equations of state.

The expansion phenomenon is identical to the gas expansion stroke in a piston engine. Assuming isentropic expansion, any thermodynamic state during the process can be computed from [5]:

$$PV^\gamma = P_0V_0^\gamma \tag{1}$$

where γ is the specific heat ratio ($\gamma = c_p/c_v = 5/3$ for monatomic and $\gamma = 7/5$ for diatomic gases). As a result, the final volume for a release from a pressure P_0 (in bar) to atmosphere ($P_1 = 1$ bar) is:

$$V_1 = P_0^{1/\gamma} V_0 = P_0^{(1-\gamma/\gamma)} RT_0 \tag{2}$$

At constant initial temperature, the final volume is a weak inverse function of pressure. Fig. 1 shows the final volume V_1 and temperature T_1 for a vessel containing a diatomic molecule ($\gamma = 7/5$) from $T_0 = 300$ K and various initial pressures P_0 . Counterintuitively, the final volume of the expanded gas is actually lower for a higher initial pressure: high pressure H_2 cools more and therefore expands less.

The amount of energy released during the gas expansion is equal to the expansion work and it is calculated as:

$$E = \int PdV \tag{3}$$

For ideal gas expansion, we substitute Equation (1) into Equation (3) and integrate from an initial thermodynamic state 0 at P_0, V_0, T_0 to a final thermodynamic state 1 at P_1, V_1, T_1 to obtain [6]:

$$E = \frac{RT_0}{1-\gamma} \left(\left(\frac{V_0}{V_1} \right)^{\gamma-1} - 1 \right) \tag{4}$$

which is equivalent to:

$$E = \frac{RT_0}{1-\gamma} \left(1 - \left(\frac{P_1}{P_0} \right)^{\frac{\gamma-1}{\gamma}} \right) \tag{5}$$

Equations (4) and (5) show a linear relationship between initial temperature and expansion energy. We also see that for a large enough initial pressure P_0 , the term in parentheses approaches 1 and the expansion energy becomes a function of temperature only:

$$\lim_{P_0 \rightarrow \infty} E = \frac{RT_0}{1-\gamma} \tag{6}$$

Assuming constant values for R, T_0, γ (7/5 for a diatomic molecule) and P_1 (1 bar) for an ideal gas, the variation of the expansion energy as a function of the initial pressure P_0 (in bar) can be mathematically described as:

$$E(P_0) = \text{constant} \cdot f(P_0) \tag{7}$$

with $f(P_0) = 1 - \frac{1}{P_0^{0.28}}$

We have $f(100 \text{ bar}) = 0.72$ and $f(1000 \text{ bar}) = 0.85$, hence the expansion energy increases only 15% as the initial pressure increases from 100 to 1000 bar. Similarly to the variation of V_1 with P_0 (Fig. 1), the isentropic expansion energy is a weak function of storage pressure for initial pressures above 100 bar. This is illustrated in Fig. 2 for a 300 K initial temperature and initial pressures up to 1000 bar ($P_1 = 1$ bar).

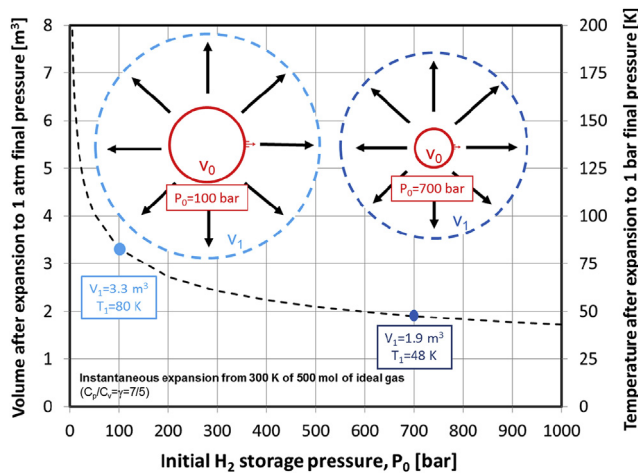


Fig. 1 – Final volume and temperature (both represented by the same dashed line) for an isentropic expansion of 500 mol (approximately equivalent to 1 kg H_2) of a diatomic ideal gas ($\gamma = 7/5$) from pressure P_0 and temperature $T_0 = 300$ K to the atmosphere ($P_1 = 1$ bar).

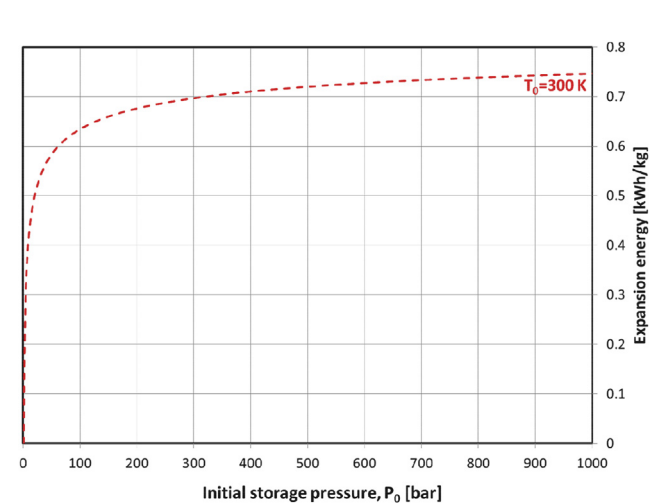


Fig. 2 – Expansion energy for the isentropic relaxation of a diatomic ideal gas with constant specific heats and a specific heat ratio of $\gamma = 7/5$ initially at 300 K and a pressure P_0 to a final pressure of $P_1 = 1$ bar.

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