

Joule-Thomson effect in case of mixtures of natural gas and hydrogen

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1. Introduction

The Joule-Thomson effect - the temperature change of real gases when forced through a throttling device, such as a valve - plays an important role in the utilisation and transportation of gases. For most of the gases and under everyday conditions the Joule-Thomson effect leads to the cooling of the gas. This is used in refrigerators, cryogenic applications and liquification of gases and has practical consequences in the handling and transportation of natural gas. However, there are a few notable exceptions, such as hydrogen. In the case of hydrogen, the Joule-Thomson effect under practical conditions leads to an increase in the gas temperature. As hydrogen is expected to play a role in the future energy system, investigating its behaviour under throttling in practical gas transport applications is of interest.

Furthermore, as injection of hydrogen in the natural gas network is investigated in several countries as an option to decrease CO₂ emissions and store excess renewable energy, the properties of admixtures of natural gas and hydrogen are under investigation. As hydrogen and natural gas behave the opposite way in terms of the Joule-Thomson effect, it is expected that their mixture will change properties with changing mixing ratios.

This report gives a short introduction to the Joule-Thomson effect, the differences between the behaviour of natural gas and hydrogen, and information about the behaviour of their admixture along with useful references.

2. The Joule-Thomson effect

In thermodynamics, the Joule-Thomson effect is the temperature change following an isenthalpic expansion of a real gas or liquid. An isenthalpic process is a process, where the enthalpy of the fluid does not change. The most straightforward example of an isenthalpic process is an irreversible adiabatic expansion through a valve or a porous plug. In everyday terms, adiabatic processes are fast processes, where there is no time for heat exchange with the environment, and these processes include expansion through a valve or expansion in a pressure regulator when the pressure is decreased.

The Joule-Thomson effect is described by the Joule-Thomson coefficient [1], which is defined as:

$$\mu_{JT} = \left(\frac{\delta T}{\delta p} \right)_{H,n} = \frac{V}{C_p} (\alpha T - 1)$$

Here, T is the temperature, p is the pressure, V is the molar volume, C_p is the heat capacity and α is the thermal expansion coefficient. There are a few consequences of the definition of the Joule-Thomson coefficient:

$\mu_{JT} = 0$ when $T = \frac{1}{\alpha}$. This is fulfilled by ideal gases [1], thus in case of an isenthalpic expansion, the temperature of ideal gases does not change.

The SI unit of μ_{JT} is K/Pa or in more practical terms $^{\circ}C/bar$ and as a first approximation gives the temperature change as a consequence of the pressure decrease by a single pressure unit.

In case of real gases and at a given pressure as the temperature is decreased, the Joule-Thomson coefficient is increasing and at some point it becomes zero, before changing sign from negative to positive. This point is the inversion point, and the temperature is the inversion temperature.

The sign of μ_{JT} determines the behaviour of the gas under expansion. If $\mu_{JT} > 0$ (under inversion temperature) the gas cools down under expansion and if $\mu_{JT} < 0$ (above the inversion temperature) the gas heats up.

It can be shown that the above equation of the Joule-Thomson coefficient can be rewritten into a form, which contains the molar specific heat capacity, the temperature, and the partial derivatives of the pressure with respect to temperature (density constant) and density (temperature constant) [2]. This means, that the coefficient can be calculated, if the equation of state describing the fluid is known.

Under conditions in the gas network, meaning not too high pressure and temperature, the components of natural gas cool down during expansion. This is the reason why in places where the pressure is decreased at going from the transmission network to the distribution network, the gas has to be preheated. However, hydrogen has exactly the opposite behaviour: it heats up during expansion.

2.1. Natural gas

The Joule-Thomson coefficient of methane and natural gas has been investigated experimentally in e.g. [3]. For natural gas at 1 bar pressure and 300K μ_{JT} is around $0.48 K/bar$ and it is decreasing slightly with increasing pressure to approx. $0.44 K/bar$ at 40 bar.

2.2. Hydrogen

Hydrogen behaves differently and has a μ_{JT} at 1 bar and 300K around -0.03 K/bar [1]. The negative sign means that under these conditions, hydrogen heats up during expansion. However, the low absolute value of the Joule-Thomson coefficient means that in practice the temperature increase of hydrogen will be negligible apart from in the case of large pressure changes.

3. Joule-Thomson effect in case of a mixture of hydrogen and natural gas

The Joule-Thomson coefficients of natural gas-hydrogen mixtures with different hydrogen blending ratios were calculated in [2] using different equations of state. In order to validate the method, the Joule-Thomson coefficients calculated for pure methane and a natural gas like mixture were compared to experimental results. Based on the calculations of the admixture, mixing up to 30% (mole fraction) hydrogen to natural gas decreases the Joule-Thomson coefficient almost linearly, but it does not invert the behaviour of the mixture. The Joule-Thomson coefficient decreases from ca. 0.5-0.6 K/bar to ca. 0.39 K/bar [2] as shown in Figure 1.

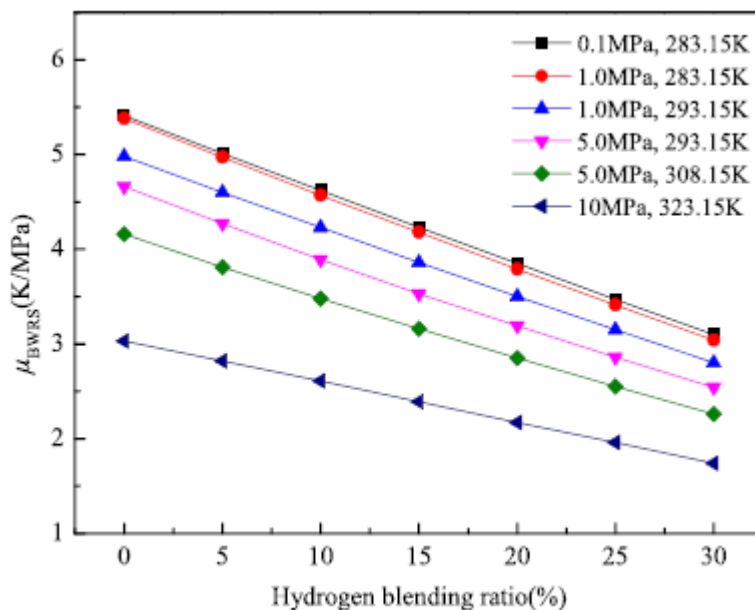


Figure 1 Joule-Thomson coefficient of natural gas-hydrogen mixture at different pressures and temperatures and a function of the hydrogen mole fraction. Figure reproduced from [2].

This means that up to practically relevant mixing ratios (20-30%), there will not be a qualitative behaviour change for the admixture. The decrease of the Joule-Thomson coefficient actually leads to a decrease in the cooling of the gas when stepping down the pressure, which for example decreases the need for pre-heating before pressure reducing units.

4. Summary

During throttling, methane and natural gas cools down as a result of the Joule-Thomson effect, i.e. when expanded in fast processes, such as through valves and pressure reducers. This well-known phenomenon is the reason behind the need to pre-heat natural gas in MR-stations before pressure reduction. However, hydrogen behaves exactly the opposite way: it heats up (under practical conditions) when expanded.

The magnitude and direction of the temperature changes are given by the Joule-Thomson coefficient, which roughly translates into the temperature change of the gas in K or °C as a result of 1 bar pressure decrease. The typical values found in literature for the gases of interest are collected in Table 1.

Even though hydrogen behaves the opposite way compared to natural gas or methane, the magnitude of temperature change is small. A 100-bar pressure reduction in case of hydrogen would lead to an approximately 4 °C temperature increase, which is negligible in most cases.

When mixing hydrogen and natural gas, the magnitude of temperature change will decrease in case of the practically relevant mixing ratios. This means that a mixture of hydrogen and natural gas will cool down less when expanded or when flowing through a pressure reducer than clean natural gas and will require less pre-heating than natural gas without hydrogen under the same conditions.

Due to no qualitative change in behaviour of hydrogen-natural gas mixtures and due to the small magnitude of temperature increase in case of pure hydrogen, the anomalous behaviour of hydrogen during expansion is not expected to cause additional engineering challenges in the gas network.

	Natural gas	Hydrogen	Natural gas – hydrogen mixture
Approximate magnitude of temperature change following 1 bar pressure drop (Joule-Thomson coefficient)	Approx. 0.5 [3]	-0.03 [1]	0.55-0.4* [2]
<i>K/bar</i>			
Behaviour	Cools down	Heats up	Cools down

Table 1: The approximate value of the Joule-Thomson coefficient of gases of interest found in literature at 1 bar and around 300K.

*: Depending on the mole fraction of hydrogen (0-30% investigated in reference)

5. References

- [1] Peter Atkins, Julio De Paula, and James Keeler, *Atkins' Physical Chemistry*, 11th ed. London, England: Oxford University Press, 2017.
- [2] J. Li, Y. Su, B. Yu, P. Wang, and D. Sun, 'Influences of Hydrogen Blending on the Joule–Thomson Coefficient of Natural Gas', *ACS Omega*, vol. 6, no. 26, pp. 16722–16735, Jul. 2021, doi: 10.1021/acsomega.1c00248.
- [3] , G. Ernst, B. Keil, H. Wirbser, and M. Jaeschke, 'Flow-calorimetric results for the massic heat capacity c_p and the Joule–Thomson coefficient of CH₄, of (0.85CH₄+0.15C₂H₆), and of a mixture similar to natural gas', *J Chem Thermodyn*, vol. 33, no. 6, pp. 601–613, Jun. 2001, doi: 10.1006/jcht.2000.0740.