

# On a Class of Thermodynamic Processes Involved in the Transport and Storage of Liquefied Petroleum Gas

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## Abstract

*This paper presents processes that may appear in liquefied petroleum gases transport and storage. We analyze the variation of thermodynamic parameters during liquefied petroleum gases utilization.*

**Key words:** *liquefied petroleum gas; isothermal expansion; isenthalpic expansion.*

## Introduction

Isothermal and isenthalpic expansions are two thermodynamic processes that may be involved in the transport and storage of liquefied petroleum gases (GPL, LPG). Such gases originate from natural gas or refinery gas and contain mainly butane ( $C_4H_{10}$ ), propane ( $C_3H_8$ ), or admixtures thereof. In addition, they contain small fractions of light and/or heavier hydrocarbons as well as sulfur compounds. Methane is usually quasi absent, and there are only traces of ethane and pentane (<1%). As per technical standards ISCIR, GPLs are Group B (liquefied gases); propane and butane are category 3b (pure flammable gases), whereas mixtures of these gases are category 4b (mixtures of flammable gases). GPL's are used as industrial and household fuel, and as solvents. Currently there is a strong trend for extensive GPL use as vehicle fuel.

Isothermal expansion processes are normally used in cryogenic processes to maintain a constant temperature during storage or transport of liquefied masses.

When a gas or vapor stream travels continuously through an area of decreasing sectional area (such as pores, small diameter tubules, or sink faucets), an isenthalpic process (lamination) takes place, characterized by a decrease in pressure. Lamination is accompanied by the Joule-Thomson effect (either increase or decrease of the gas temperature). Lamination is usually adiabatic, without production of work; it is an irreversible process accompanied by entropy increase. In practice, industrial installations take advantage of such processes for gas cooling for liquefying. However, when the flow section reduction method is used to produce expansions (namely, using lamination faucets), or flow regulation (using valves etc.), thermal effects accompanying lamination must be taken into account.

## Isothermal expansion

### Numerical relations

The second thermodynamic principle states:

$$\delta q = Tds \quad (2.1)$$

The heat exchange during a reversible isothermal transformation is given by:

$$q_{12T} = T \int_{p_1}^{p_2} \left( \frac{\partial s}{\partial p} \right)_T dp = -T \int_{p_1}^{p_2} \left( \frac{\partial v}{\partial T} \right)_p dp \quad (2.2)$$

The partial derivative  $\left( \frac{\partial v}{\partial T} \right)_p$  is computed using the gas state equation. Solving for a perfect gas, the heat consumed during an isothermal expansion from pressure  $p_1$  to  $p_2$  is obtained as:

$$q_{12T} = RT \ln \frac{p_1}{p_2} \quad (2.3)$$

Consider a liquefied gas at thermodynamic saturation, and define  $r$  as the specific latent heat of vaporization. Consider an additional heat boost  $q$ , for 1 m<sup>2</sup> sun-exposed surface per unit of time.

Given the energy balance equation:

$$\dot{m}_S r = q \quad (2.4)$$

it results:

$$\dot{m}_S = \frac{q}{r} \quad (2.5)$$

where:

$\dot{m}_S$  - the mass flow of liquefied gas, corresponding to the unit of sun-exposed surface, which evaporates and has to be cleared out the storage space [ kg/(m<sup>2</sup>s) ] ;  
 $q$  - the unit thermal flux, [W/m<sup>2</sup>].

### Case study

Maintaining low temperature of the liquefied mass is achieved by an isobar-isothermal vaporization process where the heat received by the liquefied gas (by thermal transfer from the environment) is used for the vaporization of a part of the liquid gas mass.

Since the liquefied gas is in a thermodynamic saturation state, the heat exchange by a 1 kg mass is equal to  $r$ . Table 1 shows typical values of this thermodynamic characteristic.

The intensity of the total solar radiation  $I_r$ , [W/m<sup>2</sup>] varies by geography, season, and surface positioning; various daily averages are shown in Table 2.

Consider unit thermal fluxes, corresponding to an additional heat boost for 1 m<sup>2</sup> sun-exposed surface and for the unit of time, with values  $q=100$  W/m<sup>2</sup> and  $q=150$  W/m<sup>2</sup> respectively. We

use (2.5) and the values in Table 1 to evaluate the mass flow of liquefied gas  $\dot{m}_S$  [kg/(m<sup>2</sup>s)], corresponding to the sun-exposed surface unit, which evaporates and needs to be cleared out for the storage space; the results are shown in Table 3.

**Table 1.** Latent specific heat for vaporization for propane and i-butane.

No.	Temperature, $t$ , $^{\circ}\text{C}$	Pressure, $p$ , bar	Latent specific heat for vaporization, $r$ , kJ/kg
Propane	30	10,80693	331,050
	20	8,33369	348,551
	10	6,33902	364,168
	0	4,68366	378,654
i- Butane	30	4	320
	20	3	337
	10	2,4	350
	0	1,6	360

**Table 2.** Average daily values for the solar radiation intensity  $I_r$  [ $\text{W}/\text{m}^2$ ].

No.	City	December, horizontal surface	Maximum values, horizontal surface	Maximum values, south facing surface
1	București	41,3	233,2 (August)	138,1 (August)
2	Câmpina	43,1	218,2 (June)	122,5 (September)
3	Constanța	42,2	255,1 (July)	136,6 (September)
4	Craiova	41,3	245,8 (July)	136 (September)
5	Oradea	35,6	230,9 (July)	125,9 (September)
6	Târgu-Jiu	41	238,9 (July)	130,5 (August)

## Lamination; Joule-Thomson effect

### Numerical relations

The first thermodynamics principle states:

$$\frac{w_2^2 - w_1^2}{2} + g(z_2 - z_1) + h_2 - h_1 = q_{12} - l_{t_{12}} \quad (3.1)$$

For the considered system,  $w_1 = w_2$ ,  $z_1 = z_2$ ,  $q_{12} = 0$  and  $l_{t_{12}} = 0$ , thus:

$$h_1 = h_2 \quad (3.2)$$

**Table 3.** Liquefied flow mass flow corresponding to the unit of sun-exposed surface

No.	Storage space temperature $t, ^\circ\text{C}$	Mass flow per unit of sun-exposed surface $\dot{m}_s \cdot 10^3, [\text{kg}/(\text{m}^2\text{s})]$ for $q = 100 \text{ W}/\text{m}^2$	Mass flow per unit of sun-exposed surface $\dot{m}_s \cdot 10^3, [\text{kg}/(\text{m}^2\text{s})]$ for $q = 150 \text{ W}/\text{m}^2$
Propane	30	0,3021	0,4531
	20	0,2869	0,4303
	10	0,2746	0,4119
	0	0,2641	0,3961
i-Butane	30	0,3125	0,469
	20	0,297	0,445
	10	0,286	0,429
	0	0,278	0,417

The gas enthalpy is quantitatively constant, but its quality decreases since  $h_2$  is situated at pressure  $p_2 < p_1$ . Thus, lamination is an irreversible transformation with heat loss without work. We write:

$$dh = 0 \tag{3.3}$$

Lamination is thus a transformation with constant enthalpy (isenthalpic process). The thermal effect of lamination was observed experimentally by James Prescott Joule and studied theoretically by William Thomson (Lord Kelvin). The Joule-Thomson effect relates temperature variation to pressure, under constant enthalpy conditions. Define the Joule-Thomson coefficient  $\mu_{J-T}$  as:

$$\mu_{J-T} = \left( \frac{\partial T}{\partial p} \right)_h \tag{3.4}$$

By using a series of thermodynamic relationship this can be rewritten as:

$$c_p dT + \left[ v - T \left( \frac{\partial v}{\partial T} \right)_p \right] dp = 0 \tag{3.5}$$

Thus, the Joule-Thomson coefficient can be expressed as:

$$\mu_{J-T} = \frac{T \left( \frac{\partial v}{\partial T} \right)_p - v}{c_p} = \frac{T^2}{c_p} \left( \frac{\partial \left( \frac{v}{T} \right)}{\partial T} \right)_p \tag{3.6}$$

which defines the *differential* Joule-Thomson effect in lamination. For a perfect gas:

$$\mu_{J-T} = 0 \tag{3.7}$$

The occurrence of a thermal effect at the passing of gas through an area of decreased sectional area, from a high pressure region to a low pressure region, happens only for gas behaving unlike a perfect gas. For a finite pressure variation, temperature variation is computed as:

$$(\Delta T)_h = (T_2 - T_1)_h = \int_{p_1}^{p_2} \frac{T \left( \frac{\partial v}{\partial T} \right)_p - v}{c_p} dp \quad (3.8)$$

which defines the *integral* Joule-Thomson effect in lamination.

The Joule – Thomson effect in real gases consists either in a temperature increase or decrease, as a function of the sign in the numerator of (3.8). During lamination pressure always decreases thus the following situations can be distinguished:

$$a) \quad \left( \frac{\partial v}{\partial T} \right)_p > \frac{v}{T}, \text{ thus } \left( \frac{\partial T}{\partial p} \right)_h > 0 \text{ and } \mu_{J-T} > 0 \quad (3.9)$$

which means temperature decrease;

$$b) \quad \left( \frac{\partial v}{\partial T} \right)_p < \frac{v}{T}, \text{ thus } \left( \frac{\partial T}{\partial p} \right)_h < 0 \text{ and } \mu_{J-T} < 0 \quad (3.10)$$

which means temperature increase;

$$c) \quad \left( \frac{\partial v}{\partial T} \right)_p = \frac{v}{T}, \text{ thus } \left( \frac{\partial T}{\partial p} \right)_h = 0 \text{ and } \mu_{J-T} = 0 \quad (3.11)$$

which means the temperature remains constant.

During lamination, the unit variation of entropy is expressed as:

$$\left( \frac{\partial s}{\partial p} \right)_h = -\frac{v}{T} \quad (3.12)$$

and the finite variation of entropy is expressed as:

$$(\Delta s)_h = (s_2 - s_1)_h = -\int_{p_1}^{p_2} \frac{v}{T} dp \quad (3.13)$$

For a van der Waals gas, the temperature variation during lamination with pressure decreasing from  $p_1$  to  $p_2$ , is expressed as:

$$(T_1 - T_2)_h \Big|_{p_1}^{p_2} = T_1 - 3 \sqrt{T_1^3 - 3a(p_1 - p_2) + \frac{3b}{2}(p_1^2 - p_2^2)} \quad (3.14)$$

where a and b are the van der Waals constants of the gas under study.

### Case study

We have seen that pressure always decreases during lamination; the Joule – Thomson for real gases results in either an increase or decrease in the gas temperature upon lamination, given by (3.14). Van der Waals constants for propane and butane obtained from the literature are shown in Table 4. Table 5 shows the results of computation of temperature decrease in a variety of cases obtained by using (3.14).

**Table 4** Van der Waals gas constants

Substance	Density at 0°C and 760 mmHg $\rho$ kg/m <sup>3</sup>	Van der Waals constants	
		a [Nm <sup>4</sup> /kg <sup>2</sup> ]	b [dm <sup>3</sup> /kg]
Propane	2,019	252,690	1,481
Normal butane	2,703	219,071	1,462
Iso-butane	2,668	224,024	1,508

**Table 5** Temperature decrease upon lamination.

Substance	Initial pressure, $p_1$ , [bar]	Final pressure, $p_2$ , [bar]	Initial temperature, $t_1$ , [°C]	Initial temperature, $T_1$ , [K]	Temperature variation, $\Delta T$ , [K]
Propane	8	1	15	288,15	15
Normal butane	8	1	15	288,15	15,88
Iso-butane	8	1	15	288,15	15,88

Computations were done assuming the gases obey the van der Waals type of state equations, which implies some simplifying hypotheses.

### Conclusions

- During periods with high solar intensity, an additional heat boost from the environment may occur to a fluid in a reservoir storage;
- In such situations, the simplest method of maintaining constant temperature in the storage space is by using isothermal expansion (relaxation) which consists in the evacuation of a mass of liquid by vaporization which mediates heat transfer;
- The amount of gas which vaporizes and clears out depends on:
  - the nature of the stored fluid;
  - the storage pressure and temperature;
  - the weather conditions at the place of storage;
  - the positioning of the surface of the storage container with respect to the sun.
- The method is simple and easy to use, but produces regional pollution with hydrocarbons vapors;
- Lamination occurs when gas or vapor streams continuously through an area of decreasing sectional area, and is accompanied by sudden pressure decrease;
- Lamination is an irreversible thermodynamic transformation with constant enthalpy (isenthalpic process);
- Lamination is accompanied by certain thermal effects (temperature increase/decrease) which need to be accounted for in the industrial exploitation and transport of hydrocarbons;

- For the studied gases, under the van der Waals assumption, lamination from  $T_1=288,15$  K ( $t_1=15^{\circ}\text{C}$ ) and  $p_1=8$  bar, to  $p_2=1$  bar is accompanied by a temperature decrease of 15...15,88 K.

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## Cercetări referitoare la unele procese termodinamice posibil implicate în transportul și depozitarea gazelor petroliere lichefiate

### Rezumat

În această lucrare sunt prezentate câteva procese care pot să apară în transportul și depozitarea gazelor petroliere lichefiate. Se analizează variația parametrilor termodinamici în cazul utilizării gazelor petroliere lichefiate.