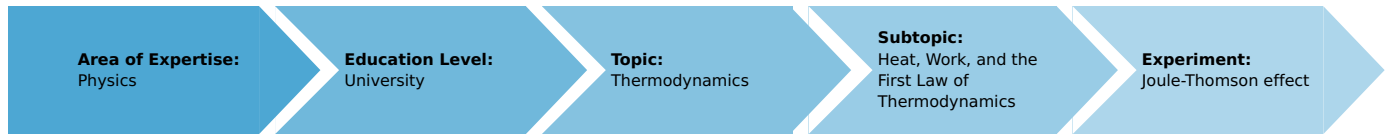


# Joule-Thomson effect (Item No.: P2320600)

## Curricular Relevance



### Difficulty



Difficult

### Preparation Time



10 Minutes

### Execution Time



30 Minutes

### Recommended Group Size



2 Students

### Additional Requirements:

### Experiment Variations:

### Keywords:

real gas, intrinsic energy, Gay-Lussac theory, throttling, Van der Waals equation, Van der Waals force, inverse Joule-Thomson effect, inversion temperature

## Overview

### Short description

#### Principle

A stream of gas is fed to a throttling point, where the gas ( $\text{CO}_2$  or  $\text{N}_2$ ) undergoes adiabatic expansion. The differences in temperature established between the two sides of the throttle point are measured at various pressures and the Joule-Thomson coefficients of the gases in question are calculated.



Fig. 1: Experimental set-up

#### Note

A detailed handbook (128 pages) containing additional experiments is included, free of charge, in the equipment.

## Safety instructions



### Carbon dioxide

H280: Contains gas under pressure; may explode if heated.  
P403: Store in a well ventilated place.

### Nitrogen

H280: Contains gas under pressure; may explode if heated.  
P403: Store in a well ventilated place.

## Equipment

Position No.	Material	Order No.	Quantity
1	Temperature meter digital, 4-2	13617-93	1
2	Joule-Thomson apparatus	04361-00	1
3	Steel cylinder, CO <sub>2</sub> , 10l, full	41761-00	1
4	Steel cylinder, nitrogen, 10l, full	41763-00	1
5	Gas-cylinder Trolley for 2 Cyl.	41790-20	1
6	Temperature probe, immersion type, Pt100	11759-01	2
7	Reducing valve for CO <sub>2</sub> / He	33481-00	1
8	Reducing valve f. nitrogen	33483-00	1
9	Wrench for steel cylinders	40322-00	1
10	Hose clip f. 12-20 diameter tube	40995-00	2

## Tasks

1. Determination of the Joule-Thomson coefficient of CO<sub>2</sub>.
2. Determination of the Joule-Thomson coefficient of N<sub>2</sub>.

## Set-up and procedure



The set-up of the experiment is shown in Fig. 1.

If necessary, screw the reducing valves onto the steel cylinders and check the tightness of the main valves. Secure the steel cylinders in their location. Attach the PVC-tubing between the reducing valve and the Joule-Thomson apparatus with hose tube clips.

On each side of the glass cylinder, introduce a temperature probe up to a few millimetres from the frit and attach with the union nut. Connect the temperature probe on the pressure side to inlet 1 and the temperature probe on the unpressurised side to inlet 2 of the temperature measurement apparatus.

### Important

The experimenting room and the experimental apparatus must be in a thermal equilibrium at the start of the measurement. The experimental apparatus should be kept out of direct sunlight and other sources of heating or cooling.

Set the temperature measurement apparatus at **temperature difference** measurement. The temperature meter should be switched on at least 30 min before performing the experiment to avoid thermal drift. Read the operating instructions for further explanations of the temperature meter. Open the valves in the following order: steel cylinder valve, operating valve, reducing valve, so that an initial pressure of 100 kPa is established. Reduce the pressure to zero in stages, in each case reading off the temperature difference one minute after the particular pressure has been established.

Perform the measurement for both gases, and determine the atmospheric pressure and ambient temperature.

## Theory and evaluation

The state for real gases is given by the van der Waals equation

$$\left(p + \frac{a}{V^2}\right) \cdot (V - b) = RT,$$

where  $p$  is the pressure,  $V$  the molar volume and  $T$  the temperature of the gas.  $R$  is the universal gas constant,  $a$  and  $b$  are the characteristic Van der Waals coefficients of the gas. The additional pressure by intermolecular forces of attraction is described by  $a$ ,  $b$  represents the volume of molecules.

In real gases the intrinsic energy  $U$  is composed of a thermocinetic and a potential component. The total change of the intrinsic energy  $U$  of a real gas therefore depends not only on the temperature and the molar heat  $C_V$  of a gas but also on the volume. The potential energy  $-a/V$  in the gas is given by the work against the intermolecular forces

$$U = C_V \cdot T - \frac{a}{V}.$$

The total differential of the intrinsic energy is given by

$$dU = \left(\frac{\partial U}{\partial T}\right)_V \cdot dT + \left(\frac{\partial U}{\partial V}\right)_T \cdot dV$$

with

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V \text{ for } \Delta V = 0$$

and

$$\left(\frac{\partial U}{\partial V}\right)_T = +\frac{a}{V^2} \text{ for } \Delta T = 0.$$

if the total differential is substituted by finite differences, one obtains

$$\Delta U = C_V \cdot \Delta T + \frac{a}{V^2} \cdot \Delta V$$

with

$$\frac{\Delta U}{\Delta T} = +C_V \text{ for } \Delta V = 0$$

and

$$\frac{\Delta U}{\Delta V} = +\frac{a}{V^2} \text{ for } \Delta T = 0.$$

The expansion of the gas at the throttle-point is adiabatic ( $\Delta Q = 0$ ). If external heat losses and friction during the flow of the gas are excluded, the total energy  $H$  of the process is constant:

$$H = U + p \cdot V = U_1 + p_1 \cdot V_1 = U_2 + p_2 \cdot V_2.$$

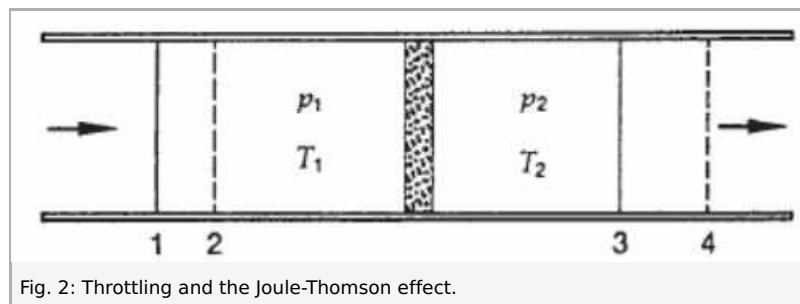


Fig. 2: Throttling and the Joule-Thomson effect.

For further calculations, pressure  $p$  can be substituted by using van der Waals equation:

$$H = C_V \cdot T - \frac{a}{V} + \left( \frac{RT}{V-b} - \frac{a}{V^2} \right) \cdot V. \quad (1)$$

After calculating the differential of (1) and substituting the total differentials by finite differences again, one obtains a relation between  $\Delta T$  and  $\Delta V$ :

$$\Delta H = C_V \cdot \Delta T + \frac{2a}{V^2} \cdot \Delta V + \frac{RV}{V-b} \cdot \Delta T - \frac{RTV}{(V-b)^2} \Delta V + \frac{RT}{V-b} \cdot \Delta V$$

$$\Delta H = \left( C_V + \frac{RV}{V-b} \right) \cdot \Delta T + \left( \frac{2a}{V^2} - \frac{RTb}{(V-b)^2} \right) \cdot \Delta V \quad (2)$$

$\Delta H = 0$  because  $H$  is constant.

In the next step,  $b$  is considered to be small compared to  $V$ .

The molar heat at constant volume  $C_V$  can be replaced with the molar heat at constant pressure  $C_p$  via the ideal gas equation and under the assumption of even gas particle masses  $m$ :

$$C_{p,m} = C_{V,m} + R. \quad (3)$$

Putting (3) into equation (2) results in

$$\frac{\Delta T}{\Delta V} = \frac{RTb-2a}{V^2 \cdot C_{p,m}}. \quad (4)$$

At the throttle point a pressure gradient  $p_1 - p_2$  and a temperature gradient  $T_1 - T_2$  are established. This effect is named the Joule-Thomson effect and is described by the coefficient

$$\mu = \frac{T_1 - T_2}{p_1 - p_2} = \frac{\Delta T}{\Delta p} \quad (5)$$

To derive a formula of this coefficient with Van der Waals forces involved, the difference  $\Delta V$  in (4) has to be expressed in terms of  $\Delta p$ . This can be approximately done via the ideal gas equation again under the assumption of even gas particle masses  $m$ :

$$V = \frac{nRT}{p}$$

After differentiating this equation to get an expression for  $dV$ , the total differentials are substituted by the finite differences, which results in the following:

$$\Delta V = \frac{RT}{p^2} \Delta p \quad (6)$$

Solving equation (4) for  $\Delta T$  gives

$$\Delta T = \frac{\Delta V}{V^2 \cdot C_{p,m}} \cdot (RTb - 2a) \quad (7)$$

After replacing  $\Delta V$  in (7) with the term in (6), one gets

$$\Delta T = \frac{-RT\Delta p}{p^2} \cdot \frac{p^2}{R^2 \cdot T^2} \cdot \frac{RTb - 2a}{C_{p,m}}$$

Putting this into (4), the equation for the Joule-Thomson coefficient results in

$$\mu = \frac{\Delta T}{\Delta p} = \frac{1}{C_{p,m}} \cdot \left( \frac{2a}{RT} - b \right) \quad (8)$$

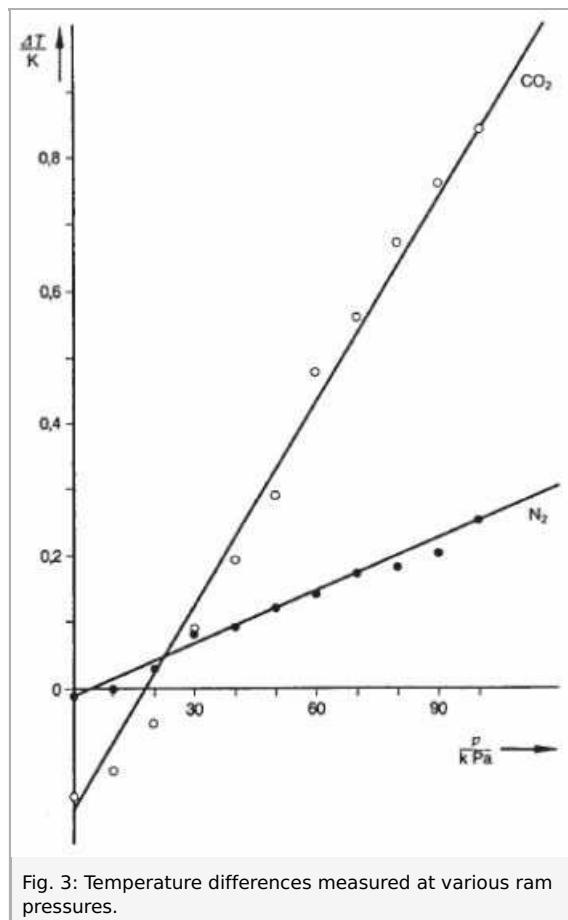


Fig. 3: Temperature differences measured at various ram pressures.

The measurement values in Fig. 3 give the straight line gradients

$$\mu_{\text{CO}_2} = (1.084 \pm 0.050) \cdot 10^{-5} \frac{\text{K}}{\text{Pa}}$$

and

$$\mu_{\text{N}_2} = (0.253 \pm 0.030) \cdot 10^{-5} \frac{\text{K}}{\text{Pa}}$$

where  $\text{N}_2$  is an approximation for air.

The two temperature probes may give different absolute values for the same temperature. But this is no problem, as only the temperature difference is important for the determination of the Joule-Thomson coefficients.

The literature values are

$$\mu_{\text{CO}_2} = 1.16 \cdot 10^{-5} \frac{\text{K}}{\text{Pa}}$$

at 20 °C and  $10^{-5}$  Pa, and

$$\mu_{\text{air}} = 0.23 \cdot 10^{-5} \frac{\text{K}}{\text{Pa}}$$

at 20 °C and  $10^{-5}$  Pa.

For  $\text{CO}_2$ , with

- $a = 3.60 \text{ Pa m}^6/\text{mol}^2$
- $b = 42.7 \text{ cm}^3/\text{mol}$
- $c_p = 366.1 \text{ J/mol K}$

equation (8) gives the coefficient

$$\mu_{\text{CO}_2} = 0.795 \cdot 10^{-5} \frac{\text{K}}{\text{Pa}} .$$

For air, with

- $a = 40 \text{ Pa m}^6/\text{mol}^2$
- $b = 39.1 \text{ cm}^3/\text{mol}$
- $c_p = 9 \text{ J/mol K}$

equation (8) gives the coefficient

$$\mu_{\text{air}} = 0.387 \cdot 10^{-5} \frac{\text{K}}{\text{Pa}} .$$

## Remarks

The formula for the Joule-Thomson coefficient indicates the condition for a cooling process

$$T_i = \frac{2a}{R \cdot b}$$

where  $T_i$  is the inversion temperature.

If  $\Delta p < 0$  the temperature  $T$  has to be lower than  $T_i$  to cool the gas with the process:

$\Delta p < 0$  and  $T < T_i$  then  $\Delta T < 0$ .

For air ( $\text{N}_2$ ) or  $\text{CO}_2$  cooling is observed at room temperature.  $\text{H}_2$  or He have a positive coefficient at room temperature, for  $\text{H}_2$  this can be hazardous because self ignition is possible.

