STUDY OF THE JOULE-THOMSON EFFECT

1.THE JOULE THOMSON EFFECT

We know from the theory of ideal gases that their internal energy is equal to the kinetic energy of molecular motion. Gay -Lussac's experiment showed that the internal energy of an ideal gas does not depend on either pressure or volume, i.e. it is not a function of the intermolecular distances, but is only a function of temperature. More detailed measurements carried out in 1883 by Joule and Thomson showed that real gases expand and change their temperature by a small amount. This effect is the subject of this exercise. At temperatures close to 0°C, most gases, including oxygen, air and nitrogen, cool down, while hydrogen, helium and neon warm up slightly. However, if expansion takes place at high temperatures, the temperature changes are smaller. We know that at high temperatures, the properties of real gases differ little from those of ideal gases. Therefore, the internal energy is a function of temperature only for ideal gases. The irreversible process of gas expansion through a porous wall that prevents pressure equalization, first realised by Joule and Thomson, has found widespread use in gas liquefaction. A schematic diagram of the experiment is shown in Figure 5.1.

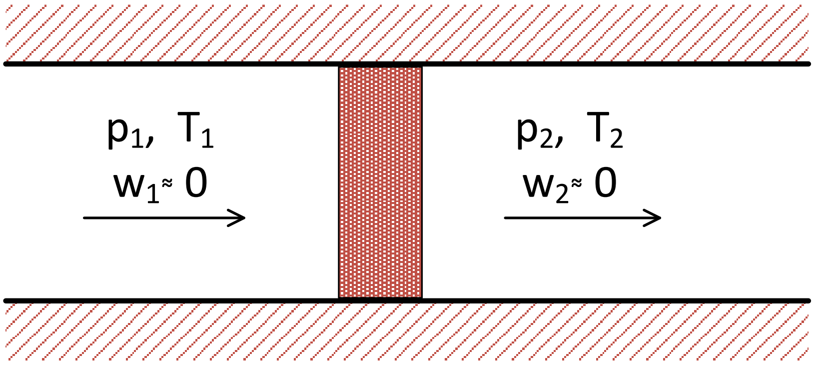

Fig.1 Joule-Thomson experiment

Throttling is the expansion of a gas in a steady state flow system without external technical work, without heat exchange with the surroundings and without any change in the kinetic energy of the medium in the inlet and outlet sections of the system. Throttling occurs wherever there is a constriction in the line in the form of a valve, a diaphragm of smaller cross-section than the line, or a porous baffle. During throttling, the external technical work corresponding to a given pressure drop is dissipated. Throttling is therefore typically an irreversible phenomenon. Figure 5.1 shows a channel through which gas flows, with a choke in the path of the gas flow. To the left of the choke the state of the gas is defined by the parameters p_1 , T_1; and w_1 , and to the right of the choke by the parameters p_2 , T_2 and w_2 , with the inflow and outflow rates w_1 and w_2 being close to zero. The channel is surrounded by an adiabatic sheath ($q_{z1,2}$ = 0).

Starting from the first law of thermodynamics for flow systems

$$q_{z1,2} = i_2 - i_1 + l_{tz1,2} \tag{1}$$

it is easy to see that in the absence of heat exchange with the surroundings and without technical work is performed, the specific enthalpy gain is zero, and therefore

$$i_2 = i_1 \tag{2}$$

that is, the specific enthalpy of the medium after throttling is equal to the specific enthalpy of the medium before throttling.

During the throttling of ideal gases, the temperature of the gas does not change because the the specific enthalpy of ideal gases is an exclusive function of temperature. The specific enthalpy of real gases is a function of temperature and pressure. The temperature change during the throttling of real gases is called the Joule-Thomson phenomenon.

If one expresses the specific enthalpy of real gases as a function of temperature and pressure, its integral differential will be of the form

$$di = \left(\frac{\partial i}{\partial T}\right)_p dT + \left(\frac{\partial i}{\partial p}\right)_T dp \tag{3}$$

after taking into account the relationship

$$\left(\frac{\partial i}{\partial T}\right)_p = c_p \tag{4}$$

and

$$\left(\frac{\partial i}{\partial p}\right)_T = -\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right] \tag{5}$$

the expression for the complete differential of the specific enthalpy becomes

$$di = c_p dT - \left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right] dp \tag{6}$$

In the throttling process, the specific enthalpies of the medium before and after throttling are the same, so that when the complete differential of specific enthalpy is set to zero, the following result is obtained

$$di = c_p dT - \left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right] dp = 0 \tag{7}$$

and the differential effect of the Joule-Thomson phenomenon is determined

$$\mu = \left(\frac{\partial T}{\partial p}\right)_i = \frac{1}{c_p}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right] = -\frac{1}{c_p}\left(\frac{\partial v}{\partial p}\right)_T\left[T\left(\frac{\partial p}{\partial T}\right)_v + v\left(\frac{\partial p}{\partial v}\right)_T\right] \tag{8}$$

It is easy to check that for the equation of state of an ideal gas

$$pv = RT \tag{9}$$

the differential effect of the Joule-Thomson phenomenon is equal to zero

$$\mu = 0 \tag{10}$$

whereas for the equations of state:

van der Waals

$$(p + \frac{a}{v^2})\,(v - b) = RT \tag{11}$$

and Berthelot

$$(p + \frac{a}{v^2})\,(v - b) = RT \tag{12}$$

This effect is equal to zero only for a specific set of points forming the inversion curve (Figure 2).

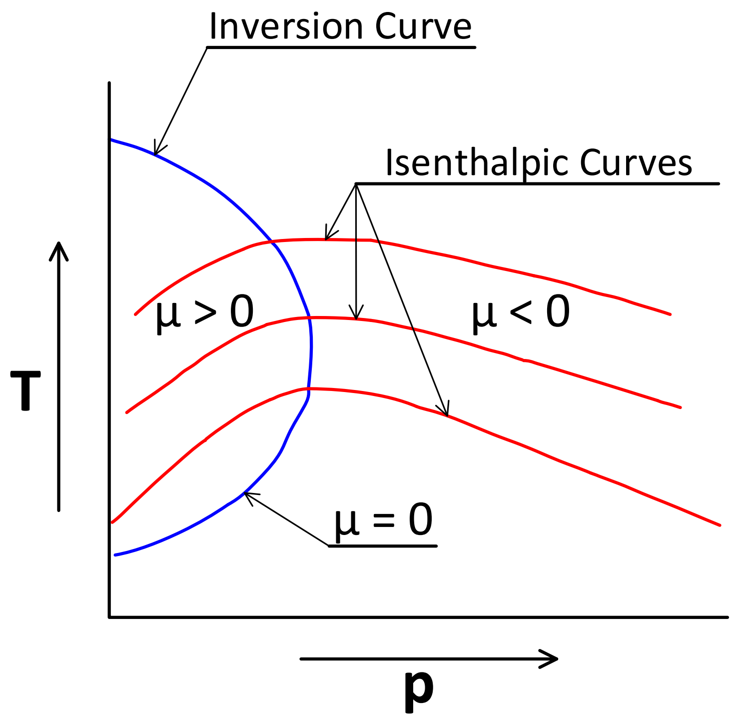

Fig.2 Example of the inversion curve for most gases

In states on the inversion curve with adiabatic throttling, the gas behaves like a ideal gas. Starting the expansion from a state located outside the inversion curve ($\mu<0$) leads to an increase of the gas temperature. The start of expansion from a state inside the inversion curve ($\mu > 0$) leads to a decrease of the temperature and can lead to liquefaction of the real gas.

The inversion temperature of most gases is higher than the ambient temperature. Nitrogen and oxygen, the two most common gases in air, have inversion temperatures (when expanded at one atmosphere of pressure) of 621K (348°C) and 764K (491°C), respectively. For a given pressure, there are usually two temperatures at which the μ coefficient changes sign.

During experimental tests, there are not elementary but finite changes in pressure and temperature. Directly from the experiments, the integral effect of the Joule-Thomson phenomenon

$$\left(\frac{\partial T}{\partial p}\right)_i = \frac{1}{\Delta \mathrm{T}} \int_p^{p+\Delta \mathrm{p}} \mu dp \tag{13}$$

In general, expansion is carried out continuously to the same ambient pressure

$$p_0 = p + \Delta p \tag{14}$$

On the basis of the data obtained in the study of the Joule-Thomson phenomenon, it is possible to determine many properties of real gases, in particular the specific heat and the form of the thermal equation of state

$$f\ (p, v, T) = 0 \tag{15}$$

2. DESCRIPTION OF THE MEASURING STAND

The measurement system, the view of which is shown in Figure 3, consists of:

- Joule-Thomson apparatus,
- two NiCr - NiAl sheathed thermocouples with a sheath diameter of 0.5 mm,

- thermos with a mixture of water and ice,
- thermocouple switch,
- millivoltmeter,
- cylinder with the tested gas equipped with reducer.

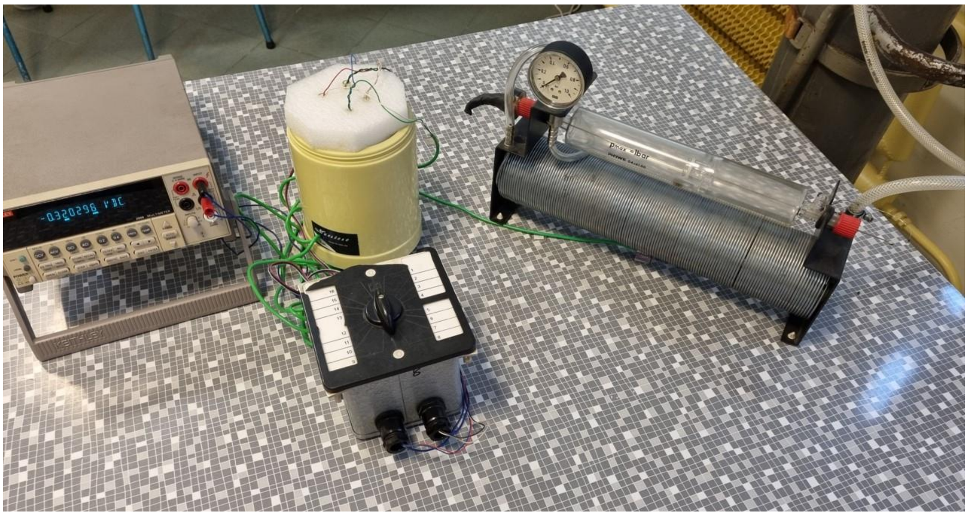

Fig.3 Laboratory stand for testing the Joule-Thomson effect

The Joule-Thomson apparatus shown in Figure 4 contains:

- an upper glass tube (1) 250 mm long and 46 mm in diameter, In the centre of the tube is a filter (2) of fused enamel which serves as a choke,

- a lower tube (3), 90 mm in diameter, consisting of 132 coils of copper and nickel-plated capillary tube,

- a pressure gauge (4) with a measuring range from 0 bar to 1 bar.

- thermocouples (5).

The glass tube (1) is coated with transparent plastic to reduce the heat loss from its surface. At a distance of 2 mm to 5 mm from the surface of the choke - on either side - are jacketed thermocouples that measure the temperature difference on either side of the choke. Gauge (4) measures the differential pressure p on both sides of the choke.

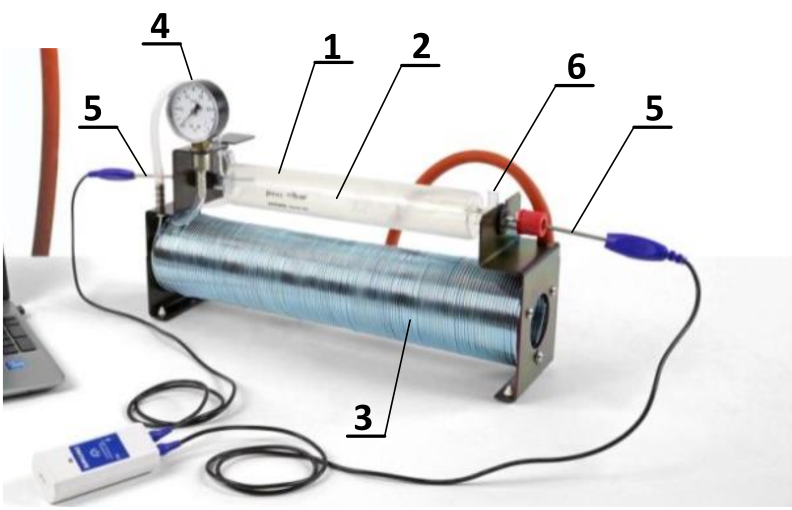

Fig.4 Joule-Thomson Apparatus

The maximum allowable overpressure p indicated by the manometer must not exceed p = 1 bar = 0.1 MPa. The pressure from the cylinder at the entrance to capillary tube should be a few bar. Care should also be taken to ensure that the temperature in the room where the tests are being carried out is constant.

3. DESCRIPTION OF THE EXPERIMENT

We investigate the Joule-Thomson effect for carbon dioxide CO_2 and nitrogen N_2.

<u>Procedure</u>

1. First connect a cylinder of CO_2 with a pressure hose to the Joule-Thomson apparatus (check Figure 4) . Check that the hose clamps are correctly attached. Carefully unscrew the regulator valve on the cylinder while observing the pressure gauge of the apparatus (4) so that the permissible overpressure of p = 1 bar is not exceeded. Make sure that the outlet opening of the glass tube (6) of the apparatus is open at all times, otherwise the tube may burst or the apparatus may be damaged.

2. Two NiCr - NiAl sheathed thermocouples with a sheath diameter of 0.5 mm are used to measure the temperature difference ΔT on both sides of the choke. Care should be taken to ensure that the sheathed thermocouples are positioned centrally to the axis of the glass tube. The accuracy of the measurement of the temperature difference ΔT should not be worse than 0.01 K.

3. When measuring pressure and temperature, record the readings of the pressure gauge p and the temperature difference ΔT. Measurements are taken for 10 values of overpressure p from 0.1 bar to 1 bar in 0.1 bar increments.

4. draw graphs ΔT = ΔT(p) for both gases tested. Compare the test results with the ΔT = ΔT(p) calibration curves shown in Figure 5 and Table 1.

Table 1

p [kPa]	0	10	20	30	40	50	60	70	80	90	100
CO_2	-0,16	-0,13	-0.05	00,09	0,19	0,28	0,48	0,56	0,67	0,75	0,83
N_2	-0,02	0	0,03	0,08	0,09	0,12	0,14	0,17	0,18	0,2	0,25

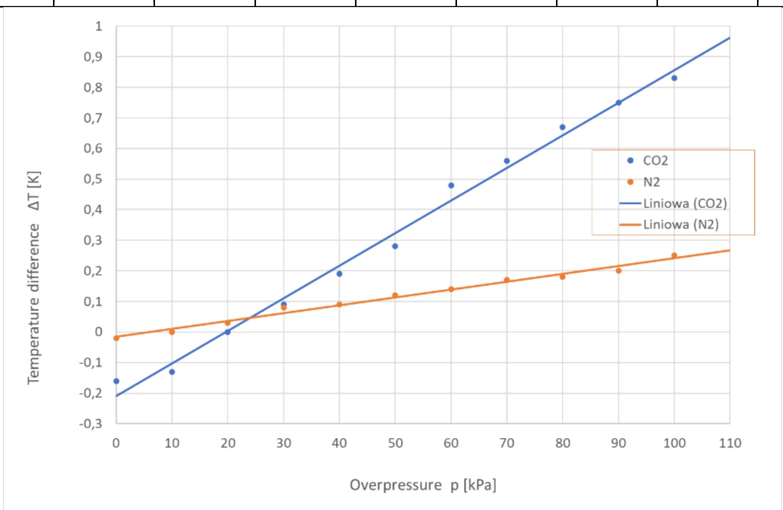

Fig.5 Dependence of temperature difference ΔT on gas overpressure p

If there is a second nitrogen cylinder at the station, we repeat the entire measurement procedure (points 1 to 4) for the second gas. We connect the second cylinder containing nitrogen to Joule-Thomson Apparatus and perform measurements. The results obtained for both gases can be presented in a common drawing (see Figure 5).

REPORT

The report should include:

a) diagrams of $\Delta T = \Delta T(p)$,

b) conclusions and evaluation of the results obtained,

c) discussion of errors.

Review questions

- What is throttling ?
- How is the enthalpy of real gases calculated ?
- What is the Joule-Thomson effect ?
- How are the rational and integral effects of the Joule-Thomson effect defined ?
- Draw and discuss the inversion curve
- How is the temperature measured in the device on which the exercise is conducted?