Joule-Thomson effect

LEP 3.2.06

Related topics

Real gas; intrinsic energy; Gay-Lussac theory; throttling; Van der Waals equation; Van der Waals force; inverse Joule-Thomson effect; inversion temperature.

Principle and task

A stream of gas is fed to a throttling point, where the gas (CO_2 or 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.

Equipment

Joule-Thomson apparatus	04361.00	1
Temperature meter digital, 4-2	13617.93	1
Temperature probe, immers.type	11759.01	2
Rubber tubing, vacuum, i.d. 8 mm	39288.00	2
Hose clip f. 12-20 diameter tube	40995.00	2
Reducing valve for CO_2 / He	33481.00	1
Reducing valve f. nitrogen	33483.00	1
Wrench for steel cylinders	40322.00	1
Steel cylinder rack, mobile	54042.00	1
Steel cylinder, CO_2, 10 l, full	41761.00	1
Steel cylinder, nitrogen, 10 l, full	41763.00	1

Problems

1. Determination of the Joule-Thomson coefficient of CO_2.
2. Determination of the Joule-Thomson coefficient of N_2.

Set-up and procedure

The set-up of the experiment is as 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 vacuum 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.

Fig. 1: Experimental set-up: Joule-Thomson effect.

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. Temperature meter should be switched on at least 30 min before performing the experiment to avoid thermal drift. Read 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

In real gases, the intrinsic energy U is composed of a thermokinetic content and a potential energy content: the potential of the intermolecular forces of attraction. This is negative and tends towards zero as the molecular distance increases. In real gases, the intrinsic energy is therefore a function of the volume, and:

$$\frac{\Delta U}{\Delta V} > 0.$$

During adiabatic expansion ($\Delta Q = 0$), during which also no external work is done, the overall intrinsic energy remains unchanged, with the result that the potential energy increases at the expense of the thermokinetic content and the gas cools.

At the throttle point, the effect named after Joule-Thomson is a quasi-stationary process.

A stationary pressure gradient $p_2 - p_1$ is established at the throttle point. If external heat losses and friction during the flow of the gas are excluded, then for the total energy H, which consists of the intrinsic energy U and displacement work pV:

$$H_1 = U_1 + p_1V_1 = U_2 + p_2\,V_2 = H_2.$$

In this equation, p_1V_1 or $p_2\,V_2$ is the work performed by an imaginary piston during the flow of a small amount of gas by a change in position from position 1 to 2 or position 3 to 4 (see Figure 2). In real gases, the displacement work p_1V_1 does not equal the displacement work p_2V_2; in this case:

$$p_1V_1 < p_2\,V_2.$$

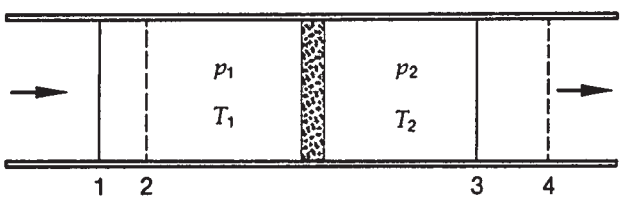
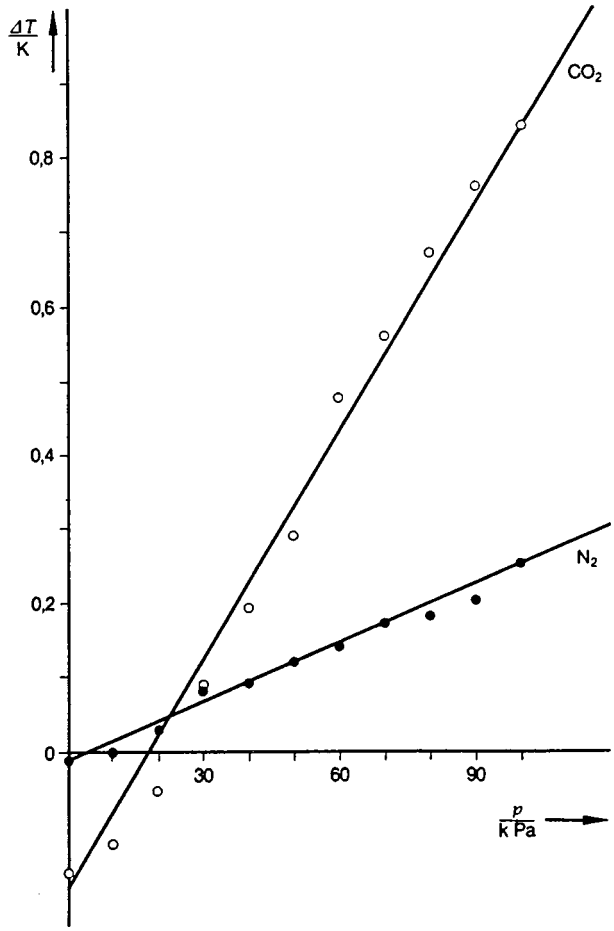


Fig. 2: Throttling and the Joule-Thomson effect.

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



This means that, from the molecular interaction potential, displacement work is permanently done and removed:

$$U_1 > U_2 \quad \text{or}$$
$$T_1 > T_2.$$

The Joule-Thomson effect is described quantitatively by the coefficients

$$\mu = \frac{T_1 - T_2}{p_1 - p_2}$$

For a change in the volume of a Van der Waals gas, the change in intrinsic energy is

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

and the Joule-Thomson coefficient is thus

$$\mu_{VdW} = \left(\frac{2a}{RT} - b\right) \cdot \frac{1}{c_p}.$$

In this equation, c_p is the specific heat under constant pressure, and a and b are the Van der Waals coefficients.

If the expansion coefficients

$$\alpha = \frac{1}{V_o} \cdot \frac{\Delta V}{\Delta T} \quad (p = \text{const.})$$

are inserted, then

$$\mu_{VdW} = \frac{VT}{c_p}\left(\alpha - \frac{1}{T}\right).$$

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

$$\mu_{CO_2} = (1\ .084 \pm 0.050) \cdot 10^{-5}\ \frac{K}{Pa}$$

and

$$\mu_{N_2} = (0.253 \pm 0.030) \cdot 10^{-5}\ \frac{K}{Pa}$$

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

The literature values are

$$\mu_{CO_2} = 1.16 \cdot 10^{-5}\ \frac{K}{Pa}$$

at 20°C and 10^{-5} Pa,

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

at 20°C and 10^5 Pa.

For $C0_2$, with

a = 3.60 Pa m^6/mol^2
b = 42.7 cm^3/mol
c_p = 366.1 J/mol K

the Van der Waals equation gives the coefficient

$$\mu_{VdW,\ CO_2} = 0.795 \cdot 10^{-5}\ \frac{K}{Pa}$$

For air, with

a = 1.40 Pa m^6/mol^2
b = 39.1 cm^3/mol
c_p = 288.9 J/mol K

the Van der Waals equation gives the coefficient

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