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Joule-Thompson throttling - starting with Maxwell's equations

$$ds = \left(\frac{\partial s}{\partial P} \right)_T dP + \left(\frac{\partial s}{\partial T} \right)_P dT \quad (1)$$

$$dh = T ds + v dP \quad (\text{substitute } ds \text{ into this equation}) \quad (2)$$

$$dh = T \left[\left(\frac{\partial s}{\partial P} \right)_T dP + \left(\frac{\partial s}{\partial T} \right)_P dT \right] + v dP \quad (3)$$

$$dh = T \left(\frac{\partial s}{\partial T} \right)_P dT + \left[T \left(\frac{\partial s}{\partial P} \right)_T + v \right] dP \quad (4)$$

Maxwell Relation

$$\left(\frac{\partial s}{\partial P} \right)_T = - \left(\frac{\partial v}{\partial T} \right)_P \quad \text{substitute this relationship into equation (4)}$$

$$dh = T \left(\frac{\partial s}{\partial T} \right)_P dT + \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right] dP$$

$$c_p = T \left(\frac{\partial s}{\partial T} \right)_P \quad \beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P \quad (\text{thermal expansion coefficient for liquids})$$

$$dT = \frac{1}{c_p} dh + \frac{1}{c_p} \left[T \left(\frac{\partial v}{\partial T} \right)_P - v \right] dP$$

$$T = T(h, P)$$

$$dT = \left(\frac{\partial T}{\partial h} \right)_P dh + \left(\frac{\partial T}{\partial P} \right)_h dP$$

$$\frac{1}{c_p} = \left(\frac{\partial T}{\partial h} \right)_P, \quad \frac{1}{c_p} \left[T \left(\frac{\partial v}{\partial T} \right)_P - v \right] = \left(\frac{\partial T}{\partial P} \right)_h = \mu_J$$

$$\alpha = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P = \frac{c_p / c_v \cdot c_p}{K_s \cdot v}$$

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 :

$$H_1 = U_1 + p_1 V_1 = U_2 + p_2 V_2 = H_2.$$

In this equation, $p_1 V_1$ 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 $p_1 V_1$ does not equal the displacement work $p_2 V_2$; in this case:

$$p_1 V_1 < p_2 V_2.$$

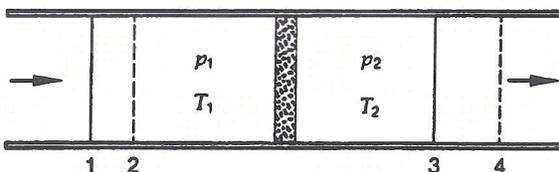
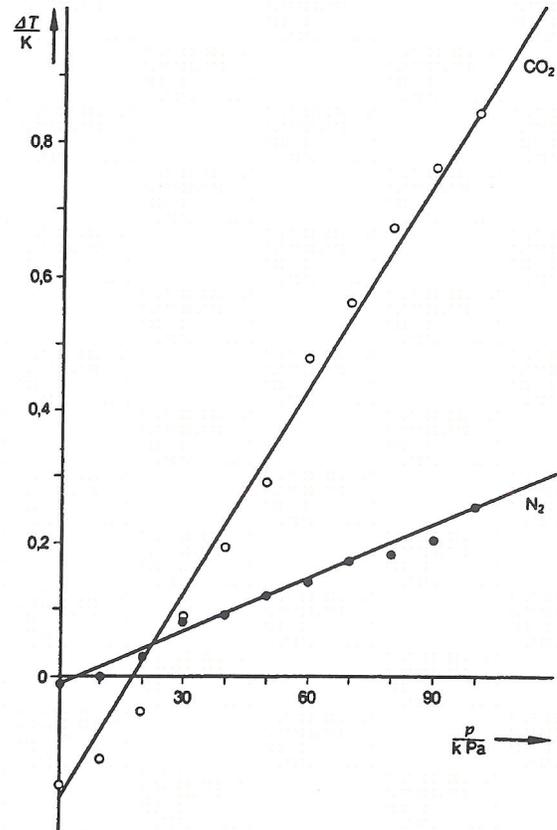


Fig. 2: Throttling and the Joule-Thomson effect.

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

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

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

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Using the solution from page 2

$$\frac{dT}{dP} = \frac{1}{mC_p} \left(\frac{2a}{RT} - b \right) \rightarrow \frac{dT}{dP} = \frac{1}{T} \cdot \frac{2a}{mC_p R} - \frac{b}{mC_p}$$

where $C_1 = \frac{2a}{mC_p R}$ and $C_2 = \frac{b}{mC_p}$ so $\frac{dT}{dP} = \frac{C_1}{T} - C_2 \rightarrow$

$$\frac{dT}{dP} + C_2 = C_1 T^{-1} \rightarrow \frac{T'}{T^{-1}} + \frac{C_2}{T^{-1}} = C_1 \rightarrow T' T + T C_2 = C_1 \rightarrow$$

$$w = T \quad w' = \frac{(1-1)}{T^{-1}} T' \rightarrow \frac{w'}{2} + w C_2 = C_1 \rightarrow M(P) \frac{w'}{2} + M(P) w C_2 = M(P) C_1$$

$$\frac{d(M(P)w)}{dP} = M(P) \frac{dw}{dP} + w \frac{dM(P)}{dP} \quad \text{where} \quad \frac{dM(P)}{dP} = 2C_2 M(P)$$

$$M(P) = \exp \int 2C_2 dP \rightarrow M(P) = \exp(2C_2 P)$$

$$w' \cdot e^{2C_2 P} + 2C_2 e^{2C_2 P} w = e^{2C_2 P} \cdot C_1 \rightarrow \frac{d}{dP} (e^{2C_2 P} \cdot w) = C_1 e^{2C_2 P} \rightarrow$$

$$\int d(e^{2C_2 P} w) = \int C_1 e^{2C_2 P} dP \rightarrow e^{2C_2 P} w = \frac{1}{2C_2} C_1 e^{2C_2 P} + C$$

Resubstitute $w = T$

$$T = \frac{C_1}{2C_2} + \frac{C}{\exp(2C_2 P)} \quad \text{where} \quad C = \left(T_1 - \frac{C_1}{2C_2} \right) \exp(2C_2 P_1)$$

which is different from the standard form of the bernoulli differential equation (so I need a more in depth explanation of the details of the solution methodology to first order non separable differential equations)

$$\text{standard Form: } T = \left(\frac{C_1}{C_2} + \frac{C}{2C_2 P_2} \right)^{1/2}$$

Both solutions gave me answers I do not believe to be correct.