

## THE THERMODYNAMIC STATES OF A FLUID IN A JOULE-THOMSON PROCESS INVOLVING PHASE CHANGES AT INTERFACES WITH LARGE CURVATURE

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### ABSTRACT

In the classical experiment of Joule and Thomson, a gas passes through a porous plug. The pressure difference between the upstream and the downstream side of the porous plug causes a temperature difference. Here, the flow process is described for the case that the fluid may condense, and the pressure loss is caused by a thin capillary. The process is calculated assuming local thermodynamic equilibrium and one-dimensional temperature and pressure distributions, respectively.

A vapor far from saturation does not condense, and the temperature and pressure distribution for the common Joule-Thomson process is recovered. A vapor close enough to saturation may condense partially or completely, and a liquid or a two-phase mixture flows through a part of the capillary. The thermodynamic path of the fluid is presented in temperature-entropy and pressure-temperature diagrams.

### INTRODUCTION

In an adiabatic throttling or Joule-Thomson process, the contribution of the kinetic energy to the energy balance is negligible. The enthalpies of the fluid are the same upstream and downstream of the region where a pressure loss occurs. For gases, the Joule-Thomson coefficient, i.e., the change of temperature with respect to pressure at constant enthalpy,  $\mu_{JT} = (\partial T / \partial p)_h$ , may be positive or negative. Vapors, i.e., fluids in a gaseous state below the critical temperature, always have a positive Joule-Thomson coefficient. Hence, a vapor undergoing a Joule-Thomson process always has a downstream temperature which is smaller than the upstream temperature.

The temperature difference causes the transport of heat, usually by conduction, in downstream direction. However, a vapor at or close to saturation upstream of the tube may not be able to release a sufficient amount of heat by cooling down. Instead, the vapor must condense, either partially or completely. The heat released by condensation is consumed further downstream by evaporation of the partially or fully condensed fluid.

The temperature field of the flow through a long, thin capillary may be approximated by a one-dimensional temperature distribution, and a one-dimensional description of the flow becomes possible. A one-dimensional description is also applicable to the flow through a porous medium, if the porous medium is modeled as a bundle of equivalent capillaries. Hence, results obtained for the flow through a porous medium may also be applied to the flow of a fluid through a capillary.

Schneider [1] described the one-dimensional flow of a fluid that is in an upstream state of a saturated vapor through a porous medium. Schneider did not account for effects of capillarity, such as capillary condensation or the pressure difference across curved menisci, but assumed that phase changes occur at plane interfaces. He observed that, due to the Joule-Thomson effect, a saturated vapor that flows through a porous medium must condense.

A critical permeability was given for the porous medium. With respect to the flow through a capillary, this is equivalent to a critical radius. For a radius of the capillary below the critical value, the vapor condenses completely. For a radius of the capillary larger than the critical radius, the fluid condenses partially, and a two-phase mixture flows through a part of the capillary. The value of the critical radius depends on the properties of the fluid and on the thermal conductivity in the flow region. For common substances, the critical radius is of the order of 10 nm. The critical radius may be much larger for very good heat conductors.

The, usually, very small value of the critical radius may be the reason that the Joule-Thomson effect did not receive much attention under conditions where phase changes occur. Confer, for instance, the remark of Tien [2], who stated, with respect to the flow of vapors through porous media, that 'Another basic thermodynamic phenomenon that may play an interesting role in heat-pipe performance under certain conditions has never been mentioned or analyzed in the literature. This is the Joule-Thomson effect of real gas flow.'

Capillary effects, which dominate the flow, were investigated more thoroughly. Rhim and Hwang [3] investigated the flow of vapors near saturation through porous Vycor glass. They did not account for the Joule-Thomson effect, but for capillary condensation, adsorption and the large capillary pressure across curved interfaces between the liquid and the vapor phase. They found that the mass flow of a fluid under conditions where condensation occurs is greatly enhanced with respect to the mass flow of a vapor that does not condense. They also observed that, because a large amount of heat is evolved due to condensation and evaporation within the porous medium, the fluid can not stay isothermal. However, later, in their seminal work Lee and Hwang [4] described the flow of a vapor through a porous medium as an isothermal process.

Based on the approach of Schneider [1], the Joule-Thomson process of a vapor was analyzed, including also the effects of

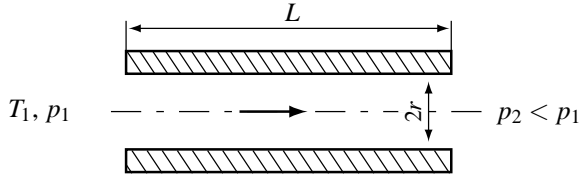


Figure 1. Sketch of the flow.

capillarity [5; 6]. A modified expression for the critical permeability [6] or for the critical radius of a capillary [7] was given. It was found that the mass flow rates calculated by applying an isothermal description were an order of magnitude larger than the mass flow rates calculated from an adiabatic, non-isothermal description [8]. Experimentally measured mass flow rates were still smaller than those obtained from the adiabatic description [8].

These results suggest that capillary forces may dominate the flow. However, in turn, the capillary forces are notably influenced by the small variation due to the Joule-Thomson effect. Consider a situation where a liquid plug is located inside a capillary. At both ends of the liquid plug curved interfaces are formed. The pressure differences across the curved interfaces are large, and large forces are exerted on the liquid on both ends of the liquid plug. However, because these forces act in opposite directions, they sum up to zero. If the thermodynamic equilibrium at one end of the plug changes, e.g., by heating up one end, a large force equal to the difference of the capillary forces remains and acts on the liquid plug. This perception is somehow supported by the observation that, over a wide range of contact angles, the mass flow rate is independent of the contact angle [7].

The states of a fluid that flows through a small capillary, with and without phase changes, are presented further below.

## THEORETICAL DESCRIPTION

The flow configuration is sketched in Fig. 1. A vapor is in a state  $p_1, T_1$  upstream of the end of a tube. The pressure  $p_2$  downstream of the tube is smaller than the pressure at the upstream side,  $p_2 < p_1$ . Due to the Joule-Thomson effect, the temperature  $T_2$  at the downstream side is also smaller than the temperature  $T_1$  upstream of the tube. The length of the capillary is  $L$ , which is large compared to the inner diameter  $2r$ . The walls of the tube contribute to the heat transfer in longitudinal direction. However, there is no heat transfer in radial direction, which can be achieved either by isolating the tube adiabatically against the surrounding or by placing a large number of the same tubes in parallel.

### Governing equations

The flow is governed by the balances of mass, momentum and energy,

$$\dot{m} = \text{constant}, \quad (1)$$

$$\dot{m} = -\frac{r^4 \pi}{8\nu} \frac{dp}{dz}, \quad (2)$$

$$\dot{m}h + r^2 \pi \dot{q} / \varepsilon = \text{constant}. \quad (3)$$

Here,  $\dot{m}$  denotes the mass flow rate,  $\nu$  refers to the viscosity of the fluid,  $p$  is the pressure,  $z$  the spatial coordinate,  $h$  refers to

the specific enthalpy of the fluid and  $\dot{q}$  denotes the heat flux. The ratio of the inner to the outer cross-sectional area of the tube is given by  $\varepsilon$ . The Reynolds-number is small, hence the law of Hagen-Poiseuille is applied, Eq. (2). The heat flux is given by Fourier's law of heat conduction,

$$\dot{q} = -k_{mf} \frac{dT}{dz}, \quad (4)$$

where  $T$  is the absolute temperature and  $k_{mf}$  is the effective thermal conductivity of the fluid-filled tube,

$$k_{mf} = (1 - \varepsilon)k_m + \varepsilon k_f. \quad (5)$$

Here,  $k_m$  and  $k_f$  refer to the thermal conductivities of the solid tube material and the fluid, respectively.

Two-phase flow within the membrane is modeled as homogeneous flow,

$$x = \frac{\alpha v_{2ph}}{v_g}, \quad \dot{x} = x, \quad (6)$$

$$v_{2ph} = \left( \frac{1 - \alpha}{v_l} + \frac{\alpha}{v_g} \right)^{-1}. \quad (7)$$

Here,  $x$  and  $\dot{x}$  are the mass fraction and the mass flow fraction of the vapor, respectively,  $\alpha$  is the vapor volume fraction and  $v_l, v_g$  and  $v_{2ph}$  refer to the specific volumes of the liquid phase, the gaseous phase and the two-phase mixture of the fluid, respectively. The effective kinematic viscosity and the effective thermal conductivity of the two-phase mixture,  $\nu_{2ph}$  and  $k_{2ph}$ , are given by

$$\nu_{2ph} = (\alpha \mu_g + (1 - \alpha) \mu_l) \nu_{2ph}, \quad (8)$$

$$k_{2ph} = \alpha k_g + (1 - \alpha) k_l. \quad (9)$$

Here,  $\mu_g$  and  $\mu_l$  refer to the dynamic viscosities and  $k_g$  and  $k_l$  to the thermal conductivities of the gaseous and the liquid phase, respectively.

At interfaces between the liquid and the gaseous phase of the fluid within the tube, the pressure difference is given by the Young-Laplace equation,

$$p_{cap} = \frac{2\sigma \cos \theta}{r}, \quad (10)$$

where  $\sigma$  refers to the surface tension and  $\theta$  is the contact angle. The pressure of the vapor phase of the fluid at a front of phase change,  $p_K$ , is given by Kelvin's equation,

$$\ln \left( \frac{p_K}{p_{sat}} \right) = -\frac{2\sigma \cos \theta}{r} \frac{v_l}{RT}. \quad (11)$$

Here,  $p_{sat}$  is the saturation pressure at a plane interface and  $R$  refers to the specific gas constant. Within the tube, a phase change occurs if the pressure of a vapor rises to  $p = p_K(T)$ , or if the pressure in the liquid falls below  $p = p_K(T) - 2\sigma(T) \cos \theta / r$ . With respect to the condition at a plane interface, the pressures at a curved interface are different in the

gaseous and the liquid phase. On both sides of the interface work is done on the fluids to bring them from their states at a plane interface to their respective states at a curved interface. These works must be added to the enthalpy of vaporization at a plane interface. Therefore, the specific enthalpy of vaporization at fronts of phase change within the porous membrane,  $h_{\text{vap,K}}$ , is given by

$$\Delta h_{\text{vap,K}} = \Delta h_{\text{vap}} + (p_{\text{K}} - p_{\text{sat}}) \times \left( \left( \frac{\partial h_{\text{g}}}{\partial p} \right)_T - \left( \frac{\partial h_{\text{l}}}{\partial p} \right)_T \right) + \left( \frac{\partial h_{\text{l}}}{\partial p} \right)_T \frac{2\sigma \cos \theta}{r}. \quad (12)$$

Here,  $\Delta h_{\text{vap}}$  is the specific enthalpy of vaporization at a plane interface and  $h_{\text{l}}$  and  $h_{\text{g}}$  denote the specific enthalpies of the liquid and the gaseous phase, respectively.

For the flow of a single phase of a fluid, Eqs. (1) to (3) and (4) yield, together with, e.g., initial conditions for  $\dot{m}$ ,  $\dot{m}h + \dot{q}$ ,  $T$  and  $p$ , a well-posed initial value problem for the variables  $T$  and  $p$  in dependence of  $z$ . For two-phase flow, pressure and temperature are not independent of each other. Instead, two independent variables are, e.g.,  $T$  and  $\alpha$ , and the dependence between  $T$  and  $p$  must be formulated. To determine the gradient  $(dp/dT)_{2\text{ph}}$  in a two-phase region in dependence of  $T$  and  $\alpha$ , the marginal cases of  $\alpha \rightarrow 1$  and  $\alpha \rightarrow 0$  are considered. The first case is equivalent to the state of a vapor that is in equilibrium with its liquid phase at a curved meniscus, hence,  $(dp/dT)_{\alpha \rightarrow 1} = dp_{\text{K}}/dT$ . The second case is equivalent to the state of the liquid at the other side of the meniscus,  $(dp/dT)_{\alpha \rightarrow 0} = d(p_{\text{K}} - 2\sigma \cos \theta / r) / dT$ . For homogeneous two-phase flow the pressure gradient is put as the volume-averaged mean of the pressures in the liquid and the gaseous phases, respectively,

$$\left( \frac{dp}{dT} \right)_{2\text{ph}} = \frac{dp_{\text{K}}}{dT} - (1 - \alpha) \frac{2 \cos \theta}{r} \frac{d\sigma}{dT}. \quad (13)$$

The boundary conditions complete the governing system of equations. They are

$$T = T_1, p = p_1, \dot{q} = 0 \quad \text{at } z \rightarrow -\infty, \quad (14)$$

$$p = p_2, \dot{q} = 0 \quad \text{at } z = L. \quad (15)$$

The system of governing equations is solved numerically. A shooting method is used to solve the boundary value problem. First, the downstream state of the fluid is completely determined. With  $h_2 = h_1$ , the downstream temperature  $T_2$  is calculated by integration along an isenthalpic line,

$$T_2 = T_1 + \int_{p_1}^{p_2} \left( \frac{\partial T}{\partial p} \right)_h dp. \quad (16)$$

Applying the initial conditions  $T = T_2$ ,  $p = p_2$  and  $\dot{q} = 0$  at  $z = L$ , the governing equations are integrated in negative  $z$ -direction. Integration is iteratively repeated, each time changing the value of  $\dot{m}$ , until the condition  $p(z=0) = p_1$  is fulfilled within a tolerance of  $(p_1 - p_2)/1000$ .

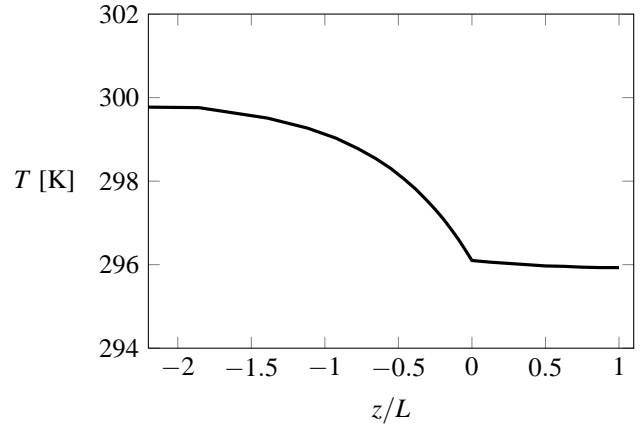


Figure 2. Temperature distribution in a Joule-Thomson process of a vapor without phase change. The tube extends from  $z/L = 0$  to  $z/L = 1$ .

## RESULTS

Results are presented for the flow of butane through a glass capillary. The thickness of the wall is half the inner radius, hence  $\varepsilon = 0.44$ . The thermal conductivity of glass is  $0.5 \text{ W/m K}$ . At a temperature of  $300 \text{ K}$ , the saturation pressure of butane is  $p_{\text{sat}}(300 \text{ K}) = 2.57 \text{ bar}$ . For a vapor that does not condense, the temperature-entropy and the pressure-temperature diagram is shown in Fig. 3. In this case, the upstream pressure is  $p_1 = 2.1 \text{ bar}$  and the downstream pressure is  $p_2 = 0.5 \text{ bar}$ . The vapor cools down isobarically in front of the tube. Within the tube, the vapor expands nearly isothermally until it reaches the downstream pressure  $p_2$ . Figure 2 shows the temperature distribution. The vapor expands nearly isothermally within the tube because the thermal conductivity of the tube material is much larger than the thermal conductivity of the vapor,  $0.5 \text{ W/m K}$  vs.  $0.016 \text{ W/m K}$ .

The path of the process in the temperature-entropy diagram in Fig. 3 shows that, even though the upstream state 1 and the downstream state 2 are both unsaturated vapors, condensation must occur if the path of the process crosses the line  $p = p_{\text{K}}$ . The line  $p = p_{\text{K}}$  is depicted as a dotted line close to the line of saturated vapor in the  $T$ - $s$  diagram. In the  $p$ - $T$  diagram, the dashed line refers to  $p = p_{\text{K}}$ .

The states of a fluid when partial condensation occurs are shown in Fig. 4. With respect to the case shown in Fig. 3, the only condition which is changed is the upstream pressure, from  $p_1 = 2.1$  to  $p_1 = 2.3 \text{ bar}$ . The two-phase mixture that flows through a part of the tube has a vapor mass fraction and also a liquid mass fraction of order unity. Hence, because the density of the liquid phase of the fluid is much larger than the density of the vapor phase, the volume fraction of the vapor is very close to one. The  $p$ - $T$  diagram shows that the pressure in the two-phase mixture within the tube is close to  $p_{\text{K}}$ , the pressure of a vapor in the tube.

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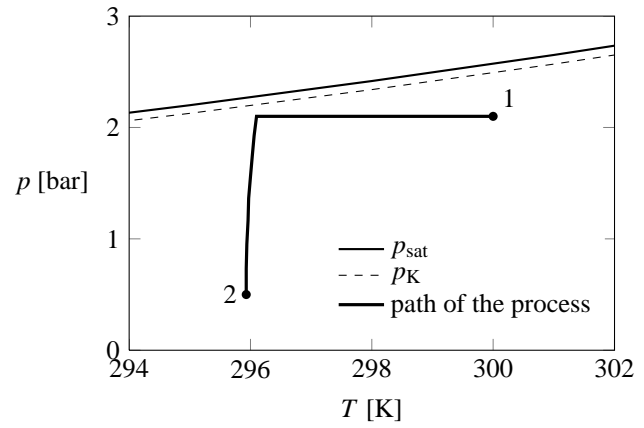
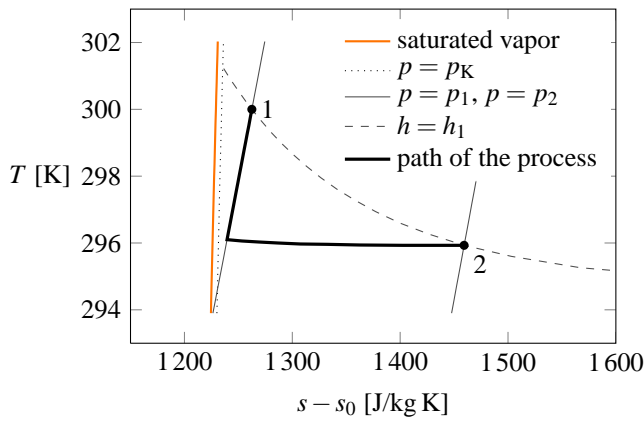


Figure 3. Joule-Thomson process of a vapor without phase change. States of the fluid in a temperature-entropy and a pressure-temperature diagram.

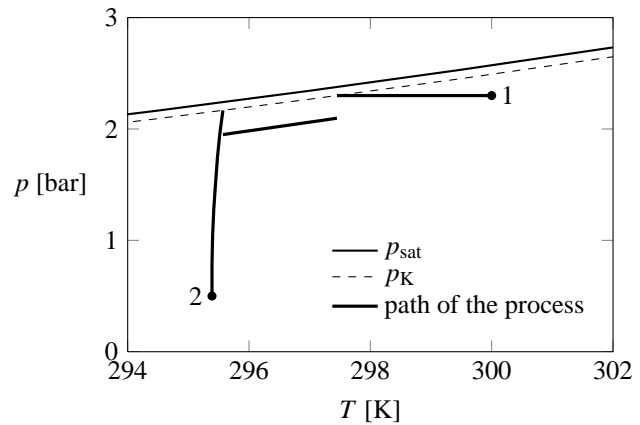
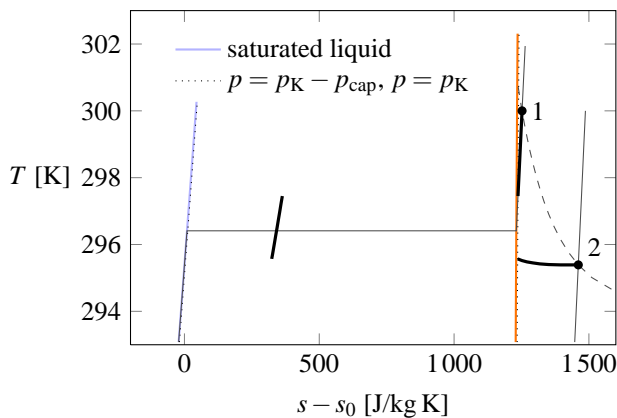


Figure 4. States of the fluid when partial condensation occurs. Temperature-entropy and pressure-temperature diagram. For remaining legend labels, see Fig. 3.

## NOMENCLATURE

$h$	Specific enthalpy [J/kg]
$k$	Thermal conductivity [W/m K]
$\dot{m}$	Mass flow rate [kg/s]
$p$	Pressure [Pa]
$\dot{q}$	Heat flux [W/m <sup>2</sup> ]
$R$	Specific gas constant [J/kg K]
$r$	Radius [m]
$T$	Absolute temperature [K]
$\nu$	Specific volume [m <sup>3</sup> /kg]
$x$	Vapor mass fraction
$\dot{x}$	Vapor mass flow fraction
$z$	Spatial coordinate [m]
$\alpha$	Greek letters to follow
$\alpha$	Vapor volume fraction [-]
$\varepsilon$	Void fraction [-]
$\theta$	Contact angle [-]
$\mu$	Dynamic viscosity [Pa s]
$\nu$	Kinematic viscosity [m <sup>2</sup> /s]
$\sigma$	Surface tension [N/m]

## Subscripts

0	Reference state
1	Upstream state
2	Downstream state
2ph	Two-phase

cap	Capillary pressure, cf. Eq. (10)
f	Fluid
g	Gaseous
l	Liquid
K	Vapor pressure at a curved interface, cf. Eq.(11)
m	Solid material
sat	Saturation pressure

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