

## On possible inversion effects in the technology of capillary-porous materials

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**Abstract:** The article discusses the possible place and role of the well-known thermodynamic Joule–Thomson effect in the technology of capillary-porous materials. The presence of the Joule–Thomson effect in these materials is substantiated by the peculiarities of the mechanism and kinetics of the diffusion physicochemical processes proceeding when they are heated. A mathematical description of the integral effects in capillary-porous materials under isothermal conditions is given.

**Key words:** Effect, material, technology, temperature, inversion

### 1. Introduction

The Joule–Thomson effect, discovered in the field of thermodynamics, is widely known today and is used in science and technology [1,2]. Later, this effect was applied in techniques as a choke effect. However, as is well known, the use of this thermodynamic effect is limited to low-temperature production and liquid dilution (Lind, Claude, etc. methods).

The results of recent physicochemical and thermophysical studies that we carried out in the field of technology of capillary-porous ceramic materials [3–5] suggest that the Joule–Thomson effect may also occur in these technological processes during the firing of ceramic materials. The assumption of the possible manifestations of the inversion effects in the technology of capillary-porous materials was first made by Professor Kulbek [3]. The fact that capillary-porous materials are widely used in the construction, chemical, energy, light, and food industries shows the role and importance of studying this thermodynamic effect in these technological processes.

The originality of this work is due to the fact that the thermodynamic side of the diffusion of physical and chemical processes remains a poorly studied problem to date. In this paper, an attempt is made, to some extent, to fill this gap.

### 2. Study of inversion effects in capillary-porous materials technology

Let us consider the kinetics and mechanism of diffusion physicochemical phenomena during the firing of capillary-porous ceramic materials.

Based on the theory of solid-phase processes (reactions) [6], they proceed through a zonal mechanism.

It was established experimentally that diffusion processes of physicochemical transformations first take place on the outer surface of the body, and then, after reaching the appropriate temperature-gas conditions,

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the localized reacting surface deepens inside the sample at a certain speed. At the same time, the formed gaseous substance is transferred through the layer of solid reaction product, in this case through the outer capillary-porous layer of the solid body into the environment, and it undergoes a sharp expansion. The speed and duration of this phenomenon are limited by the nature of the diffusion processes.

As a mathematical model for the description of diffusion processes of physicochemical transformations in ceramic samples (plate), we can take the following equation (isothermal mode) [3,4]:

$$\frac{dx}{d\tau} = \frac{D_{eff}}{x}, \quad (1)$$

where  $x$  is a coordinate,  $\tau$  is time, and  $D_{eff}$  is the effective diffusion coefficient.

Under the initial conditions  $\tau = 0, x = 0$ , Eq. (1) in integral form can be written as:

$$\frac{x^2}{2} = D_{eff} \cdot \tau. \quad (2)$$

Transforming the last equation by dividing both sides of the equation into  $d^2$  ( $d$ - for the symmetric problem, half the plate thickness, and for the asymmetric problem, thickness) we get the criterial equation:

$$\frac{x}{d} = \left( \frac{2 \cdot D_{eff} \cdot \tau}{d^2} \right)^{\frac{1}{2}}. \quad (3)$$

The expression  $\frac{D_{eff} \cdot \tau}{d^2} = F_{0,m}$  characterizes the Fourier criterion for diffusion.

The pressure difference between the gases inside the sample and the gases diffusing into the external environment in the processes under consideration is significant. Therefore, in this process, we can assume that the integral Joule–Thomson effect takes place. If we assume that the gas in the pores inside the sample is real gas and the gas that is transferred to the environment and expands is an ideal gas, then taking into account the law of enthalpy conservation during the adiabatic process, to estimate the inversion deviation, we can get the following equation [1,2]:

$$\Delta T = T_2 - T_1 = \frac{1}{c_p} \left( \frac{RbT_1}{V_{01} - b} - \frac{2a}{V_{01}} \right), \quad (4)$$

where  $T_1$  is the gas temperature inside the sample,  $T_2$  is the temperature of the gas transferred to the environment,  $R$  is the gas constant,  $c_p$  is the isobaric molar heat capacity of the gas,  $a$  and  $b$  are van der Waals constants, and  $V_{01}$  is the volume of 1 mol of gas inside the sample.

We write Eq. (4) for any gas mass ( $V_1 = \nu \cdot V_{01}$ ), and then:

$$\Delta T = T_2 - T_1 = \frac{1}{c_p} \left( \frac{\nu RbT_1}{V_1 - \nu b} - \frac{2\nu a}{V_1} \right). \quad (5)$$

Let us transform the last expression, connecting it with kinetic Eq. (2). Let us denote the initial volume of gas inside the sample by  $V_1 = \gamma \cdot V_{sam}$  ( $\gamma$  - relative degree of porosity of the sample,  $V_{sam}$  - volume of the sample) and we will assume that this volume of gas is located inside the sample where no physicochemical transformations ( $V_{d-x}$ ) have occurred. Then, based on Eq. (2), we obtain the following expression:

$$V_1 = \gamma V_{d-x} = \gamma (d - x) \cdot S = \gamma \left[ d - (2 \cdot D_{eff} \tau)^{\frac{1}{2}} \right] \cdot S, \quad (6)$$

where  $S$  is the cross-sectional area of the sample plate ( $x \perp S$ ).

Substituting this expression instead of  $V_1$  in Eq. (2.5), we get:

$$\Delta T = T_2 - T_1 = \frac{1}{c_p} \left\{ \frac{\nu R b T_1}{\gamma \left[ d - (2D_{eff}\tau)^{\frac{1}{2}} \right] S - \nu b} - \frac{2\nu a}{\gamma \left[ d - (2D_{eff}\tau)^{\frac{1}{2}} \right] S} \right\}. \quad (7)$$

The resulting expression allows us to determine the sign (direction) of the Joule–Thomson effect  $\Delta T < 0 (T_2 < T_1)$ , which takes place in the physicochemical processes that take place in capillary-porous sample plates under isothermal conditions. In addition, we can determine the amount of additional heat (spent or emitted) associated with the above inversion processes.

Traditionally, the Joule–Thomson effect is considered positive when the gas is cooled,  $\Delta T < 0 (T_2 < T_1)$ , and negative when  $\Delta T > 0 (T_2 > T_1)$ , i.e. the gas is heated. However, in terms of energy (fuel) costs in the technology of capillary-porous materials, and in particular ceramic materials, the evaluation of this effect corresponds to mathematical signs, i.e.  $\Delta T < 0$  for negative, and  $\Delta T > 0$  for positive effects.

We consider this problem for samples in the form of an unbounded cylinder ( $l > 2d$ ,  $l$  - height,  $d$  - diameter) and a ball. In [3,4,6], the following equations were obtained for describing isothermal diffusion physicochemical processes in these samples:

For a cylinder,

$$\frac{dx}{d\tau} = \frac{D_{eff}}{(r-x) \ln \frac{r}{r-x}}, \quad (8)$$

and for a ball (sphere),

$$\frac{dx}{d\tau} = \frac{D_{eff}}{x} \cdot \frac{r}{r-x}, \quad (9)$$

where  $r$  is the radius of the sample. Integrating the last expressions with regard to the initial conditions  $s = 0, x = 0$ , we obtain the following kinetic equations:

For a cylinder

$$\frac{(r-x)^2}{2} \left[ \ln(r-x) - \ln r - \frac{1}{2} \right] + \frac{r^2}{4} = D_{eff}\tau, \quad (10)$$

and for a ball (sphere),

$$\frac{x^2}{2} \left( 1 - \frac{2}{3} \cdot \frac{x}{R} \right) = D_{eff}\tau, \quad (11)$$

Dividing the right and left parts of Eqs. (10) and (11) by  $r^2$ , one can obtain kinetic equations in the criterial form.

Taking into account that for the cylinder  $V_{\gamma-x} = \pi(r-x)^2 l$ , and for the ball  $V_{\gamma-x} = \frac{4}{3}\pi(r-x)^3$ , to determine the sign (direction) of the inversion processes in capillary-porous samples of these geometric forms from Eq. (2.5), we obtain the following:

For a cylinder,

$$\Delta T = T_2 - T_1 = \frac{1}{c_p} \left[ \frac{\nu R b T_1}{\gamma \pi (r-x)^2 l - \nu b} - \frac{2\nu a}{\gamma \pi (r-x)^2 l} \right], \quad (12)$$

and for a ball (sphere),

$$\Delta T = T_2 - T_1 = \frac{1}{c_p} \left[ \frac{\nu R b T_1}{\gamma^{\frac{4}{3}} \pi (r-x)^3 - \nu b} - \frac{2\nu a}{\gamma^{\frac{4}{3}} \pi (r-x)^3} \right]. \quad (13)$$

To determine the value of  $x$ , one can use kinetic Eqs. (10) and (11).

### 3. Conclusion

In this paper we consider the possible place and role of the known thermodynamic Joule–Thomson effect in the technology of capillary-porous materials. The presence of the Joule–Thomson effect in these materials is justified by the peculiarities of the mechanism and kinetics of diffusion physicochemical processes occurring during their heating. The mathematical description of integral effects in capillary-porous materials under isothermal conditions is given. The presence of the considered thermodynamic effect in technological processes (drying, firing, etc.) is directly related to the amount of energy consumed. In this regard, a comprehensive study of these phenomena plays an important role in the technology of capillary materials.

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