JOULE–THOMPSON EFFECT IN A DISPERSE MEDIUM

E. M. Tolmachev

UDC 536.70:529.5

An expression for the Joule–Thompson coefficient of a polydisperse medium subject to throttling is derived in the relaxation approximation of thermodynamics of irreversible processes, with both temperature and velocity relaxation in the phases taken into account.

As is well known, a nonzero magnitude of the throttle effect in any gas indicates nonideality of the latter. It is interesting, from this standpoint, to examine the behavior of a fine-disperse stream passing through a region of high hydraulic drag. For this purpose, we will consider a stream which, after starting from an initial state of equilibrium, passes through an adiabatically insulated throttle and terminates in a final state of equilibrium. We consider a disperse system in the one-phase approximation, with any interphase interaction accounted for in the effective characteristics and in the internal degrees of freedom.

Let the disperse medium constitute a mixture of an ideal gas and solid particles of various sizes, without mass transfer between the two phases. Interphase heat and momentum transfer can be described with the aid of the relaxation apparatus of thermodynamics of irreversible processes and, accordingly, by introducing the exchange affinities and the relaxation parameters characterizing these processes:

temperature relaxation;

$$A_{qk}=\frac{1}{T}(T_0-T_k),\quad \xi_{qk}=\rho_k c_k(T_k-T),$$

velocity relaxation,

$$A_{fk}=\frac{1}{2}(w_0^2-w_k^2),\quad \xi_{fk}=\frac{1}{2}(w_k^2-w^2).$$

This method has been thoroughly developed in earlier studies [1-3]. Here it will only be pointed out that application of the relaxation method according to classical procedure [4] to disperse systems [1] has yielded the following equations of state for a polydisperse mixture:

thermal,

$$-\frac{\delta\rho}{\rho^{(0)}}=\beta_0\left[1-\sum_{k=1}^{N}\frac{\rho_k\beta_k c_k}{\rho c_v}\,\frac{\tau_{qk}D}{1+\tau_{qk}D}\right]\frac{\delta T_0}{T_0^{(0)}}-\beta_0\frac{\delta p}{p^{(0)}}, \tag{1}$$

and caloric

$$\delta h=(\rho c_p)^{\omega}\,\delta T_0+\rho^{\omega}\delta\,\frac{w_0^2}{2}, \tag{2}$$

where

$$(\rho c_p)=\rho c_p\left[1-\sum_{k=1}^{N}\frac{\rho_k\beta_k c_k}{\rho c_p}\,\frac{\tau_{qk}D}{1+\tau_{qk}D}\right]; \tag{3}$$

S. M. Kirov Ural Polytechnic Institute, Sverdlovsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 37, No. 5, pp. 825-829, November, 1979. Original article submitted February 5, 1979.

0022-0841/79/3705-1299$07.50

$$\rho^{\omega} = \rho\left[1 - \sum_{k=1}^{N} \frac{\rho_k \beta_k}{\rho} \frac{\tau_{fk} D}{1 + \tau_{fk} D}\right]. \tag{4}$$

As the thermodynamic parameters have been selected the density ρ of the mixture, the temperature T_0 and the pressure p of the carrier gas, and the specific kinetic energy $w_0^2/2$ of the carrier gas. Here $\rho^{(o)}$, $T_0^{(o)}$, and $p^{(o)}$ are the stream parameters corresponding to the initial equilibrium, $D \equiv d/dt$.

Assuming that functions $\rho(t)$, $T_0(t)$, $p(t)$ can be represented in the form of Fourier integrals, we change in Eqs. (1) and (2) to Fourier components:

$$y^{\omega} = \int_{-\infty}^{+\infty} y(t) \exp(-i\omega t)\, dt. \tag{5}$$

This change is formally effected by replacement of the D operator with its actual value for the corresponding harmonic $i\omega$.

The magnitude of the differential adiabatic throttle effect is given by the well-known expression

$$\alpha_h = -\frac{1}{\rho c_p}\left[1 + \frac{T}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p\right]. \tag{6}$$

In the nonequilibrium case the stream parameters will, during throttling, continuously relax to instantaneous values of corresponding equilibrium parameters in such a way that the Joule–Thompson coefficient will also relax to its final value of, obviously, zero. The total throttle effect is found by integration of $\alpha_h(t)$ with respect to time from zero to infinity, viz.,

$$\alpha_h^{\infty} = \int_{0}^{\infty} \alpha_h(t)\, dt. \tag{7}$$

In the relaxation approximation, on the other hand, the change to dynamic variables is effected by simple replacement of the derivatives with their dynamic values so that the Fourier transform of the Joule–Thompson coefficient can be written as

$$\alpha_h^{\omega} = -\frac{1}{(\rho c_p)^{\omega}}\left[1 + \frac{T_0}{\rho^{\omega}}\left(\frac{\partial \rho}{\partial T_0}\right)_p^{\omega}\right].$$

Replacing D with $i\omega$ in expressions (1)-(4) and calculating the derivative $(\partial\rho/\partial T_0)_p^{\omega}$, we obtain

$$\alpha_h^{\omega} = -\frac{1}{\rho c_p} \frac{1 - \sum\limits_k \frac{\rho_k \beta_k}{\rho} \frac{i\omega\tau_{fk}}{1 + i\omega\tau_{fk}} - \beta_0\left[1 - \sum\limits_k \frac{\rho_k \beta_k c_k}{\rho c_v} \frac{i\omega\tau_{qk}}{1 + i\omega\tau_{qk}}\right]}{\left[1 - \sum\limits_k \frac{\rho_k \beta_k}{\rho} \frac{i\omega\tau_{fk}}{1 + i\omega\tau_{fk}}\right]\left[1 - \sum\limits_k \frac{\rho_k \beta_k c_k}{\rho c_p} \frac{i\omega\tau_{qk}}{1 + i\omega\tau_{qk}}\right]}.$$

The inverse Fourier transform of this expression yields the magnitude of the relaxing differential throttle effect:

$$\alpha_h(t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \alpha_h^{\omega} \exp(i\omega t)\, d\omega, \tag{10}$$

with the integration performed along the real ω axis. For the purpose of evaluating this integral, we close the real axis through a semicircle in the upper half-plane of complex ω and then let the radius of this semicircle increase to infinity. According to the Jordan lemma, this yields

$$\alpha_h(t) = \frac{1}{2\pi} \oint \alpha_h^{\omega} \exp(i\omega t)\, d\omega = i \sum \operatorname{res} [\alpha_h^{\omega} \exp(i\omega t)], \tag{11}$$

with the summation including only residues at the poles in the upper half-plane of ω. Using the principle of the argument [5], one can easily demonstrate that all 2N poles of function (9) are located on the imaginary positive semiaxis of complex ω and thus within the integration contour.

We now express the poles of function α_h^{ω} as

$$i\Omega_{qk} \text{ and } i\Omega_{fk} \tag{12}$$

with real positive Ω_{qk} and Ω_{fk}. On the assumption that all these poles are simple ones, i.e., that there are no identical ones among them, the inverse Fourier transform yields

$$\alpha_h(t) = -\frac{1}{\rho c_p} \sum_{k=1}^{N} [A_k \Omega_{qk} \exp(-\Omega_{qk} t) + B_k \Omega_{fk} \exp(-\Omega_{fk} t)] \tag{13}$$

with real A_k and B_k obtained by evaluation of the residue at the corresponding poles.

After having integrated with respect to time over the interval $0 \leqslant t < \infty$, we obtain the Joule–Thompson coefficient for a disperse stream:

$$\alpha_h^{\infty} = -\frac{1}{\rho c_p} \sum_{k=1}^{N} [A_k + B_k]. \tag{14}$$

As an illustrative example, let us consider the behavior of a monodisperse mixture (N = 1) during adiabatic throttling, with both temperature and velocity relaxation of the phases. In this case the Fourier transform of the Joule–Thompson coefficient (9) has two simple poles at points

$$\omega_1 = i\Omega_q = i\,\frac{\rho c_p}{\rho_0 \beta_0 c_{p0} \tau_q}, \quad \omega_2 = i\Omega_f = i\,\frac{\rho}{\rho_0 \beta_0 \tau_f}, \tag{15}$$

respectively. Upon evaluation of the residues at these points on the basis of expressions (7) and (11), easy algebraic transformations yield the Joule–Thompson coefficient

$$\alpha_h^{\infty} = \frac{1}{\rho c_p} \left[\frac{\rho_1 \beta_1 c_1}{\rho_0 \beta_0 c_{p0}} + \beta_0 \left(1 - \frac{c_{v0}}{c_{p0}} \, \frac{\rho c_p}{\rho c_v} \, \frac{\rho}{\rho_0 \beta_0} \right) \right] \tag{16}$$

for a disperse mixture.

It is not surprising that the relaxation time does not appear in this expression, since the throttle effect calculated here gives the change of stream temperature between two equilibrium states, i.e., when all relaxation processes have ceased. Nevertheless, the form of expression (16) depends on whether or not some or other relaxation processes do occur. Indeed each relaxation process increases the order of the fundamental differential equations by one, but, as is well known, there is no continuous transition between solutions to differential equations of different orders. With the mechanism of velocity relaxation in a monodisperse mixture eliminated ($\tau_f = 0$), the throtte effect accordingly becomes

$$\alpha_h^{\infty} \Big|_{\tau_f = 0} = \frac{1}{\rho c_p} \left[\frac{\rho_1 \beta_1 c_1}{\rho_0 \beta_0 c_{p0}} + \beta_0 \left(1 - \frac{c_{v0}}{c_{p0}} \, \frac{\rho c_p}{\rho c_v} \right) \right], \tag{17}$$

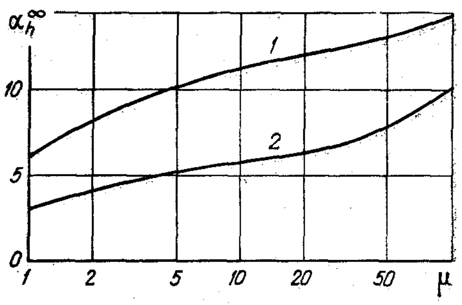

Fig. 1. Dependence of the differential throttle effect α_h^∞ (deg K/bar) on the mass concentration μ of particles: 1) corundum; 2) graphite.

while with the mechanism of temperature relaxation eliminated ($\tau_q = 0$) it becomes

$$\alpha_h^\infty \Big|_{\tau_q=0} = -\frac{1}{\rho c_p}\,\frac{\rho_1\beta_1}{\rho_0}, \tag{18}$$

and with both relaxation mechanisms eliminated ($\tau_f = 0$, $\tau_q = 0$)

$$\alpha_h^\infty \Big|_{\tau_q=0,\ \tau_f=0} = -\frac{1-\beta_0}{\rho c_p}. \tag{19}$$

According to expressions (17) and (18), a temperature lag causes cooling of the mixture and a velocity lag causes heating of the mixture during throttling. The total throttle effect depends on the relation between thermal and inertial properties of the mixture components.

The dependence of α_h^∞ on the mass concentration μ of particles in the stream has been calculated according to expression (16) and is shown in Fig. 1. The carrier phase is here atmospheric air (p = 760 mm Hg, T_0 = 300°K), and the solid phase consists of corundum particles (ρ_1 = 3900 kg/m^3, c_1 = 837 J/kg·deg K) or graphite particles (ρ_1 = 2150 kg/m^3, c_1 = 772 J/kg·deg K). The volume concentration β_0 of the carrier phase has been calculated as a function of the mass concentration μ of solid particles, viz., as

$$\beta_0 = \left(1 + \mu\,\frac{\rho_0}{\rho_1}\right)^{-1}. \tag{20}$$

The graph in Fig. 1 indicates that such a disperse stream cools down during throttling, with the Joule—Thompson coefficient reaching the absolute magnitude of 10-15 deg K/bar.

Owing to the smallness of the throttle effect in disperse media, it is difficult to name any practical technical application for it. However, it is quite possible that this effect plays a definite role in the weather, especially during movement of large dusty or snowy air masses across natural barriers.

NOTATION

A_{qk}, A_{fk}, thermal and momentum interphase exchange affinities, respectively; ξ_{qk}, ξ_{fk}, relaxation parameters; T, w, temperature and velocity of a phase relaxation in the mixture; ρ, density of the mixture; T_0, T_k, temperature of the carrier phase and of the k-th group of solid particles, respectively; p, pressure of the carrier phase; h, enthalpy of the mixture; $w_0^2/2$, specific kinetic energy of the carrier phase; β_0, β_k, volume concentration of the carrier phase and of the k-th group of solid particles, respectively; ρ_0, ρ_k, true density of the carrier phase and of the k-th group of solid particles, respectively; c_{v0} and c_{p0}, constant-volume and constant-pressure specific heats of the mixture, respectively; c_k, specific heat of the k-th group of solid particles; ρc_v, ρc_p, constant-volume and constant-pressure specific heats, respectively, of the mixture referred to volume; τ_{qk}, τ_{fk}, temperature and velocity relaxation times, respectively, of the k-th group of solid particles; t, times; ω, frequency in the Fourier series expansion; $i = \sqrt{-1}$; α_h, differential Joule–Thompson coefficient (adiabatic throttle effect); N, number of groups of particles in the mixture.

LITERATURE CITED

1. E. M. Tolmachev, Author's Abstract of Candidate's Dissertation, S. M. Kirov Ural Polytechnic Institute, Sverdlovsk (1972).
2. E. M. Tolmachev, in: Hydrodynamics and Heat Transfer [in Russian], Ural Science Center, Academy of Sciences of the USSR, Sverdlovsk (1974), p. 63.
3. E. M. Tolmachev, G. P. Yasnikov, and N. I. Syromyatnikov, in: Heat and Mass Transfer, Vol. 5, Part 1, Heat and Mass Transfer in Disperse Systems [in Russian], Naukova Dumka, Kiev (1972), p. 24.
4. R. Haase, Thermodynamics of Irreversible Processes, Addison-Wesley (1968).
5. M. A. Lavrent'ev and B. V. Shabat, Methods of the Theory of a Complex Variable [in Russian], Nauka, Moscow (1965).

TEMPERATURE–DENSITY PARAMETERS OF FREON-13 ON THE SATURATION LINE

A. M. Shavandrin and S. A. Li

UDC 533.585.536.66:537.7.717

Experimental data of a high degree of accuracy are presented on the temperature–density parameters of Freon-13 on the saturation line in the density range of $(0.08246-1.6061)\cdot 10\ kg/m^3$.

The investigation of the temperature–density parameters of argon [1], Freon-23 [2], and Freon-13B1 [3] on the saturation line by the method of quasistatic thermograms has established the possibility of using this method to study the vapor and liquid branches of the saturation line in a wide region of temperatures, including those in the vicinity of the critical point. Investigations of Freon-13 were made on the same installation to obtain more precise data on the saturation line and to test the linear diameter rule and the possibility of describing the temperature–density parameters following the hypothesis of scale similarity.

The limiting error of the density data on the saturation line is from 0.03% for $\rho \approx 1.6\ g/cm^3$ to 0.07% for the critical density on the liquid branch and from 0.07% for the critical density to 0.10% for the lowest densities on the vapor branch. The temperature of the phase transition is determined from the scale of the MPTSh-68 with an error of ±0.01°K, while its reproducibility is no worse than ±0.002°K.

The purity of the Freon-13 investigated was 99.99%, so that the sample was not subjected to any additional purification.

The experimentally obtained data on the temperature–density parameters of Freon-13 are presented in Tables 1 and 2.

The values of the critical temperature T_c and critical density ρ_c, which are presented in Table 3 in a comparison with data on the critical parameters obtained in the work of other authors, were determined by graphic analysis of the tip of the saturation line.

When a device with one container is used to investigate the temperature–density parameters on the saturation line it is impossible to determine the densities of the liquid and vapor at the same temperature; thus, to test the dependence of the average density $\bar{\rho}$ on the

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Khabarov Polytechnic Institute. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 37, No. 5, pp. 830-834, November, 1979. Original article submitted February 13, 1979.

0022-0841/79/3705-1303$07.50