A comparison with data obtained with the continuous-flow calorimeter shows that for an Ar—He mixture at a pressure of 10 bar, the excess enthalpy is approximately three times as large as the excess enthalpy of this mixture at a pressure of 18.4 bar and a 0.26 mole fraction of Ar, according to data in [8].

NOTATION

p, pressure of gaseous mixture; Δp, change in pressure during mixing; V, volume of mixture; V^E, excess volume, $Q_{T,V}$, heat of mixing at constant volume and temperature; H^E, excess enthalpy; h^E, molar excess enthalpy; T, absolute temperature; R, universal gas constant.

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MEASUREMENT OF THERMOPHYSICAL PROPERTIES OF MIXTURES BY PERIODIC HEATING OF PROBES

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We analyze the theory of the method of periodic heating of probes as applied to the study of thermophysical properties of liquid and gaseous mixtures.

One of the promising methods of investigating thermophysical properties of fluids is the method of the periodic heating of probes [1-4]. The gist of the method consists in the recording of temperature fluctuations of a probe (wire or metal foil) when heated by an alternating current. The amplitude and phase of the temperature fluctuations of the probe depend on the thermophysical properties of the fluid in which it is immersed (on the thermal conductivity λ and the volumetric heat capacity $c_p\rho$ for a cylindrical probe, and on the thermal activity $b = \sqrt{\lambda c_p \rho}$ for a plane probe). The measurement of the amplitude and phase of the temperature fluctuations of the probe by electronic means makes it possible to determine these thermophysical characteristics. The method developed can be used to study the thermophysical properties of pure gases and liquids over a wide range of states [1]. The application of the method of periodic heating to the investigation of solutions requires extension of the theory of the method.

It is well known that in gaseous and liquid mixtures a temperature gradient gives rise not only to a heat flux, but also to a diffusive flux (thermal diffusion, the Soret effect).

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On the other hand a concentration gradient causes not only a diffusive flux, but also a heat flux (diffusion heat conduction, the Dufour effect). The presence of cross effects complicates the heat-transfer process [5]. This is reflected in the introduction of two thermal conductivities to describe heat transfer in mixtures: λ_0 — the thermal conductivity of a system of uniform concentration, and λ_∞ — the thermal conductivity of a system in a stationary state when the concentration distribution produced by the temperature gradient has been established and the diffusive flux is equal to zero. The difference between λ_0 and λ_∞ is not negligible, at least for gases. Thus, for example, under normal conditions it may reach ~1.9% for a He–Ar mixture, ~2.4% for He–Xe, and ~1.7% for He–Kr [5]. The necessity of taking account of the contribution of diffusion heat conduction in solid solutions was pointed out in [6].

Steady-state methods of investigating thermal conductivity (the plane layer method, coaxial cylinders, etc.) can be used to measure λ_∞. It was shown in [7] that the method based on the recording of the temperature of a wire probe fed a step voltage records this same quantity. The question naturally arises as to which thermal conductivity is measured by the method of periodic (sinusoidal) heating.

For a stationary binary mixture the expressions for the heat and mass fluxes have the form [8]

$$\vec{J}_q = -\lambda_0 \nabla T - \rho_1 \frac{\partial \mu_1}{\partial c_1} T D' \nabla c_1, \tag{1}$$

$$\frac{\vec{J}_1}{\rho} = -c_1 c_2 D'' \nabla T - D \nabla c_1. \tag{2}$$

It is clear from Eq. (1) that λ_0 relates the heat flux and the temperature gradient for $\nabla c_1 = 0$ (i.e., for a homogeneous system). In the stationary state ($J_1/\rho = 0$), we have

$$\nabla c_1 = -c_1 c_2 (D''/D) \nabla T,$$

and substitution of the last relation into (1) gives

$$\vec{J}_q = -\left(\lambda_0 - \rho_1 \frac{\partial \mu_1}{\partial c_1} T D' c_1 c_2 \frac{D''}{D}\right) \nabla T.$$

The coefficient of proportionality in this case is λ_∞. The relation between the thermal conductivities λ_0 and λ_∞ (taking account of the Onsager reciprocal relations $D' = D''$) is thus expressed by the equality

$$\lambda_0 - \lambda_\infty = c_1 c_2 \rho_1 \frac{\partial \mu_1}{\partial c_1} T \frac{D'^2}{D}.$$

In accord with Eqs. (1) and (2) the heat-conduction and diffusion equations have the form

$$\rho c_p \frac{\partial T}{\partial t} = \lambda_0 \nabla^2 T + \rho_1 \frac{\partial \mu_1}{\partial c_1} T D' \nabla^2 c_1, \tag{3}$$

$$\frac{\partial c_1}{dt} = c_1 c_2 D' \nabla^2 T + D \nabla^2 c_1. \tag{4}$$

When a probe is heated by an alternating current of frequency ω, its temperature and that of the surrounding medium fluctuate with a frequency 2ω, and the concentration fluctuates with this same frequency. In a steady periodic process the temperature T and the concentration c_1 can be written as the sum of a constant component independent of time and a fluctuating component:

$$T = \bar{T} + \theta \exp(2i\omega t), \quad c_1 = \bar{c}_1 + \gamma \exp(2i\omega t).$$

Substituting these expressions into (3) and (4) and combining the results, we obtain the following system of equations for the fluctuating components:

$$\nabla^2 \theta = \frac{2i\omega}{a_0(1-\xi)} \theta - \frac{\xi}{1-\xi} \frac{T}{K_T} \frac{2i\omega}{D} \gamma, \tag{5}$$

$$\nabla^2 \gamma = \frac{2i\omega}{D(1-\xi)} \gamma - \frac{2i\omega}{a_0(1-\xi)} \frac{K_T}{T} \theta, \tag{6}$$

where $a_0 = \lambda_0/c_p\rho$, $\xi = (\lambda_0 - \lambda_\infty)/\lambda_0$ and $K_T = (D'/D)c_1 c_2 T$.

Let us consider first the case of a plane metal foil probe (the method of measuring the coefficient of thermal activity). We seek the solution in the form

$$\theta = A_1 \exp(-\alpha_1 x) + A_2 \exp(-\alpha_2 x) \tag{7}$$

(damped plane waves). The general form of the solution for γ follows from (5) and (7). Substituting this together with (7) into Eq. (6), we obtain the characteristic equation. Its root corresponding to the solution which is damped at infinity is

$$\alpha_{1,2} = \left\{ \frac{2i\omega(1+q)}{a_0(1-\xi)2q} \left[1 \pm \sqrt{1 - \frac{4q(1-\xi)}{(1+q)^2}} \right] \right\}^{\frac{1}{2}}, \tag{8}$$

where $q = D/a_0$. Using the boundary condition $J_1(0)/\rho = 0$ (no diffusive flux through the surface of the probe), which in the previously introduced notation takes the form

$$\frac{K_T}{T} \nabla\theta|_{x=0} + \nabla\gamma|_{x=0} = 0, \tag{9}$$

and the condition $\theta(0) = \theta_0$, where θ_0 is the amplitude of the temperature fluctuations of the probe, it is easy to determine the coefficients A_1 and A_2. Thus, we obtain the solution for θ:

$$\theta(x) = \theta_0 \left[\exp(-\alpha_1 x) - \frac{\alpha_1(1-N\alpha_1^2)}{\alpha_2(1-N\alpha_2^2)} \exp(-\alpha_2 x) \right] \left[1 - \frac{\alpha_1(1-N\alpha_1^2)}{\alpha_2(1-N\alpha_2^2)} \right]^{-1}, \tag{10}$$

where $N = a_0(1-\xi)/[2i\omega(1+\xi/q)]$. It follows from (10) that

$$\left.\frac{d\theta}{dx}\right|_{x=0} = -\theta_0 \sqrt{\frac{2i\omega}{a_0(1-\xi)}} \frac{\sqrt{1+q+2\sqrt{q(1-\xi)}}}{\sqrt{q}+\sqrt{1-\xi}}. \tag{11}$$

Taking account of (9), we write the expression for the heat flux (1) from the surface of the probe in the form

$$\vec{J}q(0) = -\lambda_0(1-\xi)\nabla\theta|_{x=0} = -\lambda_\infty \nabla\theta|_{x=0}. \tag{12}$$

Substituting (11) into (12), using the fact that $\xi = (\lambda_0 - \lambda_\infty)/\lambda_0$ is a small quantity, and limiting ourselves to terms linear in ξ, we obtain

$$J_q(0) = \lambda_\infty \theta_0 \sqrt{\frac{2i\omega}{a_\infty}} \sqrt{1+\xi(1+\sqrt{q})^{-2}}.$$

Using the last expression and the heat-balance equation for the probe [9]

$$W/s = (2c'm'\omega i/s)\theta_0 + 2J_q(0) \tag{13}$$

(W is the power expended in the probe during electrical heating, s is the surface area of the probe, and c' and m' are the specific heat and mass of the probe), it is possible to obtain an expression relating the amplitude of the temperature fluctuations of the probe to the properties of the medium in which it is located. In the present case the quantity playing the same role as the thermal activity in one-component media is

$$b^* = \sqrt{c_p \rho} \sqrt{\lambda_\infty \left[1 + \frac{\xi}{(1+\sqrt{q})^2} \right]}. \tag{14}$$

It is clear from Eq. (14) that b* is generally not directly related either to the thermal conductivity of a homogeneous system λ_0 or to the stationary thermal conductivity λ_∞, but depends on the thermal conductivity λ^*, whose value lies between them: $\lambda_\infty < \lambda^* < \lambda_0$.

It should be noted that the measurable quantity does not depend on frequency, which eliminates the apparent possibility of going over from the measurement of λ_0 to the measurement of λ_∞ with decreasing frequency ω of heating of the probe. This can be explained in the following way:

The heat-conduction Eq. (3) and the diffusion Eq. (4) used to take account of the Dufour effect are similar. As a result of this similarity the fraction of diffusion test conduction in the total heat-transfer process remains constant during a change of frequency. This is confirmed by the following considerations. The characteristic time for heating by an alternating current is its period τ. In order for a frequency dependence to be observed it is necessary to cover a range of times shorter than the time of establish equilibrium of the parameter being measured (the relaxation time τ_r) to times considerably longer than it. The characteristic time for the transition of the system from a homogeneous state characterized by λ_0 to a stationary state characterized by λ_∞ is determined by the relation [5]: $\tau_r = L^2/(\pi D)$, where L is a characteristic dimension. In probing a liquid by plane temperature waves the only characteristic dimension is the attenuation distance of the temperature wave $L = (a/\omega)^{1/2}$, and consequently the relaxation time is rigorously related to the period of heating $\tau_r = (a/(2\pi^2 D))\tau$, which eliminates the possibility of a change from $\tau < \tau_r$ to $\tau > \tau_r$.

As has already been noted, the value of ξ for certain gaseous mixtures amounts to several percent. The ratio $D/a_0 = q$ for moderately compressed and rarefied gases is of the order of unity. Thus, according to Eq. (14) the correction to λ_∞ can reach ~1%, and the measurable quantity b^* is related to the thermal conductivity λ^* lying in the middle part of the internal $\lambda_0 - \lambda_\infty$.

The value of q for liquids is small in comparison with unity ($q \sim 10^{-2}$-10^{-3}). Hence, $\lambda^* \approx \lambda_\infty(1 + \xi) \approx \lambda_0$: i.e., the measurable quantity b^* is determined by the thermal conductivity close to the thermal conductivity of a homogeneous system.

Let us now consider the probing of a solution by cylindrical waves (the method for the simultaneous determination of the thermal conductivity λ, the volumetric heat capacity $c_p\rho$, and the related quantities the thermometric conductivity $a = \lambda/c_p\rho$ and the thermal activity $b = \sqrt{\lambda c_p \rho}$).

We seek the solution of the system of equations (5) and (6) in a cylindrical coordinate system in the form of damped cylindrical waves $\theta = A_1K_0(\alpha_1 r) + A_2K_0(\alpha_2 r)$, where $K_0(\alpha r)$ is the modified Bessel function [10].

The characteristic equation with roots (8) is obtained in the same way as for a plane probe, and using boundary condition (9), the coefficients A_1 and A_2 can be determined. The solution has the form

$$\theta(r) = \theta_0 \frac{K_0(\alpha_1 r) - \dfrac{\alpha_1 K_1(\alpha_1 r_0)(1 - N\alpha_1^2)}{\alpha_2 K_1(\alpha_2 r_0)(1 - N\alpha_2^2)} K_0(\alpha_2 r)}{K_0(\alpha_1 r_0) - \dfrac{\alpha_1 K_1(\alpha_1 r_0)(1 - N\alpha_1^2)}{\alpha_2 K_1(\alpha_2 r_0)(1 - N\alpha_2^2)} K_0(\alpha_2 r_0)},$$

where $\partial K_0(\alpha r)/\partial r = -\alpha K_1(\alpha r)$, and r_0 is the radius of the probe. Using this solution, an expression can be obtained for the heat flux from the surface of the probe

$$J_q(r_0) = \lambda_\infty \theta_0 \frac{K_1(\alpha_1 r_0)}{K_0(\alpha_1 r_0)} \frac{\alpha_1 \alpha_2 N(\alpha_1^2 - \alpha_2^2)}{\alpha_2(1 - N\alpha_2^2) - \alpha_1(1 - N\alpha_1^2)\psi}, \tag{15}$$

where $\psi = K_1(\alpha_1 r_0)K_0(\alpha_2 r_0)/[K_0(\alpha_1 r_0)K_1(\alpha_2 r_0)]$.

Analysis of the general expression (15) is rather complicated, and therefore we at once take account of the fact that $\xi \ll 1$ for all gaseous and liquid mixtures with which we are familiar. We also assume that $q < 0.5$, which simplifies the expressions for the roots of the characteristic equation

$$\alpha_1^2 \approx \frac{2i\omega}{a_0(1-\xi)}\left(1 - \frac{\xi}{1-q}\right); \quad \alpha_2^2 \approx \frac{2i\omega}{D(1-\xi)}\left(1 + \frac{q}{1-q}\xi\right).$$

The last restriction is a result of our excluding from consideration rarefied and moderately dense gases for which $q \sim 1$. Analysis of the case $q \sim 1$ requires separate consideration. Taking account of the restrictions assumed, Eq. (15) is transformed to

$$J_q(r_0) = \lambda_\infty \theta_0 \frac{K_1(\alpha_1 r_0)}{K_0(\alpha_1 r_0)} \alpha_1 \left(1 + \frac{\xi}{(1-q)^2} - \frac{\sqrt{q}}{(1-q)^2}\xi\psi\right). \tag{16}$$

Substituting (16) into the heat-balance equation for the probe (13), we obtain an expression for the complex amplitude of the temperature fluctuations

$$\theta = \frac{W}{s}\left[\frac{2c'm'\omega}{s} i - b_\infty \sqrt{2\omega}\, \frac{\mathrm{hei}'\,\varkappa_1 - i\,\mathrm{her}'\,\varkappa_1}{\mathrm{hei}\,\varkappa_1 - i\,\mathrm{her}\,\varkappa_1}\left(1 + \frac{1+q}{2(1-q)^2}\xi - \frac{\sqrt{q}}{(1-q)^2}\xi\psi\right)\right]^{-1},$$

where $\varkappa_1 = r_0\sqrt{2\omega/a_\infty}\sqrt{1 - \xi/(1 - q)}$; her $\varkappa$ and hei $\varkappa$ are Thomson functions. The expression for θ yields expressions for the amplitude $|\theta|$ and phase φ of the temperature fluctuations (the lag of the temperature fluctuations behind the fluctuations of power supplied to the probe):

$$|\theta| = \frac{W}{sb_\infty\sqrt{2\omega}\varkappa_\infty\eta}\sqrt{\mathrm{hei}^2\,\varkappa_1 + \mathrm{her}^2\,\varkappa_1}\left\{\left[\mathrm{her}\,\varkappa_1 - \frac{1+L\xi}{\varkappa_\infty\eta}\,\mathrm{hei}'\,\varkappa_1 + \right.\right.$$

$$\left.\left. + \frac{M\xi}{\varkappa_\infty\eta}(\psi_1\,\mathrm{hei}'\,\varkappa_1 + \psi_2\,\mathrm{her}'\,\varkappa_1)\right]^2 + \left[\mathrm{hei}\,\varkappa_1 + \frac{1+L\xi}{\varkappa_\infty\eta}\,\mathrm{her}'\,\varkappa_1 + \frac{M\xi}{\varkappa_\infty\eta}(\psi_2\,\mathrm{hei}'\,\varkappa_1 - \psi_1\,\mathrm{her}'\,\varkappa_1)\right]^2\right\}^{-\frac{1}{2}};$$

$$\mathrm{tg}\,\varphi = -\{\varkappa_\infty\eta\,(\mathrm{her}^2\,\varkappa_1 + \mathrm{hei}^2\,\varkappa_1) + (1 + L\xi)(\mathrm{hei}\,\varkappa_1\,\mathrm{her}'\,\varkappa_1 - \mathrm{her}\,\varkappa_1\,\mathrm{hei}'\,\varkappa_1) +$$

$$+ M\xi\,[\psi_1\,(\mathrm{hei}'\,\varkappa_1\,\mathrm{her}\,\varkappa_1 - \mathrm{hei}\,\varkappa_1\,\mathrm{her}'\,\varkappa_1) + \psi_2\,(\mathrm{hei}\,\varkappa_1\,\mathrm{hei}'\,\varkappa_1 + \mathrm{her}\,\varkappa_1\,\mathrm{her}'\,\varkappa_1)]\} \times$$

$$\times \{(1 + L\xi)(\mathrm{hei}\,\varkappa_1\,\mathrm{hei}'\,\varkappa_1 + \mathrm{her}\,\varkappa_1\,\mathrm{her}'\,\varkappa_1) - M\xi\,[\psi_1\,(\mathrm{hei}'\,\varkappa_1\,\mathrm{hei}\,\varkappa_1 - \mathrm{her}'\,\varkappa_1\,\mathrm{her}\,\varkappa_1) + \psi_2\,(\mathrm{hei}\,\varkappa_1\,\mathrm{her}'\,\varkappa_1 + \mathrm{hei}'\,\varkappa_1\,\mathrm{her}\,\varkappa_1)]\}^{-1},$$

where $L = (1 + q)/[2(1 - q)^2]$; $M = \sqrt{q}/(1 - q)^2$; $\psi = \psi_1 + i\psi_2$. For solutions ($q \ll 1$) the last expressions for the amplitude $|\theta|$ and $\tan\varphi$ reduce to expressions for one-component liquids in which the thermal conductivity is the thermal conductivity of a homogeneous system λ_0. Actually, as $q \to 0$, $\varkappa_1 \to \varkappa_0 = r_0\sqrt{2\omega/a_0}$, $M \to 0$, $L \to 0.5$ and $\varkappa_\infty\eta/(1 + L\xi) \to \varkappa_0\eta$, which reduces $|\theta|$ and $\tan\varphi$ to forms corresponding to the solution for pure liquids [9], with $\varkappa_0$ replacing $\varkappa$.

Thus, the method of periodic heating with both plane and cylindrical temperature waves can be used to measure the thermal conductivity λ_0 and the related quantities the thermometric conductivity $a_0 = \lambda_0/c_p\rho$ and the thermal activity $b_0 = \sqrt{\lambda_0 c_p \rho}$ in solutions ($q \ll 1$).

NOTATION

λ, thermal conductivity; c_p, specific heat; ρ, density; c_1 and c_2, weight concentrations; $\vec{J}_g$, reduced heat flux; $\vec{J}_1$, diffusive flux; T, absolute temperature; t, time; D, interdiffusion coefficient; D', Dufour coefficient; D", thermal diffusion coefficient; K_T, thermal diffusion ratio; μ, chemical potential; a, thermometric conductivity; b, thermal activity; ω, angular frequency of electric current heating probe.

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