

based on the analysis of the data in [2]. A comparison of the values of the coefficient of thermal conductivity calculated according to this formula for light homologs with the recommended values [3] showed that the disagreement between the experimental values and the computed values does not exceed +2.1%. Therefore, the proposed formula (1) also describes with adequate accuracy the available experimental data on the thermal conductivity of light homologs of the formiates that we studied. Thus there is the possibility of calculating  $\lambda = f(T)$  for formiates that have not been studied or are difficult to study experimentally, thereby avoiding laborious and expensive investigations.

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#### NONISOTHERMAL TRANSFER PROCESSES IN A SINGLE COMPONENT GAS

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Expressions relating the true thermal conductivity coefficient of a gas to the effective value measured by various experimental methods are obtained.

All of the methods used for experimental determination of gas thermal conductivity are based on the principle of heat transfer from a solid surface preheated to the required temperature and maintenance of a temperature gradient within a system containing the gas to be studied.

Existing thermal conductivity measurement methods can be divided into two classes:

- 1) pressure gradient present in system ( $\rho = \text{const}$ ): non-steady-state heated filament method, steady-state plane layer and thermal conductivity column methods;
- 2) constant gas pressure ( $\rho \neq \text{const}$ ): non-steady-state shock tube method, steady-state heated filament method, etc.

All these methods only permit determination of an effective thermal conductivity which is never equal to the true value because of various side effects.

With consideration of the classification presented above, we will examine nonisothermal transfer processes within a single component gas, neglecting viscous momentum transfer. The linear phenomenological expressions relating energy and mass-transfer processes in any single component system will be written in the form [1]

$$\vec{J}_M = L_{11}\vec{X}_M + L_{12}\vec{X}_U, \quad \vec{J}_U = L_{21}\vec{X}_M + L_{22}\vec{X}_U. \quad (1)$$

If the gas is ideal and the specific volume of the system is practically constant ( $\rho = \text{const}$ ,  $p \neq \text{const}$ ), then we can express the thermodynamic forces in the form of [1]

$$\vec{X}_U = -\nabla T/T^2, \quad \vec{X}_M = -\frac{v\nabla p}{T} + \frac{h\nabla T}{T^2}. \quad (2)$$

Considering Eq. (2), we rewrite Eq. (1):

$$\vec{J}_M = -\frac{L_{11}k}{mp}\nabla p + \left(\frac{5}{2}\frac{L_{11}kT}{m} - L_{12}\right)\frac{\nabla T}{T^2}, \quad (3)$$

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$$\vec{J}_U = -\frac{L_{21}}{mp} \nabla p + \left( \frac{5}{2} \frac{L_{21}kT}{m} - L_{22} \right) \frac{\nabla T}{T^2}. \quad (4)$$

In Eq. (3) the coefficient of  $\nabla p$  characterizes mass transfer under the action of pressure difference, while the coefficient of  $\nabla T$  characterizes the action of the temperature gradient. In Eq. (4) the coefficient of  $\nabla p$  characterizes energy transfer due to the thermo-mechanical effect, while the coefficient of  $\nabla T$  is the thermal conductivity coefficient.

Equations (3), (4) can be written in terms of effective thermal conductivity  $\lambda_{ef}$  and diffusion  $D_{ef}$  coefficients with consideration of the fact that

$$\vec{J}_M = -\frac{L_{12}}{T^2} \left( 1 - \frac{3}{2} q^* \right) \nabla T = -D_{ef} \nabla T, \quad (5)$$

where

$$q^* = \frac{L_{11}}{L_{12}} \frac{kT}{m}; \quad D_{ef} = \frac{L_{12}}{T^2} \alpha, \quad 0 < \alpha < 1;$$

$$\vec{J}_U = -\frac{L_{22}}{T^2} \left( 1 - \frac{3}{2} Q^* \right) \nabla T = -\lambda_{ef} \nabla T, \quad (6)$$

and  $Q^* = \frac{L_{21}}{L_{22}} \frac{kT}{m}$ .

Initially we will limit ourselves to the steady-state mass transfer process

$$\vec{J}_M = -\frac{L_{12}}{T^2} \left( 1 - \frac{3}{2} q^* \right) \nabla T = 0.$$

Whence

$$L_{12} = \frac{3}{2} L_{11} \frac{kT}{m}.$$

We express the coefficient  $L_{11}$  which characterizes nonisothermal diffusion caused by a pressure difference in the form

$$L_{11} = b\rho Dm/k, \quad (7)$$

where  $b$  is some proportionality coefficient. According to the Onsager reciprocity theorem:

$$L_{12} = L_{21} = \frac{3}{2} b\rho DT. \quad (8)$$

We will evaluate  $Q^*$  for the steady-state process. For this purpose, substituting Eq. (8) in the expression for  $Q^* = \frac{L_{21}kT}{L_{22}m}$ , we obtain

$$Q^* = \frac{3}{2} L_{22}^{-1} b\rho D (k/m) T^2 = b\rho D / f\eta,$$

since  $L_{22}/T^2 = \lambda_{tr} = f\eta c_v$ ,  $c_v = (3/2)(k/m)$ ,  $f = 2.5$  is the Aiken factor,  $\rho D/\eta = (6/5)A^*$ ,  $A^* = \Omega^{(2,2)*}/\Omega^{(1,1)*}$ .

With the aid of Eq. (3) we obtain the well-known expression for thermodynamic pressure difference in the steady state [1]:  $\Delta p/\Delta T = -\theta^*/vT$ , or with consideration of the fact that  $\Delta \ln p = \Delta \ln T$ , we find  $p\theta = -\theta^* = -kT/m$ , where  $\theta^* = h - (L_{12}/L_{11})$ ,  $h = \frac{5}{2} \frac{kT}{m}$ .

To describe the process of mass transfer in the nonsteady state we use Eq. (3):

$$J_M = -\frac{L_{12}}{T^2} \left[ q^* \frac{\Delta \ln p}{\Delta \ln T} + \left( 1 - h \frac{L_{11}}{L_{12}} \right) \right] \Delta T = -D_{ef} \Delta T,$$

with the aid of which we obtain

$$\frac{\Delta p}{\Delta T} = \frac{k - \frac{L_{12}}{L_{11}}(1 - \alpha)}{vT} = -\frac{\theta_H^*}{vT},$$

where  $0 < \alpha < 1$ ,  $\alpha = \frac{D_{\text{ef}} T^2}{L_{12}}$ . Consequently, for an ideal gas

$$pv = -\theta_H^* = -\frac{kT}{m}(1 - \alpha).$$

According to Eq. (6), the relationship between the true ( $\lambda_{\text{tr}}$ ) and effective thermal conductivity coefficient, which is measured by the non-steady-state heated filament method (we assume that  $\alpha = 0.6$ ) has the form

$$\lambda_{\text{tr}} = \lambda_{\text{ef}} \left(1 - \frac{3}{2} b \frac{\rho D}{\eta}\right)^{-1}, \quad b > 0,$$

while the relationship between the true thermal conductivity and the effective value measured by the stationary plane layer method has the form

$$\lambda_{\text{tr}} = \lambda_{\text{ef}} \left(1 - \frac{3}{5} b \frac{\rho D}{\eta}\right)^{-1}, \quad b > 0.$$

In the case where the system specific volume changes ( $\rho \neq \text{const}$ ,  $p = \text{const}$ ), in order to find an expression for the thermodynamic forces  $\vec{X}_U$  and  $\vec{X}_M$ , appearing in Eq. (1), it is necessary to use the expression

$$TdS = dU - \mu dM + p dV. \quad (9)$$

Differentiating Eq. (9) with respect to  $dU$  at  $M = \text{const}$ , we obtain [2]

$$\vec{X}_U = \nabla \left(\frac{1}{T}\right) + \nabla \left(\frac{p}{T} \frac{dV}{dU}\right) = -\frac{5}{3} \frac{\nabla T}{T^2}. \quad (10)$$

Differentiating Eq. (9) with respect to  $dM$  at  $U = \text{const}$ , we find

$$\vec{X}_M = -\nabla \left(\frac{\mu}{T}\right) + \nabla \left(\frac{p}{T} \frac{dV}{dM}\right) = \frac{k}{m} \left(\frac{5}{2} \nabla \ln T + \nabla \ln \rho\right). \quad (11)$$

Using Eqs. (10), (11) we rewrite Eq. (1) in the form

$$\vec{J}_M = \frac{L_{11}}{\rho} \frac{k}{m} \nabla \rho - \frac{5}{3} \frac{L_{12}}{T^2} \left(1 - \frac{3}{2} q^*\right) \nabla T, \quad (12)$$

$$\vec{J}_U = \frac{L_{21}}{\rho} \frac{k}{m} \nabla \rho - \frac{5}{3} \frac{L_{22}}{T^2} \left(1 - \frac{3}{2} Q^*\right) \nabla T, \quad (13)$$

where

$$q^* = \frac{L_{11}}{L_{12}} \frac{kT}{m}, \quad Q^* = \frac{L_{21}}{L_{22}} \frac{kT}{m}.$$

In Eq. (12) the coefficient of  $\nabla \rho$ , equal to  $\frac{L_{11}}{\rho} \frac{k}{m} = aD$ , characterizes nonisothermal diffusion, which develops due to density differences, the temperature gradient coefficient  $\frac{5}{3} \frac{L_{12}}{T^2} \left(1 - \frac{3}{2} q^*\right)$  is related to mass transfer produced by temperature difference.

Nonisothermal diffusion was studied experimentally by the authors of [3].

In Eq. (13) the coefficient  $\frac{L_{21} k}{\rho m}$  standing before  $\nabla \rho$  characterizes energy transfer due to density difference, as discussed in [4]. The coefficient  $\frac{5}{3} \frac{L_{22}}{T^2} \left(1 - \frac{3}{2} Q^*\right)$  before  $\nabla T$  is the thermal conductivity coefficient.

We will simplify Eqs. (12), (13), assuming that  $\nabla \ln \rho = -\nabla \ln T$ :

$$\vec{J}_M = -\frac{5}{3} \frac{L_{12}}{T^2} (1 - 0.9 q^*) \nabla T = -D_{\text{ef}} \nabla T, \quad (14)$$

$$\vec{J}_U = -\frac{5}{3} \frac{L_{22}}{T^2} (1 - 0.9 Q^*) \nabla T = -\lambda_{\text{ef}} \nabla T. \quad (15)$$

We will limit ourselves to steady-state mass transfer, setting Eq. (14) equal to zero for this purpose. Then

$$L_{12} = L_{21} = 0.9 L_{11} \frac{kT}{m}.$$

We define

$$L_{11} = a \frac{\rho D}{(k/m)}, \quad (16)$$

where  $a$  is some proportionality coefficient. With consideration of Eq. (16)

$$L_{12} = L_{21} = 0.9 a \rho D T. \quad (17)$$

Substituting Eq. (17) in the expression for  $Q^* = \frac{L_{12}}{L_{22}} \frac{kT}{m}$ , we find

$$Q^* = 0.24 a \frac{\rho D}{\eta}, \quad (18)$$

Then using Eq. (15), we obtain

$$\lambda_{\text{tr}} = \frac{3}{5} \lambda_{\text{ef}} (1 - 0.216 a \rho D / \eta)^{-1}, \quad a > 0. \quad (19)$$

This expression establishes the relationship between the true gas thermal conductivity and the effective value determined experimentally, for example, by the steady-state heated filament method.

We will now consider the nonsteady-state of the mass-transfer process:

$$\vec{J}_M = -\frac{5}{3} \frac{L_{12}}{T^2} (1 - 0.9 q^*) \nabla T = -D_{\text{ef}} \nabla T,$$

where  $D_{\text{ef}} = \frac{5}{3} \frac{L_{12}}{T^2} \alpha$ ;  $0 < \alpha < 1$ . Considering that  $1 - 0.9 q^* = \alpha$ , we obtain

$$L_{12} = L_{21} = 0.9 \frac{kT}{m} L_{11} (1 - \alpha)^{-1}. \quad (20)$$

We will now write an expression for the effective gas thermal conductivity measured by the non-steady-state shock tube method ( $\lambda_{1\text{ef}}$ ), using the expression for total energy flux

$$\vec{J}_U = \vec{J}_U + h \vec{J}_M = -\lambda_{\text{ef}} \nabla T,$$

and considering the fact that in the thermal conductivity measurement experiment the gas moves as a whole. Here  $\vec{J}_U$  is the normalized energy flux.

The stationary thermal conductivity coefficient measured, for example, by the steady-state heated filament method ( $\lambda_{2\text{ef}}$ ) can be characterized by the expression

$$\vec{J}_U = -\lambda_{1\text{ef}} \nabla T - h \vec{J}_M = -(\lambda_{1\text{ef}} + \lambda_0) \nabla T = -\lambda_{2\text{ef}} \nabla T; \quad \lambda_0 = h D_{\text{ef}},$$

whence  $\lambda_{1\text{ef}} = \lambda_{2\text{ef}} - \lambda_0$ , i.e.,  $\lambda_{1\text{ef}} < \lambda_{2\text{ef}}$ , which is confirmed by experimental data.

It can be shown that the true gas thermal conductivity coefficient can be expressed in terms of the effective coefficient measured by the shock tube method in the following manner (it is assumed that  $\alpha = 0.76$ ):

$$\lambda_{\text{tr}} = \frac{3}{5} \left( 1 + a \frac{\rho D}{\eta} \right)^{-1} \lambda_{\text{ef}}; \quad a < 0.$$

The relationships obtained herein may be used to calculate true gas thermal conductivity over a wide temperature range from experimental data obtained by various methods.

#### NOTATION

U, energy; T, temperature; p, pressure;  $\rho$ , density; V, volume; v, specific volume; S, entropy; h, specific enthalpy; M, gas mass; m, molecular mass;  $L_{ij}$ ,  $L_{ij}$ , phenomenological coefficients;  $\lambda$ , thermal conductivity coefficient;  $\lambda_{tr}$ , true thermal conductivity;  $\lambda_{ef}$ , effective thermal conductivity; D, self-diffusion coefficient;  $\eta$ , viscosity coefficient;  $c_v$ , specific heat at constant volume; k, Boltzmann's constant;  $\theta^*$ , heat of transfer.

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#### AN ANALYTICAL MODEL FOR REVERSIBLE RADIATION EFFECTS ON POLYMER SPECIFIC HEAT

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A study is made of the energy balance in gas release by radiation in polymers as one of the possible mechanisms for reversible effects on the specific heat.

There are papers on irreversible radiation effects on the specific heats of polymers for polyethylene [1-3] and polystyrene [2, 4]. The effects are usually related to macrostructural transformations on irradiation and are examined when the radiation ceases.

Nothing is known about the reversible (instantaneous) effects on the specific heats of polymers. Moreover, it is not even clear whether such changes actually occur, although it is logical to assume that short-lived radiolysis products may affect individual modes in the collective vibrations (individual segments or the polymer chain as a whole) and can thus give rise to reversible effects.

We have examined one of the possible mechanisms for reversible change in the specific heat associated with the thermodynamics of gas production by radiolysis.

I. Theoretical Analysis. Although nearly all of the absorbed energy ultimately goes to heat the specimen, some is used in producing cross-linking chemical bonds, transvinylene unsaturation, etc. A certain fraction of the energy accumulates in the radiolytic gas in the free volume of the polymer.

If the relative rate of diffusion to the surface is sufficiently small, the gas pressure gradually increases and attains a certain critical value  $P_{cr}$  corresponding to the recrystallization stress  $\sigma_y$  (the yield point). From this time on, gas bubbles are formed, whose number and sizes gradually increase. This volume change occurs essentially at constant  $P_{cr}$ , since the stretching curve for an unoriented crystallized polymer is as shown in Fig. 1. Bubble growth corresponds to the part AB on the deformation curve.

The gas performs work  $p dv$  in this isobaric process. There is correspondingly a change in the internal energy  $du$ . The total amount of heat  $dq$  supplied to the gas is

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