MEASUREMENT OF THE CONCENTRATION PROFILES AND COEFFICIENTS OF INTERDIFFUSION OF THE VAPORS OF SOME LIQUIDS IN ARGON

L. I. Kurlapov and S. N. Chernyak

UDC 533.15

The concentration profiles, the local and integral coefficients of interdiffusion, and the time of establishment of steady diffusion of vapors of ether, acetone, benzene, and ethyl alcohol in argon are measured.

The coefficients of diffusion of vapors in a gas can be used in calculations of the mass transfer in various technological devices. The application of kinetic theory also permits their use for finding the molecular-kinetic parameters of vapors [1]. Measurements of coefficients of interdiffusion by the Stefan method have revealed the influence of the dimensions of the diffusion cell on the results obtained [2, 3], which can explain the pronounced concentration dependence of the coefficients of interdiffusion, as occurs for gaseous systems [4]. The concentration dependence of the coefficients of interdiffusion leads to the fact that the concentration profiles of a diffusing mixture will differ from those expected for the Stefan method with a constant coefficient of interdiffusion, as well as to the fact that one must use local coefficients of interdiffusion to find the molecular-kinetic parameters.

In the present communication we present the results of measurements of the concentration profiles and local coefficients of interdiffusion of the vapors of 1) $(C_2H_5)_2O$; 2) $(CH_3)_2CO$; 3) C_6H_6; 4) C_2H_5OH in argon by the method described earlier [5, 6]. The measurements were conducted at atmospheric pressure (702 mm Hg on the average) and at a temperature of 300°K.

The profiles of the vapor concentration c_2 for the four respective systems are presented in Fig. 1. The errors in the relative volume concentrations of the vapors with an accuracy of 0.95 were ±0.006, ±0.002, ±0.001, and ±0.002 for systems 1-4, respectively. It is seen from Fig. 1 that the measured values of c_2 at a certain $X = x/L_{ef}$ (x is the coordinate along the axis of the diffusion capillary and L_{ef} is the effective length of the capillary with allowance for the end corrections for systems 1-3) differ from the theoretical values [7] found with the condition of independence of the coefficients of interdiffusion from the concentration. The experimentally obtained profiles can be represented by polynomials, whose coefficients were found by the least-squares method on a Minsk-22 computer:

$$1)\ c_2 = -1.277X^5 + 2.883X^4 - 2.765X^3 + 0.7566X^2 - 0.3904X + 0.7991,$$

$$2)\ c_2 = -0.05442X^5 + 0.1265X^4 - 0.1310X^3 - 0.01811X^2 - 0.2905X + 0.3693,$$

$$3)\ c_2 = -0.01260X^4 + 0.01968X^3 - 0.02681X^2 - 0.1240X + 0.1445,$$

$$4)\ c_2 = 0.003718X^2 - 0.07525X + 0.07527.$$

Differentiation of function $c_2(X)$ allows one to find the local values of the concentration gradients and hence the local coefficients of interdiffusion [5, 6]. In Fig. 2 we plot the local coefficients of interdiffusion D_{12} (points), reduced to standard pressure, for systems 1, 2, 3, and 4, respectively. The mean values of the

TABLE 1. Coefficients of Interdiffusion of Vapors of Liquids into Argon, Reduced to Standard Pressure

Vapor of liquid	T, °K	$\bar{D}_{12} \cdot 10^4$, m^2/sec	
1	2	3	4
$(C_2H_5)_2O$	300	0,0919±0,0013	0,099±0,003
$(CH_3)_2CO$	300	0,098±0,002	0,098±0,003
C_6H_6	300	0,083±0,003	0,084±0,003
C_2H_5OH	299	0,101±0,008	0,109±0,010

S. M. Kirov Kazakh State University, Alma-Ata. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 35, No. 2, pp. 287-291, August, 1978. Original article submitted June 22, 1977.

0022-0841/78/3502-0946 $07.50 © 1979 Plenum Publishing Corporation

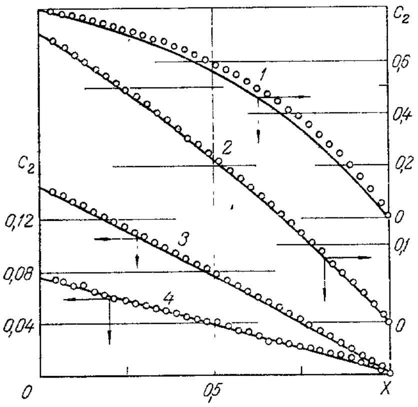

Fig. 1

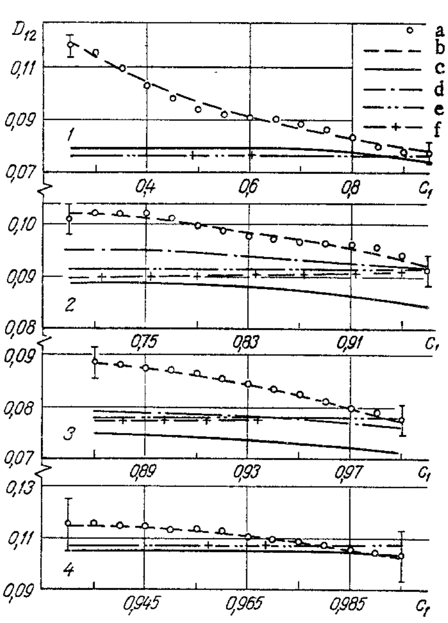

Fig. 2

Fig. 1. Distributions of vapor concentration along axis of diffusion capillary of a Stefan cell (concentration profiles) for the following systems: 1) Ar – $(C_2H_5)_2O$; 2) Ar – $(CH_3)_2CO$: 3) Ar – C_6H_6; 4) Ar – C_2H_5OH; points) experiment; curves) theory under the assumption of independence of coefficient of interdiffusion from the concentration.

Fig. 2. Dependence of coefficients of interdiffusion (10^{-4} m^2/sec) on concentration for systems 1-4: a) experiment; b) polynomials (1); c) Maxwell – Boltzmann theory with $\sigma_{11}(Ar) = 0.332$, $\sigma_{22}((C_2H_5)_2O) = 0.674$, $\sigma_{22}((CH_3)_2CO) = 0.632$, $\sigma_{22}(C_6H_6) = 0.676$, and $\sigma_{22}(C_2H_5OH) = 0.559$ N/m, found from viscosity [8, 9]; d) Maxwell – Boltzmann theory with $\sigma_{11}(Ar) = 0.344$ [4, 11], $\sigma_{22} \cdot ((CH_3)_2CO) = 0.580$, and $\sigma_{22}(C_6H_6) = 0.630$ N/m, found from $D_{12}(c_1 \rightarrow 1)$; e) second approximation of rigorous kinetic theory [1]; f) from equations of [10] with viscosity parameters taken from [1, 9].

test temperatures were the same as for the integral coefficients of interdiffusion, since the local and integral coefficients of interdiffusion were measured in parallel using different analyzers. It is seen from Fig. 2 that the concentration dependence cannot be neglected for systems 1-3, since it exceeds the error in the measurements of the local coefficients of interdiffusion. For the fourth system the concentration dependence, although it does lie within the limits of the experimental error, should not be neglected since the local coefficients of interdiffusion were obtained from continuous curves of the concentration distributions over the length of the capillary. This dependence is approximated for systems 1, 2, 3, and 4 by the following respective polynomials:

$$\begin{aligned}
&1)\ D_{12} = 0.05762c_1^2 - 0.1244c_1 + 0.1449,\\
&2)\ D_{12} = -0.06610c_1^2 + 0.07496c_1 + 0.08184,\\
&3)\ D_{12} = -0.3740c_1^2 + 0.6033c_1 - 0.1532,\\
&4)\ D_{12} = -2.859c_1^2 + 5.309c_1 - 2.349.
\end{aligned} \qquad (1)$$

As seen from Fig. 2, not one of the existing equations of kinetic theories describes the experiment fully. In the concentration range under consideration, the second approximation of the rigorous theory of [1] gives an almost constant value of the coefficient of interdiffusion. The Maxwell – Boltzmann theory for the rigid-sphere potential [11] describes the experiment better than the others. The use of σ_{11} and σ_{22} found from the coefficients of viscosity of the pure components [8, 9] (solid line) for systems 2 and 3 gives understated values, which is explained by the inexact relationship between the coefficients of viscosity and self-diffusion given by the Maxwell – Boltzmann theory.

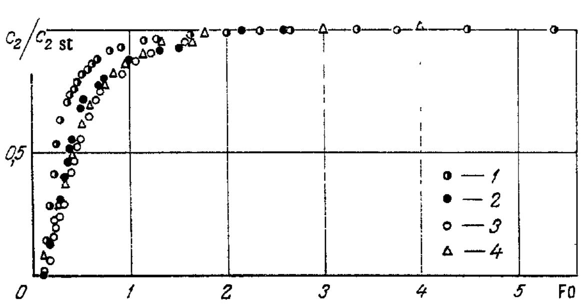

Fig. 3. Establishment of a steady vapor concentration c_2 in the diffusion cell during diffusion of the following systems: 1) Ar — $(C_2H_5)_2O$; 2) Ar — $(CH_3)_2CO$; 3) Ar — C_6H_6; 4) Ar — C_2H_5OH.

As noted above, from the measured coefficient of interdiffusion one can calculate σ. If the concentration dependence of the coefficient of interdiffusion is significant then σ_{12} must be derived from the trace coefficient of interdiffusion [10]. In the Maxwell — Boltzmann theory the trace coefficient of diffusion with $c_1 = 1$ is expressed through σ_{12}. Its values for systems 2 and 3 are found from (1) with $c_1 = 1$. From these values one calculates σ_{12} and then, using the known collision diameters of the gases, found from the coefficients of self-diffusion [4, 11], e.g., and the combination rule, one finds the rigid-sphere diameters for the vapors. Under the experimental conditions we obtained the following values for acetone and benzene vapors, respectively: 2) $\sigma_{22} = 0.580$ N/m and 3) $\sigma_{22} = 0.630$ N/m.

The method used allows one to measure the integral coefficient of interdiffusion $\bar{D}_{12}$, usually presented in the literature, simultaneously with the concentration distribution. The results of the measurements are presented in Table 1. The values of $\bar{D}_{12}$ using the vapor concentration at the lower end of the diffusion capillary, corresponding to the saturating vapor pressure, are presented in the third column while the values obtained by extrapolation of the function $c_2(X)$ to $X = 0$ are presented in the fourth column. For the majority of systems these values coincide within the error limits. This indicates that the diffusion of the vapor is the limiting process in the diffusion cell. The differences for ether vapor might have originated from the fact that with intense evaporation the correction to the temperature of the liquid surface, which we estimated for all the systems from the condition of energy balance, was less well-founded for ether, so that an uncontrolled systematic error in the saturating vapor pressure is possible for this system. In such a case it is preferable to use the value from the fourth column of the table. The integral values of $\bar{D}_{12}$ lie within the range of variation of the local values of D_{12} (Fig. 2).

All the measurements described were carried out in a steady state. The time of onset of steady diffusion was measured in control experiments. For this the value of the vapor concentration c_2 at a certain cross section of the diffusion capillary was recorded at certain times. The results of the measurements are presented in Fig. 3.

As seen from the figure, a steady process sets in at a dimensionless diffusion time $Fo > 2$ for all the systems. This agrees with the predictions of the analytical theory of heat conduction with allowance for the triple analogy [12]. The moment of the introduction of the liquid at the bottom of the diffusion cell filled with the test gas was taken as the starting point in our tests, and therefore the agreement of the measured time of onset of the steady process with the theory indicates that the time in which the vapor reaches saturation above the surface of the liquid itself is negligibly small.

NOTATION

$X = x/L_{ef}$; x, coordinate along axis of diffusion capillary; L_{ef}, effective length; c_1, c_2, relative volume concentrations of gas and vapor; D_{12}, $\bar{D}_{12}$, local and integral coefficients of interdiffusion; σ, collision diameter of molecules; $Fo = 4D\tau/L^2$, diffusional Fourier number; T, temperature.

LITERATURE CITED

1. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids, Wiley, New York (1954).
2. C. J. Lee and C. R. Wilke, Ind. Eng. Chem., 46, 2381 (1954).

3. A. F. Bogatyrev, É. N. Bondareva, and T. S. Rumyantseva, in: Diffusion in Gases and Liquids [in Russian], Kazakh State Univ., Alma-Ata (1974), p. 57.
4. G. P. Martynova, L. I. Kurlapov, and N. D. Kosov, Izv. Akad. Nauk KazSSR, Ser. Fiz.-Mat., No. 2 (1975).
5. L. I. Kurlapov and S. N. Chernyak, in: Diffusion in Gases and Liquids [in Russian], Kazakh State Univ., Alma-Ata (1974).
6. N. D. Kosov, L. I. Kurlapov, and S. N. Chernyak, in: Applied and Theoretical Physics [in Russian], Kazakh State Univ., No. 9, Alma-Ata (1977).
7. S. N. Chernyak and L. I. Kurlapov, in: Diffusion in Gases and Liquids [in Russian], Kazakh State Univ., Alma-Ata (1974).
8. L. I. Kurlapov and G. P. Martynova, Teor. Osn. Khim. Tekhnol., 4, No. 3 (1970).
9. I. F. Golubev and N. E. Gnezdilov, Viscosity of Gas Mixtures [in Russian], Gos. Kom. Stand. Sov. Min. SSSR, Moscow (1971).
10. L. I. Kurlapov, Zh. Tekh. Fiz., 46, No. 8 (1976).
11. A. F. Bogatyrev, N. D. Kosov, and L. I. Kurlapov, in: Some Problems of General and Applied Physics [in Russian], Nauka, Alma-Ata (1972).
12. A. V. Lykov, The Theory of Heat Conduction [in Russian], Vysshaya Shkola, Moscow (1967).

INFLUENCE OF HEAT CONDUCTION OF THE WALL ON THE TURBULENT PRANDTL NUMBER IN THE VISCOUS SUBLAYER

P. I. Geshev

UDC 532.517.4

Temperature pulsations in the viscous sublayer and in the heat-conducting wall are analyzed. The analytical dependence of the criterion Pr_t on the parameters Pr and Λ and the coordinate y_+ is determined.

In [1-2] it is shown that in the viscous sublayer of a turbulent boundary stream the characteristics of the wall material affect the magnitude of the temperature pulsations, and a dimensionless criterion is obtained for this effect: $\Lambda = \sqrt{(\rho c_p \lambda)_2/(\rho c_p \lambda)_1}$. The influence of the molecular Prandtl number (or the Schmidt number Sc in the case of mass transfer [3]) on the turbulent transfer in the viscous sublayer was investigated theoretically in [3-5]. The influence of the wall material was partially taken into account in [3-5] by setting up different boundary conditions: of the first kind $[\theta(y=0) = 0]$ or of the second kind $[(\partial\theta/\partial y)(y=0) = 0]$. This corresponds to $\Lambda = \infty$ and $\Lambda = 0$. In the present paper the theory of [3-5] is generalized to arbitrary values of Λ.

We will start from the following equations for the temperature pulsations:

$$\frac{\partial\theta}{\partial t} + v\frac{dT}{dy} = a\frac{\partial^2\theta}{\partial y^2} \quad (y>0), \tag{1}$$

$$\frac{\partial\varphi}{\partial t} = b\frac{\partial^2\varphi}{\partial y^2} \quad (y<0), \tag{2}$$

$$\theta = \varphi \quad (y=0), \tag{3}$$

$$\lambda_1\frac{\partial\theta}{\partial y} = \lambda_2\frac{\partial\varphi}{\partial y} \quad (y=0). \tag{4}$$

Equation (1) describes the temperature pulsations in the viscous sublayer; (2) is the equation of heat propagation in the solid wall; the conditions (3)-(4) express the continuity of the temperature and of the heat flux at the boundary. In (1) we neglected the dependence of v and θ on the coordinates x and z. The applicability of such an approximation can be justified rather rigorously in the case of large Prandtl numbers (see [3-5]), but

---

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 35, No. 2, pp. 292-296, August, 1978. Original article submitted July 25, 1977.

0022-0841/78/3502- 0949 $07.50 © 1979 Plenum Publishing Corporation