THERMAL DIFFUSION IN GAS MIXTURES

T. N. Abramenko and K. A. Shashkov

UDC 533.735

Theories describing the process of separation by thermal diffusion in gas mixtures are considered. It is known that such thermodiffusion can be found in mixtures of ideal gases.

Experimental data demonstrates that in nonisothermal systems consisting of several components mass transfer occurs because of a temperature gradient which produces "separation" in an initially homogeneous mixture, i.e., leads to a nonequilibrium distribution of components over space. This transfer phenomenon has been termed thermodiffusion.

A number of studies [1-15] have considered thermodiffusion separation in gas mixtures, but the question of the nature of this process has still not been answered decisively.

In contrast to other transfer phenomena, thermodiffusion is significantly dependent on the nature of intermolecular interactions [6, 7, 16]. As a rule, this dependence is dealt with by commencing from the fact that to determine the thermodiffusion constant a larger number of collision integrals are used than in determination of other transfer properties. The poor agreement between experimental and theoretical results on thermodiffusion is usually related to the significant dependence of the latter on the nature of intermolecular interactions [7].

A special place in thermodiffusion theory is occupied by the question of the absence of thermodiffusion separation in mixtures of gases, the molecules of which interact by a law inversely proportional to the fifth power of distance (Maxwell molecules). This fact also explains the strong dependence of thermodiffusion on the nature of the intermolecular interactions.

Meizner [17, 18] and Haase [19-21] feel that thermodiffusion exists in mixtures of ideal gases. Kotousov [6] has demonstrated that thermodiffusion and the diffusion thermoeffect disappear in such mixtures.

Grew and Mundy [22], in an experimental study of the temperature dependence of the thermodiffusion constant in a constant mixture of argon and neon, found a minimum in this dependence (anomalous behavior) at a temperature of 149°K. This can be related to the theoretical temperature dependence of the thermodiffusion constant of an equimolar mixture of He^3-He^4, which has a solution at $T \approx 0.2°K$ (Fig. 1) [25]. A number of investigators [23, 24] have related the presence of a minimum in the temperature dependence of the thermodiffusion constant of the constant Ar−Kr mixture to formation of dimers − "products" of intermolecular interaction. All these facts indicate that the thermodiffusion separation process is dependent on the nature of intermolecular interactions, since the temperature dependence of the thermodiffusion constant is regarded as a characteristic of the intermolecular interaction process.

Such divergence in opinions on the thermal separation process in gas mixtures is aggravated by the absence of any clear explanation of the nature of the thermodiffusion separation process [1]. We should note that a clear explanation of the mechanism of any transfer process implies description of its elementary molecular-kinetic theory. Fürth [26] has developed such an elementary theory, using the assumption of the existence of two molecular free path lengths for transfer, of mean numerical density (l_i) and mean velocity ($l_i^!$) of molecules, such that $l_i^! = al_i$, with the quantity a entering the expression characterizing the thermodiffusion constant of the gas mixture. Laranjeira [27-29] treated a as a characteristic of the degree of influence possessed by the nature of intermolecular forces on the thermodiffusion process. In the limiting case of an ideal one-component gas, his elementary kinetic theory indicates the presence of a flow of molecules at constant gas pressure far from the state of rarefaction, which is not supported by either the thermodynamics of irreversible processes or strict molecular-kinetic theory of gases.

Monchick and Mason [30] treated the mechanism of thermodiffusion separation in gas mixtures in terms of the theory of "free flight" of molecules. In their opinion, thermodiffusion develops only as a consequence of

---

A. V. Lykov Institute of Heat and Mass Transfer, Academy of Sciences of the Belorussian SSR. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 36, No. 4, pp. 676-684, April, 1979. Original article submitted August 29, 1978.

0022-0841/79/3604-0448$07.50

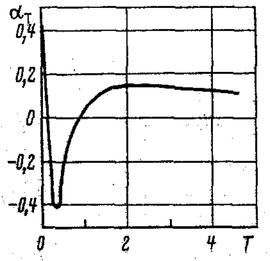

Fig. 1. Thermodiffusion constant of constant isotopic mixture He^3-He^4 versus temperature; $x_1 = 0.5$; T, °K.

a dependence of molecular collision frequency upon velocity. While giving a formally correct explanation of the process of thermodiffusion separation, the authors of [30] gave an incorrect graphic interpretation of the mechanism, based upon the existence of two "wings" in the molecular distribution function over velocity (Fig. 2). The two "wings" of this function were treated in [30] as two flows of molecules moving in opposite directions relative to the temperature gradient, leading to thermodiffusion separation of the gas mixture. However it should be noted that $\Delta f_i / |\nabla \ln T|$ is not a molecular flow, and the presence of a "negative" wing in the molecular distribution over velocity indicates that within the gas mixture there has occurred a redistribution of molecules over velocity due to the presence of a temperature gradient, which leads to development of a molecular flow. We note that this theory does not support the absence of thermodiffusion in the mixtures $Ne^{22}-NH_3$ ($x_1 = 0.38$) and $Ne^{20}-NH_3$ ($x_1 = 0.72$) [8].

Dickel [31] notes that the effect of thermal separation appearing in a mixture with temperature gradient conditions is composed of two components: a) thermodiffusion, which causes the appearance of a concentration gradient in the mixture; b) thermal concentration shift, developing in mixtures of real gases because of excess thermodynamic functions.

Thus in Dickel's classification thermodiffusion is an effect observed only in ideal mixtures.

The review presented above demonstrates that the literature cited is not of a single opinion on the nature of thermodiffusion separation in gas mixtures, and that the concept of the greater sensitivity of thermodiffusion to the nature of intermolecular interactions, as compared to other transfer properties, relies upon the assumption of the existence of two free path lengths, and absence of thermodiffusion in mixtures of Maxwell molecules.

In [6] it was shown that the presence of thermodiffusion and the diffusion thermoeffect characterizes the nonidealness of the mixture components. This fact was proved in [6] in the following manner. Since in the stationary state the condition $\operatorname{div} J'_q = -J_1 \nabla \partial \bar{h}/\partial c_1$, where $J'_q = J_q - \partial \bar{h}/\partial c_1 J_1$, then by specifying stationary boundary conditions for temperature or concentration, we can find a stationary state such that $\nabla(\partial \bar{h}/\partial c_1) = 0$, so that $\operatorname{div} J'_q = 0$ also. The condition $\nabla(\partial \bar{h}/\partial c_1) = 0$ permits determination of the unique ratio $\nabla T/\nabla c_1$ at which

$$\operatorname{div} \mathbf{J}'_q = 0,\ \mathbf{J}'_q = \mathbf{J}_1 \alpha_T c_1 c_2 \frac{\partial^2 \bar{g}}{\partial c_1^2} - \lambda_\infty \nabla T = 0,\ \left(\frac{\partial \bar{g}}{\partial c_i} = \bar{\mu}_i - \bar{\mu}_n \right),$$

$$\frac{\nabla T}{\nabla c_1} = -\frac{\partial^2 \bar{h}/\partial c_1^2}{\partial^2 \bar{h}/\partial T \partial c_1}.$$

Using these conditions and the relationship

$$\mathbf{J}_1 = -\rho D_{12} \left(\alpha_T c_1 c_2 \frac{\nabla T}{T} + \nabla c_1 \right),$$

we can find

$$\frac{\partial^2 h}{\partial x_1^2} = (0.5 - 1)\, \alpha_T \frac{n D_{12}}{\lambda_\infty} \left(\frac{M_2 - M_1}{M_1 x_1 + M_2 x_2} c_p + \frac{\partial c_p}{\partial x_1} \right) x_1 x_2 \frac{\partial^2 g}{\partial x_1^2}.$$

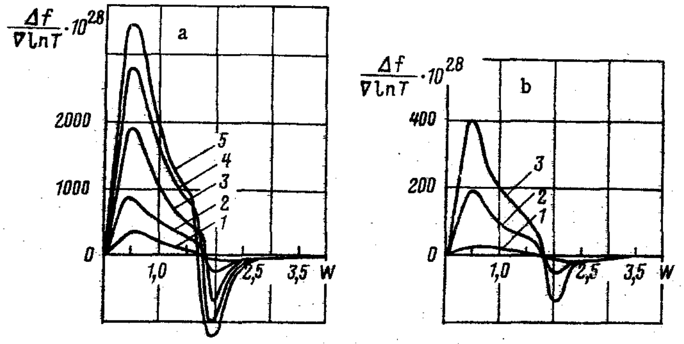

Fig. 2. Molecular distribution over velocity: a) H_2–He, T = 500°K; 1) x_1 = 0.1; 2) 0.25; 3) 0.5; 4) 0.75; 5) 0.9; b) He–Ar, T = 80°K; 1) x_1 = 0.25; 2) 0.5; 3) 0.75.

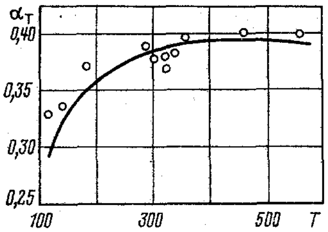

Fig. 3. Thermodiffusion constant of He–Ar mixture versus temperature, x_1 = 0.512.

According to this expression, thermodiffusion in mixtures of ideal gases is absent, since in this case $\partial^2 h/\partial x_1^2 = 0$. Calculations with this expression show that for an equimolar He–Ar mixture at T = 300°K and p = 1 atm $|\alpha_T| = 10^{-2}$. Calculation of α_T with experimental data on the excess thermodynamic functions h^E [6] shows that $|\alpha_T| \approx 0.4$, which is confirmed by the data of [32] (Fig. 3).

We will now turn to an evaluation of the temperature dependence of the thermodiffusion constant of an argon–krypton mixture. Later experimental data [33] obtained from the temperature dependence of the thermodiffusion constant of this mixture demonstrate that the presence of a minimum in this function is related to condensation of the heavy component in the measurement cell, while the "sharp" minimum in the temperature dependence of the thermodiffusion constant of He^3–He^4 at very low temperatures is in our opinion related to the fact that the mean free path length of molecules in He^3 tends to infinity as T → 0°K and a continuous hydrodynamic description of transfer processes is impossible. It is then necessary to describe the transfer processes with the aid of quasiparticle (elementary excitation) concepts [31, 36].

We will now consider the mechanism of thermodiffusion separation in gas mixtures [37]. We limit our description of the thermodiffusion process to the framework of the phenomenological thermodynamics of irreversible processes. In a coordinate system moving at the mean-mass velocity,

$$\mathbf{J}_q = \mathbf{J}_1 c_1 \frac{\partial \bar{\mu}_1}{\partial c_1} \alpha_T + \mathbf{J}_1 \frac{\partial \bar{h}}{\partial c_1} - \lambda_\infty \nabla T, \quad \mathbf{J}_1 = -\rho D_{12} \left(\nabla c_1 + \alpha_T c_1 c_2 \frac{\nabla T}{T} \right).$$

We rewrite the expressions for heat and mass fluxes in the form

$$\mathbf{J}_q = -\lambda \nabla T = \mathbf{J}_1 \left(\alpha_T c_1 c_2 \frac{\partial^2 \bar{g}}{\partial c_1^2} + \frac{\partial \bar{h}}{\partial c_1} \right) - \lambda_\infty \nabla T = q^* \mathbf{J}_1 - \lambda_\infty \nabla T,$$

where $q^* = \theta^* + \partial \bar{h}/\partial c_1$ is the transfer energy; $\theta^* = \alpha_T c_1 c_2 \partial^2 \bar{g}/\partial c_1^2$ is the transfer heat. From these, the total mass flux is

$$\mathbf{J}_1 = -\frac{\lambda - \lambda_\infty}{\alpha_T c_1 \frac{\partial \bar{\mu}_1}{\partial c_1} + \frac{\partial \bar{h}}{\partial c_1}} \nabla T = -\frac{\lambda - \lambda_\infty}{q^*} \nabla T.$$

We define the thermal conductivity coefficient in the nonstationary state

$$\lambda = \lambda_\infty + \lambda_{D^\mathrm{T}} \exp(-t/\tau).$$

For the total heat flux

$$\lambda_{D^\mathrm{T}} = \lambda_0 - \lambda_\infty = \left(\alpha_\mathrm{T} c_1 \frac{\partial \bar{\mu}_1}{\partial c_1} + \frac{\partial \bar{h}}{\partial c_1}\right) \frac{\rho D_{12}}{T} k_\mathrm{T}.$$

For the reduced flux

$$\lambda_{D^\mathrm{T}} = \alpha_\mathrm{T} c_1 \frac{\partial \bar{\mu}_1}{\partial c_1} \frac{\rho D_{12}}{T} k_\mathrm{T}.$$

With the aid of these experiments we obtain

$$\mathbf{J}_1 = -\rho D_1^\mathrm{T} \exp(-t/\tau) \nabla T; \quad \mathbf{J}_2 = \rho D_1^\mathrm{T} \exp(-t/\tau) \nabla T.$$

The same results may be obtained with the methods of strict molecular-kinetic theory of gases.

From this it is evident that thermodiffusion separation in a binary mixture is related to the development of two mass flows, moving in opposite directions under the influence of the temperature gradient.

We will now offer an elementary molecular-kinetic theory of thermodiffusion [37].

We assume that a binary gas mixture of weakly interacting molecules* is located between two infinite horizontal planes, the temperatures of which are constant, but unequal, with the temperature gradient being sufficiently small. It is obvious that both the temperature and concentration of the mixture will be functions of the z coordinate. We define the molecular flow of the first sort through a unit area moving at the mean-numeric velocity in the plane $z = 0$. The molecular flow of the first sort through one side of elementary area is equal to $^1/_4\, {}_1\bar{v}_1$, and each molecule transfers its mass and velocity on the average not to the plane $z = 0$, but to the plane $z = -u_1 l_1$, where there exists a probability of encountering another molecule before arriving in the plane $z = 0$. Here u_1 is a numerical factor. Then

$$I_{1+} = \frac{1}{4} (n_1 \bar{v}_1)_{z=-u_1 l_1} = \frac{1}{4}\left(n_1 - u_1 l_1 \frac{\partial n_1}{\partial T} \frac{\partial T}{\partial z}\right) \bar{v}_1 \left(1 - \frac{1}{2} u_1 l_1 \frac{1}{T} \frac{\partial T}{\partial z}\right) \approx$$

$$\approx \frac{1}{4} \bar{v}_1 \left(n_1 - u_1 l_1 \frac{\partial n_1}{\partial T} \frac{\partial T}{\partial z} - \frac{1}{2} n_1 u_1 l_1 \frac{1}{T} \frac{\partial T}{\partial z}\right).$$

The plus index in the notation for the molecular flow of the first component indicates that it is considered in the direction from the negative to the positive side. Similarly,

$$I_{1-} \approx \frac{1}{4} \bar{v}_1 \left(n_1 + u_1 l_1 \frac{\partial n_1}{\partial T} \frac{\partial T}{\partial z} + \frac{1}{2} n_1 u_1 l_1 \frac{1}{T} \frac{\partial T}{\partial z}\right).$$

The total flux of molecules of the first component is equal to

$$I_1 = I_{1+} - I_{1-} \approx -\frac{1}{2} \bar{v}_1 \left(u_1 l_1 \frac{\partial n_1}{\partial T} + \frac{1}{2} n_1 u_1 l_1 \frac{1}{T}\right) \frac{\partial T}{\partial z} = -\frac{n_1 D_{12}}{T}\left(\frac{\partial n_1}{\partial T} \frac{T}{n_1} + \frac{1}{2}\right) \frac{\partial T}{\partial z} = 0,$$

since in the case of a gas of solid spheres as T → ∞

$$k(\sqrt{T})^{-1} n \left(\frac{T}{n} \frac{dn}{dT} + \frac{1}{2}\right) = 0$$

or

$$\left(\frac{T}{n_i} \frac{dn_i}{dT} + \frac{1}{2}\right) = 0.^\dagger$$

---

*The solid sphere model describes weak molecular interaction well at high temperatures where mutual attraction of the molecules becomes insignificant: $B(T) = -2\pi\tilde{N} \int_0^\infty \{\exp(-\varphi(r)/kT) - 1\} r^2 dr \to 0$ as $T \to \infty$.

†This same result follows from Laranjeira's theory [27-29] at $l_i = l_i'$.

Similarly,

$$I_2 \approx -\frac{n_2 D_{12}}{T}\left(\frac{\partial n_2}{\partial T}\,\frac{T}{n_2}+\frac{1}{2}\right)\frac{\partial T}{\partial z}=0, \text{ где } D_{12}=\frac{1}{2}u_1 l_1 \bar{v}_1=\frac{1}{2}\,u_2 l_2 \bar{v}_2 .$$

If the pressure in the mixture is constant, then the condition dp/dz = 0 must be satisfied. In the case of an ideal gas considered here from the condition dp/dz = d(nkT)/dz = 0 we obtain

$$x_1\left(1+\frac{dn_1^*}{dT}\,\frac{T}{n_1}\right)=-x_2\left(1+\frac{dn_2^*}{dT}\,\frac{T}{n_2}\right),$$

since $x_1(1+(dn_1^*/dT)\,T/n_1^*)=T\cdot dx_1/dT=s_T$ (in the stationary state $s_T = k_T$ and $k_{T_1} = -k_{T_2} = k_T$). Here k_T is the thermodiffusion ratio, characterizing the process of thermodiffusion separation in the stationary state; $s_T = k_T \cdot f(t/\tau)$ is the thermodiffusion ratio characterizing the same process in the nonstationary state. Then

$$I_1=-nD_1^T f(t/\tau)\frac{\partial T}{\partial z}, \quad I_2=nD_1^T f(t/\tau)\frac{\partial T}{\partial z} .$$

According to the strict molecular-kinetic theory of gases [1-2], the dynamics of the molecular collision process, which are related to the nature of the intermolecular forces, affect the transfer processes through the so-called collision integrals

$$\Omega^{(l,s)}=\sqrt{\frac{2\pi kT}{\mu_{ij}}}\int_0^\infty\int_0^\infty e^{-\gamma_{ij}^2}\,\gamma_{ij}^{2s+3}\,(1-\cos^l \chi)\,b\,db\,d\gamma_{ij},$$

where

$$\gamma_{ij}=\sqrt{\mu_{ij}/2kT}\,(v_i-v_j), \quad \chi=\pi-2b\int_{r_m}^{b}\frac{dr/r^2}{\sqrt{1-\dfrac{\varphi(r)}{\frac{1}{2}\mu g^2}-\dfrac{b^2}{r^2}}},$$

which appear in the form of dimensionless groups in the expressions for the transfer coefficients

$$A=\Omega^{(2,2)}/\Omega^{(1,1)}, \quad B=(5\Omega^{(1,2)}-4\Omega^{(1,3)})/\Omega^{(2,1)}, \quad C=\Omega^{(1,2)}/\Omega^{(1,1)}.$$

In the case of an ideal gas $\varphi(r) \to 0$, $r_m = b$, $\chi = \pi - 2\arcsin 1 = 0$. It can be shown, for example, that

$$C=\frac{\int_0^\infty\int_0^\infty e^{-\gamma^2}\gamma^7\,b\,db\,d\gamma}{\int_0^\infty\int_0^\infty e^{-\gamma^2}\gamma^5\,b\,db\,d\gamma}$$

and the value of this quantity should be close to unity. Consequently, the transfer coefficients of a mixture of ideal (weakly interacting) gases depend only on the magnitude of the molecular mass of the components, the composition of the mixture, the temperature, and the pressure.

We will now consider a binary mixture of real gases located under a temperature gradient condition. Limiting ourselves to consideration of collisions of only two molecules for the sake of simplicity, we write the equation of state of the gas in the form

$$pv=kT\left(1+\frac{B(T,\,x_1)}{v}\right).$$

Since the gas mixture is under constant pressure, the constant pressure condition ($\nabla p=0$) leads to the expression

$$x_1\left[1+\frac{dn_1}{dT}\,\frac{1}{1+nb_0}\,\frac{T}{n_1}(1+2nB)\right]\frac{1+2nB-B'_{n_2}}{1+2nB-B'_{n_1}}=-x_2\left[1+\frac{dn_2}{dT}\,\frac{1}{1+nb_0}\,\frac{T}{n_2}(1+2nB)\right],$$

[†] A similar relationship can be obtained for the equation of state

$$pv=kT\left[1+\frac{B(T,\,x_1)}{v}+\frac{C(T,\,x_1)}{v^2}+\ldots\right].$$

where

$$b_0 = B(T,\ x_1) + T\frac{\partial B(T,\ x_1)}{\partial T}, \qquad B'_{n_i} = n_i \frac{\partial B(T,\ x_i)}{\partial x_i},$$

and

$$x_i\left[1 + \frac{dn_i}{dT}\ \frac{1}{1+nb_0}\ \frac{T}{n_i}(1+2nB-B'_{n_i})\right] \times \frac{1+nb_0}{1+2nB-B'_{n_i}} = T\frac{\partial x_i}{\partial T} = k_{\mathrm{T}}.$$

In the stationary state $k_{T_1} = -k_{T_2} = k_T$, while

$$k_{\mathrm{T}}^{E} = k_{\mathrm{T\,real}} - k_{\mathrm{T\,ideal}} = x_i \frac{n(b_0 - 2B) + (1+2nB)\dfrac{d\ln n_i/n_i^*}{d\ln T} + B'_{n_i}\left(1 + \dfrac{d\ln n_i^*}{d\ln T}\right)}{1 + 2nB - B'_{n_i}}$$

characterizes the thermal concentration shift produced by the excess thermodynamic function.

We will now consider the concept of an ideal gas. Strictly speaking an ideal gas is a set of mathematical (imaginary) points of infinitely small dimensions. There are no interaction forces between these points, i.e., an ideal gas is a mathematical abstraction. In statistical physics the concept of an ideal gas implies a gas which has interactions between molecules so weak that they may be neglected. Physically, such neglect is possible either when the molecular interaction is weak at any molecular separation, or when the gas is sufficiently rarefied [38].

The examination of the process of thermodiffusion performed here treated the case of weak interaction between the gas molecules, when the equation of state $pv = kT$ is valid, and the case where binary molecular collisions are considered and the equation of state contains a term considering the "nonidealness" of the gas. It has been shown that thermodiffusion does not depend on the nature of molecular interactions and occurs in mixtures of both ideal and real gases.

We note that in the case of a thermally inhomogeneous Knudsen gas there is no thermodiffusion, since the latter transforms to thermoeffusion. In such a gas at an inhomogeneous temperature the pressure is no longer constant but satisfies the condition $p/\sqrt{T} = \mathrm{const}$ and mass flows of each component are absent [3].

Unfortunately, it appears impossible to obtain the condition for absence of thermodiffusion and the diffusion thermoeffect in mixtures of real gases at the present time.

The authors regard it their pleasant duty to thank Professor L. S. Kotousov for his valuable remarks made in evaluating the present study.

NOTATION

T	is the temperature;
x_1	is the molecular fraction of lighter component;
c_1	is the mass concentration;
J_q	is the thermal flux in mean-mass velocity system;
J'_q	is the reduced thermal flux;
h	is the specific enthalpy;
α_T	is the thermodiffusion constant;
k_T	is the thermodiffusion ratio;
μ_i	is the chemical potential of i-th component;
ρ	is the density of mixture;
n	is the numerical density of component molecules;
D_{12}	is the mutual diffusion coefficient;
k	is the Boltzmann's constant;
v	is the volume;
$B(T, x_1)$, $C(T, x_1)$	are the second and third virial coefficients;
J_1	is the mass flow of first component;
I_1	is the particle flow of first component;
λ_∞, λ_0, λ	are the mixture thermal conductivity coefficients in stationary state, at initial time, and in nonstationary state;

λ_D^T	is the contribution of diffusion thermoeffect to mixture thermal conductivity;
t	is the time;
τ	is the time for establishment of stationary state in system;
$\bar{v}$	is the mean velocity;
l	is the mean molecular free path length;
D_1^T	is the thermodiffusion coefficient of first component;
p	is the pressure;
μ_{ij}	is the reduced molecular mass;
γ_{ij}	is the reduced velocity;
χ	is the angle of inclination;
b	is the impact parameter;
r_m	is the distance of closest molecular approach;
r	is the intermolecular distance;
$\varphi(r)$	is the intermolecular interaction potential;
g	is the relative velocity;
h^E	is the excess enthalpy;
$\tilde{N}$	is the Avogadro's number.

LITERATURE CITED

1. S. Chapman and T. Cowling, Mathematical Theory of Non-Uniform Gases, Cambridge Univ. Press (1970).
2. J. O. Hirschfelder et al., Molecular Theory of Gases and Liquids, Wiley (1964).
3. S. R. De Groot, Thermodynamics of Irreversible Processes [Russian translation], Moscow (1956).
4. S. R. De Groot and P. Mazur, Non-Equilibrium Thermodynamics, American Elsevier (1962).
5. R. Haase, Thermodynamics of Irreversible Processes, Addison-Wesley (1968).
6. L. S. Kotousov, Thermodiffusion, A Method for Study of Nonideal Systems [in Russian], Leningrad (1973).
7. J. Ferziger and G. Kaper, Mathematical Theory of Transfer Processes in Gases, North-Holland.
8. In: Thermodynamics of Gases [in Russian], V. S. Zuev (ed.), Moscow (1970).
9. In: Thermodynamics of Irreversible Processes [in Russian], Moscow (1972).
10. P. Glansdorff and I. Prigogine, Thermodynamic Theory of Structure, Stability, and Fluctuations, Wiley (1971).
11. D. N. Zubarev (ed.), Nonequilibrium Statistical Thermodynamics, Plenum Pub. (1974).
12. K. E. Grew and T. L. Ibbs, Thermal Diffusion in Gases, Cambridge Univ. Press (1952).
13. L. D. Landau and E. M. Lifshitz, Mechanics of Continuous Media [in Russian], Moscow (1953).
14. A. V. Lykov and Yu. A. Mikhailov, Theory of Heat and Mass Transfer [in Russian], Moscow (1963).
15. A. G. Shashkov and T. N. Abramenko, Crossover Effects in Gas Systems [in Russian], Minsk (1976).
16. B. A. Kalinin, P. E. Suetin, and A. É. Loiko, in: Diffusion in Gases and Liquids [in Russian], Alma-Ata (1972).
17. J. Meixner, Ann. Phys. (5), 39, 333 (1941).
18. J. Meixner, Z. Phys. Chem. Abt. B, 53, 235 (1943).
19. R. Haase, Z. Electrochem. Angew. Phys. Chem., 54, 450 (1950).
20. R. Haase, Z. Phys., 127, 1 (1949).
21. R. Haase, Z. Phys. Chem., 197, 219 (1950).
22. K. E. Grew and J. N. Mundy, Phys. Fluids, 4, 1325 (1961).
23. W. W. Wakeham, J. Phys. B, 4, 1564 (1971).
24. D. E. Stogrin and J. O. Hirschfelder, J. Chem. Phys., 31, No. 6, 1545 (1959).
25. E. G. D. Cohen, M. J. Offerhaus, and J. De Boer, Physica, 20, 501 (1954).
26. R. Fürth, Proc. R. Soc. London, Ser. A, 179, 461 (1942).
27. M. F. Laranjeira, Physica, 26, 409 (1960).
28. M. F. Laranjeira, Physica, 26, 417 (1960).
29. M. F. Laranjeira, Physica, 26, 431 (1960).
30. L. Monchick and E. A. Mason, Phys. Fluids, 10, No. 7 (1967).
31. G. Dickel, Z. Phys. Chem., 33, 337 (1962).
32. A. P. Zolotukhina, "Concentration dependence of the thermodiffusion constant of binary gas mixtures," Author's Abstract of Candidate's Dissertation, ITMO Akad. Nauk Beloruss. SSR (1973).

33. V. L. Zhdanov, Inzh.-Fiz. Zh., 35, No. 3 (1978).
34. L. D. Landau, Zh. Eksperim. Teor. Fiz., 30, No. 6 (1956).
35. A. A. Abrikosov and I. M. Khalatnikov, Usp. Fiz. Nauk, 66, No. 2 (1958).
36. D. Paines and P. Nosier, Theory of Quantum Liquids [Russian translation], Moscow (1957).
37. T. N. Abramenko and E. A. Shashkov, Problems of Heat and Mass Exchange, 77 [in Russian], Minsk (1977).
38. L. D. Landau and E. M. Lifshitz, Statistical Physics, Pergamon.

METHOD OF CRITICAL-TEMPERATURE DETERMINATION FOR INDICATOR MATERIALS

B. G. Abramovich, V. V. Matveev,
and V. V. Gavrilov

UDC 536.522.3

A method is described for measuring the switching temperature of an indicator coating in the range 50-1200°C.

Temperatures can be monitored by means of temperature-sensitive coatings, which provide rapid, fairly simple, and exact monitoring of thermal processes [1, 2]. Sometimes such coatings are used in conjunction with traditional temperature transducers to provide additional information on the thermal state, but sometimes they are the only devices that can be employed.

Previously, these indicators were used only when high accuracy was not necessary or when other methods could not be used, but nowadays new types make it possible to measure temperature very precisely, and the error may be comparable with that of many thermometers. For example, the TI indicators [3] clearly allow one to measure a temperature to 0.01 degree. However, the practical accuracy is dependent on the error involved in measuring the critical temperature of the indicator itself.

There is therefore a need for precision methods of measuring switching temperatures, since this is the only way the devices can be fully utilized; the phase transition in such an indicator always occurs at the same temperature, no matter what the conditions of use. The problem is therefore to determine the melting point with the highest precision.

Current methods of switching-point measurement employ visual definition of the melting boundary or color transition in conjunction with temperature measurement at the boundary [1, 4]. There is a subjective error in visual measurements, and this results in a substantial spread in the results, even though it is usual to perform a series of measurements in order to obtain a reliable result.

We have developed an objective method of switching-point definition that provides very precise melting-point measurement over a wide temperature range.

The indicator is heated along with a thermally indifferent substance, and the melting is detected from the temperature difference as recorded with a differential thermocouple. The temperature difference is plotted as a function of the temperature itself on a chart recorder.

We used standard instruments made in this country; for example, the TPP thermoelectric thermometer was used with a PDS-021 XY recorder, an F-116 photoelectronic amplifier, and an SUOL oven.

Figure 1 shows the block diagram; the signal from the differential couple passes to the amplifier 5 and then to the Y input, while the X input receives the heating temperature, which is provided by one of the junctions in the differential couple.

The indicator (temperature-sensitive substance and bonding agent) is placed in the quartz crucible and compacted; the crucible is then placed in the oven along with one junction of the differential couple, which is

---

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 36, No. 4, pp. 685-688, April 1979. Original article submitted June 15, 1978.