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A PHENOMENOLOGICAL DESCRIPTION OF DIFFUSION PROCESSES IN NONIDEAL GASES

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A phenomenological approach to the diffusion problem is presented which allows one to determine the behavior of the coefficient of interdiffusion in nonideal binary gaseous solutions in a rather wide region of variation of the parameters.

The theory of diffusion in dense nonideal gases still remains underdeveloped. In this connection a phenomenological approach to the diffusion problem is offered which permits a satisfactory description of the behavior of the coefficient of interdiffusion near the critical region of vaporization of binary solutions except for a small vicinity of the critical point. This approach is based on propositions of nonequilibrium thermodynamics, and its success is due to the experimentally established relationship consisting in the fact that the mobility of particles in dense gases depends smoothly on the parameters of the system and, in a number of cases, is subject to calculation or experimental determination. Thus, in the given approach principal attention is paid to the analysis of the thermodynamic force – the gradient of the chemical potential. One can be sure that a successful explanation of some of the observed dependences of the coefficient of diffusion on the parameters of the system through such an approach will promote the more intensive development of experiment in this field.

According to nonequilibrium thermodynamics, in a one-phase, two-component system without external fields, with P = const and T = const,

$$j_2 = -L_{12}\frac{\nabla\mu_2}{T} = -nD_{12}\nabla c, \quad j_2 = -j_1, \tag{1}$$

where the fluxes of the components are treated in a relative coordinate system moving with the numerical-mean velocity, and hence D_{12} is treated in the same coordinate system.

One can show [1] that

$$D_{12} = bc(1-c)\left(\frac{\partial\mu}{\partial c}\right)_{P,T}. \tag{2}$$

The mobility entering into Eq. (2) must be distinguished from molecular mobility. They coincide if the concentration approaches zero. Henceforth we have the latter case in mind. It is seen from (2) that the coefficient of interdiffusion depends on the mobility and the derivative of the chemical potential with respect to the concentration. First let us consider the mobility and cite experimental data allowing us to make an assumption about the weakness of its variation. In Fig. 1 we present data on self-diffusion in different gases in a wide range of

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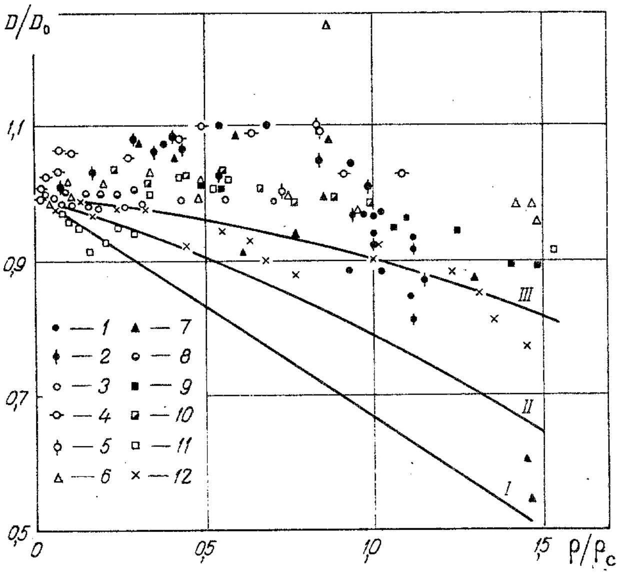

Fig. 1. Dependence of ratio D/D_0 on reduced density ρ/ρ_c from data on self-diffusion in the following systems: Ar (1, 2) [2]; Kr (3, 4, 5) [3]; CO_2 (6, 7) [4]; N_2 (8) [5]; CH_4 (9, 10, 11) [6]; SF_6 (12) [7]; 11, 12) data on the boundary curve. Curve I is constructed using the Van der Waals equation; II) from the Berthelot equation with $T^* = 2$; III) the same with $T^* = 1$; 1) $T/T_c = 1.00013$; 2) 1.025; 3) 1.423; 4) 1.472; 5) 1.064; 6) 1.013; 7) 1.030; 8) 2.324; 9) 1.022; 10) 1.433.

densities at different temperatures [2-5] and on the curve of coexistence [6, 7] (the ratio D/D_0 is laid out along the ordinate axis, where D_0 is the coefficient of self-diffusion calculated by the Chapman – Enskog method [8] with the parameters of the intermolecular potential determined in such a way as to satisfy the experimental values of D in the given system at low densities). It follows from Fig. 1 that the coefficients of self-diffusion in nonideal gases, which are determined by the mobility of the particles, depend on the density just as in the case of rarefied gases. One can arrive at the same conclusion by examining the graphic functions given in reports on the measurement of the coefficients of self-diffusion in Xe on the boundary curve and in the critical region [9], as well as in C_2H_4 and H_2 [10]. One should also note [11], in which a similar conclusion was drawn. We note that such a dependence is observed at densities somewhat exceeding the critical density. Curves with allowance for the influence of the nonideal nature of the system on particle mobility with the help of some equations of state are also given in Fig. 1. For this we used the expression [8]

$$\frac{DV}{D_0 b_0} = \frac{1}{y}, \text{ where } b_0 = B(T) + T\frac{dB(T)}{dT};$$

$$y = \frac{V^*}{T^*}\left[T^*\left(\frac{\partial P^*}{\partial T^*}\right)_{V^*}\right]\frac{P_c V_c}{RT_c} - 1, \tag{3}$$

to calculate the coefficient of self-diffusion. To calculate the quantity $(\partial P^*/\partial T^*)_{V^*}$ we used the Van der Waals equation $P^* = 8T^*/(3V^* - 1) - 3/V^{*2}$ and the Berthelot equation $P^* = 8T^*/(3V^* - 1) - 3/(T^*V^{*2})$. With allowance for the nonideal nature of the gas the quantity D/D_0 does not remain constant. If the Berthelot equation is used it depends on T and ρ while if the Van der Waals equation is used it depends only on ρ. It is also seen from Fig. 1 that the use of the Berthelot equation (curve III) permits a better description of the experimental data. In this case the approximation error is ~10%.

Now let us consider the question of the behavior of the mobility of molecules in nonideal gas mixtures. The mobility of molecules in such systems can be determined with the help of (2) from known experimental values of D_{12} and $(\partial\mu/\partial c)_{P,T}$ or by measuring this quantity directly, such as by the spin echo method.

By using Eq. (2) to determine b from values of D_{12} and $(\partial\mu/\partial c)_{P,T}$ taken from [12, 13] it was established that this quantity, just as in the case of one-component systems, behaves in accordance with the laws of rarefied gases, despite the considerable densities, exceeding the critical value. One can draw the same conclusion if one considers the results of measurements of the mobility by the spin echo method [14]. Thus, we propose to calculate the mobility in nonideal gas mixtures from the Chapman – Enskog equation [8]

$$D_{12}^{0}=b(1-c)kT=0.32024\cdot10^{-6}\frac{M_1c+M_2(1-c)}{\rho\sigma_{12}^{2}\Omega_{12}^{(1,1)\star}}\sqrt{\frac{TM_1M_2}{2(M_1+M_2)}}\,. \tag{4}$$

Since the particle mobility b has no singularities in a rather wide region of variation of the parameters of the equation of state and even near the boundary of separation into phases, the behavior of the coefficient of diffusion in nonideal gaseous solutions of low concentration will be determined, in accordance with (2), by the dependence of $(\partial\mu/\partial c)_{P,T}$ on the parameters of the system, especially in those regions where the relative variation in the mobility of the diffusing particles is considerably less than the variation of the derivative $(\partial\mu/\partial c)_{P,T}$.

Let us consider the dependence of $(\partial\mu/\partial c)_{P,T}$ on the parameters of the system and clarify some experimentally observed properties of the behavior of the coefficient of diffusion. An explicit expression for the derivative $(\partial\mu/\partial c)_{P,T}$ through the equation of state was obtained in [1] under certain assumptions about the behavior of the free energy of a solution in the form

$$\left(\frac{\partial\mu}{\partial c}\right)_{P,T}=\frac{kT}{c}\left[1-\frac{c}{kT}\,\frac{(\partial P/\partial c)_{T,V}^{2}}{-(\partial P/\partial V)_{T,c}}\right] \tag{5}$$

or in the form [15]

$$\left(\frac{\partial\mu}{\partial c}\right)_{P,T}=\left[\frac{\partial\mu(P_0,T,c)}{\partial c}\right]_{P,T}+\int\limits_{P_0}^{P}(1-c)\left[\frac{\partial^2V(P,T,c)}{\partial c^2}\right]_{P,T}dP. \tag{6}$$

Thus, to determine the quantity $(\partial\mu/\partial c)_{P,T}$ one must know the equation of state. It is interesting to analyze the behavior of $(\partial\mu/\partial c)_{P,T}$ in the region of applicability of the Van der Waals – Landau theory. We perform the analysis within the framework of the Van der Waals equation for a mixture of two gases,

$$P=\frac{RT}{V-b}-\frac{a}{V^2}, \tag{7}$$

where $a=a_{11}c^2+2a_{12}c(1-c)+a_{22}(1-c)^2$, $b=b_{11}c^2+2b_{12}c(1-c)+b_{22}(1-c)^2$. The constants a_{11} and b_{11} for an $Ar-CO_2$ solution were determined from the values of T_c and V_c of pure Ar [16], while a_{22} and b_{22} were found by the least-squares method from the data of [17] for CO_2. The constants a_{12} and b_{12} were determined by the least-squares method from data for an $Ar-CO_2$ mixture [13] by substituting the already known a_{11}, b_{11}, a_{22}, and b_{22} into Eq. (7). The results obtained are presented in Table 1. Now that we have the equation of state (7), we can find the derivative $(\partial\mu/\partial c)_{P,T}$ from (5) and (6) and, using Eq. (2), we can find the ratio of the coefficient of diffusion of the nonideal gas mixture to the coefficient of diffusion of an ideal solution calculated from (4) at the same values of ρ and T as for the nonideal solution:

$$\frac{D}{D_{12}^{0}}=\frac{c}{RT}\left(\frac{\partial\mu}{\partial c}\right)_{P,T}=1-\frac{c(1-c)^2}{T^{*2}}\left\{\frac{(\partial P^*/\partial c)_{T,V}^{2}}{-(\partial P^*/\partial V^*)_{T,c}}-\frac{1}{b_{22}}\,\frac{8T^*}{3V^*-b/b_{22}}\right.$$
$$\left.\times\left[\frac{d^2b}{dc^2}+\frac{1}{3V^*-b/b_{22}}\,\frac{1}{b_{22}}\left(\frac{db}{dc}\right)^2\right]+\frac{9}{V^*}\,\frac{1}{a_{22}}\,\frac{d^2a}{dc^2}\right\}. \tag{8}$$

Here V and T are reduced to the critical values $V_c=3b_{22}$ and $T_c=8a_{22}/27b_{22}R$ for pure CO_2.

Of course, Eq. (8) is valid in that region where one can assume that the mobility of the molecules is determined by Eq. (4). In addition, for the reasonable application of (8) one must determine the region of separation of the solution into phases. The metastable region, in the coordinates V, T, c, e.g., is determined by the equation

$$\mu_1^{l}=\mu_1^{n},\ \mu_2^{l}=\mu_2^{n}, \tag{9}$$

TABLE 1. Constants of the Van der Waals Equation

Ar		CO_2		$Ar-CO_2$ mixture	
a_{11}, bar·cm^6/mole^2	b_{11}, cm^3/mole	a_{22}, bar·cm^6/mole^2	b_{22}, cm^3/mole	a_{12}, bar·cm^6/mole	b_{12}, cm^3/mole
1,06·10⁶	25,1	3,20·10⁶	35,9	1,77·10⁶	31,0

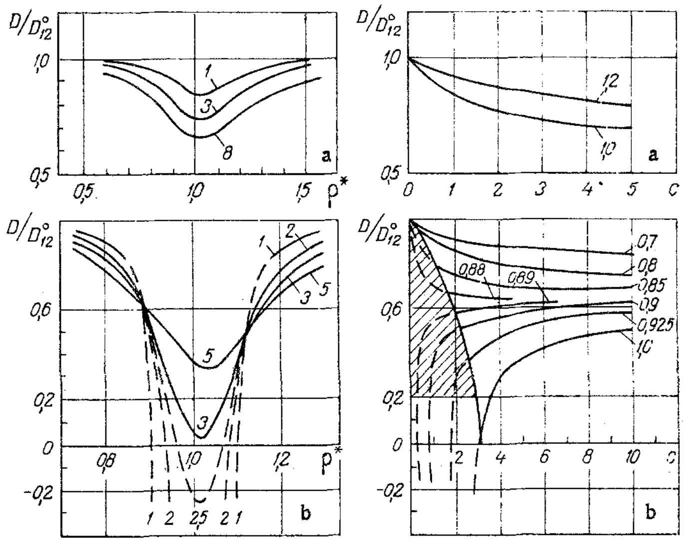

Fig. 2. Dependence of D/D^0_{12} on the reduced density $\rho^* = \rho/\rho_c$ and the concentration c.

where

$$\mu_1(P(T, V, c), T, c) - \chi_1(T) = \ln\frac{cRT}{V-b} + \frac{b+(1-c)\dfrac{db}{dc}}{V-b} - \frac{2a+(1-c)\dfrac{da}{dc}}{VRT}, \qquad (10)$$

$$\mu_2(P(T, V, c), T, c) - \chi_2(T) = \ln\frac{(1-c)RT}{V-b} + \frac{b-c\dfrac{db}{dc}}{V-b} - \frac{2a-c\dfrac{da}{dc}}{VRT}, \qquad (11)$$

$$\mu_i^{id} = RT\ln(Pc_i) + \chi_i(T).$$

The resulting dependences of D/D^0_{12} on T, V, and c for an Ar – CO_2 mixture near the region of separation of the solution, which is adjacent to the critical point of vaporization of pure CO_2, are presented in Fig. 2 [at $T^* = T/T_c$ equal to 1.013 (a) and 0.99 (b)]. The dependence on the reduced density $\rho^* = \rho/\rho_c$ (the values of ρ_c and T_c are taken for pure CO_2) for solutions with different Ar concentrations is shown on the left. The dependence of D/D^0_{12} on c at ρ^* = const is shown on the right. The numbers on the curves are the concentration in mole % (left) and the values of the relative density (right). The dashed lines and the hatched region correspond to the two-phase region. Negative values of $(\partial\mu/\partial c)_{P,T}$ correspond to the region of absolute instability.

In Fig. 3 dependences of D/D^0_{12} on T at constant P and c near the separation region, calculated using (8), are compared with experimental data obtained in [18]. The calculation (solid lines) was made at pressures which were adjusted so as to match the temperature of separation into phases. The dashed lines are drawn through the experimental points. Here some of the data obtained at high temperatures far from the boundary curve were used to calculate D^0_{12} from Eq. (4) at the following values of the parameters of the potential of the intermolecular interaction: $\sigma_{12} = 4.8$ Å, $\varepsilon_{12}/k = 480$°K; they were found from the condition of the best approximation of these data by Eq. (4). The satisfactory agreement between the results obtained by the proposed

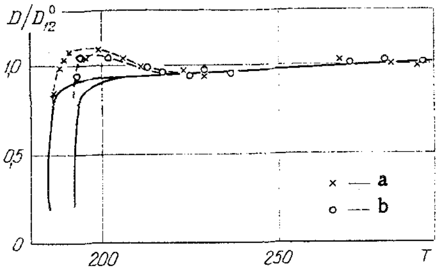

Fig. 3. Dependence of D/D^0_{12} on temperature T, °K, at P = const and c = const: a) 1 atm; b) 2 atm, data of [18] on diffusion in an Ar – CO_2 system.

calculation method and experiment is seen from Fig. 3. It should also be noted that the experiment confirms the sharp decrease in the coefficient of diffusion as the two-phase region is approached, which we assumed.

Now let us determine the region of values of the parameters where the given approach to the diffusion problem is inapplicable. This is primarily the region of the liquid state ($\rho^* > 1.5$), as well as the region near the critical point of vaporization of binary solutions, in which the Onsager coefficient can no longer be considered to be slowly varying. In fact (see [19], for example), this coefficient has a singularity, and its temperature dependence can be written as

$$L^*_{12} = A_0\tau^{-\gamma+\nu}. \tag{12}$$

The behavior of the coefficient of diffusion itself near the critical point is described by the equation

$$D_{12} = L^*_{12}/(\partial c/\partial\mu)_{P,T} = \frac{kT}{6\pi\eta r_{cor}}, \tag{13}$$

where $r_{cor} = r_0\tau^{-\nu}$ and $(\partial c/\partial\mu)_{P,T} \approx a_0\tau^{-\gamma}$.

Thus, in the general case, the coefficient of diffusion can be represented in the form of two terms:

$$D_{12} = bc(1-c)\left(\frac{\partial\mu}{\partial c}\right)_{P,T} + \frac{kT}{6\pi\eta r_{cor}}. \tag{14}$$

Far from the critical point the first term is larger than the second and it plays the main role in diffusion processes. In the region close enough to the critical point the second term prevails and the diffusion is determined by it. The first term corresponds to the contribution to the diffusional flux arising due to the diffusion of molecules whose mobility varies weakly under the action of the thermodynamic force $\vec{\Delta}\mu/T$. The second term coincides in form with the Einstein equation and corresponds to the coefficient of diffusion of clusters with a size $\sim r_{cor}$, isolated with respect to concentration, which undergo Brownian motion. An estimate [12] shows that for a CO_2–Ar system the second term in (14) starts to have an appreciable influence on the behavior of the coefficient of interdiffusion only for $\tau \leq 10^{-3}$, when $c \lesssim 3$ mole %.

Thus, one can conclude that to describe the diffusion processes at some distance from the critical point one can, as in [12, 13], take the mobility of the molecules as depending weakly on the parameters of the system, and Eq. (2) and an approximate equation of state of the Vander Waals – Landau type can be used to calculate the coefficient of diffusion.

NOTATION

P, pressure; T, temperature; V, molar volume; ρ, density of solution, g/cm^3; R, gas constant; L_{12}, Onsager kinetic coefficient; j_1, j_2, fluxes of mixture components; B(T), second virial coefficient; μ, chemical potential; μ_i^{id}, chemical potential of i-th component of a mixture of ideal gases under the same conditions as in the mixture of nonideal gases; μ_i, chemical potential of i-th component of the actual mixture; n, number density of particles; c, concentration of second component, molar fraction; b, mobility of molecules, cm/sec · dyn; D_{12}, coefficient of interdiffusion; D_{12}^0, Chapman – Enskog coefficient of interdiffusion; $\Omega_{12}^{(1,1)*}$, collision integral; M_1, M_2, molecular weights of diffusing molecules; D, coefficient of self-diffusion; D_0, Chapman – Enskog coefficient of self-diffusion; ε_{12}, σ_{12}, parameters of Lennard-Jones potential; k, Boltzmann constant; a_{11}, a_{12}, a_{22}, b_{11}, b_{12}, b_{22}, constants of Vander Waals equation of state of the mixture; $\tau = (T - T_c)/T_c$, reduced temperature; γ, ν, critical indices of compressibility and correlation radius, respectively; r_{cor}, correlation radius. Critical values are denoted by the index c; values reduced to critical values are denoted by *; η, viscosity; σ_{12}, Å.

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DEPENDENCE BETWEEN THE COEFFICIENT OF DIFFUSION AND THE CONCENTRATION OF NONAZEOTROPIC BINARY MIXTURES

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An empirical relation is obtained between the coefficient of diffusion and the difference in equilibrium molar fractions of the low-boiling-point component in the vapor and liquid phases of six nonideal binary systems.

Because of the complexity and inadequate study of the process of diffusion in liquid mixtures, the dependence of the coefficient of molecular interdiffusion of the components on the composition cannot yet be expressed strictly analytically. Various approximate equations allowing for one or another factors, which are not always known in practice, have been proposed for calculating the coefficients of diffusion of binary mixtures [1-3]. For example, the Wilke equation includes the dependence of the activity and viscosity of the components on the composition, while the Darken equation includes the dependence of the coefficient of activity of the components on the concentration. In the majority of cases, however, neither the activities nor their coefficients are known, nor the equilibrium concentrations of the components in the liquid and vapor phases of the mixture.

The forces of interaction of the molecules of the components have the determining influence on the intensity of interdiffusion of the components and the phase equilibrium of nonideal mixtures. These forces are very small in mixtures which are ideal or close to it. For such mixtures the total and partial pressures and the coefficient of diffusion can be calculated sufficiently reliably by the additivity rule with allowance for their linear dependence on the concentrations of the components. The composition of the vapor phase of an ideal solution of a mixture is also easy to calculate, knowing the composition of the equilibrium liquid phase. For nonideal mixtures a departure from the ideal (linear) dependence occurs because of the influence of the forces of molecular interaction. The value of the excess concentration of one of the components in the vapor phase relative to the concentration of the same component in the liquid phase evidently can characterize to a greater or lesser degree the nonideal nature of the processes of vaporization and diffusion. The excess concentration ΔX in the vapor phase is a function of the thermodynamic parameters (temperature, pressure, and concentration of the mixture) and of the processes taking place in the liquid layer at the boundary between the vapor phase and the main mass of liquid far from the phase interface. Therefore, greater correspondence should be observed between the coefficient of diffusion D_l in the boundary layer and the value of the excess concentration ΔX than between ΔX and the coefficient of diffusion D for the main mass of liquid.

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