Differentiating (41) with respect to time, we obtain (13), thus demonstrating the equivalence of the two approaches.

In conclusion, we derive a general formula for the LQY. We note for this purpose that the general definition of the LQY is none other than the Laplace transform of the function $m(t)=e^{-\varepsilon(t)}$, where $p=\tau_D^{-1}$. Therefore, using (38), we obtain for the LQY the general expression

$$\eta=\frac{Y(\tau_D{}^{-1}+\tau_0{}^{-1})}{1-\tau_0{}^{-1}Y(\tau_D{}^{-1}+\tau_0{}^{-1})}. \qquad (42)$$

In the case of a donor—acceptor dipole-dipole interaction we have $m=6$ and the formulas (42), (39) and (17) yield for the LQY the relation

$$\eta=\frac{Y(\tau'^{-1})}{1-\tau_0{}^{-1}Y(\tau'^{-1})},\quad \tau'=\frac{\tau_D\tau_0}{\tau_D+\tau_0}, \qquad (43)$$

while $Y(\tau')$ is given by

$$Y(\tau'^{-1})=\tau'\left[1-\frac{\alpha}{2}(\tau'\pi)^{1/2}\exp\left(\frac{\alpha^2\tau'}{4}\right)\operatorname{erf}\left(\frac{\alpha\tau'^{1/2}}{2}\right)\right], \qquad (44)$$

where $\operatorname{erf}(x)=1-\Phi(x)$, and $\Phi(x)$ is the error integral.[14]

We note that Watts[16] solved the equations of[2] by numerical methods.

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Diffusion near the critical point under conditions of large concentration gradients

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Binary diffusion in a capillary is computed by a perturbation theory method for the case when the mutual-diffusion coefficient and the solution density depend on the concentration. The calculation is in agreement with experiments performed on diffusion in a CO_2–Ar solution near the critical point for vaporization of CO_2. It is shown that, at low Ar concentrations, the obtained experimental dependence of the mutual-diffusion coefficient on the reduced temperature τ can be described with satisfactory accuracy for values of τ up to 10^{-4}–10^{-5} by a theory in which the Onsager coefficient (mobility) is regular.

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Systematic experimental investigations on diffusion near the critical point, which have established a strong slowing down of the concentration relaxation processes, were begun in the fifties by Krichevskiĭ and his coworkers.[1] An explanation of this slowing down was given by Leontovich within the framework of the self-consistent field theory for the case when the particle mobility is regular at the critical point.[2]

The application of laser techniques to the measurement of Rayleigh line widths at the end of the sixties made it possible[3] (see also Swinney and Cummin's review article[4]) to come close to the critical point without significantly perturbing the system and to discover a new competing diffusion mechanism. An interpretation of these results has been given in a number of papers[3–7] on the basis of the theory of interacting modes and the scaling-law hypothesis. The main result of this interpretation, in so far as the problem of interest to us here is concerned, is that, in a region sufficiently close to the critical point, the mutual-diffusion coefficient D_{12} can be represented thus:

$$D_{12}=L^s(\partial\mu/\partial C)_{p,T}+L^r(\partial\mu/\partial C)_{p,T}, \qquad (1)$$

where L^s and L^r are the singular and regular parts of

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the Onsager coefficient, C is the concentration, and μ is the chemical potential. The first term in (1) is, according to the coupled-mode theory, equal to

$$L^s(\partial\mu/\partial C)_{p,T}=kT/6\pi\eta\xi, \tag{2}$$

where η is the viscosity, ξ is the correlation length, and k is the Boltzmann constant. According to the fluctuation theory of second-order phase transitions, the dependence on temperature of the correlation length and the susceptibility is as follows[8]:

$$\xi=\xi_0\tau^{-\nu}, \tag{3}$$

$$(\partial C/\partial\mu)_{p,T}\approx C/RT+a\tau^{-\gamma}; \tag{4}$$

here $R=kN_0$, where N_0 is the Avogadro number, ξ_0 is a parameter whose value is of the order of the interatomic distance, a is some constant, and τ is the reduced temperature. According to the scaling theory of second-order phase transitions, the corresponding critical indices have the values $\nu=0.65$ and $\gamma=1.25$.[8] In the self-consistent field theory these critical indices are equal to $\nu=0.5$ and $\gamma=1$.

The second term of Eq. (1) describes diffusion in a region some distance away from the critical point. Here we use the self-consistent field theory. This theory, which is based on the expansibility into series of the thermodynamic quantities of the system in terms of the parameters of the system, has certain advantages connected with its simplicity, and is sufficiently exact for the description of certain critical phenomena. According to this theory, near the critical point of the solvent we can obtain[2]

$$D_{12}=L^r(\partial\mu/\partial C)_{p,T}, \tag{5}$$

$$\left(\frac{\partial\mu}{\partial C}\right)_{p,T}=\frac{RT}{C}\left(\frac{\Delta V^2+a_1\Delta T+(a_2-a_3)C}{\Delta V^2+a_1\Delta T+a_2C}\right), \tag{6}$$

where ΔV and ΔT are the deviations of the specific volume and the temperature from the critical values for the pure solvent,

$$a_1=2(\partial^2p/\partial V\partial T)_c/(\partial^3p/\partial V^3)_c,\quad a_2=2(\partial^2p/\partial V\partial C)_c/(\partial^3p/\partial V^3)_c \tag{7}$$
$$a_3=-2(\partial p/\partial C)_c^2/RT(\partial^3p/\partial V^3)_c.$$

Here the values of the derivatives are taken at the critical point of the solvent.

For the coefficient L^r near the critical point the following estimates will do:

$$L^r=bC(1-C)/N_0\approx C/6\pi\eta rN_0 \tag{8}$$

or

$$L^r=CD_{12}^0/RT,$$

where

$$D_{12}^0=0.32024\cdot10^{-4}\frac{M_1C+M_2(1-C)}{\rho\sigma_{12}^2\Omega_{12}^{(1,1)*}}\left[\frac{T(M_1+M_2)}{2M_1M_2}\right]^{1/2}, \tag{9}$$

b is the mobility of the molecules of the solute relative to a coordinate system moving with the mean velocity of the molecules of the solvent, r is the radius of the molecules of the solute, D_{12}^0 [cm^2/sec] is the mutual-diffusion coefficient for a dense gaseous mixture, for the computation of which an expression obtained for a rarefied gas is used, ρ [g/cm^3] is the density, σ_{12} [Å] is the effective diameter for the scattering cross section, $\Omega_{12}^{(1,1)*}$ is the collision integral, and M_1 and M_2 are the molecular weights of the solvent and the admixture. The error in the estimate (9) does not exceed 10% in our case.

Below we describe experiments on the diffusion of argon in a binary solution near the critical point of vaporization of the CO_2 solvent. Let us consider the equalization of the concentration in the capillary (the one-dimensional case). One end of the capillary is sealed, while a constant admixture concentration, C_0, is maintained at the other end. Let the pressure and temperature of the gas be kept constant, and let there be no significant pressure gradient. Under these conditions the diffusion equations have the form[2]:

$$\partial C/\partial t+\mathbf{v}\nabla C=\rho^{-1}\operatorname{div}(\rho D_{12}\operatorname{grad}C), \tag{10}$$

$$\partial\rho/\partial t=-\operatorname{div}\rho\mathbf{v}, \tag{11}$$

$$D_{12}=bkT\left(1-\frac{a_3C}{\Delta V^2+a_1\Delta T+a_2C}\right); \tag{12}$$

here $\mathbf{v}$ is the mean mass velocity in the gas motion, t is the time, a_1, a_2, and a_3 are coefficients which can be determined from the equation of state obtained in Ref. 9 for the CO_2-Ar solution:

$$\Delta p=AC+A_1\Delta T+BC\Delta V+B_1\Delta T\Delta V+C_1\Delta V^3+D_1C^2$$
$$+F\Delta T^2+EC\Delta T+G\Delta T\Delta V^2+G_1C\Delta V^2, \tag{13}$$

where

$$A=224,\ A_1=1.65,\ B=-3.97,\ B_1=-0.0176,\ C_1=-0.000048,$$
$$D_1=582,\ F=0.0076,\ E=1.67,\ G=0.00047,$$
$$G_1=0.082,\ p_c=74.0408\ \text{bar},\ V_c=94.0171\ \text{cm}^3/\text{mole}$$
$$T_c=31.0128^\circ\text{C},\quad a_1=B_1/3C_1=0.122\cdot10^3,\quad a_2=B/3C_1=0.27\cdot10^5,$$
$$a_3=-A^2/3RTC_1=0.14\cdot10^5.$$

The numerical values of the coefficients in (13) have been obtained for the case when the pressure is expressed in bars, the specific volume in cm^3/mole, the temperature in degrees Kelvin, and the concentration in mole fractions.

We solved the system of equations (10)–(12) by a perturbation-theory method with the use of iterations, the concentration distribution along the length of the capillary at a distance x from the sealed end at the moment of time t having in the first approximation in the perturbation the form

$$C(x,t)=\Delta C_0-\varphi(x,t)-\frac{64\Delta C_0}{\pi^3}\sum_{n,m,k=0}^{\infty}\chi_{nmk}(t)\sin\frac{(2n+1)\pi x}{2l}; \tag{14}$$

here

$$\varphi(x,t)=\frac{4\Delta C_0}{\pi}\sum_{n=0}^{\infty}(2n+1)^{-1}\sin\frac{(2n+1)\pi x}{2l}\exp\left(-\left[\frac{(2n+1)\pi}{2l}\right]^2D_{12}t\right),$$

$$\chi_{nmk}(t)=\left\{\left[\frac{2}{\rho}\left(\frac{\partial\rho}{\partial C}\right)_{p,T}+\frac{1}{D_{12}}\left(\frac{\partial D_{12}}{\partial C}\right)_{p,T}\right]\Delta C_0\right.$$

$$\times\frac{2n+1}{[(2n+1)^2-(2m+2k+2)^2][(2n+1)^2-(2m-2k)^2]}$$

$$-\frac{2}{D_{12}}\left(\frac{\partial D_{12}}{\partial C}\right)_{p,T}\Delta C_0\frac{2n+1}{[(2n+1)^2-(2m+2k+2)^2][(2n+1)^2-(2m-2k)^2]}$$
$$\times\frac{(2k+1)^2}{(2n+1)^2-(2m+1)^2-(2k+1)^2}\bigg\}\bigg\{\exp\left(-\left[\frac{(2n+1)\pi}{2l}\right]^2D_{12}t\right)$$
$$-\exp\left(-[(2m+1)^2+(2k+1)^2]\left(\frac{\pi}{2l}\right)^2D_{12}t\right)\bigg\}. \qquad (15)$$

Denoting by $C(t)$ the mean concentration in the capillary up to the time t, we obtain by integrating (14) over the length of the capillary the expression

$$C(t)=\Delta C_0[1-\Lambda(t)-H(t)]; \qquad (16)$$

where

$$\Lambda(t)=\frac{8}{\pi^2}\sum_{n=0}^{\infty}(2n+1)^{-2}\exp\left(-\left[\frac{(2n+1)\pi}{2l}\right]^2D_{12}t\right),$$
$$H(t)=\frac{2}{\pi}\sum_{n,m,k=0}^{\infty}\frac{\chi_{nmk}(t)}{2n+1} \qquad (17)$$

It is immediately evident from these expressions that the perturbation series expansion is in the two parameters:

$$\Delta\rho=\rho^{-1}(\partial\rho/\partial C)_{p,T}\Delta C, \quad \Delta D_{12}=D_{12}^{-1}(\partial D_{12}/\partial C)_{p,T}\Delta C.$$

Near the critical point for vaporization of the solvent, these parameters can be large, and can vary considerably in the course of the diffusion. Indeed, from (13) it follows that

$$\left(\frac{\partial V}{\partial C}\right)_{p,T}=\frac{-1}{\rho^2}\left(\frac{\partial\rho}{\partial C}\right)_{p,T}=\frac{A+B\Delta V+2D_1C+E\Delta T+G_1\Delta V^2}{BC+B_1\Delta T+3C_1\Delta V^2+2G\Delta T\Delta V+2G_1C\Delta V}. \qquad (18)$$

At the critical point for the pure liquid this expression has different limits, including infinitely large limits, depending on the approach path.[10] To take account of the considerable variation of these parameters in the course of the diffusion, we assumed them to be functions of $C_0(t)=\Delta C_0[1-\Lambda(t)]$, and computed them from the formulas (12) and (13) for each moment of time. This case corresponds to that approximation in which ρ and D_{12} are expanded in power series, but the iterations are performed not only for the concentration, but also for the coefficients of this expansion. Such an iterative procedure converges significantly more rapidly, and the discarded terms are equal in order of magnitude to

$$2\rho^{-2}(\partial\rho/\partial C)_{p,T}(\partial^2\rho/\partial C^2)_{p,T}\Delta C^3,$$

which does not exceed 6% in the most unfavorable of the considered cases.

The dependence, computed with the use of the equation of state, of the mean concentration on time can be compared with the experimentally observed diffusion. The construction of the diffusion cell used for the observation of such a dependence is shown in Fig. 1. The capillary is of length $l=22$ mm and diameter 1 mm. The concentration of the gaseous solutions was determined with an MI-1305 mass spectrometer. To maintain a constant pressure in the course of the diffusion and a constant concentration at the open end of the capillary, the ratio of the volume of the capillary to that of the internal cavity of the diffusion bomb was chosen to be large (about 2000). The constancy of the temperature was ensured by a reliable thermostatic control, a good thermal conductivity of the capillary walls, and a sufficiently small diameter of the capillary. The error made in the determination of the concentration was not worse than 0.002% Ar. The procedure and errors are described in greater detail in Ref. 11.

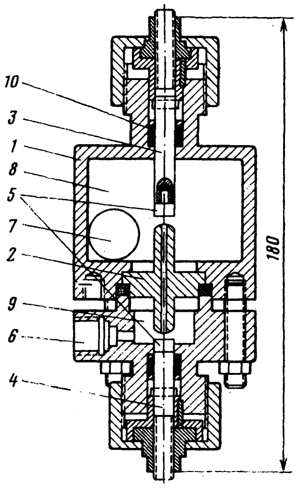

FIG. 1. Measuring cell: 1) high-pressure bomb, 2) capillary, 3) internal valve, 4) external valve, 5) silver end pieces, 6) connecting pipe socket for connecting the cell with the inlet and filling systems, 7) steel ball for intermixing the gas mixture, 8) interior volume of bomb, 9) external volume, 10) teflon packing gland.

The experiment was performed in the following sequence. The internal cavity of the bomb 8 (Fig. 1) was filled with a gaseous Ar-CO_2 mixture of known concentration C_0 and density ρ_b. Then the evacuated capillary 2 was filled with pure CO_2, or CO_2 diluted to a concentration of C^0_{cap}, at a temperature well above the critical temperature for CO_2, so as to preclude the stratification of the gas. The gas density in the capillary was chosen such as to secure a small pressure excess in the capillary over the gas pressure in the cavity of the bomb. This precluded the suction of the mixture into the capillary from the bomb cavity at the moment of opening of the value 3 at the very beginning of the diffusion process. The gas-filled bomb was placed in a thermostat in the vertical position, so that the valve 3 was directed upwards to prevent the outflow from the capillary of the denser gas. After the attainment of thermal equilibrium the valve 3 was opened. This moment was recorded as the beginning of the diffusion process. After some time (diffusion time t), the valve 3 was opened and the bomb was connected to the inlet system of the mass spectrometer for the determination of the Ar concentration, $C_{cap}(t)$, in the capillary.

For the purpose of increasing the accuracy, and to eliminate the extraneous calibrations of the mass spectrometer, the Ar content, C_0, in the bomb cavity was redetermined immediately after the determination of $C_{cap}(t)$ (see Ref. 11). For this purpose, gas was first drawn from the cavity 8 into the capillary with the valve

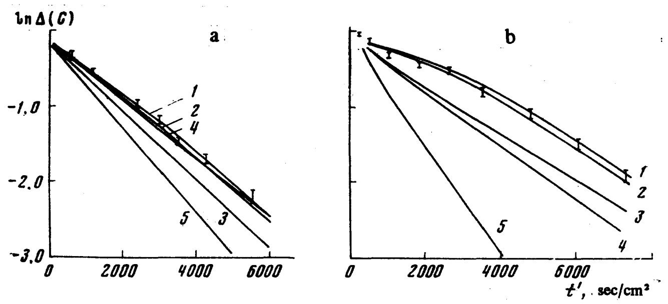

FIG. 2. Dependence of lnΔ(C) on t': a) for $T=35°$ C, $\rho_b=0.45$ g/cm³, $C^0_{cap}=0$, and $C_0=2.06\%$ Ar; b) for $T=31.3°$ C, $\rho_b=0.36$ g/cm³, $C^0_{cap}=0$, $C_0=4.55\%$ Ar. The curves 1 are plots of the solution to the nonlinear Eq. (10); 2) solution of the linear Fick equation (Eq. (10) $\mathbf{v}\nabla C=0$); 3) solution of the linear Fick equation with the diffusion coefficient (12) in the case when $\Delta V=$ const and $C=$ const and are equal to the values which they assume at the end of the diffusion process; 4) solution of the linear Fick equation with the diffusion coefficient (9) and ρ equal to the initial density of the gas mixture in the capillary; 5) solution of the linear Fick equation with the diffusion coefficient (9) for ρ equal to the gas density, ρ_b, in the bomb; the points are experimental points.

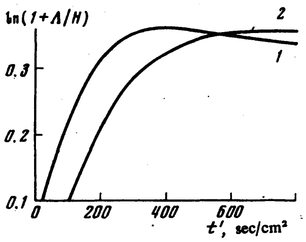

FIG. 3. Dependence of the logarithm of the ratio of the sum of the linear terms to that of the nonlinear terms of the solution (17): 1) for $T=35°$ C, $\rho_b=0.45$ g/cm³, $C^0_{cap}=0$, $C_0=2.06\%$ Ar; 2) for $T=31.3°$ C, $\rho_b=0.366$ g/cm³, $C^0_{cap}=0$, $C_0=4.55\%$ Ar.

4 closed, and then fed into the inlet system of the mass spectrometer for analysis. Such a procedure enabled us to determine at the same time the densities of the mixtures being analyzed from the pressures produced by the test samples in the inlet system, since the gas density in the internal cavity of the bomb was known beforehand from the accurately measured volume of this cavity and the difference between the weights of the filled and empty bomb.

In Fig. 2 we show the dependences of the measured mean concentration in the capillary on the time in the coordinates

$$\ln\left(1-\frac{C_c(t)-C_c^0}{C_0-C_{cap}^0}\right)\equiv\ln\Delta(C),\quad t'=\frac{\pi^2t}{4l^2}.$$

The curves 1 were constructed from Eq. (16) with allowance for the dependence of the parameters $\Delta\rho$ and ΔD_{12} on $C_{cap}(t)$. To give an idea about the magnitude of the contribution to the diffusion process from the flow of the gas as a whole, a flow which arises during the mixing of the gases, we present in Fig. 2 the curves 2. They were constructed in the same way as the curves 1, but under the condition that $\mathbf{v}\cdot\nabla C=0$ (see Eq. (10)).

We show in the same figure for comparison the solutions to Eq. (10) for the case when $\mathbf{v}\cdot\nabla C=0$ and the density and diffusion coefficient are assumed to be constants. The curves 3 represent the case when D_{12} is determined by Eq. (12) for the case when ΔV and C are constants and are equal to those values which they assume at the very end of the diffusion process. Finally, the curves 4 and 5 describe the dependences that should be obtained in the case when D_{12} is computed from Eq. (9). In this case the curves 4 were constructed under the assumption that the density was equal to the initial gas density, ρ^0_{cap}, in the capillary, while the curves 5 are for the case when the density corresponds not to the initial, but to the final mean $\rho_{cap}(t)$ value that it assumes as a result of actual diffusion.

It can be seen from these same figures that, at points sufficiently far from the critical point for the pure solvent, CO$_2$, i.e., for $T-T_c\geq 4$ K and $C\leq 2.06\%$ Ar (see Fig. 2a), the computational methods corresponding to the curves 1, 2, and 4 give approximately the same picture for the diffusion process. However, for departures from the critical point equal, for example, to $T-T_c\approx 0.3$ K, $C\approx 4.55\%$, and $|\rho-\rho_{cr}|<0.3$ g/cm³ (see Fig. 2b), the solution can in no way be considered to be an ideal solution and, to obtain the correct picture of the process, it is necessary to allow for the gas streams arising from the mixing of the components and for the dependence of the diffusion coefficient on concentration.

Figure 3 shows the dependence $\ln(1+\Lambda/H)$ as a function of the time, where Λ/H is the ratio of the linear terms of the solution of the diffusion equation to the nonlinear terms. Since at large times this function varies insignificantly, the asymptotic value of D_{12} can be found from the limiting slope of the experimental $\ln\Delta(C)=f(t')$ curve for $t'\to\infty$, the error being largely determined by the accuracy of the concentration measurement.

In Fig. 4 we show the dependence of the ratio of the experimentally measured diffusion coefficient to the value computed from Eq. (9) on the reduced temperature $\tau=(T-T_c)/T_c$, where T_c is the critical temperature of the solution in degrees Kelvin.

Since in the capillary method, in contrast, for example, to the gradientless method of measuring Rayleigh line widths, the concentration and the density vary and

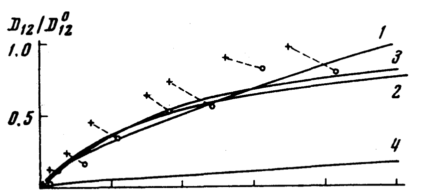

FIG. 4. Dependence of the experimentally measured diffusion coefficients on the reduced temperature $\tau=(T-T_c)/T_c$ and the approximating functions: the curve 1 was computed from Eq. (19), 2) from (20) for $C=4.34\%$ Ar, 3) from (21), 4) from (22) for $\nu=0.65$; +) experimental points corresponding to the D^0_{12} and τ values computed with ρ^0_{cap} and C^0_{cap} values; o) experimental points computed with $\rho_{cap}(t)$ and $C_{cap}(t)$ values.

TABLE I.

Temperature of experiment, °C	C_0 %Ar	C^0_{cap}, %Ar	$C_{\text{cap}}(t)$, %Ar	t, sec	$D_{12}\cdot 10^4$, cm²/sec	$\rho_б$, g/cm³	ρ^0_{cap}, g/cm³	$\rho_{\text{cap}}(t)$ g/cm³	$\left(\frac{D_{12}}{D^0_{12}}\right)_0$	$\left(\frac{D_{12}}{D^0_{12}}\right)_t$	$\tau_0\cdot 10^2$	$\tau_t\cdot 10^2$
40	4.850	2,135	4,579	8653	4.85	0,40	0.51	0.41	0,978	0,786	3,50	4,14
37	4.850	2.551	4.418	6270	4.74	0.40	0.48	0.43	0,903	0.815	2.62	3,13
35	4.850	2,071	4.342	8990	4.33	0.40	0.56	0.42	0,743	0.557	1.83	2,44
33	4.850	3,318	4.471	7313	3.25	0.40	0,49	0.42	0,636	0.533	1.50	1,81
31.5	4.850	2.199	3.822	7419	1.83	0.40	0.62	0.47	0,455	0.345	0,711	1,14
29,5	4.850	3.496	4.343	16264	0.953	0.40	0,65	0.44	0.249	0.169	0.395	0.615
28,3	4.850	4.083	4.547	21082	0.688	0,40	0.45	0.42	0.124	0.116	0,149	0.269
27.8	4.850	4.194	4.549	53990	0.213	0.40	0.47	0.43	0.039	0.035	0,050	0.159

do possess gradients in the course of the measurements, we give some parameters for the characterization of the experiment in Table I. Thus, the diffusion-coefficient values given in Fig. 4 are some mean values for Ar-CO_2 solutions with concentrations of 2.1–4.4% Ar and densities of 0.4–0.65 g/cm³. In view of the fact that in the course of diffusion at a constant temperature the critical temperature of the solution varies owing to the variation of the concentration, the D_{12} values pertain also to some mean reduced temperature. As was found earlier,[9] for CO_2-Ar solutions the decrease of T_c with increasing concentration is linear, and constitutes approximately 0.8° per 1% Ar.

The obtained temperature dependence of D_{12} (the small circles in Figs. 4 and 5) can be approximated by a function of the type

$$D_{12}/D_{12}^0=A_0\tau^{-\nu}, \tag{19}$$

where $\nu=0.7$ and $A_0=8$ (see Fig. 4, curve 1), the ν and A_0 values having been chosen from the condition that the mean square error functional have its minimum value. However, this dependence can also be approximated within the limits of the spread by the function following from the self-consistent field theory in the case of a regular mobility:

$$\begin{aligned}D_{12}/D_{12}^0&=C(\partial\mu/\partial C)_{p,T}/RT\\&=a_1T_c\tau/(a_3C+a_1T_c\tau),\end{aligned} \tag{20}$$

where $V=V_c=91$ cm³/mol and $T_c=299.287$ K is the critical temperature of the solution: see the curve 2 in Fig. 4. This curve was drawn for a solution of concentration 4.34% Ar and with the a_1 and a_3 values given in Eq. (13).

If we assume that the Eqs. (4), (5), and (9) are applicable, then the function approximating the experimental dependence will be representable in the form

$$D_{12}/D_{12}^0=(1+a'\tau^{-\gamma})^{-1}, \tag{21}$$

(see Fig. 4, curve 3, which was drawn with the fitting coefficient $a'=aRT/C=6.9\times 10^{-3}$.

Let us now estimate the temperature dependence of the diffusion coefficient under the assumption that the coupled-mode theory is applicable. In this case, taking (2), (3), (8), and (9) into account, we obtain

$$D_{12}/D_{12}^0=r_0\xi_0^{-1}\tau^{-\nu}. \tag{22}$$

For $r_0\xi_0^{-1}=1$ and $\nu=0.65$ this dependence is represented by the curve 4 in Fig. 4. Actually, $r_0\xi_0^{-1}<1$, and the deviation from the experimental data will be even greater. In Fig. 5 the dependences (19)–(22) are shown on a logarithmic scale. It can be seen from this figure that a dependence of the type (22) becomes of the same order of magnitude as the dependence (20) only in the region $\tau\sim 10^{-4}$ and exceeds it only when $\tau<10^{-5}$.

It is interesting to note that the dependence (20) goes over into the linear, rapidly-decreasing dependence $D_{12}/D_{12}^0\sim\tau$ at temperatures $\tau\approx a_3C/a_1T_c$, i.e., this transition depends on the concentration, and occurs earlier at higher, than at lower, concentrations. In the coupled-mode theory Eq. (2) does not depend on the concentration. Having this in view, let us now compare the magnitudes of the first and second terms of Eq. (1) as we approach the critical point of the solution with respect to temperature. It is clear that the temperature at which the first term becomes greater than the more rapidly decreasing second term also depends on the concentration. Thus, at sufficiently high concentrations the region, $10^{-4}<\tau<10^{-2}$, of singular behavior of the Onsager coefficient characterizing the diffusion near the critical point for vaporization of the solution turns out to be experimentally accessible.

Let us now estimate the temperature region where the second term of Eq. (1) assumes the asymptotic form τ^{γ}, using the isomorphism theory of critical phenomena[8]:

$$\tau_\text{T}\leqslant\left[\frac{AC}{T_c^2}\left(\frac{dT_c}{dC}\right)^2\right]^{1/\gamma}\approx 10^{-1.6},$$

where $A\approx 5.6$ is the coefficient attached to the singular part of the specific heat[12]

$$C_V/R=A\tau^{-\alpha}+B.$$

The first term of Eq. (2) with a singularity in the On-

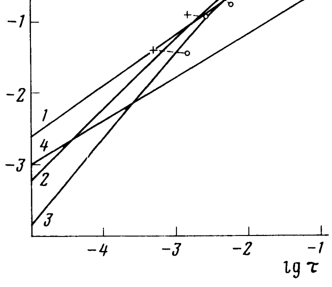

FIG. 5. Same as in Fig. 4, but on a logarithmic scale.

sager coefficient should in our case be taken into account at temperatures

$$\tau_\nu \leqslant \left[\frac{AC}{T_c^2} \left(\frac{dT_c}{dC} \right)^2 \right]^{1/\nu} \approx 10^{-3,2}.$$

Thus, the estimate obtained for the reduced temperatures on the basis of the isomorphism theory of critical phenomena agrees with the characteristic temperatures shown in Fig. 5.

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Contribution to the theory of the optical properties of imperfect cholesteric liquid crystals

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A theory of the optical properties of imperfect (mosaic) cholesteric liquid crystals (CLC) is developed. The optical characteristics are determined on the basis of the transport equations for the light-polarization tensor. The use of these equations is made possible by the statistical character of the imperfections of the mosaic CLC. The case of light propagation along the optical axis is considered in detail. It is shown that the optics of imperfect CLC is subject to qualitative singularities in comparison with the case of ideal CLC. These are, in particular, the polarization of the light, the broadening of the frequency regions of the selective reflection, the independence of the specific rotatory power on the sample thickness, and the selective attenuation of light circularly polarized in either direction. It is noted that the equations obtained in the paper for the polarization tensor can be useful for a description of the scattering of radiation of different types from imperfect crystals.

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INTRODUCTION

Many experimental and theoretical studies have been made of the optics of cholesteric liquid crystals (CLC) (see, e.g., [1–8]). It has been well established that the unusual character of the optical properties of CLC is due to diffraction of light by their periodic structure. There is, however, a wide gap between the theoretical and experimental papers. Whereas in experiment one deals usually with crystals that are non-ideal to a greater or lesser degree, the theoretical papers consider almost exclusively the optics of an ideal planar cholesteric structure. It appears that the only theoretical relation used for the interpretation of measurements made on non-ideal CLC is the improved Bragg formula,[3,4] which connects the period of the cholesteric helix with the wave length of the diffraction-reflected light and with the angles of incidence and reflection relative to the CLC surface.

Yet there are many problems in the optics of imperfect cholesteric crystals, of importance both from the experimental and the fundamental points of view, which have not been dealt with theoretically. Foremost among them are the dependence of the light reflection and transmission coefficients on the degree of perfection of the cholesteric samples, the influence of the imperfections on the polarization characteristics of the light and on the rotation of the plane of polarization, and others. Naturally, in these cases the phenomena are likewise determined by the diffraction of the light in the CLC, but to answer the foregoing questions it is necessary in most

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