An optical method for measuring the positions of spinodals in stratified solutions

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We show that during pulsed irradiation of a thin cuvette containing one of the phases of a stratified associated solution (the phase with the lower critical point) the conjugate phase of the solution precipitates within the laser spot. As the temperature T of the cuvette varies smoothly the fraction of precipitated phase changes discontinuously at two points T_1 and T_2 ($T_1 < T_2$). We have established experimentally that T_1 coincides with the binodal temperature, and that the concentration dependence of the position of the point T_2 can be related to the spinodal temperature of the solution.

It is well-known that phase equilibrium curves are ordinarily very difficult to measure experimentally. This is particularly true of measurements of the position of inherently first-order phase transitions of spinodal type, i.e., boundaries between regions on the phase diagram where the system state is metastable and where it is labile (reviewed, e.g., in Ref. 1). For this reason, the search for new and efficient methods of making this type of measurement is a problem of considerable current interest. In this paper we propose a new method for determining experimentally the position of the spinodal T_s in the coordinates (T,x) for stratified binary solutions with a lower critical point T_c (where T is the temperature and x is the concentration of one of the components of the solution).

We recall that the spinodal curve $T_s(x)$ is determined by the equation $(\partial\mu/\partial x)_{p_0,T} = 0$, where $\mu(p_0,T,x)$ is the chemical potential of one component of the solution with concentration x for a given constant value of the pressure $p = p_0$; the binodal $T_b(x)$ is the solution to the equation $\mu^{\rm I}(p_0,T,x) = \mu^{\rm II}(p_0,T,x)$, where $\mu^{\rm I}$ and $\mu^{\rm II}$ are the chemical potentials of this component in the two unmixed phases. At the critical point $x = x_c$ both of these curves are tangent to one another: $T_b(x_c) = T_s(x_c)$. In the metastable region located between the binodal $T_b(x)$ and spinodal $T_s(x)$ in the (T,x) coordinate plane, the derivative of the chemical potential satisfies $(\partial\mu/\partial x)_{p_0,T} > 0$; in the labile region, which lies within the spinodal, $(\partial\mu/\partial x)_{p_0,T} < 0$.

The method we propose to determine the position of the spinodal is based on the use of optical methods to identify the temperature $T = T(x)$ at which $\partial\mu/\partial x$ changes sign. Our method involves an experimentally observable response to optical excitation; however, this response is not the usual signal due to light scattering,[1] but is rather a change in the amount of a new phase (the conjugate fraction of the solution) that appears when the solution is irradiated with a laser in the temperature range $T \geqslant T_b(x)$. We observed that when a given phase of the system (i.e., fraction of the stratified solution) held within this range of temperatures is irradiated by a pulse of laser light sufficiently intense that the solution is transparent to this light, the pulse induces precipitation of the conjugate phase of the solution (within the region of irradiation); furthermore, the temperature dependence of the amount of precipitated phase for a fixed radiation intensity undergoes a discontinuity with positive derivative at the point $T = T_2$. The temperature T_2 is a function of the concentration x of the original phase. We take this temperature $T_2(x)$ to be the spinodal temperature.

Our experiments were carried out using an associated solution of trimethylpyridine (TMP) $C_8H_{11}N$ in water (for which $T_c = 5.7$ °C at a critical molecular concentration of water $x_c = 97\%$). The associated nature of this solution is due to the presence of H...O bonds between water molecules and N...H bonds between molecules of water and TMP. Our interest in this particular solution stems from the observation of a sizable number of anomalies in its physical characteristics.[2,3]

An important clue to the physical interpretation of this light-induced phase separation, which we observed and used to determine $T_s(x)$, is the fact that the molecular weight of the solute TMP (equal to 121) exceeds the molecular weight of the solvent (water). It is well-known that the diffusion current of a given component in a mixture is in general determined not only by the gradient of its concentration x but also by gradients in the temperature (thermodiffusion) and pressure (barodiffusion) of the mixture.[4] However, inclusion of barodiffusion is required only when sizable pressure gradients are present in the liquid due, to, e.g., an external electric field, a fact that has often been emphasized in the literature (see, e.g., Ref. 4). Apparently this situation obtains in our experiments: the laser pulse used to illuminate the solution had an intensity $I \approx 50$ MW/cm^2 over an illuminated spot with diameter $d \approx 0.15$ cm; in this case the gradient of the electrostrictive pressure equaled

$$|\nabla p_{\rm str}| \approx \rho(\partial\varepsilon/\partial\rho)\,2I/cd \approx 2 \text{ atm/cm}$$

[here c is the velocity of light, ρ is the density of the solution, and $\rho(\partial\varepsilon/\partial\rho) \approx 1$].

The coefficient of barodiffusion $D_p = (\alpha p/p)(\partial V/\partial x)_{p,T}$ [where V is the specific volume of the solution, p is the pressure and the coefficient $\alpha > 0$ (see Ref. 4)] is negative for the heavy component of a binary solution (i.e., the component with the larger molecular weight).[1)] This implies that barodiffusion should pull the heavy molecules into regions where the pressure is high; in our experiment the region of laser irradiation is such a region. Of course, this latter conclusion is valid only when the solution is transparent, so that the irradiated region does not become hot and thereby give rise to thermodiffusion.

The coefficient of ordinary diffusion (i.e., determined by the gradient of the concentration) $D = (\alpha/\rho)(\partial\mu/\partial x)_{p,T}$ is always positive outside the labile region of the state diagram (both for heavy and light components of the mix-

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ture[2]). In the labile region, where $\partial\mu/\partial x < 0$, the coefficient $D < 0$, which corresponds to extreme instability of the states of the solution in this region.

When barodiffusion is included (and thermodiffusion neglected) the vector **j**, i.e., the mass current density of the heavy component at the boundary of the irradiated region of the solution, can be written in the form

$$\mathbf{j}=\alpha\left|\frac{\partial V}{\partial x_1}\right|_{p,T}\left[\nabla p_{\text{str}}-\frac{(\partial\mu/\partial x_1)_{p,T}}{|\partial V/\partial x_1|_{p,T}}\nabla x_1\right]. \tag{1}$$

Here and in what follows we use x_1 to denote the concentration of the heavy component, i.e., $x_1 = 1 - x$, where x is the concentration of the light component (in our case, water; see Fig. 1). In the laser experiment the directions of the gradients ∇p_{str} and ∇x_1 coincide; therefore, for a large enough light intensity $I > I_0$ the current j is directed towards the axis of the laser beam (i.e., into the irradiated region). Setting $|\nabla p_{\text{str}}| \approx 2I/cd$ and $|\nabla x_1| \approx 2\hat{x}_1/d$ (where $\hat{x}_1$ is the value of the concentration of the heavy component on the axis of the beam; for our experiment we can always assume $\hat{x}_1 \ll 1$), for the metastable region of the state diagram where $(\partial\mu/\partial x_1)_{p,T} > 0$ we obtain the following necessary condition for the light intensity to induce a flow toward the beam axis:

$$I>I_0=\hat{x}_1 c\,\frac{(\partial\mu/\partial x_1)_{p,T}}{|\partial V/\partial x_1|_{p,T}}. \tag{2}$$

From (1) it follows that as the temperature of the solution increases above $T_b(x)$ at a fixed light intensity I [satisfying condition (2)] the flux of TMP molecules into the region of irradiation within the time of the laser pulse can change discontinuously at the point $T = T_s(x)$ (i.e., where $\partial\mu/\partial x_1$ changes sign). The magnitude of this discontinuity can be rigorously estimated knowing only the dependence of the quantities $(\partial\mu/\partial x_1)_{p,T}$ and $(\partial V/\partial x_1)_{p,T}$ on temperature (in both the metastable and labile regions).

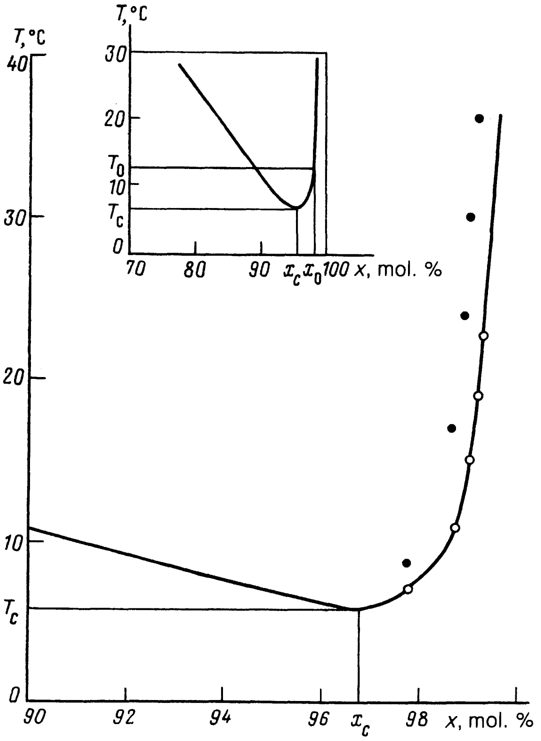

FIG. 1. Phase diagram of a solution of TMP in water; the solid curve is the binodal from Ref. 4; ○ denotes the series of experimental points T_1, ● are the corresponding spinodal points T_2. In the inset we show the general form of the binodal.

As we have already said, in our experiments the measured response was the amount of new phase of the solution induced by the laser pulse. The experimental setup (see below) was such that this amount of new phase (the light fraction) was proportional to the flux of TMP molecules into the region of irradiation during the laser pulse, leading to a concentration x_1 of the heavy fraction which was excessive for the given temperature. Consequently, the observed response should undergo a positive discontinuity at the point $T = T_s(x)$.

Let us turn now to a description of our experiment involving the solution TMP + water, for which the binodal curve $T_b(x)$ is known (see Ref. 5 and the inset to Fig. 1). In our experiment (see Fig. 2) we used a pulse-periodic ($f = 10$ Hz) YAG:Nd^{3+} laser in the Q-switched regime ($\lambda = 1.06\,\mu$m, the pulse width was $\tau = 15$ nsec, and the oscillation linewidth of the radiation equaled 3 cm^{-1}). The energy in the pulse after attenuation by filters came to $W = 20$ mJ. The irradiated solution was placed in a rather thin cuvette (in the majority of our trials we used a cuvette for which the distance between windows was 25 μm). The response consisted of the formation of microdroplets of solution of the other phase with a rather long lifetime in the irradiated region (hydrodynamic processes in this cuvette were suppressed to a significant degree). The cuvette was itself connected to a liquid thermostat and attached to a 2-coordinate stage, making it possible for us to shift the cuvette transverse to the beam. These shifts were implemented using two ShVR-711 stepping motors, which were programmably controlled (the program resided in an IBM-PC-XT computer) through a CAMAC module. The need for a way to translate the cuvette transverse to the beam will become clear in what follows.

In order to obtain a solution with a specific concentration of water x_0, we poured an initial solution (a mixture of TMP and water in a volume ratio 1:3) into a capillary tube with diameter 5 mm and left it standing at a temperature

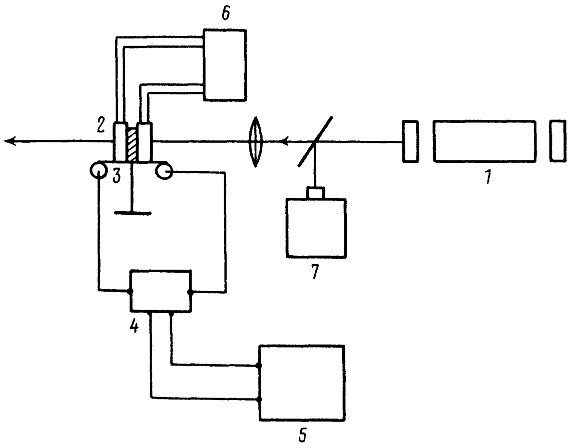

FIG. 2. Schematic experimental setup: *1*—YAG:Nd^{3+}-laser, *2*—cuvette with solution, *3*—2-coordinate stage, *4*—CAMAC module, *5*—IBM-PC-XT, *6*—thermostat, *7*—IMO-2H energy meter for measuring the laser radiation.

$T_0 > T_c$ (over the course of an hour in the majority of trials). This resulted in stratification of the solution into light and heavy fractions (LF and HF), whose concentrations are determined by the left-hand (for the LF) and right-hand (for the HF) points where the line $T = T_0$ intersects the binodal (see Fig. 1). It is important to emphasize that the concentration of heavy TMP molecules in the LF is always higher than in the HF; this is clear from the figure. All of the experimental data presented below involve values of the concentration $x_0 > x_c$; therefore we will be dealing only with the right-hand branch of the spinodal.

Next, the HF is placed in a cuvette with windows at the same temperature T_0. The cuvette itself consists of two quartz films (windows) of thickness 5 mm with a teflon lining of thickness 25 μm between them. Before placing the film in the thermostat to fix its initial temperature, we cleansed the surface of the film of dust, degreased it using acetone, and dried it under an exhaust fan. After we cleaned the films and brought them to the required temperature T_0, a drop of the HF at the same temperature was deposited at the surface of one of them (see above). After this the two films with the droplet squeezed between them were fastened with clamp mounts. The geometry of these mounts allowed us to eliminate the possibility of evaporation of the liquid from the cuvette. The mounts also had a "water jacket" circuit for coupling with the thermostat. In all the subsequent manipulations of the filled cuvette we were able to vary its temperature (to within 0.1 K) using the liquid thermostat connected to it through an external circuit. In these experiments the cuvette itself could be placed in the field of view of a microscope and simultaneously irradiated by laser pulses. The microscope was used to identify microdroplets of the HF in the solution when they appeared.

In each case it was important to verify that the settling temperature T_0 of the solution in the cuvette corresponded to the temperature of the binodal $T_b(x_0)$. At this temperature we observed a background of microdroplets with dimensions ~ 1–3 μm in the field of the microscope that was uniform over the area of the cuvette (see Fig. 3; the photographs were obtained in a dark-field microscope). Lowering the temperature by one degree caused the microdroplets to disappear. This shows that the droplets consist of the LF, which appear in the HF as a result of fluctuations at the binodal. As the temperature of the cuvette was increased from the point T_0, the density of microdroplets and their dimensions increased as well. We regarded this as experimental confirmation that the settling temperature T_0 of the solution in the cuvette coincided with the binodal temperature $T_b(x_0)$.

The cuvette was irradiated by single laser pulses selected from a pulse train by an electromechanical shutter. By doing this we were able to keep heating the solution in the irradiated region below $\Delta T \approx \varkappa W/d^2 C_V \approx 0.05$ K (where $\varkappa \approx 0.2$ cm^{-1} is the absorption coefficient, C_V is the heat capacity per unit volume, and W is the energy in the pulse). Figure 4 shows the response of the solution to a pulse "shooting through" the cuvette at a temperature $T > T_0$. A cloudiness consisting of an appreciably higher density of LF microdroplets has formed within the laser spot. The lifetime of the dark area was 5–10 min. As a quantitative characterization of this response we chose the area S of the dark region (the linear dimension of the dark area was measured using a ruler in the microscope). Because the shape of this dark spot was irregular as well as washed-out at its edges, the relative error $\Delta S/S$ in measuring S for a single laser shot was on the order of 100%. In order to increase this accuracy we collected an ensemble of statistical data based on a sequence of 250 laser pulse shots through a cuvette kept at a fixed temperature, so that each pulse in the sequence was incident on a new portion of the cuvette. Within the pauses between pulses, which lasted ~ 10 sec, we used the 2-coordinate stage to shift the cuvette in the plane perpendicular to the beam by 3–4 mm. By averaging the areas S over the set of 250 independent values, we obtained a relatively accurate measurement of the area, such that $(\langle \Delta S^2 \rangle)^{1/2}/\langle S \rangle \sim 5\%$.

Towards the end of the series of 250 pulses (and after complete relaxation of all the dark areas) we changed the temperature of the cuvette and repeated the same procedure for measuring S. In this way, we determined the temperature dependence of the area of darkness, $S = S(T, x_0)$, for each initial concentration x_0 of solution. A set of five of these dependences is shown in Figs. 5a–5e for settling temperatures $T_0 = 7$, 11, 15, 19, and 23 °C and the corresponding water concentrations $x_0 = 98$, 99, 99.15, 99.3, and 99.5

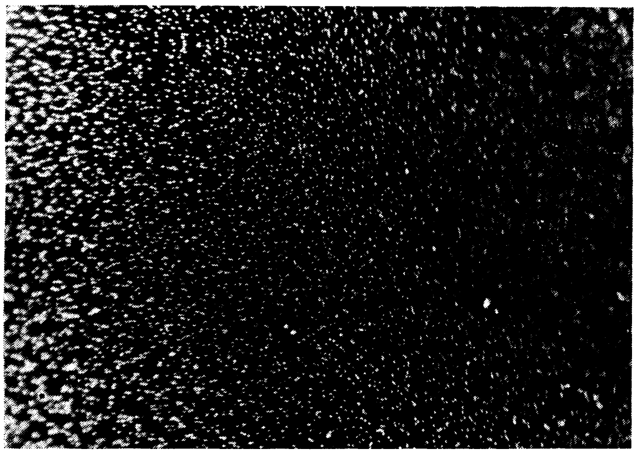

FIG. 3. General form of microdroplets of the LF in an HF solution for $T_0 = T_b(x_0)$.

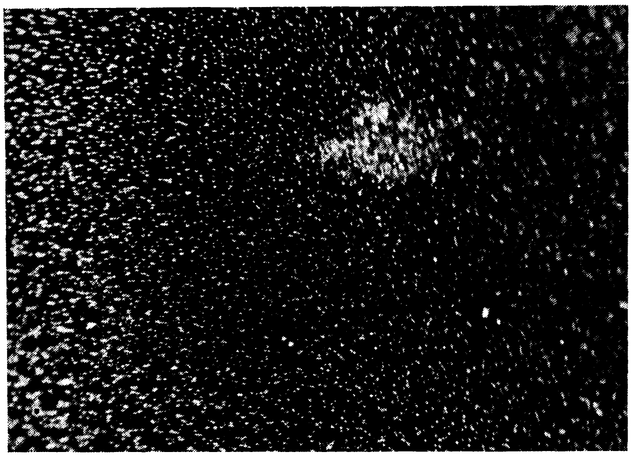

FIG. 4. Formation of a dark spot with an increased quantity of microdroplets of the LF as a result of a laser shot.

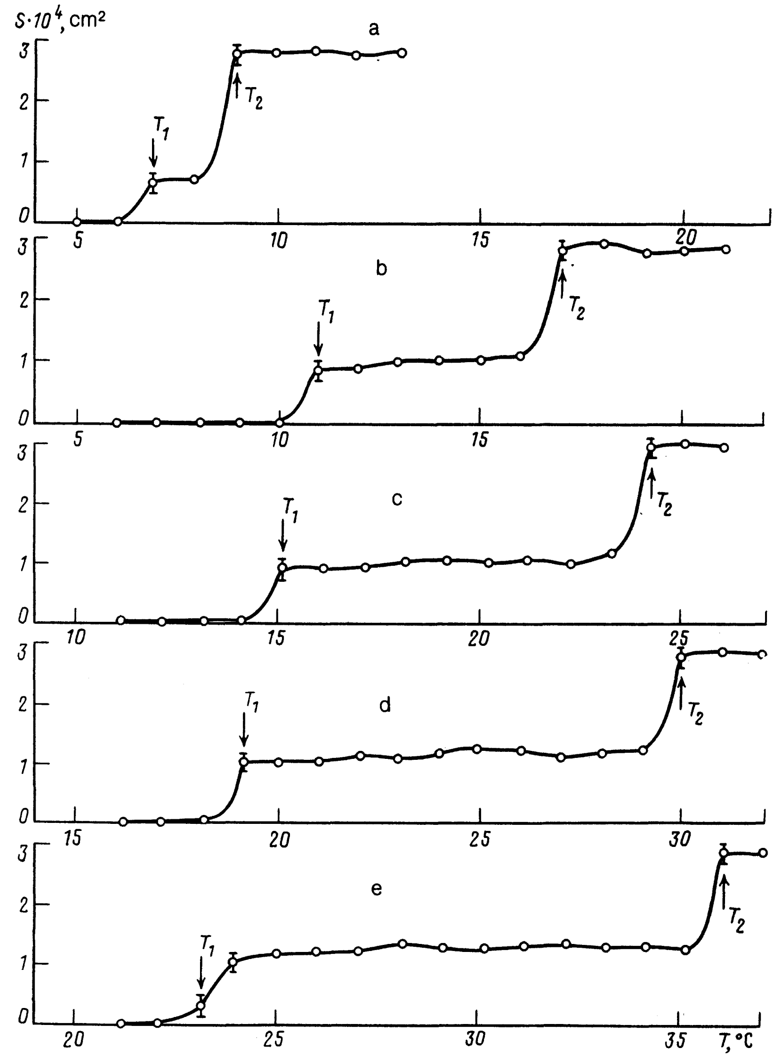

FIG. 5. Temperature dependence of the area S produced by laser action: a) $T_0 = 7\,^\circ\mathrm{C}$, $x_0 = 98$ mole %; b) $T_0 = 11\,^\circ\mathrm{C}$, $x_0 = 99$ mole %; c) $T_0 = 15\,^\circ\mathrm{C}$, $x_0 = 99.15$ mole %; d) $T_0 = 19\,^\circ\mathrm{C}$, $x_0 = 99.3$ mole %; e) $T_0 = 23\,^\circ\mathrm{C}$, $x_0 = 99.5$ mole %.

mol. %. In all five cases we began the first series of laser shots after cooling the cuvette down to a temperature $T < T_0(x_0)$ (at this temperature the droplets of LF had disappeared); each subsequent series then followed an increase in the temperature by 1 °C. It is clear from Fig. 5 that at the temperature T_1 that coincided with the temperature $T_0 = T_b(x_0)$, the magnitude of $S(T)$ rose rapidly from zero to a level of $\sim 10^{-4}$ cm² (showing that we could use the experiment as an independent way to determine the binodal temperature $T_b = T_1$). Beyond this temperature the function $S(T)$ had no features until a temperature T_2 was reached, at which $S(T)$ again exhibited a discontinuity. At higher temperatures $S(T)$ reached a plateau.

It follows from our theoretical discussion that the second discontinuity is necessarily associated with a change in the sign of $(\partial\mu/\partial x_1)_{p,T}$, i.e., with passage through a spinodal, and that the temperature T_2 can be identified with the spinodal temperature $T_s(x_0)$. As we decreased the initial concentration x_0 the experimental value of the difference $\Delta T = T_2 - T_1$ decreased, which is in agreement with the thermodynamic argument stating that the temperatures $T_s(x)$ and $T_b(x)$ should coincide at the critical point $x = x_0$. Of course the validity of our conclusions should be verified by some parallel experiment, e.g., choosing a solution with a known spinodal temperature and verifying its location using the method proposed here.

However, the following fact should be noted. In practice, for the majority of experiments the position of the spinodal of a solution is studied near the critical point (see Ref. 1), i.e., for $T - T_c \approx 0.1$–1 K, whereas the method that we are proposing here is almost useless near the critical point because it requires extremely stable specification of the temperature within the cuvette and capillary tube (to an accuracy of hundredths of a degree), which is difficult to attain by using an ordinary thermostat, as the results will be distorted by the thermal effect of the laser pulse. The discussion given above shows that our method allows us to obtain data on the position of the spinodal in the range $T - T_c \approx 10$ K with the help of standard thermostat techniques (using the methods described in Ref. 1, it would be very difficult to obtain such results for liquid solutions at the present time). Therefore, the idea of verifying this method in a parallel experiment must remain a purely speculative one at this time.

We also carried out analogous experiments using the LF, in which we poured out the fraction from the capillary tube corresponding to the intersection of the horizontal line $T_0 = \mathrm{const}$ with the left-hand branch of the binodal into a cuvette at temperature T_0. In this case we also observed a uniform background of microdroplets of the conjugate phase in the cuvette (which in this case corresponded to the HF; the HF droplets differed from droplets of the LF by their lack of an abrupt surface and their larger size). This homogeneous background also disappeared for $T < T_0$. When we fired the laser pulses through the cuvette, we found that the action of the light did not lead to an increase in the number of droplets of the conjugate phase even when the intensity of the laser radiation was increased by an order of magnitude (compared with the experiments carried out with the HF). Since increasing the amount of the conjugate phase would imply an increase in the concentration of water in this case (see Fig. 1), and since barodiffusion should, on the other hand, repel water molecules, which are the lighter component of the mixture, from the region of irradiation, the absence of an effect here provides indirect confirmation of its "barodiffusive" origin.

In conclusion we should say that, as far as we know, the experimental results presented in this paper and their theoretical interpretation constitute the first observation of laser-induced barodiffusion in a liquid mixture and the first experimental confirmation of a negative coefficient of barodiffusion of its heavy component. The details of the effects we have observed and the possibility of using them to determine spinodals in stratifying solutions as yet have not been investigated.

We the authors are grateful to F. B. Bunkin for useful discussions of this work.

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1) A rigorous proof that the sign of D_p is negative for the heavy component is available only for mixtures of ideal gases (see Ref. 4, the problem in Sec. 59). However, it can also be argued for liquid mixtures on the basis of self-evident qualitative considerations.

2) For nonstratifying solutions the coefficient D is positive for all regions of concentration and temperature.

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