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INVESTIGATION OF THE FORMATION OF LOCAL CONCENTRATIONS NEAR THE CRITICAL LIQUID-GAS POINT BY THE ELECTRON PARAMAGNETIC RESONANCE TECHNIQUE

A. Yu. SHAULOV, N. I. ANDREEVA, A. G. SKLYAROVA, A. L. BUCHACHENKO, N. S. ENIKOLOPYAN, and Yu. Kh. SHAULOV

Institute of Chemical Physics, USSR Academy of Sciences

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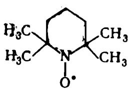
The formulation of long-lived high local concentration clusters of the stable radical in the binary systems ethane + R (stable radical) and ethylene + R is investigated near the critical liquid-gas point of the mixture by the paramagnetic probe technique. The local concentrations exceed the average radical concentrations by one or two orders of magnitude and are manifest by the strong exchange narrowing of the EPR lines. It is shown that near the critical point there exist regions with a high local concentration (clusters) and with a low concentration of the radicals. The cluster distribution with respect to density and concentration of radicals in them is assessed and the size and lifetime of the clusters are estimated. It is suggested that the stabilization of the density and concentration fluctuations which is observed reflects the existence of stable, thermodynamically favorable formations, the fluctuons. The results may be interpreted as being due to a drop in solubility of the second component in the gas mixture near the critical liquid-gas point. An EPR spectrum with a highly resolved hyperfine structure in the gas phase is obtained.

ACCORDING to the thermodynamic theory of critical phenomena, the critical point of a binary solution is characterized by the vanishing of the first and second derivatives of the chemical potential of the second component with respect to its molar fraction[1]. This leads, in particular, to the appearance in the vicinity of the critical point of such phenomena as the formation of developed density fluctuations [2,3], a strong decrease of the diffusion coefficient [4,5], the appearance of a λ singularity in the specific heat [6] and others, all of which are attributed in modern phenomenological theory of generalized critical phenomena to the change of the correlation radius in the system [7,8]. Another feature of the liquid-gas critical point, namely the extremal point on the state curve, is the exceedingly large value of the coefficient of isothermal compressibility, which leads to a gravitational effect, namely the distribution of the matter over the weight of the vessel [9-12]. The present paper is devoted to the diffusion and the concentration behaviors of the second component of a binary mixture in a phase transition with respect to critical parameters.

The systems investigated were the mixtures ethane + R and ethylene + R. The second component R was the stable radical 2, 2, 6-tetramethylpiperidine-1-oxyl



which is a paramagnetic particle. The purity of the ethane was 99.99 wt.%, that of the ethylene 99.95 wt.%, and the content of the stable radical in the mixture was about 0.2 wt.%. The ampules were filled in a vacuum not lower than 10^{-3} mm Hg with accuracy ±0.15%. The "criticality" of the sample was monitored visually and revealed by the vanishing of the meniscus after thorough stirring of the content of the ampule and sufficiently slow temperature approach to the critical point. The monitoring was in a thermostat in which the accuracy was maintained constant within ±0.001°. This procedure has made it possible to choose samples best satisfying the requirements of the experiment. The critical parameters of pure ethane are $T_{cr} = 32.2°C$ and $d_{cr} = 0.209$ g/cm^3; those of pure ethylene are $T_{cr} = 9.7°C$ and $d_{cr} = 0.215$ g/cm^3. The critical parameters of the ethane + R mixture are $T_{cr} = 32.5°C$ and $d_{cr} = 0.195$ g/cm^3, and those of ethylene + R are $T_{cr} = 9.9°C$ and $d_{cr} = 0.194$ g/cm^3.

The sample was thermostatically controlled in the resonator of an EPR spectrometer in a quartz Dewar, using a gas stream stabilized in velocity and in temperature. The thermostat accuracy was not less than ±0.003°C. To equalize the temperature field over the volume of the sample, the mixture was stirred with a solenoid. The stirrer was a steel endpiece to which a copper coil was soldered; this coil introduced no significant distortion in the antinode of the magnetic field of the resonator, the height of which was about 5 mm. The distribution of the substance over the height of the vessel was determined with the aid of the device that varied the depth of immersion of the sample in the resonator without upsetting the thermostat operating conditions (Fig. 1). The investigation was performed with the EPR-2 instrument of our Institute.

To investigate the behavior of the system, we used the paramagnetic-probe method [13-15]. In this case the probe was the second component. We note that in view of the small amount of the second component it can be assumed that the system under the conditions of the phase transition was near the critical point of the pure substance.

The EPR spectrum of the stable radical in ethane and ethylene, at the chosen radical concentration, is the first derivative of the absorption curve and consists

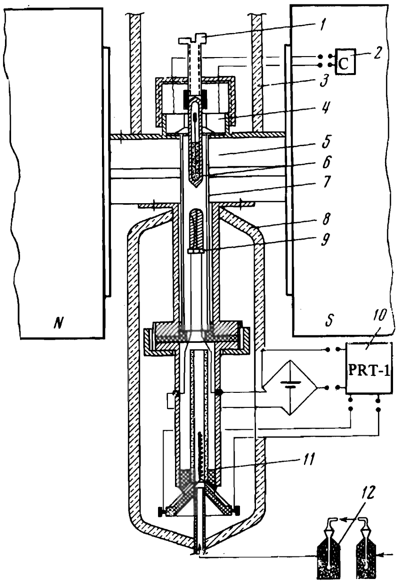


FIG. 1. Thermostat system for the ampule in the resonator of the EPR spectrometer: 1–regulator for the vertical displacement of the ampule, 2–chopper for the solenoid used to produce stirring inside the ampule, 3–"parolon" heat insulation, 4–solenoid, 5–EPR spectrometer resonator, 6–ampule with investigated substance, 7–quartz Dewar, 8–"parolon" heat insulation, 9–platinum resistance thermometer, 10–temperature regulator, 11–heater, 12–stabilizer for the flow of the heat-transfer gas.

of three lines with an isotropic hyperfine interaction constant 16 Oe at the nitrogen nucleus. (We note that this is the first time that an EPR spectrum with a well resolved hyperfine structure has been observed in the gas phase.) The width of the spectral components in the liquid increased with increasing temperature and concentration, for this increase raises the frequency of encounters of the radicals and the exchange interactions of the unpaired electrons in the radical pairs leads to a broadening of the EPR lines (case of weak exchange). The broadening is in accordance with the equation

$$\delta H_e = pKn_R, \quad p = {}^2/_3 j^2\tau_p{}^2(1 + j^2\tau_p{}^2)^{-1}, \tag{1}$$

where K is the bimolecular constant of the rate of radical encounters, p is the exchange probability, j is the average exchange energy in the radical pair, τ_p is the lifetime of the radical pair, and n_R is the concentration of the radicals. Usually $j\tau_p \gg 1$ and $p = {}^2/_3$ in a liquid, but under experimental conditions the density of the medium is much less than the density of an "ordinary" liquid and the exchange probability is possibly also lower.

Figure 2 shows the temperature dependence of δH_e and $S(n_R)$, the latter being a quantity proportional to the radical concentration for the ethane + R and ethylene + R mixtures in a wide range of temperatures (the measurements were performed in the lower part of the sample, and at small waiting times (15 min) the stirring did not lead to significant changes). In the reduction of the data we took into account the distortion of the spectrum as the result of line superposition; the area was determined on the basis of dependences obtained experimentally in model systems, using the formula

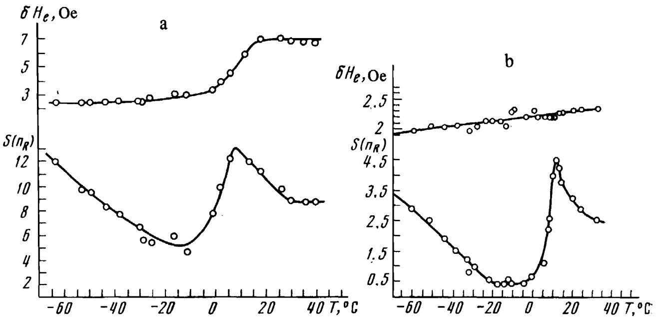


FIG. 2. Temperature dependence of the line width (δH_e) and of the radical concentration ($S(n_R)$) in the lower part of the sample: a–for ethane + R mixture, b–for ethylene + R mixture.

$$S(n_R) = \varkappa(\delta H_e) h \delta H_e^2,$$

where δH_e and h are the width and the amplitude of the first derivative of the spectrum, and $\kappa(\delta H_e)$ is a correction coefficient that takes into account the superposition of the spectral lines. We also took into account the distribution of the radical in the gas phase with increasing temperature, and the change of the magnetic susceptibility with changing temperature[16].

We note that the change of the concentration of the radical in the upper part of the ampule with rising temperature, at an average concentration of R near 1% in "noncritical" samples, has shown that this change is well described by an exponential dependence, and the heat of evaporation of the radical is 1.5 kcal/mol, which is close to the heat of evaporation of pure ethane 1.4 kcal/mol[17] (the employed method may be convenient in many cases to determine the heat of evaporation of liquids). As can be seen from Fig. 2, the concentration of the radical in the lower part, starting with $T_{cr} - T \approx 20°C$, increases and reaches a maximum near the critical point, after which it decreases. This can be attributed to the formation, in broad temperature intervals, of stable products of concentration fluctuations, which settle in the lower part of the vessel in the gravitational field. Since these results agree well with measurements of the fluctuation formations in pure ether and benzene, performed by the method of x-ray scattering at small angles[18], it can be stated that the radical is concentrated on the sections with increased density (which we shall call clusters). This means that a potential barrier is produced and prevents the radical from leaving such a cluster, and the probability of finding the radical in the cluster increases strongly. What is possibly observed here is stabilization of the density fluctuations of the clusters, which settle on the bottom during the lifetime, and the stabilization of which is due to the presence of the radical. We emphasize that the critical point is close to the extremal point on the plot of $S(n_R)$ against T.

Measurements in the immediate vicinity of the critical point were performed in two regimes: in a more uniform field in the case of thorough stirring inside the sample, and under the conditions of a temperature gradient in the absence of stirring. In addition, the

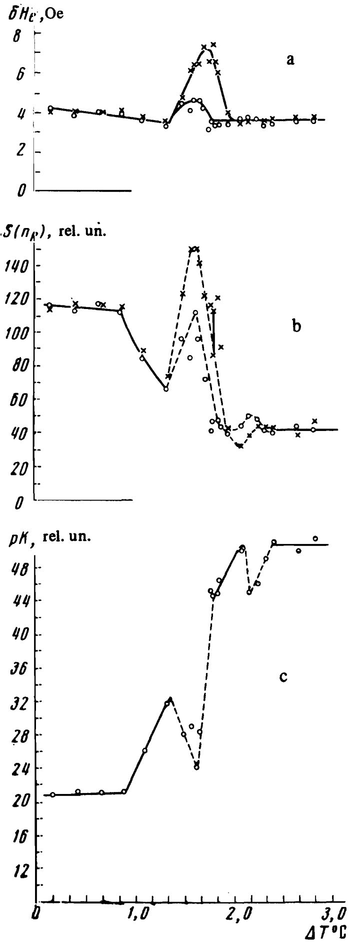


FIG. 3. Temperature dependence of the line width of the triplet spectrum of the radical (a) of its concentration (b), and of the value of pK(c) in the lower part of the ampule in the vicinity of the critical point (the experiments were performed with large temperature intervals between the measurement points and with stirring): O–measurement immediately after stirring, X–measurement after a waiting time of 10 minutes.

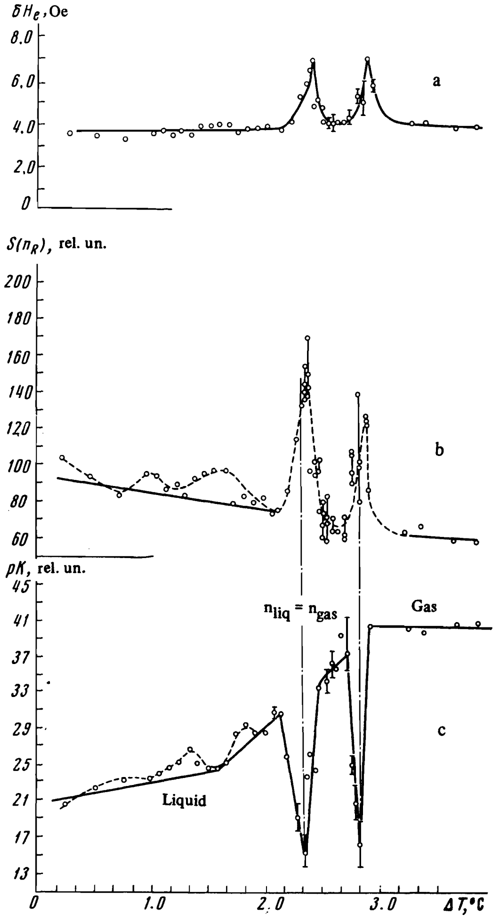


FIG. 4. Temperature dependence of the line width of the triplet spectrum of the radical (a), of its concentration (b), and of the value of pK(c) in the lower part of the ampule in the vicinity of the critical point (the experiments were performed with smaller temperature intervals between measurements and with stirring).

critical point was approached in temperature steps of varying sizes.

Let us examine the phenomena that were observed in measurements under stirring conditions, using ethane as an example. The working equation was (1), and the parameter characterizing the molecular mobility was chosen to be the product pK. An investigation of the temperature dependence of pK has revealed an abrupt change of this parameter on going from the liquid to the gas, and a sensitivity of this parameter to the properties of the medium. On the basis of the obtained data we can single out three states: liquid, gas, and transition region. From the behavior of pK in the transition region we can assess the fraction of the gas phase in the liquid and the density of the medium. The critical point of the system can apparently be regarded as the point at which the fractions of the gas and liquid phases are equal, i.e., the average value of pK in the transition region.

Figure 3 shows the temperature dependences of δH_e, $S(n_R)$, and pK in the transition region of the lower part of the ampule plotted with large temperature steps. It can be seen that an increase of the concentration, accompanied by a decrease of pK, takes place near the critical point and in a region close to the gas phase (pK was calculated under the assumption that all the radicals are in clusters). The increase of the concentration in the lower part of the ampule, i.e., the uneven distribution of the radicals over the height of the sample, was discussed by us earlier. It is seen in Fig. 3b that a wait of ten minutes after the stirring leads to an intensification of the concentration distribution of the radical in the vessel and to an increase of its content in the lower part. We see that pK in these regions is close to the value of pK for the liquid. It follows therefore that the radical in the lower part of the medium has a density close to the density of liquid ethane. In the upper part of the sample, on the other hand, there is an antibatic decrease of the radical concentration and an increase of pK, and these can be attributed to a decrease of the ethane density in this part of the ampule.

It is interesting to note the wave-like character in the temperature dependence of δH_e and $S(n_R)$ in the case of a smoother approach to the phase-equilibrium curve (Fig. 4).

An investigation of the behavior of pK on approaching the equilibrium curve has shown in certain samples

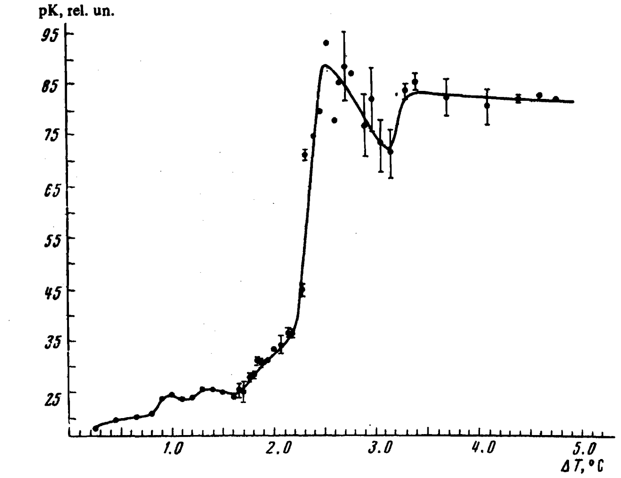


FIG. 5. Temperature dependence of pK (the measurements were performed in the lower part of the sample and with stirring).

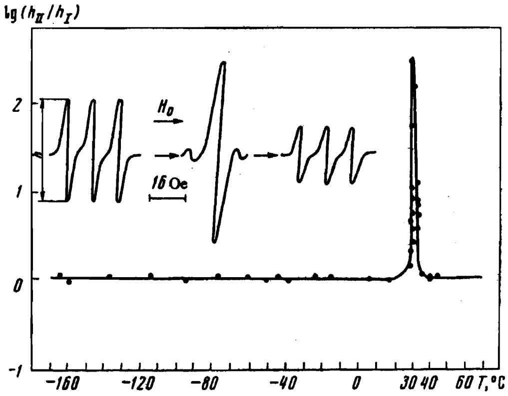


FIG. 6. Temperature dependence of the logarithm of the ratio of the intensities of the central component of the EPR spectrum (H_{II}) to the intensity of the outtermost component (H_I) (for the ethane + R mixture).

a more abrupt variation of this parameter, apparently due to the fact that the experiment was performed far from the critical region, where a sharp transition through the phase equilibrium curve should be observed. There is an interesting strongly increased scatter of the data near the pure gas phase—"turbulent zone"—and is accompanied by a small decrease of pK (Fig. 5).

On the basis of the obtained data we can conclude, accurate to a factor of 2, that there are no anomalous changes in the molecular mobility of the second component in the ethane clusters near the liquid-gas critical point. However, as shown earlier, the macrodiffusion of the radical is determined by the clusters. The clusters themselves are in this case sufficiently stable long-lived structure formations. Thus, it is meaningful to speak of two types of molecular-kinetic organization at the critical point, and, depending on the organization of the experiments, one can measure diffusion of either submolecular type (diffusion from the clusters) or of molecular type (diffusion in the clusters). The inconsistency observed in the literature is apparently connected precisely with this fact. Thus, measurements by the diffusion-cell method[5,19] and measurements based on the kinetics of iodine and chlorine atoms recombination[20,21], in which strong effects were noted, can be regarded as diffusion measurements of the submolecular type.

On the other hand, measurements of the molecular diffusion type yielded the following results. In the investigation of the self-diffusion coefficient, by the NMR method, in pure Xe[22] and SF_6[23], and also by the spin-echo method in CH_4[24], the authors reached the conclusion that there is no anomalous behavior of the molecular mobility near the critical point. However, when the spin-echo method was used, a deviation from the ρ-D dependence was observed in a C_2H_6-O_2 mixture (ρ is the density and D the self-diffusion coefficient of oxygen)[25], a fact that can be attributed to density changes in analogy with the changes of pK in the present study (cf. Figs. 3 and 4). A similar conclusion was arrived at by measurements of the diffusion coefficient of ^{36}Ar in the natural mixture (capillary method)[26]. Investigations of the quasi-elastic scattering of neutrons in CO_2 have shown a decrease in the broadening of the quasielastic peak[27], something that can be attributed to a decrease of the self-diffusion of CO_2, but the result was not confirmed in pure C_2H_6 when the same method was used[28]. The cited published data and the results obtained in the present study apparently allow us to state that there is no anomalous variation of the molecular mobility of matter near the liquid-gas critical point, accurate to a coefficient 2—3.

We consider next the phenomena observed in measurements near the critical point under the conditions of a temperature gradient ($\Delta T = 0.1°C$), using ethane as an example. Measurements under these conditions have revealed that the EPR spectrum experiences abrupt changes, the triplet line intensity decreases sharply, and a very intense singlet line appears at the center of the triplet spectrum (Fig. 6). Beyond the critical point (in the gas phase), the singlet line disappears and the ordinary triplet spectrum characteristic of radicals in a liquid is restored. As seen from Fig. 6, near the critical point, the total EPR spectrum is a superposition of an intense singlet line at the center over the ordinary low-intensity triplet spectrum (the figure shows its two outermost components, and the central component is covered by the singlet). Such a behavior of the spectrum means that near the critical point the radical is in the main in a state of concentrated solution, and its smaller fraction is in a state of dilute solution, i.e., strong inhomogeneities of the radical concentration in the volume are observed. We assume that the sections with increased local radical concentration (singlet) are clusters and the sections with the decreased local concentration (triplet) are radicals which do not fall into the clusters and are located in the space between the clusters. We see that in the clusters, owing to the high local concentration of the radicals, the frequency of their encounters is large, the volume interactions average out the hyperfine interaction, the triplet lines "contract" towards the center, and the EPR spectrum should constitute a singlet with line width

$$\Delta H_s = a^2 / pKn_R, \tag{2}$$

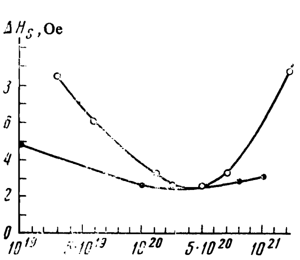


FIG. 7

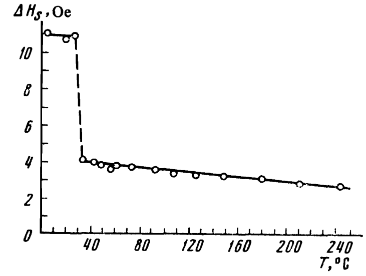


FIG. 8

FIG. 7. Dependence of the line width of the singlet EPR spectrum (ΔH_S) of the radical on its concentration in different solvents at room temperature (O—in heptane, +—in diethyl ether).

FIG. 8. Temperature dependence of the line width of the EPR spectrum of the pure radical.

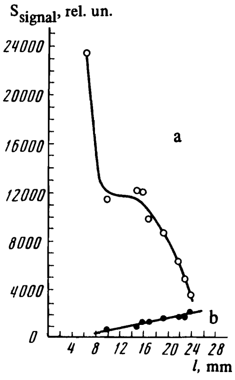


FIG. 9

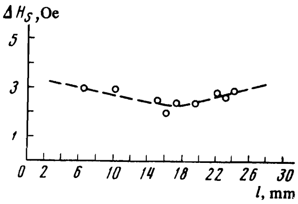


FIG. 10

FIG. 9. Dependence of the concentration of the radicals in the clusters (a) and in the space between the cluster (b) on the distance l to the bottom of the ampule.

FIG. 10. Dependence of the width of the singlet line of the anomalous spectrum, obtained near the critical point, on l.

where a is the hyperfine-interaction constant. Since, as we have seen earlier, the translational mobility of the radicals in the clusters is approximately the same as in liquid ethane near T_{cr}, we can estimate, using Eq. (2), the local concentration of the radical in the cluster from the width ΔH_S of the singlet. We present below the principal investigated characteristics of the clusters.

A. Local Concentrations of Radicals in Clusters

To determine this parameter, we simulated the exchange broadening of the spectral line in the clusters and investigated the dependence of ΔH_S (in the region of strong exchange) on the radical concentration in liquid solutions (heptane, diethyl ether), and also in the pure radical below and above the melting temperature (Figs. 7 and 8). An analysis of the line widths has shown that the substance in the cluster is not a pure radical, since ΔH_S in the cluster is much smaller than ΔH_S in the radical solution. This means that the concentration of the radical in the cluster is high enough to cause the exchange interactions to make the line much narrower, but still not concentrated enough for the dipole interactions to start to broaden them (as in the pure radical). From a comparison of ΔH_S in the cluster with ΔH_S in n-heptane and in diethyl ether (Fig. 7), we can conclude that the local concentrations in the cluster are of the order of 5×10^{19}–5×10^{20} spins/cm^3. Thus, the local concentration is 10–100 times larger than the average concentration, and the content of the radial in the cluster is 1–10% of the ethane. It is obvious that the presence of stable local concentrations in the system is evidence of a strong decrease of the macroscopic diffusion coefficient of the radical.

B. Distribution of Clusters with Respect to Density and Concentration

The EPR spectrum near the critical point was investigated at different points along the height of the ampules. Superposition of the spectra was observed up to 25 mm from the bottom at an approximate total ampule length 60 mm. We observed two interesting phenomena. First, it turned out that the relative fractions of the radicals in the cluster and in the medium between the clusters vary with the height. The fraction of the radicals in the clusters decreases with increasing distance from the bottom of the ampule l (Fig. 9a), while the fraction of the radicals in the medium between the clusters exhibits an inverse linear dependence (Fig. 9b). This result can be interpreted as indicating that the long-lived clusters settle to the bottom of the ampule in the gravitational field so that the cluster density acquires a height distribution. These data agree qualitatively with the density distribution of pure ethane over the height of the vessel [29] [1] and with the distribution of the impurity concentration in CO_2 [12].

Second, the width of the singlet is somewhat different in different points of the ampule and its variation recalls the concentration dependence of the line width in heptane and in ether (see Sec. 7). Apparently, the clusters distributed over the height have different local radical concentrations. However, the slight difference in ΔH_S at different heights in the vessel (Figs. 9, 10) and the weak dependence of ΔH_S on n_R near the point of maximum ΔH_S (Fig. 8) do not lead to an unambiguous conclusion concerning the concrete form of the cluster concentration distribution.

C. Cluster Dimensions

An estimate of the average cluster dimensions was obtained with the aid of the parametric formula

$$\frac{n_{h1}}{n_{h2}} = \exp\left(-\frac{mgh}{kT}\right), \tag{3}$$

where m is the mass of the cluster and n_{h1} and n_{h2} are the radical concentrations in the clusters in the upper and lower points of the measurement. We start here from the assumption that the dependence of S_{singl} and of the local radical concentration n_h on the height reflect the distribution of the cluster density over the height of the vessel. In the calculation it was assumed that the cluster density is 0.20 g/cm^3. The cluster diameter calculated with the aid of (3) is approximately 700 Å. These estimates coincide in order

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[1] In [29] there are cited results obtained by H. B. Palmer.

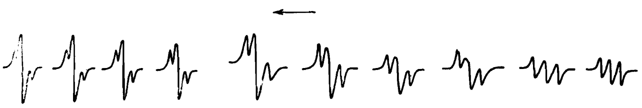


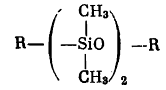
FIG. 11. Kinetics of reconstruction of the anomalous spectrum after stirring (the time between the recording of two spectra is ~30 sec).

of magnitude with estimates of the density fluctuation diameters in ethylene [3], ether [9], xenon [30], and CO_2 [31], and confirm once more the conclusion that the radical is concentrated in sections with increased density, where it becomes stabilized.

D. Cluster Lifetime

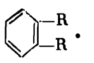
The EPR spectrum near the critical point is a superposition of the spectra of the radical in two states, and both states are observed simultaneously. To this end it is necessary that the exchange between states be slow, i.e., that the lifetime τ of the cluster be much longer than the reciprocal constant of the hyperfine interaction, i.e., $\tau \gg a$ or $\tau \gg 2.3 \times 10^{-8}$ sec. We note that the condition for the transition from the region of weak exchange into the region of strong exchange depends on the hyperfine-interaction constant of the employed radical (Eq. (2)). This means that the singlet-triplet transition is not observed at sufficiently small average radical concentrations, when the local concentrations in the clusters are insufficient to satisfy the strong-exchange condition. Stirring the system under conditions when the superposition of the spectra is observed leads to a vanishing of the singlet (the local concentration is insufficient for the singlet-triplet transition); the singlet is then restored under static conditions within ~2 minutes. Figure 11 shows the kinetics for the establishment of the anomalous spectrum and apparently reflects the kinetics of establishment of the temperature gradient over the height of the sample and the rate of settling of the clusters to the bottom. We note that an increase of the gradient leads to a sharp intensification of the foregoing effects. It is interesting that the changes in the spectrum after stirring are analogous to the changes occurring when the critical temperature is approached. We might add that the phenomenon of concentration and percipitation of the radical is observed also when the radical has much larger average concentrations.

The formation of long-lived regions with increased local radical concentration can be interpreted as a decrease of the solubility of the second component and its "percipitation" from the system near the liquid-gas critical point. Analogous phenomena were observed by us in the systems ethane + the biradical



$$R-\left(-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{Si}}}}O\right)_2-R$$

and ethylene + the biradical



We note that ordinary concentration fluctuations cannot explain the observed strong concentration of the substance. A possible explanation may be the formation of clusters with very large lifetimes and high surface tension, which leads to the appearance of a potential barrier hindering the emergence of the radical into the volume. On the other hand, a temperature drop deviates the system from the critical point towards the liquid and leads to an increase of the barrier, i.e., to an increase of the observed effect. Such an interpretation of the data can be reconciled with the theoretical conclusion of the feasibility of stable thermodynamically favored formations, fluctuons, near the critical points and phase-transition points, due to the interaction of the free electrons with regions in which the order, composition, or magnetization is disturbed[32-35]. In addition, it has been shown that under certain conditions, when the concentration is varied, a boundary between the two phases is produced in the vicinity of the fluctuon at a certain distance from its center [34]. It can be assumed that the role of the free electron is played in our case by the second component--the stable radical.

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[1] J. W. Gibbs, Scientific Papers, Vol. 1, Thermodynamics, Dover.

[2] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Nauka, 1964 [Addison-Wesley, 1969].

[3] H. Cataldi and H. G. Drickamer, J. Chem. Phys. 18, 650 (1950).

[4] I. R. Krichevskiĭ and N. E. Khazanova, in: Kriticheskie yavleniya i fluktuatsii v rastvorakh (Critical Phenomena and Fluctuations in Solutions), AN SSSR, 1960, p. 45.

[5] N. E. Khazanova and L. S. Lesnevskaya, Zh. Fiz. Khim, 40, 464, 2330 (1966).

[6] M. I. Bagatskiĭ, A. V. Voronel' and V. G. Gusak, Zh. Eksp. Teor. Fiz. 43, 728 (1962) [Sov. Phys.-JETP 16, 517 (1963)].

[7] L. P. Kadanoff and J. Swift, Phys. Rev. 166, 89 (1962).

[8] V. L. Pokrovskiĭ, Usp. Fiz. Nauk 94, 127 (1968) [Sov. Phys.-Usp. 11, 66 (1968)].

[9] C. A. Winkler and O. Maass, Canad. Journ. of Res. 9, 613 (1933).

[10] H. L. Lorentzen and B. D. Hansen, in: Critical Phenomena, ed. by M. S. Green, J. V. Sengers, Proc. of a Conf., Washington, 1966, p. 213.

[11] I. V. Zavalin and Yu. I. Shimanskiĭ, Ukr. Fiz. Zh. 9, 491, 1122 (1964).

[12] D. L. Timrot and K. F. Shuĭskaya, Inzh. Fiz. Zh. 10, 478 (1966).

[13] D. E. Pake and T. R. Tuttle, Phys. Rev. Lett. 3, 9, 423 (1959).

[14] C. H. Johnson, Mol. Phys. 12, 125 (1963).

[15] A. M. Vasserman, A. L. Kovarskiĭ, A. L. Buchachenko and M. B. Neiman, coll. Vysokomolekulyannye soedineniya (High-molecular Compounds), IKhF, AN SSSR, 1970.

[16] Kazuo Mukai, Bull. Chem. Soc. Japan 42, 40 (1969).

[17] M. E. Tester, Thermodynamics Functions of Gases, 3, ed. by F. Din, London, 1961.

[18] N. V. Mokhov and Ya. M. Lobkovskiĭ, Ukr. Fiz. Zh. 9, 465 (1964).

[19] I. R. Krichevskiĭ, N. E. Khazanova and L. R. Lin-

shitz, Dokl. Akad. Nauk SSSR **141**, 397 (1961).

[20] I. R. Krichevskiĭ and Yu. V. Tsekhanskaya, Inzh. Fiz. Zh. 5, 105 (1962).

[21] I. R. Krichevskiĭ, Yu. V. Tsekhanskaya, and Z. A. Polyakova, Zh. Fiz. Khim 6, 1333 (1966).

[22] R. S. Erlich and H. Y. Carr, Phys. Rev. Lett. 25, 341 (1970).

[23] J. K. Tison,and E. R. Hunt, J. Chem. Phys. 54, 1526 (1971).

[24] N. J. Trappeniers and P. H. Oostung, Phys. Lett. 23, 455 (1966).

[25] J. D. Noble and M. Bloom, Phys. Rev. Lett. **14**, 250 (1965).

[26] M. de Paz, ibid. 20, 183 (1968).

[27] L. Bata, E. Koszo, L. Kroo, and L. Pal, Phys. Letters 24A, 57 (1967).

[28] L. A. Bulavin, A. V. Voronel', Yu. M. Ostanevich, A. P. Silkina, and A. V. Strelkov, Reprint from Neutron Inelastic Scattering 1, 525 (1968).

[29] J. O. Hirschfelder, C. Curtiss, and R. Byrd, Molecular Theory of Gases and Liquids, Wiley, 1964.

[30] Y. Yeh, Phys. Rev. Lett. 18, 1043 (1967).

[31] H. Swing and H. Z. Cummins, Phys. Rev. 171, 152 (1968).

[32] M. A. Krivoglaz, Fiz. Tverd. Tela 11, 2230 (1969) [Sov. Phys.-Solid State 11, 1802 (1970)].

[33] M. A. Krivoglaz and A. A. Trushchenko, ibid. 11, 3119 (1969) [11, 2531 (1970)].

[34] A. M. Dykhne and M. A. Krivoglaz, ibid. 12, 1705 (1970) [12, 1349 (1970)].

[35] M. A. Krivoglaz and A. A. Trushchenko, ibid. 15, 1940, 1956 (1970) [sic!].

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