A STATISTICAL EVALUATION OF THE PHENOMENOLOGICAL COEFFICIENTS OF PHOTODISSOCIATION IN THE CRITICAL REGION

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At the critical point of a binary solution, molecular diffusion is stopped (see review [1]). This ought certainly to exert a considerable effect on the kinetics of processes taking place in the critical phase. Thus, for example, bimolecular reactions in which one of the components of the binary solution takes part should be greatly retarded or perhaps completely prevented.

An unusual confirmation of this is provided by the work of Krichevskii et al. [2] on the photodissociation of an infinitely dilute component in the critical phase of the solvent; using the dissociation of iodine in solution in carbon dioxide (molar fraction of iodine $N_b \cong 10^{-6}$), they have shown that the recombination after irradiation is greatly retarded, which is quite different from the behavior above the critical region. Similar results were also obtained on pure chlorine [3].

In the former case, a ternary metastable system is formed (I_2-I-CO_2), while in the latter, photodissociation results in the formation of the binary system ($Cl-Cl_2$). The formation of a new system leads to a shift in the critical point which was also measured in these experiments. This shift occupies a considerable time, which confirms the view developed in [4, 5] about the movement of Brownian particles in the critical phase.

The phenomenological theory starts from the view that the concentration of atoms formed during photodissociation is proportional to the change in the critical temperature (we shall consider below the transition from a pure substance into a binary dilute system), that is,

$$\Delta n_b = k\Delta T, \tag{1}$$

where Δn_b is the number of atoms produced by dissociation (so that the number of dissociated molecules is, correspondingly, $\Delta n_a = \Delta n_b/2$; the subscript a refers to the solvent); $\Delta T = T - T_{cr}$ (where T_{cr}^a is the critical temperature of the pure solvent, and T that of the solution); k is a proportionality constant which has to be determined.

It is then suggested that the rate of formation of the atoms is proportional to the number of absorbed light quanta,

$$\frac{d\Delta \dot{n}_b}{dt} = 2M, \tag{2}$$

where M is the number of moles of light (einstein $\cdot$ cm$^{-3} \cdot$ sec^{-1}).

The recombination process is described by the equation

$$\frac{d\Delta n_b}{dt} = -\lambda\Delta n_b^2. \tag{3}$$

When a stationary regime is set up, the following relation applies [taking account of Eq. (1)]:

$$M = 2\lambda k^2\Delta T^2. \tag{4}$$

From the quantities in (4), as already indicated, experiment gives directly only the value ΔT. It follows that the determination of the remaining parameters is a very important task.

Information about dissociation coefficients may be obtained statistically. With this in view we refer to the statistical theory of phase transitions which uses as its basis the so-called method of conditional distribution [6, 7]. In this method we consider, not the position of individual groups of molecules, but a collection of selected positions for all particles. If the total volume V is divided into n equal cells (where n is the number of particles), then in the case of condensed systems, the principle importance in the configuration integral attaches to those distributions of molecules which lead to the presence of one particle in each cell.

In this approximation for a binary solution, the temperature of phase transition (including the critical temperature) is determined by the expression

$$T = -\frac{1}{2k v}\left[N_a K_{aa} + N_b K_{bb} + \sqrt{N_a^2 K_{aa}^2 + N_b^2 K_{bb}^2 + 2N_a N_b(2K_{ab}^2 - K_{aa}K_{bb})} \right], \tag{5}$$

where v is the molecular volume; N_i is the mole fraction of the i-th component ($N_b \ll 1$); k is the Boltzmann constant; and the functionals K are determined through the intermolecular potentials of the corresponding homogeneous mixed sorts of particles.

At the critical point of the pure a component (solvent) $K_{ab} = K_{aa}$ [8]. Then

$$T_{\text{cr}}^a = -\frac{1}{kv} K_{au}. \tag{6}$$

By making use of the resolution of (5) into a series with respect to N_b, and the condition given by (6), we find the value of the shift of the critical temperature due to a change in the composition of the mixture (caused by the dissociation of Δn_a molecules into Δn_b atoms). Using only the first two terms of the expression we may write

$$\Delta T = 2T_{\text{cr}}^a \Delta n_b. \tag{7}$$

From this it follows that the desired proportionality constant in the phenomenonological expression (1) is

$$k = \frac{1}{2T_{\text{cr}}^a}. \tag{8}$$

Knowledge of k makes it possible to evaluate the other quantities. If, in harmony with the theory of Smolukhovskii [9], we assume that the recombination of atoms occurs in a similar way to the coagulation of colloidal particles, then

$$\lambda = 8\pi NDr, \tag{9}$$

where N is the Avogadro number, D is the diffusion coefficient, and r is the radius of the atom.

From the experimental data of Krichevskii we have calculated the value of $b-\lambda k$. Thus for chlorine (in the binary system $Cl-Cl_2$) when $\Delta T \sim 10^{-2}$ degrees, the value of b is of the order of 10^{-1} $\deg^{-1} \cdot \sec^{-1}$. This in its turn makes it possible to evaluate λ, and also the diffusion coefficient D. For the example given, $D \sim 10^{-15}$ $cm^2 \cdot \sec^{-1}$, and is many orders of magnitude smaller than the diffusion coefficient above the critical region, which confirms the fact that diffusion practically ceases in the critical region. For the value of M we obtain by a corresponding calculation 10^{-8}.

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