Critical slowing down of chemical reactions

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An analysis is made of the conditions of anomalous slowing down of chemical reactions near the critical points of solution. Such slowing down is possible at isolated points of the critical hypersurface of a solution. The most likely effect to be observed is the slowing down of the reactions of separation of weakly dissolved components from a solvent.

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It is well known that the diffusion processes in liquids slow down greatly near the critical points. This suggests the possibility of anomalous slowing down of chemical reactions occurring under near-critical conditions. Krichevskiĭ *et al.*[1,2] were the first to observe such critical slowing down of chemical reactions and they explained this effect by the slowing down of the diffusion of molecules of the reacting components. This point of view was criticized by Leontovich[3] who pointed out that the diffusion understood as the motion of separate molecules is never slowed down and the reduction in the rate of equalization of the concentration gradients by diffusion is associated with an anomaly of the quantity $\partial\mu/\partial c$ (μ is the chemical potential and c is the concentration). Recently Procaccia and Gitterman[4] attempted to explain from a similar standpoint the slowing down of chemical reactions. It seems to us that in spite of the correct general approach, Procaccia and Gitterman's treatment suffers from a number of inaccuracies, so that it is worth to consider the subject once again. We shall show that the slowing down of a chemical reaction near a critical point may occur provided certain additional fairly stringent conditions are satisfied, so that the slowing down is observed only at isolated points of intersection of the critical hypersurface with the hypersurface of chemical equilibrium. In addition to a general analysis, we shall discuss in detail the case of reactions in dilute solutions. We shall show that the effect most likely to be observed is the slowing down of reactions in which weakly dissolved components separate out in a solvent.

1. GENERAL ANALYSIS

We shall consider a chemical reaction in a n-component mixture and we shall describe this mixture by

$$\nu_i M_i = 0,$$

where ν_i are integers and M_i are the substances. We shall assume that the number of particles of a substance M_i is N_i. We shall define a chemical reaction of the coordinate ξ by

$$V^{-1} dN_i = \nu_i d\xi + e_i^{(\alpha)} \eta^{(\alpha)}. \tag{1}$$

The vectors $\{\nu_i, e_i^{(\alpha)}\}$ form an orthogonal basis in the N_i vector space and V is the volume of the system. Near a chemical equilibrium described by

$$A = \nu_i \mu_i = 0 \tag{2}$$

(μ_i are the chemical potentials of the substances M_i) the reaction rate is proportional to A:

$$\frac{d\xi}{dt} = -\Gamma A = -\Gamma \nu_i \frac{\partial \mu_i}{\partial N_k} (N_k - N_k^{(0)}). \tag{3}$$

Introducing the matrix $\chi_{ik}^{-1} = V(\partial\mu_i/\partial N_k)_{P,T}$ and using Eq. (1), we obtain

$$\frac{d\xi}{dt} = -\Gamma \nu_i \chi_{ik}^{-1} \nu_k (\xi - \xi_0) - \Gamma \nu_i \chi_{ik}^{-1} e_k^{(\alpha)} (\eta^{(\alpha)} - \eta_0^{(\alpha)}). \tag{4}$$

As is usual in the Landau–Khalatnikov theory, we shall assume that Γ is a constant. The reaction does not alter the values of the "orthogonal" coordinates $\eta^{(\alpha)}$ so that if the diffusion is ignored, we can assume that the quantities $\eta^{(\alpha)}$ have the equilibrium values $\eta_0^{(\alpha)}$ ($\eta^{(\alpha)} - \eta_0^{(\alpha)} \neq 0$ leads simply to a shift of ξ_0).

Our task will be to investigate the behavior of the quantity

$$\chi_r^{-1} = \nu_i \chi_{ik}^{-1} \nu_k$$

near the critical points. We note first of all that the natural variables which specify the chemical reaction conditions are the pressure P, temperature T, and concentration $c_i = N_i/N$ ($N = \sum_i N_i$). The proportion of changes in the numbers of all the particles $N_i \to \lambda N_i$ under conditions of constant P and T do not alter the chemical potentials μ_i, so that the matrix χ_{ik}^{-1} is always degenerate:

$$\chi_{ik}^{-1} N_k^{(0)} = 0. \tag{5}$$

We must stress that the degeneracy condition (5) is always satisfied and does not imply any instability of the state of matter. The critical state of a substance is characterized by the appearance of a second eigenvector X_i with the zeroth eigenvalue:

$$\chi_{ik}^{-1} X_k = 0. \tag{6}$$

Denoting the corresponding coordinate X_i by φ we find the conditions for a critical point in the form

$$\frac{\partial^2 \Phi}{\partial \varphi^2} = 0, \quad \frac{\partial^3 \Phi}{\partial \varphi^3} = 0; \quad \Phi = \sum_i N_i \Phi_i (P, T, c_i), \tag{7}$$

where Φ is the free energy of the system.

The two conditions in Eq. (7) define a critical $(n-1)$-dimensional hypersurface in the space of $n+1$ parameters P, T, and c_i defining the state of the system. If the chemical equilibrium condition (2) is satisfied anywhere on the critical hypersurface, then we have to consider the question of the critical kinetics of states with a weak chemical nonequilibrium.

At an arbitrary point on this hypersurface the matrix

χ_{ik}^{-1} has two zero eigenvalues which define the "zero" plane $\alpha N_i^{(0)}+\beta X_i$; the other eigenvalues of this matrix are positive. Therefore, the critical slowing down of a chemical reaction associated with vanishing of the quantity

$$\chi_r^{-1}=\nu_i\chi_{ik}^{-1}\nu_k$$

at a critical point occurs when and only when the vector ν_i can be represented in the form

$$\nu_i=\alpha N_i^{(0)}+\beta X_i.$$

This imposes additional $n-2$ restrictions on the parameters of the system, leaving one free parameter which is fixed by the condition (2).

Therefore, for any value of n the critical slowing down may occur at isolated points on the critical hypersurface of a system.

It should be noted that in the important case of a two-component ($n=2$) mixture any critical point close to a chemical equilibrium is also a reaction slowing-down point, as pointed out in Ref. 4. In this case an anomaly of the relaxation time $t_r=(\Gamma\chi_r^{-1})^{-1}$ is in the form of $t_r \propto \tau^{-\gamma}$, where τ is the proximity to a critical point and $\gamma\approx 1.3$ is a critical susceptibility index for a one-component system.[5] If $n>2$, the nature of the anomaly depends on the direction in which the parameters of a system approach the critical slowing-down point. If the approach occurs along the critical hypersurface, i.e.,

$$\nu_i=\alpha N_i^{(0)}+\beta X_i+\tau Y_i,$$

where Y_i is orthogonal to $N_i^{(0)}$ and X_i, then

$$\nu_i\chi_{ik}^{-1}\nu_k=\tau^2 Y_i\chi_{ik}^{-1}Y_k$$

and $t_r\propto\tau^{-2}$. In all other cases, we have $t_r\propto\tau^{-\gamma}$.

2. SLOWING DOWN OF REACTIONS IN A DILUTE SOLUTION

The above general analysis shows that the critical slowing down of a chemical reaction occurs at isolated points of the critical hypersurface but it does not give the conditions of existence of such points. In this section we shall consider in greater detail the case of a dilute solution near a critical point of a solvent and in analyzing the critical point we shall confine ourselves to the self-consistent field approximation. A change in the free energy Ω in the case of small density fluctuations of the components of a dilute solution is given by

$$\delta\Omega=\frac{\tau}{2}(\delta n_0)^2+\tilde{g}_i\delta n_0\delta n_i+\sum_{i=1}^{n-1}\frac{(\delta n_i)^2}{2n_i}. \tag{8}$$

Here, δn_0 is a fluctuation of the solvent density n_0, δn_i ($i=1,\dots,n-1$) are fluctuations of the densities n_i of the solutes, which obey the condition $n_i\ll n_0$. Proximity to the critical point of a solvent means that $\tau\ll 1$. The quantities $\tilde{g}_i n_0$ representing the interaction of a solute with the solvent are of the order of $T\ln c_i\gtrsim T$. The expression (8) is simplified by omitting unimportant terms of the type $g_{ik}\delta n_i\delta n_k$ ($i\neq k$). We shall write down Eq. (8) in the form

$$\delta\Omega={}^1/_2(\delta n_\alpha)\tilde{\chi}_{\alpha\beta}^{-1}(\delta n_\beta),\quad \alpha,\ \beta=0,\ 1,\dots,n-1, \tag{9}$$

$$\tilde{\chi}_{\alpha\beta}^{-1}=\frac{1}{V}\left(\frac{\partial^2\Omega}{\partial n_\alpha\,\partial n_\beta}\right)_{V,T}=\left(\frac{\partial\mu_\alpha}{\partial n_\beta}\right)_{V,T}. \tag{10}$$

It follows from Eq. (8) that

$$\tilde{\chi}_{00}^{-1}=\tau,\quad \tilde{\chi}_{0i}^{-1}=\tilde{g}_i,\quad \tilde{\chi}_{ik}^{-1}=\delta_{ik}n_i^{-1}. \tag{11}$$

It should be stressed that Eq. (10) defines the matrix $\tilde{\chi}_{\alpha\beta}^{-1}$ which is not identical with the matrix χ_{ik}^{-1} introduced earlier because the derivatives in Eq. (10) are obtained under constant-volume rather than constant-pressure conditions. A critical point of a solution is given by the degeneracy of the matrix $\tilde{\chi}_{\alpha\beta}^{-1}$:

$$\det\tilde{\chi}_{\alpha\beta}^{-1}=\left(\tau-\sum_k\tilde{g}_k^2 n_k\right)\prod_j\frac{1}{n_j}=0. \tag{12}$$

In calculating the determinant we shall retain only the principal terms, assuming τ and n_i are small quantities of the same order of magnitude. Thus, at a critical point we should have

$$\tau-\sum_k g_k^2 c_k=0, \tag{13}$$

where we have introduced the concentrations $c_k=n_k/n_0$ and denoted $\tilde{g}_k n_0^{1/2}$ in terms of g_k. The "critical" vector **x** in the density space has the components

$$\mathbf{x}=(1,\ -g_1c_1,\dots,-g_{n-1}c_{n-1})=(1,\ -g_ic_i). \tag{14}$$

The stability of a system at a critical point requires vanishing of the derivative $\partial^3\Omega/\partial\varphi^3$, where φ is the critical coordinate corresponding to **x**. The cubic terms in the expansion of $\partial\Omega$ are

$$\delta\Omega^{(3)}=\theta(\delta n_0)^3+(\delta n_0)^2\sum_i p_i\delta n_i+O(c^2), \tag{15}$$

where $\theta\ll 1$ because of the proximity to a critical point of the pure solvent; p_i are certain coefficients. Allowing for Eq. (14), we have

$$\delta\Omega^{(3)}=(\delta n_0)^3\left[\theta-\sum_i p_ig_ic_i+O(c^2)\right]. \tag{16}$$

Thus, the critical set is defined by the conditions

$$\tau-\sum_k g_k^2c_k=0,\quad \theta-\sum_k g_kp_kc_k=0. \tag{17}$$

The condition for critical slowing-down of a reaction obtained in Sec. 1 is

$$\alpha(1,\ c_i)+\beta(1,\ -g_ic_i)=(\nu_0,\ \nu_i), \tag{18}$$

where α and β are arbitrary numbers. The chemical equilibrium condition

$$\nu_0\mu_0+\sum_k\nu_k\mu_k=0,$$

can—as is known—be written down in the form of the law of mass action

$$\prod_k(c_k)^{\nu_k}=K, \tag{19}$$

where K is the equilibrium constant.

For example, a chemical reaction in a dilute solution near an equilibrium point undergoes critical slowing down when the conditions (17)–(19) are satisfied simultaneously. We shall now test this system of equations for compatibility. We shall assume that $\nu_0\neq 0$. It then follows from Eq. (18) that

$$c_i=\frac{\nu_i}{\nu_0}\,\frac{\alpha/\beta+1}{\alpha/\beta-g_i}.$$

Assuming that $\alpha/\beta+1=-q\nu_0$, where $q \ll 1$, we obtain

$$c_i=\frac{\nu_i q}{1+g_i+q\nu_0}\approx\frac{\nu_i}{1+g_i}q. \tag{20}$$

It is clear from Eq. (20) that the quantity ν_0 does not occur in the expression for c_i. This expression will have the same form also if $\nu_0=0$. The parameters τ and θ can be expressed in terms of q by means of Eq. (17):

$$\tau=q\sum_k\frac{g_k^2\nu_k}{1+g_k},\quad \theta=q\sum_k\frac{g_k p_k \nu_k}{1+g_k}. \tag{21}$$

Finally, substituting Eq. (20) into Eq. (19), we obtain the following equation for q:

$$q^s\prod_k\left(\frac{\nu_k}{1+g_k}\right)^{\nu_k}=K;\quad s=\sum_k \nu_k. \tag{22}$$

The expressions in Eq. (22) are compatible with the condition $K \ll 1$ and $q \ll 1$ if $s \neq 0$. An even more stringent condition is imposed by Eq. (20): since all the concentrations satisfy $c_i > 0$ and ν_i can be both positive and negative, it follows that Eq. (20) is obeyed only for the case of a very specific relationship between the signs of ν_i and $1+g_i$. This condition is not obeyed only in the case of a two-component solution. If such a solution is dilute in equilibrium, there is always a critical slowing-down point. In the case of a multicomponent solution the phenomenon of critical slowing down may occur in the reactions involving separation of weakly dissolved substances from a solvent. In this case we find that $\nu_k > 0$ and $g_k > 0$ are always satisfied and the conditions (20)–(22) may be obeyed.

3. CONCLUSIONS

We have shown that the critical slowing down of reactions occurring near equilibrium can occur only at isolated points on the critical hypersurface of the parameters of a system. In particular, slowing down should occur in a dilute solution of one substance in another at the point of intersection of a critical line with the chemical equilibrium surface.

Krichevskiĭ *et al.*[2] studied the $Cl_2 \rightarrow 2Cl$ photodissociation reaction near the critical point of molecular chlorine. They examined the $2Cl \rightarrow Cl_2$ recombination curve after the end of optical pumping and concluded that the reaction exhibited critical slowing down. In the investigated range of concentrations the spontaneous dissociation could be ignored completely. The dependence of the concentration of atomic chlorine on time was hyperbolic: $c=A/(t-t_0)$. Krichevskiĭ *et al.*[2] tried to find the moment in time corresponding to zero concentration. Clearly, such a moment does not exist and the time found in this way is simply evidence of the sensitivity of the method. An analysis of the recombination curves given in Ref. 2 for a constant pumping rate shows that in reality there is no anomalous slowing down of the reaction. This is easily understood since the reaction occurs far from a thermodynamic equilibrium. Chemical reactions near the critical points of solutions were investigated also by Snyder and Eckert[6] and the anomalous slowing down was not observed. This is easily understood because in the investigated multicomponent mixture such critical behavior should be observed only at isolated points of the critical set. The critical slowing down of reactions in multicomponent solutions requires a special set of the parameters t, P, and c_i.

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