

Asymptotic form of the approach to equilibrium and concentration fluctuations

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We consider the kinetics of the reversible chemical reaction $B + C \rightleftharpoons A$. We show that this kinetics is determined by the process of diffusion formation of the spectrum of the equilibrium density fluctuations, so that the equilibrium is approached in accord with the power law $t^{-3/2}$.

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Consider the reversible dissociation $A \rightleftharpoons B + C$ ¹; the equilibrium state is determined by the effective-mass law. The equilibrium constant is expressed in terms of the chemical potentials of the reacting substances A , B , and C . It is assumed here that each of them is in a state that is by itself in equilibrium at the given concentration. Consequently, it is tacitly assumed that the substances A , B , and C have a Poisson distribution in space, i.e., that in each small volume V , containing on the average $\bar{N} = Vn$ molecules, the rms deviation is $\Delta N = \sqrt{(N - \bar{N})^2} = \sqrt{\bar{N}}$, and the fluctuations δA , δB and δC are not correlated with one another. Only in such a state is the total energy minimal and the law of effective masses holds for concentrations averaged over a large volume, $\overline{BC} = k_p \overline{A}$ with the "thermodynamic" value of k_p .

As will be shown below, the kinetics of the establishment of the complete equilibrium at a long time after the start of the reaction is limited precisely by the rate at which the concentration fluctuations assume their steady state. This depends on the diffusion, so that asymptotically, at $t \rightarrow \infty$, the relations of the formal chemical kinetics

$$\bar{A}(t) = A(\infty) + f e^{-wt}, \quad \bar{B}(t) = \bar{C}(t) = B(\infty) - f e^{-wt}, \quad (1)$$

are replaced by

$$\bar{A}(t) = A(\infty) + g t^{-3/2}, \quad \bar{B}(t) = \bar{C}(t) = B(\infty) - g t^{-3/2}, \quad (2)$$

where the averaging, as before, is over the volume.

We consider the simplest case $t=0$, $A=A_0$, $B=C=0$, where at equilibrium $A(\infty)=C(\infty) \ll A(0)$, so that we can neglect the variation of A during the dissociation time, $A(t) \approx A_0$, as well as the fluctuations of the initial substance A . We consider now the fluctuations and distinguish between the correlated ones $q = \delta B + \delta C$ and the anticorrelated ones $p = \delta B - \delta C$.

Individual acts of the decay of the molecules A , as well as the act of joining of B with C , are random events; they consequently cause fluctuations. It is clear, however, that since only correlated fluctuations are produced, the chemical reaction does not change the concentration difference. Only the diffusion of B and C in space can alter the value of p .

Consider a sufficiently late instant when local thermodynamic equilibrium has been established everywhere, as well as the equilibrium distribution $q(\infty)$, but the quantity $p(t)$ connected with the slow process—diffusion—has not yet reached equilibrium. During this period, the following relation holds:

$$C(x, t) B(x, t) = B^2(\infty). \quad (3)$$

Averaging this relation, we obtain, recognizing that $\overline{B} = \overline{B(\infty)} + \frac{1}{2}p + \frac{1}{2}q$, $\overline{C} = \overline{C(\infty)} + \frac{1}{2}p - \frac{1}{2}q$, $\overline{p} = \overline{q} = \overline{pq} = 0$

$$\overline{B^2(t)} = B^2(\infty) - \frac{1}{4} \overline{q^2(\infty)} + \frac{1}{4} \overline{p^2(t)}. \quad (4)$$

The problem has been reduced to a calculation of the mean square of the anticorrelated part of the fluctuations. By way of estimate we note that at the instant t the fluctuations of p with the characteristic dimension \sqrt{Dt} , where D is the diffusion coefficient, have not yet been excited; the equilibrium amplitude of these fluctuations would be $\overline{p^2(t)} \cong B(\infty)/V$. Here the volume is $V \approx D^{3/2} t^{3/2}$, and B is expressed in absolute units (number of particles per cm^3). At equilibrium $q^2(\infty) = p^2(\infty)$, and $\overline{B} = B(\infty)$, but at the instant t , owing to the incomplete excitation of the anticorrelated fluctuations, we have

$$p^2(t) - q^2(t) \approx p^2(t) - p^2(\infty) \approx -\frac{B(\infty)}{D^{3/2} t^{3/2}}, \quad (5)$$

and ultimately

$$B(t) = B(\infty) - \frac{\alpha}{D^{3/2} t^{3/2}}, \quad (6)$$

where α is a dimensionless factor of the order of unity. It is easy to make the foregoing estimate more accurate by changing over to the Fourier representation $p(x, t) = \int p_k \exp(ikx) d^3k$. To determine p_k we use the diffusion equation. The classical equation $\partial p / \partial t = D \Delta p$ would have given $dp_k / dt = -k^2 D p_k$.

Actually, however, it is necessary to use the diffusion equation with a random force describing the fluctuations. The equation is then written not for a determined p_k , but for the probability distribution of the systems with respect to the quantity p_k

$$\Phi = \prod_k \Phi_k(p_k, t), \quad \frac{\partial \Phi_k}{\partial t} = -\frac{\partial}{\partial p_k} (k^2 D p_k \Phi_k) + D_k \frac{\partial^2 \Phi_k}{\partial p_k^2}, \quad (7)$$

where D_k is the diffusion coefficient in p_k space. For our purposes, however, it suffices to set up the equation for the second moment

$$\frac{d}{dt} \int_{-\infty}^{\infty} p_k^2 \Phi_k dp_k = -2k^2 D p_k^2 + 2D_k. \quad (8)$$

Thus, each $\overline{p_k^2(t)}$ tends to its own stationary value exponentially. The stationary value $\overline{p_k^2(\infty)}$ is determined by the equilibrium spectrum, $\overline{p_k^2(\infty)} = \text{const}(k)$ (white noise). This yields again the same result (6):

$$\overline{p^2(x, t)} = \text{const} \int p_k^2(t) d^3k = \infty - \text{const} D^{-3/2} t^{-3/2}.$$

The infinite term is cancelled by a like term in expression for q^2 . The calculation of the dimensionless constants and a discussion of the possible experiment will be presented in a detailed article now in preparation.

We note also that the change in the asymptotic form takes place also in the case of a decay into two identical molecules ($A \rightleftharpoons 2B$), although the constant in (6) will have a different absolute value.

Thus, the $t^{-3/2}$ law holds for all reactions as equilibrium is approached. It is possible that small angle light scattering will make it possible to trace the evolution of definite Fourier components of the concentration, and not only their mean values. The physical interaction of A , B , and C alter the equilibrium constants and gives rise to corrections to the law of effective masses, but it does no

change the conclusions concerning the kinetics. Exceptions are the long-range Coulomb forces in electrolytic dissociation $A \rightleftharpoons B^+ + C^-$. However, even here, in the presence of other ions that do not take part in the reaction, the condition of electroneutrality no longer requires $B^+ = C^-$ and our arguments again become valid.

¹The irreversible reaction was considered in^[1].

Ya.B. Zel'dovich, *Elektrokhimiya* **13**, 677 (1977); A.A. Ovchinnikov and Ya.B. Zeldovich, *Chem. Phys.* (1977), in press.