The mass action law and the kinetics of chemical reactions with allowance for thermodynamic fluctuations of the density

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A general theory of chemical reactions, in which account is taken of the thermodynamic fluctuations of the density of the reacting particles, is developed. The reversible reaction $B+B\rightleftarrows A$ is used in the analysis as an example. It is shown that the particle-density fluctuations lead at equilibrium to correction of the mass-action law: $b^2/a=K_p(T)$, where b and a are respectively the densities of the numbers of particles A and B, and $K_p(T)$ is the equilibrium constant. These corrections, which can be called kinetic, are small if the density of the reacting particles is small, but differ from the corrections usually calculated in statistical physics and necessitated by the potential interaction of the particles. On the other hand, these corrections influence strongly the kinetics of the approach to equilibrium, since the evolution of the fluctuating part of the particle density is connected with diffusion. It turns out that as $t\rightarrow\infty$ the exponential relation given by the equations of the formal chemical kinetics is replaced by $a(t)=c/(Dt)^{3/2}$. Thus, during the later stages, any reaction is diffusion-dominated (i.e., is determined by the rate of encounter of the reacting particles). The analysis method consists of reducing the system-evolution equation to that of the evolution of a mixture of two quantum Bose gases. This problem is analyzed by the method of separating the condensate and approximate second quantization, developed by Bogolyubov in the theory of a weakly nonideal Bose gas.

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1. INTRODUCTION

The role of diffusion in chemical kinetics is splendidly elucidated in a monograph by Frank-Kamenetskiĭ[1] and in later review articles.[2] New questions arise when account is taken of thermodynamic fluctuations of the concentrations of the reacting substances. "Uniform" distribution of the matter is uniform only in the mean—averaged over a large volume or over a long time interval, but in small volumes short-period fluctuations are inevitable, as is also Brownian motion. The diffusion equations for the concentrations of the reagents usually employed in chemical kinetics only smooth out the initial inhomogeneities of the density. It must be remembered, however, that in such a situation we are actually dealing with a multiparticle system, and in the absence of a reaction the number of particles N in a certain volume V has even in a fully homogeneous system a variance

$$\langle (N-\langle N\rangle)^2\rangle=\langle N\rangle,\quad \langle N\rangle=nV,$$

where n is the density of the number of particles and $\langle\ldots\rangle$ denotes averaging over the coordinates of all the particles. When a reaction takes place, the total number of particles of any sort, say N_A, cannot be regarded as given even at equilibrium, since the reaction acts take place statistically at random and only in the mean is the total number of the particles A equal to its equilibrium value $\langle N_A\rangle$. The effect of such fluctuations of the total number of particles in a chemical reaction was considered in a number of studies.[3-5] Their general conclusion is that, in the thermodynamic limit (i.e., at $N_A\rightarrow\infty$, $V\rightarrow\infty$, $N_A/V=n_A$) the influence of these fluctuations vanishes. No account was taken in these studies, however, of the spatial fluctuations of the number of particles, or else it was assumed that they become equalized rapidly enough (the so-called local-equilibrium hypothesis). Yet the process that equalizes the spatial fluctuations due to the chemical reactions is particle diffusion, which is quite slow, especially for long-wave fluctuations. Thus, a fluctuation with characteristic dimension l becomes equalized within a time l^2/D_A (D_A is the diffusion coefficient of the particles of sort A). It will be shown below that these spatial fluctuations come into play, at low densities of the reacting particles, only in the next higher terms in the density of the reacting particles. The spatial fluctuations of the number of particles in the reacting system call thus for certain corrections to the mass-action law, and these corrections are small at low density.1) These corrections, however, have a substantially different time behavior and, in particular, can determine the temporal behavior of the quantities.

Thus, in another paper[6] we have considered the irreversible reaction $A+B\rightarrow C$ and obtained new asymptotic laws for the decrease of the concentration n_A as $t\rightarrow\infty$. If $n_A=n_N$ (stoichiometric mixture of the reagents), then $n_A\sim 1/t^{3/4}$ replaces the $1/t$ law of formal kinetics; if $n_A\ll n_B$, then $n_A\sim\exp(-ct^{3/5})$ in place of $\exp(-ct)$.2)

2. THE REACTION $B+B\leftrightarrows A$, ESTIMATES

We consider in this article the theory of chemical reactions in the presence of spatial fluctuations, using as an example the dissociation reaction $A\rightarrow B+B$ and its inverse, the recombination reaction $B+B\rightarrow A$. Particular attention will be paid to corrections to the mass-action law (whose form without allowance for the fluctuation is $b^2/a=K_p(T)$, where a and b are respectively the densities of the particles A and B, and $K_p(T)$ is the equilibrium constant) and to the asymptotic laws that govern the approach to equilibrium. (The reaction $B+C\rightleftharpoons A$, where the effects are larger, was considered by us earlier).[12]

We precede the rigorous solution by some heuristic considerations. Consider the following hypothetical experiment: first A is kept at low temperature, so that a fluctuation distribution of A is fully established, but there is no dissociation. The entire volume is then uniformly heated to a temperature at which the dissociation is noticeable, and the produced particles B are measured. The kinetics of the local establishment of chemical equilibrium is assumed to be fast enough. The reaction results in local equilibrium, and until diffusion alters the concentrations we have according to the mass-action law

$$b(x)=[K_p(T)a(x)]^{1/2}. \tag{1}$$

Owing to the thermodynamic fluctuations, the densities a and b depend here on the coordinate x. The exact equality (1) is a restriction imposed on the fluctuations of the reaction products B. It is not surprising that this limitation increases their chemical potential and therefore decreases the dissociation compared with true equilibrium.

The conclusion that the dissociation decreases in the initial period can be reached in a different manner, on the basis of the mass-action law in the classical formulation, without resorting to the concepts of statistical mechanics. We obtain from (1)

$$\langle b(x)\rangle=\langle (K_p(T)a(x))^{1/2}\rangle$$

(the averaging is over space). Since the curve $f(a)=\sqrt{a}$ is convex upward, it is obvious that

$$\langle (K_p(T)a(x))^{1/2}\rangle<(K_p(T)\langle a(x)\rangle)^{1/2}.$$

To state it in words: if the particles A have a nonuniform distribution the local-equilibrium amount of the dissociation products yields a total smaller amount (or, equivalently, a smaller average concentration) compared with a calculation from the average concentration of the initial product A.

It is easy to indicate a quantitative measure of the discrepancy. We write

$$a(x)=\langle a\rangle+\delta a(x),\quad \delta a(x)\ll\langle a\rangle. \tag{2}$$

We next have

$$a^{1/2}(x)=\langle a\rangle^{1/2}+\frac{1}{2}\frac{\delta a(x)}{\langle a\rangle^{1/2}}-\frac{1}{8}\frac{[\delta a(x)]^2}{\langle a\rangle^{3/2}}. \tag{3}$$

Averaging yields

$$\langle a^{1/2}(x)\rangle=\langle a\rangle^{1/2}\left(1-\frac{1}{8}\frac{\langle[\delta a(x)]^2\rangle}{\langle a\rangle^2}\right). \tag{4}$$

According to the preceding arguments,

$$\langle[\delta a(x)]^2\rangle=\left\langle\left(\frac{\Delta N_A}{V}\right)^2\right\rangle=\frac{\langle N_A\rangle}{V^2}=\frac{\langle a\rangle}{V}\qquad\frac{\langle[\delta a(x)]^2\rangle}{\langle a\rangle^2}=\frac{1}{\langle a\rangle V}. \tag{5}$$

After a time t, the diffusion produces equilibrium fluctuations in a region with linear dimension $(Dt)^{1/2}$, i.e., in a volume $V\sim(Dt)^{3/2}$ for the new $\langle a\rangle=\langle a_0\rangle-\frac{1}{2}\langle b\rangle$. Substituting this in (5), we obtain the law that governs the asymptotic approach of the density of the particles B to equilibrium:

$$b(t)=b_{eq}\,[1-\alpha/\langle a\rangle(Dt)^{3/2}]. \tag{6}$$

The usual formally kinetic approach leads to the equations

$$\frac{db}{dt}=2w_+{}^0a-2w_-{}^0b^2,\qquad 2a+b=\text{const}, \tag{7}$$

where w_+^0 and w_-^0 are the rate constants of the dissociation and recombination, respectively, and $K_p(T)=w_+^0/w_-^0$. The solution of this system under the same conditions yields

$$b(t)=b_{eq}\,[1-\exp(-\omega_0t)],\quad \omega_0=w_+{}^0+4b_{eq}\,w_-{}^0, \tag{8}$$

i.e., an exponentially rapid approach to equilibrium.

In chemical kinetics it is customary to distinguish between diffusion-controlled reactions, i.e., reactions whose rate is limited by the process of the encounter of the reagents with each other, and reactions that proceed in the kinetic region, i.e., determined by the elementary chemical reaction rate itself. It follows from our analysis that all reactions are diffusion-controlled during the last stages.

3. OPERATOR FORM OF THE FUNDAMENTAL EQUATIONS

For a consistent description of the chemical reaction $B+B\rightleftharpoons A$ with allowance for the density fluctuations we need a more detailed description of the direct and inverse chemical processes. We consider for this purpose only two B particles. The probability density for finding the first particle at point x_1 and the second particle at x_2 will be specified by the function $u_{2,0}(x_1,x_2)$, while the probability density that the one produced particle A is located at the point y will be specified by the function $u_{0,1}(y)$. For this two-particle problem, the condition for normalization to unity of the total probability of finding the system at some state is

$$\iint dx_1\,dx_2\,u_{2,0}(x_1,x_2)+\int dy\,u_{0,1}(y)=1. \tag{9}$$

The probability that two particles B (at points x_1 and x_2) will be transformed into a particle A is specified by the function $w_-(x_1-x_2)$, and the probability that a particle A located at a point A will be transformed into two B particles, one at y and the other at x, will be assumed equal to $w_+(y-x)$. We need not differentiate between the particles B, so that we can regard $u_{2,0}(x_1,x_2)$ as a function symmetrical in its arguments.

We can now write equations for the evolution of this system:

$$\frac{\partial u_{2,0}(x_1,x_2)}{\partial t}=D_b(\Delta_{x_1}+\Delta_{x_2})u_{2,0}(x_1,x_2)$$

$$-2w_-(x_1-x_2)u_{2,0}(x_1,x_2)+w_+(x_1-x_2)u_{0,1}(x_2)+w_+(x_2-x_1)u_{0,1}(x_1), \tag{10a}$$

$$\frac{\partial u_{0,1}(x)}{\partial t}=D_a\Delta_x u_{0,1}(x)+2\int w_-(x-x_2)u_{2,0}(x,x_2)\,dx_2$$

$$-2\int w_+(x-x_2)\,dx_2 u_{0,1}(x). \tag{10b}$$

The terms with creation and annihilation of particles A and B in the right-hand sides of (10) are quite obvious from the definitions of the functions $w_+(x)$ and $w_-(x)$; D_a and D_b are the diffusion coefficients of particles A and B, respectively. From (10) we can easily obtain the condition for the conservation of the total probability (9).

To generalize equations of type (10) to a system of many particles we must introduce the functions

$$u_{N,M}(x_1,x_2,\ldots,x_N|y_1,y_2,\ldots,y_M), \tag{11}$$

which are separately symmetrical in the coordinates x_i and y_i. Without writing out the corresponding cumbersome system of equations in the x-representation, we note, examining the system (10), that it is reminiscent of the quantum field-theoretical system with creation and annihilation of particles in the Fock representation.[8] Taking account also of the symmetry of the functions in the variables x and y separately, we can attempt to write this system with the aid of creation and annihilation operators $\psi_a^+(x)$, $\psi_a(x)$ and $\psi_b^+(x)$, $\psi_b(x)$, for these particles; these operators satisfy the Bose-operator permutation relations

$$[\psi_a(x),\psi_a^+(y)]=\delta(x-y),\quad [\psi_a^+(x),\psi_a^+(y)]=0,$$
$$[\psi_a(x),\psi_a(y)]=0. \tag{12}$$

Analogous relations are chosen also for the particles B. The operators of particles A and B commute.

This is possible if we introduce the operator function

$$\Phi=\sum_{M,N=0}^{\infty}\int\ldots\int dx_1\ldots dx_N\,dy_1\ldots dy_M u_{N,M}(x_1,\ldots,x_N|y_1,\ldots,y_M)$$
$$\times\psi_b^+(x_1)\psi_b^+(x_2)\ldots\psi_b^+(x_N)\psi_a^+(y_1)\psi_a^+(y_2)\ldots\psi_a^+(y_M) \tag{13}$$

and the system "Hamiltonian"

$$\hat{H}=-D_b\int dx\,\nabla_x\psi_b^+(x)\nabla_x\psi_b(x)-D_a\int dx\,\nabla_x\psi_a^+(x)\nabla_x\psi_a(x)$$
$$+{}^1/_2\iiint dx_1\,dx_2\,dy[\delta(y-x_1)+\delta(y-x_2)]w_+(x_1-x_2)\psi_b^+(x_1)\psi_b^+(x_2)\psi_a(y)$$
$$+{}^1/_2\iiint dx_1\,dx_2\,dy[\delta(y-x_1)+\delta(y-x_2)]w_-(x_1-x_2)\psi_b(x_1)\psi_b(x_2)\psi_a^+(y)$$
$$-\iint dx_1\,dx_2 w_-(x_1-x_2)\psi_b^+(x_1)\psi_b^+(x_2)\psi_b(x_2)\psi_b(x_1)$$
$$-\iint w_+(x-x')\psi_a^+(x)\psi_a(x)\,dx\,dx'. \tag{14}$$

The equation for the evolution of the system then takes the form

$$\partial\Phi/\partial t=\hat{H}\Phi, \tag{15}$$

i.e., it is similar to the Schrödinger equation.

For all this outward analogy, there are also significant differences. Thus, the operator H is not Hermitian, $H\neq H^+$. It is more important, however, that the physical quantities—the mean values—are determined with the aid of the operator Φ in accordance with entirely different rules. Thus, to set up the norm

$$\sum_{N,M=0}^{\infty}\int\ldots\int dx_1\ldots dx_N\,dy_1\ldots dy_M u_{N,M}(x_1,\ldots,x_N|y_1,\ldots,y_M) \tag{16}$$

with the operator Φ we must take the usual field-theoretical scalar product of Φ with the function Φ_0 defined by

$$\langle\Phi_0|=\langle 0|\sum_{k,k'=0}^{\infty}\frac{[\int\psi_b(x)dx]^k}{k!}\frac{[\int\psi_a(x)dx]^{k'}}{k'!}$$
$$=\langle 0|\exp\left\{\int[\psi_a(x)+\psi_b(x)]dx\right\}. \tag{17}$$

The normalization condition then takes the form of the equality

$$\langle\Phi_0|\Phi\rangle=1. \tag{18}$$

It is actually satisfied if it is recognized that

$$\langle\Phi_0|\hat{H}=0. \tag{19}$$

The number of particles (say, A) is expressed as the mean value of the operator

$$\hat{N}_A=\int\psi_a^+(x)\psi_a(x)\,dx, \tag{20}$$

namely

$$N_A(t)=\langle\Phi_0|\hat{N}_A|\Phi\rangle. \tag{21}$$

There is also a Heisenberg representation of the operators, as seen from the fact that

$$|\Phi(t)\rangle=\exp(\hat{H}t)|\Phi_{in}\rangle; \tag{22}$$

$|\Phi_{in}\rangle$ is the initial function of the system, and a mean value of the type (21) can be written as follows:

$$N_A(t)=\langle\Phi_0|\exp(-\hat{H}t)\hat{N}_A\exp(\hat{H}t)|\Phi_{in}\rangle. \tag{23}$$

The operator $\hat{N}_A(t)$ takes thus in the Heisenberg representation the form

$$\hat{N}_A(t)=\exp(-\hat{H}t)\hat{N}_A\exp(\hat{H}t)$$

and satisfies the usual equations of motion

$$d\hat{N}_A/dt=[\hat{N}_A,\hat{H}]. \tag{24}$$

Thus, the equations of motion of a classical system can be written in a "quantum" form. We note that the idea of expressing the classical Liouville equation in quantum form was first advanced by Prigogine.[9]

It will be convenient in what follows to express the Hamiltonian $\hat{H}$ in terms of the creation operators in the momentum representation, as is customary in statistical mechanics[10]:

$$\alpha_k^+=\frac{1}{V^{1/2}}\int\psi_a^+(x)e^{ikx}dx,\qquad \beta_k^+=\frac{1}{V^{1/2}}\int\psi_b^+(x)e^{ikx}dx. \tag{25}$$

We then have

$$\begin{aligned}\hat{H}=&-\sum_k D_b k^2\beta_k^+\beta_k-\sum_k D_a k^2\alpha_k^+\alpha_k\\&+\frac{1}{2V^{1/2}}\sum_{k_1+k_2=q}[w_+(k_1-q)+w_+(k_2-q)]\beta_{k_1}^+\beta_{k_2}^+\alpha_q\\&+\frac{1}{2V^{1/2}}\sum_{k_1+k_2=q}[w_-(k_1-q)+w_-(k_2-q)]\beta_{k_1}\beta_{k_2}\alpha_q^+\\&+\frac{1}{V}\sum_{\substack{k_1+k_2=\\=k_1'+k_2'}}\beta_{k_1}^+\beta_{k_2}^+\beta_{k_2'}\beta_{k_1'}w_-(k_1-k_1')-\sum_k w_+^0\alpha_k^+\alpha_{k'}.\end{aligned}\tag{26}$$

Here $w_+(k)$ and $w_-(d)$ are the Fourier transforms of the functions $w_+(x)$ and $w_-(x)$, while w_+^0 is the value of $w_+(k)$ at $k=0$.

4. EQUATIONS FOR THE EVOLUTION OF THE PARTICLE DENSITIES AND THE FLUCTUATUION SPECTRUM IN THE COURSE OF A CHEMICAL REACTION

The Hamiltonian (26) is similar to the Hamiltonian of an interacting Bose gas (even though it is not Hermitian). The methods of determining its eigenfunctions will be taken from the Bogolyubov theory of a weakly nonideal Bose gas.[11] Weakness of the interaction is guaranteed here by the low particle density, i.e., by the parameter $n_A r_A^3 \ll 1$ (where r_A is the radius of the A particles). So as not to complicate the calculations unnecessarily, we shall regard also the functions $w_+(k)$ and $w_-(k)$ (suitably reduced to dimensionless form) as small.[3]

We make use of the fact that at low density there is a macroscopically small number of particles A and B with nonzero momentum, and consequently the operators α_0^+, β_0^+, α_0, β_0 can be regarded as c-numbers. Expanding, following Bogolyubov, the Hamiltonian up to term quadratic in α_k, β_k, β_k^+, α_k^+ $(k\neq 0)$, we write $\hat{H}$ in the form of a sum of two terms:

$$\hat{H}=\hat{H}_0+\hat{H}_1,\tag{27}$$

where

$$\hat{H}_0=\frac{1}{V^{1/2}}w_+^0\beta_0^{+2}\alpha_0+\frac{1}{V^{1/2}}w_-^0\beta_0^2\alpha_0^+-\frac{1}{V}w_-^0\beta_0^{+2}\beta_0^2-w_+^0\alpha_0^+\alpha_0\tag{28}$$

and $\hat{H}_1$ is that part of the Hamiltonian $\hat{H}$ which is quadratic in β_k, α_k, α_k^+, β_k^+ $(k\neq 0)$ and which we shall write out later on. Since α_0 and β_0 are in essence classical variables, we can obtain equations of motion for them as for Heisenberg operators and then declare them to be c-numbers. We thus obtain

$$\begin{aligned}\frac{d\beta_0}{dt}&=2\frac{w_+^0}{V^{1/2}}\alpha_0\beta_0^+-\frac{2w_-^0}{V}\beta_0^+\beta_0^2-\frac{2}{V}\beta_0^+\left\langle\sum_k w_-(k)\beta_k(t)\beta_{-k}(t)\right\rangle,\\\frac{d\alpha_0}{dt}&=\frac{1}{V^{1/2}}w_-^0\beta_0^2-w_+^0\alpha_0+\frac{1}{V^{1/2}}\left\langle\sum_k w_-(k)\beta_k(t)\beta_{-k}(t)\right\rangle.\end{aligned}\tag{29}$$

These equations are accurate to within certain mean values which will subsequently turn out to be equal to zero. The equations for α_0^+ and β_0^+ are similar in form (although they cannot obtained from (29) by the conjugation operation, since the Hamiltonian is not Hermitian), and are satisfied at

$$\alpha_0^+=\beta_0^+=\sqrt{V}.\tag{30}$$

Taking (30) into account, and introducing in plane of α_0 and β_0 the respective densities $a=\alpha_0/V^{1/2}$ and $b=\beta_0/V^{1/2}$,[4] of the particles A and B, we can rewrite the Hamiltonian $\hat{H}_1$ in the form

$$\begin{aligned}\hat{H}_1=&-\sum_k\varepsilon_1(k)\beta_k^+\beta_k-\sum_k\varepsilon_2(k)\alpha_k^+\alpha_k\\&+\sum_k\mu_+(k)\beta_k^+\alpha_k+\sum_k\mu_-(k)\alpha_k^+\beta_k+\sum_k\lambda(k)\beta_k^+\beta_{-k}^+,\end{aligned}\tag{31}$$

where

$$\begin{gathered}\varepsilon_1(k)=D_b k^2+2b[w_-^0+w_-(k)],\quad\mu_+(k)=w_+^0+w_+(k),\\\varepsilon_2(k)=D_a k^2+w_+^0,\quad\mu_-(k)=w_-^0+w_-(k),\\\lambda(k)=aw_+(k)-b^2w_-(k).\end{gathered}\tag{32}$$

The equations of motion with the Hamiltonian $\hat{H}_1$ for the mean values

$$\begin{gathered}\sigma_{\beta\beta}(k,t)=\langle 0|\beta_k(t)\beta_{-k}(t)|\Phi_{in}\rangle,\\\sigma_{\alpha\alpha}(k,t)=\langle 0|\alpha_k(t)\alpha_{-k}(t)|\Phi_{in}\rangle,\\\sigma_{\alpha\beta}(k,t)=\langle 0|\alpha_k(t)\beta_{-k}(t)|\Phi_{in}\rangle=\sigma_{\beta\alpha}(-k,t)\end{gathered}\tag{33}$$

are of the form

$$\begin{gathered}\frac{d\sigma_{\beta\beta}(k,t)}{dt}=-2\varepsilon_1(k)\sigma_{\beta\beta}(k,t)+2\mu_+(k)\sigma_{\beta\alpha}(k,t)+2\lambda(k),\\\frac{d\sigma_{\alpha\alpha}(k,t)}{dt}=-2\varepsilon_2(k)\sigma_{\alpha\alpha}(k,t)+2\mu_-(k)\sigma_{\beta\alpha}(k,t),\\\frac{d\sigma_{\alpha\beta}(k,t)}{dt}=-[\varepsilon_1(k)+\varepsilon_2(k)]\sigma_{\alpha\beta}(k,t)+\mu_+(k)\sigma_{\alpha\alpha}(k,t)+\mu_-(k)\sigma_{\beta\beta}(k,t).\end{gathered}\tag{34}$$

If we add to them the first equation of (29), written in the same notation:

$$\frac{db}{dt}=2w_+^0a-2w_-^0b^2-\frac{2}{V}\sum_k w_-(k)\sigma_{\beta\beta}(k,t)\tag{35}$$

as well as the particle-number conservation law

$$b+2a=\text{const},\tag{36}$$

which follows from the second equation of (29), then we obtain the sought system of equations. It determines simultaneously both the dynamics of the variation of the particle number as a result of the occurring chemical reaction, and the dynamics of the development of the fluctuations with time. We note that while the system of equations for $\sigma_{\alpha\alpha}$, $\sigma_{\alpha\beta}$, $\sigma_{\beta\beta}$ is linear, its coefficients ϵ_1 and $\lambda(k)$ depend on the time via $b(t)$ and $a(t)$.

5. CORRECTIONS TO THE MASS-ACTION LAW

To determine the corrections to the mass-action law we must consider the equilibrium situation, i.e., time-independent $a(t)$, $b(t)$, and $\sigma_{\alpha\alpha}$, $\sigma_{\alpha\beta}$, $\sigma_{\beta\beta}$. We determine first $\sigma_{\beta\beta}$ from (34) and substitute it in (35). Neglecting the fluctuations, (i.e., $\sigma_{\beta\beta}$), we get from (35) the mass-action law in its classical form:

$$b^2/a=w_+^0/w_-^0=K_p(T).$$

Adding (36), we determine the equilibrium concentrations a_0 and b_0. Allowance for the fluctuation terms leads to a correction to the equilibrium concentrations: $a_{eq}=a_0+\delta a$, where

$$\delta a=-\frac{\delta b}{2}=\frac{1}{\omega_0 V}\sum_k w_-(k)\lambda(k)\frac{\varepsilon_1(k)\varepsilon_2(k)-\mu_+(k)\mu_-(k)+\varepsilon_2^2(k)}{[\varepsilon_1(k)\varepsilon_2(k)-\mu_+(k)\mu_-(k)][\varepsilon_1(k)+\varepsilon_2(k)]}$$

$$\omega_0=w_+{}^0+4b_0w_-{}^0. \tag{37}$$

We shall not evaluate the integrals contained here for any concrete functions $w_+(k)$ and $w_-(k)$. It is important for us in principle that such corrections exist. It should be noted that, generally speaking, the corrections of next order in the density to the mass-action law can be of two kinds. First, potential corrections due to the fact that the reacting particles interact with one another in potential manner. The second type of correction, which we shall call dynamic, is due to the fact that the particles have a certain probability of reacting. It is these kinetic corrections that are given by formula (37). Of course, the detailed balancing principle for $w_\pm(k)$ ensures agreement of the final result with the equilibrium result calculated by thermodynamics.

6. ASYMPTOTIC BEHAVIOR OF THE DENSITIES *a(t)* AND *b(t)*

To determine the characteristic time-dependent asymptotic densities $a(t)$ and $b(t)$ we consider the simplest nonstationary problem. Let initially the system of particles A and B be in equilibrium at a certain temperature T. The particle densities a_0 and b_0 are determined in this case as in Sec. 5. Assume that the temperature is suddenly raised by a small amount δT. The system characteristics such as the diffusion coefficients or the dissociation and recombination probabilities $w_+(k)$ and $w_-(k)$ also change suddenly. In accordance with the fundamental system of equations, the equilibrium concentrations of the particles A and B should also change. We shall consider the approach of $a(t)$ and $b(t)$ to their new values.

Since the initial and final densities do not differ greatly (in view of the small increase of the temperature), the variation of $\epsilon_{1,2}$ and $\mu_\pm$ with time can be neglected, and the entire system (34)–(36) becomes linear with constant coefficients.

Consider, for example, the general solution of the linear system of equations (34) without the term with $\lambda(k)$. In this case $\sigma_{\beta\beta}(k,t)$ contains time exponentials of the form

$$\exp[-2\omega_1(k)t],\ \exp\{-[\omega_1(k)+\omega_2(k)]t\},\ \exp[-2\omega_2(k)t], \tag{38}$$

where

$$\omega_{1,2}(k)=\frac{\varepsilon_1(k)+\varepsilon_2(k)}{2}\pm\left[\frac{[\varepsilon_1(k)-\varepsilon_2(k)]^2}{4}+\mu_+(k)\mu_-(k)\right]^{1/2}. \tag{39}$$

The asymptotic form, as $t\to\infty$, of the quantity

$$\frac{1}{V}\sum_k\sigma_{\beta\beta}(k,t)w_-(k)$$

in (35) is determined by small k. If k is small, $\omega_1(k)$ tends to ω_0, i.e., to a finite value, and $\omega_2(k)$ tends in this case to $D_{eff}k^2$ and leads to a quantity that depends on time in power-law fashion

$$\frac{1}{V}\sum_k\sigma_{\beta\beta}(k,t)w_-(k),$$

and with it to the particle density $a(t)$.

In fact, at $t\omega_0\gg 1$ the terms in $\sigma_{\beta\beta}(k,t)$ containing the exponential $\exp[-\omega_1(k)t]$ can be neglected. Obtaining the solution from (34), we get for $\sigma_{\beta\beta}(k,t)$

$$\sigma_{\beta\beta}(k,t)\to\tilde{\sigma}_{\beta\beta}(k,t)=\frac{1}{(\omega_1-\omega_2)^2}[\mu_+^2(k)\delta\sigma_{\alpha\alpha}^{(0)}(k)+$$

$$+(\varepsilon_1-\omega_1)^2\delta\sigma_{\beta\beta}^{(0)}(k)-2\mu_+(k)(\varepsilon_1-\omega_1)\delta\sigma_{\alpha\beta}^{(0)}(k)]\exp[-2\omega_2(k)t], \tag{40}$$

where $\delta\sigma_{\alpha\alpha}^{(0)}(k)$, $\delta\sigma_{\alpha\beta}^{(0)}(k)$ and $\delta\sigma_{\beta\beta}^{(0)}$ are the changes of the quantities at equilibrium, due to the temperature rise δT. If

$$\frac{1}{V}\sum_k w_-(k)\tilde{\sigma}_{\beta\beta}(k,t)$$

has a power-law dependence on t, then we can discard from (35) at large t the term with the derivative db/dt and we have the following asymptotic behavior with change in t:

$$\delta a(t)\approx\frac{1}{V\omega_0}\sum_k w_-(k)\tilde{\sigma}_{\beta\beta}(k,t)=-\frac{\delta b(t)}{2}. \tag{41}$$

To calculate the integral with respect to k as $t\to\infty$, we must put $k=0$ everywhere in the pre-exponential factor, after which we have

$$\delta a(t)=\frac{w_+{}^0}{8\omega_0{}^3}\frac{1}{(2\pi D_{eff}t)^{3/2}}\left(\frac{\delta\varkappa}{\delta T}\right)\delta T. \tag{42}$$

Here D_{eff} is the effective diffusion coefficient, which is expressed in terms of the initial parameters in the form

$$D_{eff}=\frac{w_+{}^0D_b+4bw_-{}^0D_a-2bw_-{}^0w_+{}'}{w_+{}^0+4bw_-{}^0},\qquad w_\pm{}'=\left.\frac{dw_\pm(k)}{dk^2}\right|_{k=0}. \tag{43}$$

For $\varkappa$ we have

$$\varkappa=(w_+{}'w_-{}^0-w_+{}^0w_-{}')a/w_-{}^0D_{eff}. \tag{44}$$

An interesting feature of the expression for the effective diffusion coefficient is that it does not vanish even if both diffusion coefficients, D_a and D_b, are rigorously equal to zero. The reason for the remaining effective diffusion coefficient is that the very process of creation and annihilation of particles at points different from the initial position leads to diffusion and to equalization of the concentration. We note that the exponent in the asymptotic form coincides with that obtained by us on the basis of heuristic considerations.

To complete the analysis, we note that the function $|\Phi\rangle$, which is a solution of the equation

$$\partial|\Phi\rangle/\partial t=H|\Phi\rangle,$$

has the structure

$$|\Phi\rangle=\exp\left\{\sum_k[\alpha_k{}^+\alpha_{-k}{}^+\gamma_{\alpha\alpha}(k,t)+\alpha_k{}^+\beta_{-k}{}^+\gamma_{\alpha\beta}(k,t)+\beta_k{}^+\beta_{-k}{}^+\gamma_{\beta\beta}(k,t)]\right\},$$

and consequently all the mean values of the type

$$\langle 0|\alpha_k{}^+\alpha_k|\Phi\rangle,\ \langle 0|\beta_k{}^+\alpha_k|\Phi\rangle,\ \langle 0|\beta_k{}^+\beta_k|\Phi\rangle,\ \langle 0|\alpha_k{}^+\beta_k|\Phi\rangle,\ \langle 0|\alpha_k{}^+\alpha_{-k}{}^+|\Phi\rangle,\ldots$$

vanish, thus justifying the discarding, mentioned in Sec. 4, of the mean values in the derivation of the fundamental equations.

1) We note that the classification of the contribution to any quantity by the degrees of the density of the reacting particles is not trivial, since the effective-mass law relates quantities of different order in density.

2) The last formula was derived earlier by Balagurov and Vaks.[7]

3) Otherwise it is necessary to carry out an extra summation of the ladder diagrams of perturbation theory, to take into account the dynamics of motion with a potential $w_-(x)$. Our approximation is equivalent to the Born approximation in quantum mechanics.

4) It will subsequently be shown that

$$a=\frac{N_A(t)}{V}=\left\langle \Phi_0\left|\sum_k\alpha_k{}^+\alpha_k\right|\Phi\right\rangle=\frac{\alpha_0}{V^{1/2}},\quad \frac{N_B(t)}{V}=b(t)=\frac{\beta_0}{V^{1/2}}.$$

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Induced reflection and bleaching effects in electro-optic crystals

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Partial bleaching of a crystal or total reflection of light were observed during propagation of monochromatic laser radiation parallel to the optic axis of the ferroelectric $LiNbO_3$. It was found theoretically and experimentally that both effects are due to the appearance of a periodic refractive index grating under the influence of the transmitted and reflected (from the rear face) light waves. The nature of the effect is governed entirely by the direction of the polar axis of the crystal.

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§1. EXPERIMENTAL RESULTS

Action of monochromatic laser radiation of $\lambda = 5145$ Å wavelength on $LiNbO_3$:Fe crystals produced the following effects: a beam of $I_0 \gtrsim 1$ W/cm² intensity incident normally parallel to the optic axis1) ($k_0\uparrow\uparrow c$) resulted in almost complete transformation into a reflected beam. The intensity of the radiation transmitted by a crystal 0.3 cm thick was less than 5% although its initial value was 60%. The time dependences of the reflection $R = I_r/I_0$ and transmission $F = I_t/I_0$ coefficients were determined (Fig. 1). The time taken to establish the final pattern decreased on increase of the intensity of light (Fig. 1). A change in the direction of the optic axis ($k_0\uparrow\downarrow c$) altered drastically the nature of the effect. The crystal became bleached, i.e., the transmission coefficient F increased and the reflection coefficient R decreased. The maximum increase in F amounted to 14%. When the direction of incidence deviated from the normal, the reflection and bleaching effects of narrow