CALCULATION OF PROBABILITIES OF VIBRATIONAL—TRANSLATIONAL AND VIBRATIONAL—VIBRATIONAL EXCHANGES BETWEEN ISOTOPIC VARIANTS OF NITROGEN MOLECULES AT LOW TEMPERATURES

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UDC 539.196.5

Recently a number of theoretical and experimental reports have appeared devoted to questions of isotope separation in chemical reactions taking place under conditions of thermodynamic nonequilibrium [1-5]. In this case the working gas is usually at a low translational temperature (φ300°K). Theoretical calculations require knowledge of the probabilities of vibrational—vibrational (V—V) and vibrational—translational (V—T) exchanges between molecules of the working gas.

Unfortunately, there are extremely few experimental data on the probabilities of V—T and V—V exchanges at a temperature of ≲300°K and they cover a limited range of molecules [6-8], while experimental data on V—V exchange for nitrogen molecules are entirely absent.

The purpose of the present report is the calculation of the probabilities of V—V and V—T exchanges between isotopic variants of nitrogen molecules. This calculation was preceded by a search for and selection of the most suitable methods for calculations of the probabilities of V—T and V—V exchanges which exist in the literature. In addition, the probabilities of V—T exchange were calculated for several other pairs of molecules.

§1. The probability $p_{10}(T)$ of vibrational—translational exchange was calculated within the framework of the quasiclassical approximation, which was sugggested in [9, 10] and yields satisfactory agreement with experiment in the temperature range of 150-300°K for the process CO(V = 1) + He = CO(V = 0) + He + 0.2657 eV. The quantity $P_{10}(T)$ was calculated just as in [10] from the equation

$$P_{10}(T) = \frac{1}{kT} \int\limits_0^\infty P_{10}(E)\, e^{-\frac{E}{kT}}\, dE. \tag{1.1}$$

The integration was carried out with the help of the Laguerre quadrature formula [11] with an accuracy of 0.001%. The Morse potential was written in the form [12]

$$U(r) = D\{e^{-r/L} - 2e^{-r/2L}\}.$$

The values of the depth D of the potential well were taken from [12]. For a comparison with experimental data the probabilities $P_{10}(T)$ were converted to characteristic relaxation times pτ [13].

The parameter L of the Morse potential was chosen so that in the temperature range of 1000-5000°K the slope of the linear section of the graph of the dependence of the logarithm of the theoretically calculated values of pτ on $T^{-1/3}$ coincided with the slope of the straight line approximating the experimentally measured values of log (pτ). The steric factor Z was chosen so as to obtain agreement between the theoretical and experimental values of pτ in the temperature region of 1000-5000°K. The quantity L was assumed to be the same for all the isotopic variants of the nitrogen molecules. The logarithms of the probabilities $P_{10}(T)$ obtained were approximated by polynomials by the method of least squares

$$\ln [P_{10}(T)] = \sum_{i=1}^{N} a_i (T \cdot 10^{-3})^i. \tag{1.2}$$

The accuracy of the approximation was 0.001%. The values of D, L, Z, and a_i are presented in Table 1. The temperature dependence of log (pτ) for different pairs of combinations of O_2, N_2, and Ar molecules is shown in Fig. 1. The dashed lines correspond to extrapolation of the high-temperature experimental data into the low-temperature region in accordance with a

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Moscow. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 5, pp. 5-12, September-October, 1977. Original article submitted September 1, 1976.

0021-8944/77/1805-0593$07.50

TABLE 1

No.	Process	$D\cdot10^{12}$, erg	σ, Å	L, Å	$Z-1$	a_0	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
1	$N_2(V=1)+N_2(V=0)=N_2(V=0)+N_2(V=1)$	0,0126	3,681	—	3	−8,25649	−18,6955	208,670	−1116,85	3627,53	−7397,50	9251,35	−6484,60	1950,54
2	$N^{14}N^{14}(V=1)+N^{14}N^{14}(V=0)=N^{14}N^{14}(V=0)+N^{14}N^{14}(V=1)$	0,0126	3,681	—	3	−8,25690	−18,6953	208,678	−1116,84	3627,50	−7397,43	9251,27	−6484,55	1950,53
3	$N^{14}N^{15}(V=1)+N^{14}N^{15}(V=0)N^{14}N^{15}(V=0)+N^{14}N^{15}(V=1)$	0,0126	3,681	—	3	−8,25382	−18,6944	208,672	−1116,82	3627,44	−7397,31	9251,14	−6484,46	1950,50
4	$N^{15}N^{15}(V=1)+N^{15}N^{15}(V=0)+N^{15}N^{15}(V=0)+N^{15}N^{15}(V=1)$	0,0126	3,681	—	3	−8,25778	−18,6948	208,675	−1116,83	3627,46	−7397,36	9251,18	−6484,48	1950,51
5	$N^{15}N^{15}(V=1)+N^{14}N^{14}(V=0)=N^{15}N^{15}(V=0)+N^{14}N^{14}(V=1)$	0,0126	3.681	—	3	−13,7455	48,5610	−300,472	1310,11	−3828,51	7321,93	−8774,22	5967,57	−1755,57
6	$N^{14}N^{15}(V=1)+N^{14}N^{15}(V=0)=N^{15}N^{15}(V=0)+N^{14}N^{15}(V=1)$	0.0126	3,681	—	3	−10.7445	14,0336	−44,7163	104,181	−143,918	71,4970	86,3041	−144,668	617,600
7	$N^{14}N^{14}(V=1)+N^{14}N^{15}(V=0)=N^{14}N^{14}(V=0)+N^{14}N^{15}(V=1)$	0,0126	3,681	—	3	−8,71106	−15,3925	191,388	−1053,97	3471,00	−7136,44	8972,93	−6313,17	1904,23
8	$N_2(V=1)+N_2=N_2(V=0)+N_2$	0,0126	—	4,11	0,272	−46,1901	73,6029	266,121	−3592,21	17031,0	−44996,0	69258,3	−58039,2	20479,0
9	$N^{14}N^{14}(V=1)+N^{14}N^{14}=N^{14}N^{14}(V=0)+N^{14}N^{14}$	0,0126	—	4,11	0,272	−46,1911	73,5480	266.589	−3594,63	17039,0	−45013,2	69281,3	−58056,6	20484,7
10	$N^{14}N^{14}(V=1)+N^{14}N^{15}=N^{14}N^{14}(V=0)+N^{14}N^{15}$	0,0126	—	4,11	0,272	−46.6689	76,0095	253,620	−3547,09	16924,3	−44838,2	69123,7	−57985,2	20474,3
11	$N^{14}N^{14}(V=1)+N^{15}N^{15}=N^{14}N^{14}(V=0)+N^{15}N^{15}$	0,0126	—	4.11	0,272	−45.1040	13,9976	1079.85	−9375,06	41189,0	−106383	162551	−135973	47995,1
12	$N^{14}N^{15}(V=1)+N^{14}N^{14}=N^{14}N^{15}(V=0)+N^{14}N^{14}$	0,0126	—	4,11	0,272	−46,1402	75,5270	249.194	−3503,96	16734,5	−44353,2	6839,09	−57377,9	20261,7
13	$N^{14}N^{15}(V=1)+N^{14}N^{15}=N^{14}N^{15}(V=0)+N^{14}N^{15}$	0,0126	—	4,11	0,272	−46.6261	78.0743	235,468	−3452,10	16604,1	−44141,4	68180,8	−57264,5	20237,0
14	$N^{14}N^{15}(V=1)+N^{15}N^{15}=N^{14}N^{15}(V=0)+N^{15}N^{15}$	0,0126	—	4,11	0,272	−45,7812	38,8139	765,399	−7207,62	32270,5	−83920,3	128606	−107727	38049,9
15	$N^{15}N^{15}(V=1)+N^{14}N^{14}=N^{15}N^{15}(V=0)+N^{14}N^{14}$	0.0126	—	4,11	0,272	−46,0461	77,3754	232,031	−3412,06	16420,1	−43661,6	67447,1	−56651,8	20021,3
16	$N^{15}N^{15}(V=1)+N^{14}N^{15}=N^{15}N^{15}(V=0)+N^{14}N^{15}$	0,0126	—	4,11	0,272	−46,5393	80,0034	217,584	−3356,06	16274,4	−43414,4	67186,3	−56497,8	19982,8
17	$N^{15}N^{15}(V=1)+N^{15}N^{15}=N^{15}N^{15}(V=0)+N^{15}N^{15}$	0,0126	—	4,11	0,272	−47,0131	82,5649	203.206	−3298,84	16120,5	−43142,3	66884,0	−56307.2	19930,9
18	$N_2(V=1)+Ar=N_2(V=0)+Ar$	0.0147	—	2,1	0,276	−51,2403	134,277	−387,369	740,593	−577,864	−814,846	2538,29	−2485,03	896,750
19	$N^{14}N^{14}(V=1)+Ar=N^{14}N^{14}(V=0)+Ar$	0,0147	—	2,1	0,276	−51,2479	134,259	−387,156	739,485	−574,383	−821,757	2546,46	−2490,96	898,481
20	$N^{14}N^{15}(V=1)+Ar=N^{14}N^{15}(V=0)+Ar$	0,0147	—	2,1	0,276	−51,2653	136,566	−404,939	822,150	−821,948	−343,024	1969,92	−2097,45	782,571
21	$N^{15}N^{15}(V=1)+Ar=N^{15}N^{15}(V=0)+Ar$	0,0147	—	2,1	0,276	−51,2304	138,653	−421,633	900,736	−1058,82	116,824	1414,42	−1717,88	670,591
22	$O_2(V=1)+Ar=O_2(V=0)+Ar$	0,0164	—	6,06	0,248	−34,6386	79,5392	−141,523	−138,106	−1669,19	−4724,78	6907,55	−5302,28	1691,63
23	$CO(V=1)+Ar=CO(V=0)+Ar$	0,0163	—	2,19	0,272	−46,5090	114,183	−274,074	267,277	−773,518	−3363,61	5564,94	−4530,53	1495,73
24	$N_2(V=1)+O_2=N_2(V=0)+O_2$	0,0140	—	1,75	0,285	−50,2947	131,470	−376,470	709,510	−517,403	−891,333	2596,69	−2508,10	899,813
25	$N_2(V=1)+CO=N_2(V=0)+CO$	0,0139	—	2,26	0,284	−48,7392	122,761	−329,854	526,573	−22,0256	−1787,13	3625,77	−3185,53	1094,04

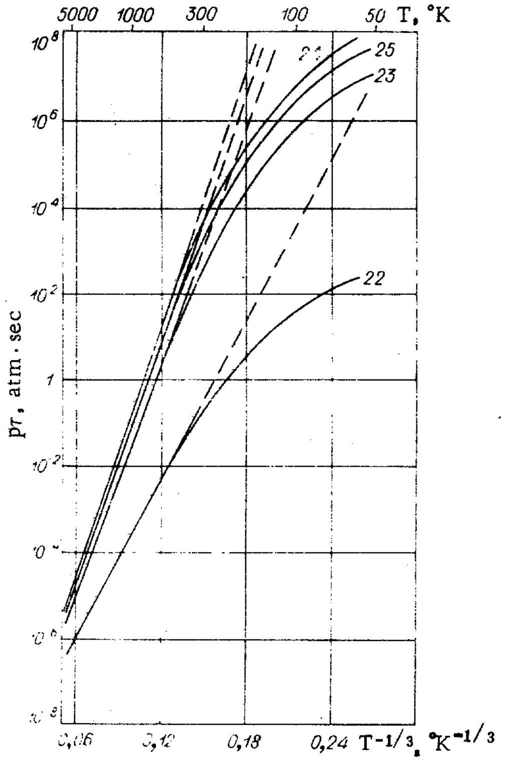

Fig. 1

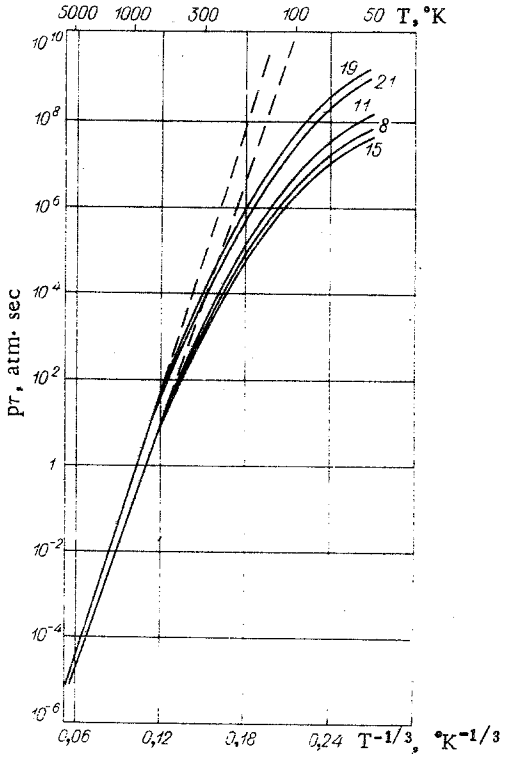

Fig. 2

$\sim T^{-1/3}$ law [14]. The numbers on the curves indicate the serial number of the corresponding process in Table 1. As seen from Fig. 1, for T < 500°K one observes a departure from the Landau–Teller dependence, reaching two to three orders of magnitude for T = 100°K, depending on the pair of molecules. According to the experimental data of [6] the Landau–Teller approximation is not satisfied at low temperatures.

The temperature dependence of log (pτ) for different isotopic variants of nitrogen molecules and for isotopic variants for nitrogen and argon molecules in shown in Fig. 2.

§2. The theory developed in [15, 16] was set at the basis of the calculation of the probabilities $P_{10}^{01}(T)$ of vibrational–vibrational exchange between isotopic variants of nitrogen molecules. Some changes were introduced into the calculating method, however. The probability of V–V exchange was determined from the equation

$$P_{10}^{01}(T) = \frac{1}{2} Z \exp(D/kT) \exp(-\hbar(\omega_1 - \omega_2)/2kT) \times$$
$$\times \sum_{i=1}^{2} \sum_{j=1}^{2} \frac{1}{4} \int_0^\infty \operatorname{sech}^2 \left\{ \sqrt{\frac{2M}{kT\beta}} (\omega_1 - \omega_2) L \right\} \sin \left\{ \sqrt{\frac{2kTM}{\omega_1\omega_2\mu_1\mu_2}} \frac{\gamma_i\gamma_j}{L} \sqrt{\beta} \right\} e^{-\beta} d\beta, \qquad (2.1)$$

where $\beta = Mv^2/2kT$; $\gamma_1 = m_A/(m_A + m_B)$; $\gamma_2 = m_B/(m_A + m_B)$; $\gamma_3 = m_C/(m_C + m_D)$; $\gamma_4 = m_D/(m_C + m_D)$; ω is the transition frequency; μ is the reduced mass of the oscillator; M is the reduced mass of the colliding molecules; v is the relative translational velocity of the molecules; ħ is Planck's constant; m is the mass of the corresponding atom in a molecule. The indices 1 and 2 pertain to the molecules AB and CD, respectively, taking part in the process

$$AB(V = 1) + CD(V = 0) = AB(V = 0) + CD(V = 1) + \hbar(\omega_1 - \omega_2).$$

The factor exp(D/kT) roughly allows for the attraction of the molecules [17], the coefficient 1/2 appears due to averaging over the impact parameter of the collision of molecules AB and CD [18], and the factor $\exp[-\hbar(\omega_1 - \omega_2)/2kT]$ is introduced to make the probability equations symmetrical relative to the final and initial velocities of the colliding molecules [19]. The double summation is carried out in order to average over the collisions AB–CD, AB–DC, BA–CD, and BA–DC.

In Eq.(2.1) the argument of the sine is written in a more general form than in [16], a form suitable for different molecules.

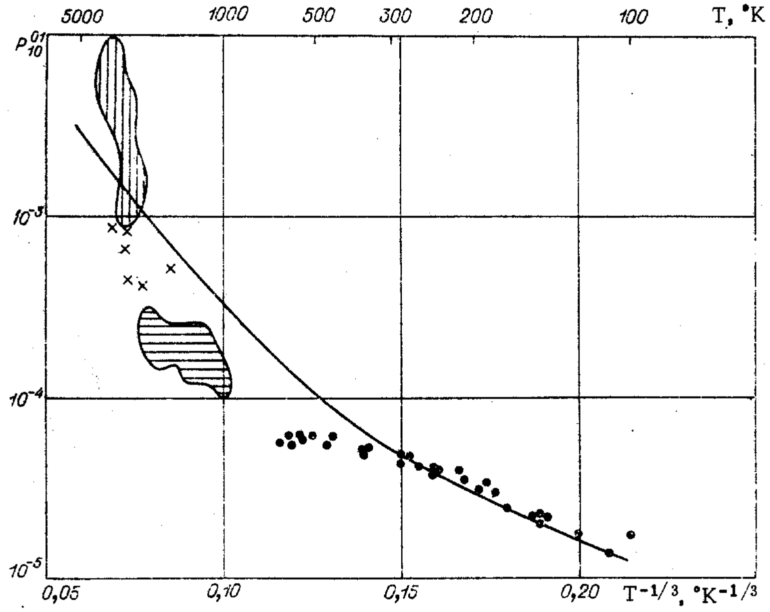

Fig. 3

The parameter L in the interaction potential $U(r) = Ae^{-r/L} - D$ was determined with the help of the parameter σ of the Lennard-Jones potential by method A of [13]. The values of σ presented in Table 1 were taken from [12]. The steric factor Z was taken as equal to 1/3 in the calculations.

The integral of (2.1) was not replaced by an approximate analytical formula as in [16] but was determined by numerical integration with an accuracy of 0.001%.

The results of a calculation of the exchange probability $P_{10}^{01}(T)$ by Eq. (2.1) for the process $N_2(V = 1) + CO(V = 0) = N_2(V = 0) + CO(V = 1) + 0.0231$ eV are presented in Fig. 3. The known results presented in [7] are plotted with dots, those presented in [20] by crosses, the region where the experimental values of [21] lie is hatched with horizontal lines, and that for [22] by vertical lines.

The agreement with the experimental data is very good in the region of low temperatures. But in the region of high temperatures the spread between the published experimental data reaches almost an order of magnitude, and our results agree best with the results of [22].

The exchange probabilities for the processes

$$N_2(V = 1) + O_2(V = 0) = N_2(V = 0) + O_2(V = 1) + 0.0958 \text{ eV},$$
$$CO(V = 1) + O_2(V = 0) = CO(V = 0) + O_2(V = 1) + 0.0728 \text{ eV}$$

were also calculated by Eq. (2.1) and good agreement with the experiments was found.

This gives reason to assume that in the case of V—V exchange between nitrogen molecules, for which experimental data are entirely absent, the results of a calculation by Eq. (2.1) will also be close to the true probabilities.

The temperature dependence of the probabilities $P_{10}^{01}(T)$ for isotopic variants of nitrogen molecules is shown by solid lines in Fig. 4 while the results of a calculation by Eq. (2) of [16] for the process

$$N_2(V = 1) + N_2(V = 0) = N_2(V = 0) + N_2(V = 1)$$

with a steric factor Z = 1/3 is shown by a dashed line.

As follows from Fig. 4, in the case of resonance vibrational—vibrational exchange the $P_{10}^{01}(T)$ are practically the same for all three isotopic variants of nitrogen molecules, but with an increase in the isotopic shift the probabilities of quasiresonance V—V exchange decrease, with the difference between them becoming more noticeable with a decrease in temperature.

§3. On the basis of the results presented one can conclude that the mass number has an important effect on the probabilities of vibrational—vibrational and vibrational—translational exchanges.

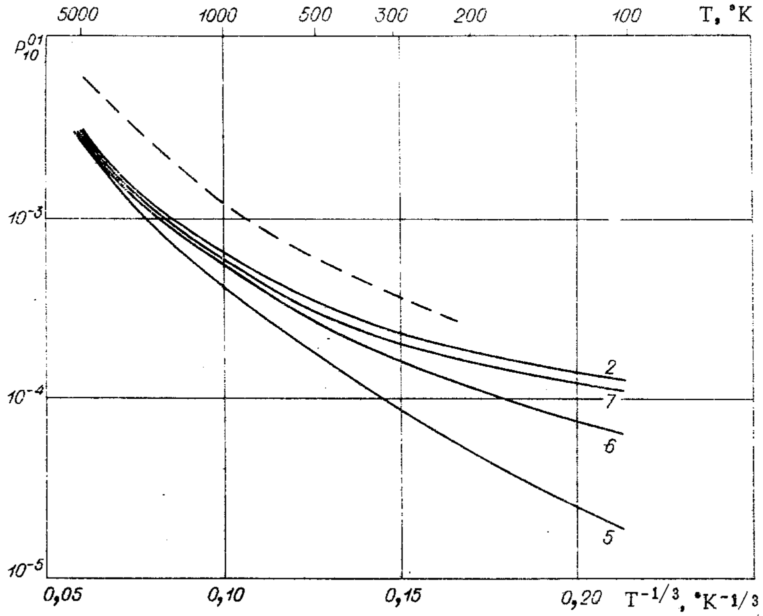

Fig. 4

In the calculations it was found that the difference between the probabilities at T = 100°K for the processes

$$N^{14}N^{14}(V=1)+N^{15}N^{15}=N^{14}N^{14}(V=0)+N^{15}N^{15}+0.289\text{ eV}, \tag{3.1}$$

$$N^{15}N^{15}(V=1)+N^{14}N^{14}=N^{15}N^{15}(V=0)+N^{14}N^{14}+0.279\text{ eV} \tag{3.2}$$

is 51%, while for the processes

$$N^{14}N^{14}(V=1)+\text{Ar}=N^{14}N^{14}(V=0)+\text{Ar}+0.289\text{ eV}, \tag{3.3}$$

$$N^{15}N^{15}(V=1)+\text{Ar}=N^{15}N^{15}(V=0)+\text{Ar}+0.279\text{ eV} \tag{3.4}$$

it is 15%.

Such a difference is connected with the fact that the energy of the $N^{14}N^{14}$ oscillator is greater than that of the $N^{15}N^{15}$ oscillator, while the mass of the argon atom is greater than that of $N^{14}N^{14}$ or $N^{15}N^{15}$. The indicated tendency of a decrease in the exchange probability with a decrease in the oscillator energy and the mass of the incident molecule was also brought out in [23], where the experimental data on the characteristic times of vibrational–translational relaxation were analyzed for a whole series of molecules.

The differences in the probabilities become smaller with an increase in temperature, and at T = 3000°K they are 24 and 9% for the processes (3.1), (3.2) and (3.3), (3.4), respectively.

In the case of V–V exchange for isotopic variants of nitrogen molecules it was found that the maximum difference in probabilities is observed for processes 2 and 5 (see Table 1), where the energy defect is maximal, and it reaches 82% at T = 100°K.

The larger difference in probabilities in comparison with V–T exchange is due to the fact that with an increase in the energy defect, i.e., with departure of the system from resonance, the probability of V–V exchange decreases sharply by an exponential law [14].

As noted in a number of reports (see [24], for example), the multipole interaction can make a significant contribution to the probability of V–V exchange at low temperatures. The probabilities of V–V exchange for CO molecules with allowance for the dipole–dipole interaction are calculated in [18]. It is shown that allowance for this interaction leads to an increase in the probability and that the effect of the weaker dipole–quadrupole interaction is small. This gives reason to assume that the relatively weak quadrupole–quadrupole interaction changes the results of the calculation insignificantly, since the N_2 molecule does not have a permanent dipole moment.

The results of the present work make it possible to proceed to the numerical calculation of processes of separation of nitrogen isotopes in chemical reactions taking place under conditions of thermodynamic nonequilibrium at a low translational temperature. Up to now we know of examples in the literature of such calculations [4, 5] which were made without allowance for the difference in the probabilities of V–T exchange for different isotopic variants of nitrogen.

However, the difference in the probabilities of V—T exchange indicated above can obviously affect the coefficient of separation calculated, for example, in [5]. Thus, for the processes

$$N^{14}N^{14}(V = 10) + Ar = N^{14}N^{14}(V = 9) + Ar + 0.257 \text{ eV}, \tag{3.5}$$

$$N^{15}N^{15}(V = 10) + Ar = N^{15}N^{15}(V = 9) + Ar + 0.243 \text{ eV} \tag{3.6}$$

the ratio of the probability $P_{10,9}(T)$ of the process (3.6) to the analogous probability of the process (3.5) equals about 3-4 and increases with the level number, which can lead to depletion of the upper vibrational levels of the heavy isotope.

The authors thank E. E. Nikitin, S. Ya. Umanskii, and E. A. Andreev for useful discussions.

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A METHOD FOR INTEGRATING THE FOKKER–PLANCK EQUATION

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UDC 533.72

A method for analyzing kinetic processes described by the Fokker–Planck equation is proposed. The method is based on a series expansion of the distribution function in the powers of an evolution operator acting on the equilibrium function (or on the series of temporal derivatives of some parameter). To be specific, the following equation is considered which describes a wide range of effects in standard plasma as well as in a solid-body one:

$$\frac{\partial f}{\partial t} + v_i \frac{\partial f}{\partial r_i} = \frac{\partial}{\partial v_i}\left(D_{ij}\frac{\partial f}{\partial v_j} - A_i f\right) = \hat{H} f. \tag{1}$$

In the case of a spatially homogeneous distribution function f of electrons which only depend on the modulus of the velocity vector v provided the equilibrium temperature T_e of the electron distribution is known Eq. (1) can be reduced to

$$g\frac{\partial u}{\partial t} = \frac{\partial}{\partial v}\left(gD\frac{\partial u}{\partial v}\right), \tag{2}$$

where $u = \exp(mv^2/2T_e)f$; $g = v^2\exp(-mv^2/2T_e)$; D is the diffusion coefficient; v is the modulus of the velocity vector.

By integrating both sides of (2) twice with respect to v and assuming the derivative $\partial u/\partial v$ to be bounded at zero one has

$$u = u_0 + \hat{E}u, \tag{3}$$

where the evolution operation $\hat{E}$ is defined as follows:

$$\hat{E} = \int_0^v \frac{dv'}{gD}\int_0^{v'} dv'' g\frac{\partial}{\partial t} = \hat{H}^{-1}\frac{\partial}{\partial t}.$$

The operator $\hat{E}$ now acts on the equilibrium distribution function $u = u_0$ on the right-hand side of (3); the result is called a quasiequilibrium distribution function (QDF) of the first order. By acting with the operator $\hat{E}$ on the right-hand side of (3) on the QDF of the first order one finds a QDF of the second order, etc. Thus, the sought distribution function is now represented in the form of an infinite series in the powers of the evolution operator $\hat{E}$ or in the form of a series of time derivatives of the parameter u_0:

$$u = \sum_{n=0}^{\infty} \hat{E}^n u_0 = \sum_{n=0}^{\infty} \beta_n \frac{d^{(n)}u_0}{dt^n}, \tag{4}$$

in which the expansion coefficients are found from the formula

$$\beta_n = \int_0^v \frac{dv'}{gD}\int_0^{v'} dv'' g\beta_{n-1}, \quad \beta_0 = 1.$$

Terms with higher derivatives in (4) play an important part only in the initial stages of the procedure. They become smaller in due time, and starting from an instant the expansion (4) can be limited to a finite number of terms. The assumption that an infinite series can be "curtailed" is based on the fact that gradually the system "forgets" the data on the ini-

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Moscow. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 5, pp. 13-16, September-October, 1977. Original article submitted September 30, 1976.

0021-8944/77/1805-0599$07.50