KINETIC EQUATIONS FOR VIBRATIONAL RELAXATION

IN A MIXTURE OF POLYATOMIC GASES

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Kinetic equations are derived for the relaxation of the vibrational energy in a mixture of polyatomic gases, which are ones with molecules simulated by harmonic oscillators. The most general case is envisaged, where the energy relaxation occurs not only via vibrational—translational transitions but also via multiquantum vibrational exchange involving an arbitrary number of vibrational modes. The analysis also incorporates the possible degeneracy of each mode when the molecules colliding are the same. An expression is derived that extends previous results [1-6] and that relates the vibrational temperatures in the case of quasiequilibrium. Equations are derived for the vibrational relaxation for the $CO_2 - N_2$ case.

There have recently been various papers [7-14] dealing with the theory of vibrational relaxation in a gas consisting of polyatomic molecules. For instance, in [7-11, 13] there are discussions of the vibrational relaxation of CO_2 or $CO_2 - N_2$, $CO_2 - N_2 - He$, $CO_2 - N_2 - H_2O$ mixtures for detailed conditions of nonequilibrium, such as excitation of vibrations by electron impact or rapid cooling of gas on flow through a slot or nozzle. Use has been made [7, 8, 10, 13] of approximate kinetic equations that do not take into account transitions between highly excited states.

Equations have also been derived [9, 12, 14] for various particular cases with allowance for the transitions between the upper levels, and equations have been derived for relaxation of the vibrational energy of molecules represented by a set of harmonic oscillators. All the same, the use of these equations leads to errors, since they were derived neglecting the degeneracy of the vibrations, or else considering it incorrectly. Also, in [9, 12, 14] there was no correct consideration of the features of relaxation in the gas consisting of identical molecules.

Another aspect of the theory of vibrational relaxation in a multicomponent mixture of molecular gases is the distribution of the energy between the various vibrational modes in quasiequilibrium, when the energy exchange rate between these modes substantially exceeds the rate of vibrational—translational relaxation. The first relationships to be derived were those of [1, 2] for the mean number of vibration quanta and the vibrational temperatures in rapid one-quantum exchange in a binary mixture of diatomic gases; subsequently these were extended to the particular case of a multicomponent mixture [3] and for a binary mixture of diatomic gases with two rapid exchange channels [4, 6] and with one channel for multiquantum exchange [5]. However, the expressions found in [1-6] relate the temperatures only for two vibrational modes and do not reflect the position that may exist when there is rapid vibrational exchange in the mixture of polyatomic molecules.

The object of the present study is to derive the kinetic equations for the relaxation of the vibrational modes of a polyatomic molecule represented as a set of harmonic oscillators, together with the derivation of a general relationship between the vibrational temperatures in rapid vibrational exchange between modes.

1. Relaxation Equation for a Vibrational Mode in a Binary Mixture of Polyatomic Gases. Consider the vibrational relaxation in a mixture of the polyatomic gases A and B; we take into account only transitions due to collisions of A and B, which corresponds to the case where gas A is a minor impurity in B. The relaxation in the one-component gas will be considered in Sec. 2. Let the molecules A and B have

altogether L types of modes, which are represented by harmonic oscillators. In this case, an arbitrary vibrational state of the A + B system may be described by a set of vibrational quantum numbers $(v_1, v_2, \ldots, v_L)$; one of the possible relaxation channels for the populations of the vibrational levels when A and B collide may be put in the form

$$(v_1, \ldots, v_k; v_{k+1}, \ldots, v_L) \equiv \{v_i; v_j\} \to (v_1 \pm l_1, \ldots, v_k \pm l_k;$$
$$v_{k+1} \mp l_{k+1}, \ldots, v_L \mp l_L) \equiv \{v_i \pm l_i; v_j \mp l_j\} \quad (i = 1 - k, \; j = k+1 - L) \tag{1.1}$$

This formula means that the system A + B starts from some initial state $\{v_i; v_j\}$ and as a result of collision passes to a new state such that the modes enumerated by subscript i undergo steps of l_i quanta upwards (downwards), while the other modes, which are enumerated by subscript j, undergo transitions by l_j quanta downwards (upwards). In groups i and j there may be modes belonging to different molecules. We distinguish in molecule A an arbitrary mode ξ belonging for instance to the group of modes i, and we consider the change in the mean number of vibrational quanta ε_ξ for this mode. First of all we write down the balance equations for the change in the populations $N_A(v_\xi)$ of the v_ξ levels as a result of the process of (1.1) on collision of A and B:

$$\frac{dN_A(v_\xi)}{dt} = \frac{Z_{AB}}{N_B} \sum_{v_i \neq r_\xi} \left[P_{AB} \begin{Bmatrix} v_i - l_i \to v_i \\ v_j + l_j \to v_j \end{Bmatrix} N_A \{v_{i_A} - l_{i_A};$$
$$v_{j_A} + l_{j_A}\} N_B \{v_{i_B} - l_{i_B}; v_{j_B} + l_{j_B}\} - P_{AB} \begin{Bmatrix} v_i \to v_i - l_i \\ v_j \to v_j + l_j \end{Bmatrix} \times$$
$$\times N_A \{v_{i_A}; v_{j_A}\} N_B \{v_{i_B}; v_{j_B}\} + P_{AB} \begin{Bmatrix} v_i + l_i \to v_i \\ v_j - l_j \to v_j \end{Bmatrix} N_A \{v_{i_A} + l_{i_A}; v_{j_A} - l_{j_A}\} \times$$
$$\times N_B \{v_{i_B} + l_{i_B}; v_{j_B} - l_{j_B}\} - P_{AB} \begin{Bmatrix} v_i \to v_i + l_i \\ v_j \to v_j - l_j \end{Bmatrix} N_A \{v_{i_A}; v_{j_A}\} N_B \{v_{i_B}; v_{j_B}\} \right] \tag{1.2}$$
$$N_A(v_\xi) = \sum_{v_{i_A} \neq v_\xi} N_A \{v_{i_A}; v_{j_A}\}$$

Here $N_A\{v_{i_A}; v_{j_A}\}$ and $N_B\{v_{i_B}; v_{j_B}\}$ are the populations of the vibrational states $\{v_{i_A}; v_{j_A}\}$ and $\{v_{i_B}; v_{j_B}\}$ respectively of molecules A and B, while N_A and N_B are the total numbers of molecules A and B in unit volume, Z_{AB} is the number of collisions of particles A and with B molecules in unit time, and P_{AB} is the probability of a composite vibrational transition in the A + B system in one collision. The summation in (1.2) is taken over all levels of all modes in both molecules, apart from the distinguished mode ξ in A.

We assume that each mode i or j may have degeneracy r_i or r_j; then the principle of detailed balancing gives the probabilities of the forward and reverse processes as related by relationships of the form

$$P_{AB} \begin{Bmatrix} v_i - l_i \to v_i \\ v_j + l_j \to v_j \end{Bmatrix} = \frac{g\{v_i; v_j\}}{g\{v_i - l_i; v_j + l_j\}} P_{AB} \begin{Bmatrix} v_i \to v_i - l_i \\ v_j \to v_j + l_j \end{Bmatrix} \prod_{i=1}^{k} \beta_i^{l_i} \prod_{j=k+1}^{L} \beta_j^{-l_j} \tag{1.3}$$

$$\beta_s = \exp\left(-\frac{h\nu_s}{kT}\right), \qquad \left(\begin{matrix} s = i = 1 - k \\ s = j = k + 1 - L \end{matrix} \right)$$

Here ν_s is the frequency of the normal vibrations of mode s, T is the gas temperature, and $g\{v_i; v_j\}$ is the statistical weight of the $\{v_i; v_j\}$ vibrational state of A + B:

$$g\{v_i; v_j\} = g(v_1) \ldots g(v_k) g(v_{k+1}) \ldots g(v_L) = \prod_{i=1}^{k} \frac{(v_i + r_i - 1)!}{v_i!(r_i - 1)!} \times$$
$$\times \prod_{j=k+1}^{L} \frac{(v_j + r_j - 1)!}{v_j!(r_j - 1)!} = \prod_{i=1}^{k} \binom{v_i + r_i - 1}{v_i} \prod_{j=k+1}^{L} \binom{v_j + r_j - 1}{v_j} \tag{1.4}$$

To derive from (1.2) the relevant equation for the vibrational energy of mode ξ, we express the value of P_{AB} for transitions between arbitrary upper states in terms of the corresponding probabilities for transitions between the lowest levels involved in transition. In this case [15]

$$P_{AB} \begin{Bmatrix} v_i + l_i \to v_i \\ v_j - l_j \to v_j \end{Bmatrix} = \frac{g\{v_j\}}{g\{v_j - l_j\} g\{l_j\}} P_{AB} \begin{Bmatrix} l_i \to 0 \\ 0 \to l_j \end{Bmatrix} \prod_{i=1}^{k} \binom{v_i + l_i}{v_i} \prod_{j=k+1}^{L} \binom{v_j}{v_j - l_j} \tag{1.5}$$

Further, for each type of normal vibration (mode) we introduce a vibrational temperature T_s, which characterizes the quantity of vibrational energy in that mode. This is possible because, as for diatomic molecules, the vibrational exchange within each type of vibration occurs in a time much less than the time needed for transition of energy to translational degrees of freedom and exchange of energy between different vibrational modes. The temperatures T_s will generally differ one from another and from the gas temperature T. Then the populations in (1.2) may be put in the form

$$N_A\{v_{i_A}; v_{j_A}\} = N_A g\{v_{i_A}; v_{j_A}\} \prod_{i_A} x_{i_A}^{v_{i_A}}(1 - x_{i_A})^{r_{i_A}} \prod_{j_A} x_{j_A}^{v_{j_A}}(1 - x_{j_A})^{r_{j_A}} \tag{1.6}$$

or in more compact form, omitting the subscripts A and B,

$$N_A\{v_{i_A}; v_{j_A}\} N_B\{v_{i_B}; v_{j_B}\} = N_A N_B g\{v_i; v_j\} \prod_{i=1}^{k} x_i^{v_i}(1 - x_i)^{r_i} \prod_{j=k+1}^{L} x_j^{v_j}(1 - x_j)^{r_j} \tag{1.7}$$

$$x_s = \exp\left(-\frac{h\nu_s}{kT_s}\right) \qquad \left(\begin{matrix} s = i = 1 - k \\ s = j = k+1 - L \end{matrix}\right) \tag{1.8}$$

If some mode s belongs, for instance, to molecule A, then the mean reserve of vibrational quanta ε_s in this mode per molecule may be expressed in terms of x_s; here we multiply (1.6) by v_s and sum over all $\{v_{i_A}; v_{j_A}\}$ that include v_s from 0 to ∞. We sum using (1.4) and (1.8) and omit the subscript A to get

$$\varepsilon_s = r_s x_s/(1 - x_s) \tag{1.9}$$

The summation over all $\{v_{i_A}; v_{j_A}\}$ in (1.9) has taken into account the contribution from combination levels to the total ε_s in mode s.

Now we return directly to derivation of the kinetic equation for the vibrational energy in mode ξ. We multiply both parts of (1.2) by v_ξ and then sum over all $\{v_i; v_j\}$ including v_ξ from 0 to ∞ and use (1.3)-(1.9) to get after transformation that

$$\frac{d\varepsilon_\xi}{dt} = Z_{AB}P_{AB}\begin{Bmatrix} l_i \to 0 \\ 0 \to l_j \end{Bmatrix} \frac{l_\xi}{g\{l_j\}}\left(\prod_{i=1}^{k}\beta_i^{l_i}\prod_{j=k+1}^{L}\beta_j^{-l_j}x_j^{l_j} - \prod_{i=1}^{k}x_i^{l_i}\right) \times$$
$$\times \prod_{i=1}^{k}(1 - x_i)^{r_i}\sum_{v_i=0}^{\infty}\frac{(v_i + l_i + r_i - 1)!}{v_i!\,l_i!\,(r_i - 1)!}x_i^{v_i}\prod_{j=k+1}^{L}(1 - x_j)^{r_j} \times$$
$$\times \sum_{v_j=0}^{\infty}\frac{(v_j + l_j + r_j - 1)!}{v_j!\,l_j!\,(r_j - 1)!}x_j^{v_j} = Z_{AB}l_\xi g\{l_i\}P_{AB}\begin{Bmatrix} l_i \to 0 \\ 0 \to l_j \end{Bmatrix} \times$$
$$\times \left(\prod_{i=1}^{k}\beta_i^{l_i}\prod_{j=k+1}^{L}\beta_j^{-l_j}x_j^{l_j} - \prod_{i=1}^{k}x_i^{l_i}\right)\prod_{i=1}^{k}(1 - x_i)^{r_i}F(l_i + r_i, 1; 1; x_i) \times$$
$$\times \prod_{j=k+1}^{L}(1 - x_j)^{r_j}F(l_j + r_j, 1; 1; x_j) \tag{1.10}$$

From (1.10) we get the final form for the equation by using the explicit form for the hypergeometric functions:

$$\frac{d\varepsilon_\xi}{dt} = Z_{AB}P_{AB}\begin{Bmatrix} l_i \to 0 \\ 0 \to l_j \end{Bmatrix} l_\xi\left(\prod_{i=1}^{k}\beta_i^{l_i}\prod_{j=k+1}^{L}\beta_j^{-l_j}x_j^{l_j} - \prod_{i=1}^{k}x_i^{l_i}\right) \times$$
$$\times \prod_{i=1}^{k}\binom{l_i + r_i - 1}{l_i}(1 - x_i)^{-l_i}\prod_{j=k+1}^{L}(1 - x_j)^{-l_j} \tag{1.11}$$

We use (1.9) and the equilibrium value ε_{0s} for the gas temperature T

$$\varepsilon_{0s} = r_s\beta_s/(1 - \beta_s)$$

to rewrite (1.11) in the form

$$\frac{d\varepsilon_\xi}{dt} = Z_{AB}P_{AB}\begin{Bmatrix} l_i \to 0 \\ 0 \to l_j \end{Bmatrix} l_\xi\prod_{i=1}^{k}\binom{l_i + r_i - 1}{l_i}[r_i(r_i + \varepsilon_{0i})]^{-l_i}\prod_{j=k+1}^{L}(r_j\varepsilon_{0j})^{-l_j}\left\{\prod_{i=1}^{k}[\varepsilon_{0i}(r_i + \varepsilon_i)]^{l_i}\prod_{j=k+1}^{L}[\varepsilon_j(r_j + \varepsilon_{0j})]^{l_j} - \right.$$
$$\left. - \prod_{i=1}^{k}[\varepsilon_i(r_i + \varepsilon_{0i})]^{l_i}\prod_{j=k+1}^{L}[\varepsilon_{0j}(r_j + \varepsilon_i)]^{l_j}\right\} \tag{1.12}$$

The probability $P_{AB}\begin{Bmatrix} l_i \to 0 \\ 0 \to l_j \end{Bmatrix}$, appearing in (1.11) and (1.12) is dependent on the degeneracy of the modes i and j involved in the transition; it has been shown [15]

$$P_{AB}\begin{Bmatrix} l_i \to 0 \\ 0 \to l_j \end{Bmatrix} = P_{AB}^{SSH}\begin{Bmatrix} l_i \to 0 \\ 0 \to l_j \end{Bmatrix} \prod_{i=1}^{k} r_i^{l_i} \prod_{j=k+1}^{L} r_j^{l_j} \left[\prod_{i=1}^{k} \binom{l_i + r_i - 1}{l_i} \right]^{-1} \tag{1.13}$$

where P_{AB}^{SSH} is the transition probability calculated without allowance for the degeneracy by the usual SSH method [16, 17]. We substitute (1.13) in (1.12) to get a form for the kinetic equation

$$\frac{d\varepsilon_\xi}{dt} = Z_{AB} P_{AB}^{SSH} \begin{Bmatrix} l_i \to 0 \\ 0 \to l_j \end{Bmatrix} l_\xi \prod_{i=1}^{k} (r_i + \varepsilon_{0i})^{-l_i} \prod_{j=k+1}^{L} \varepsilon_{0j}^{-l_j} \left\{ \prod_{i=1}^{k} [\varepsilon_{0i}(r_i + \varepsilon_i)]^{l_i} \times \right.$$
$$\left. \times \prod_{j=k+1}^{L} [\varepsilon_j(r_j + \varepsilon_{0j})]^{l_j} - \prod_{i=1}^{k} [\varepsilon_i(r_i + \varepsilon_{0i})]^{l_i} \prod_{j=k+1}^{L} [\varepsilon_{0j}(r_j + \varepsilon_j)]^{l_j} \right\} \tag{1.14}$$

Equations (1.11), (1.12), and (1.14) describe the relaxation of the vibrational quanta or energy in mode ξ via one channel, which is specified by giving the numbers $\{l_i; l_j\}$; if there are several channels, the rates as calculated via (1.11), (1.12), and (1.14) become somewhat more complicated. Naturally, the resulting equation for ε_ξ in the general case must be solved in conjunction with other equations describing the energy relaxation in the other modes.

Equations (1.11), (1.12), and (1.14) are the most general form of the equations for the vibrational energy of quanta in a mixture of harmonic oscillators, and they describe the relaxation on the collision of different molecules; if $l_i = l_j = 0$ (for $i \neq \xi$), $l_\xi = 1$, and then (1.11), (1.12), and (1.14) become the usual Landau–Teller expression for vibrational–translational relaxation. If $L = 2$, $l_\xi = 1$, $l_j = 1$, $r_\xi = 1$, $r_j = 1$ they correspond to one-quantum exchange in the binary mixture of diatomic molecules. In the particular case $\{l_i; l_j\} \leq 1$, (1.11), (1.12), and (1.14) become the formula derived in [12] for $\{r_i; r_j\} = 1$, which describes the one-quantum exchange involving many modes. However, in [12] and also in [9, 14] there was an incorrect consideration of the case of degenerate oscillators; also, in [9, 12, 14] there was no correct discussion of some features of the relaxation when identical molecules collide.

2. Relaxation of a Mode Energy in a One-Component Polyatomic Gas. There are special features in the relaxation in A + A collisions because there is a difference from the A + B case in that the arbitrary energy state is not defined unambiguously by the sole choice of the set of quantum numbers $\{v_i; v_j\}$ for the two molecules, and the result is the same if, for instance, in one molecule for a mode we consider instead of level v_i the level $v_i + k$, while for the other molecule in the same mode we consider in place of level w_i a level $w_i - k$. In fact this means that in A + A collisions part of the energy or some of the quanta lost by mode ξ from one molecule A may be distributed differently in the two molecules. Formally, this case corresponds to doubling the degeneracy of each mode, so the equation for the relaxation of the vibrational quanta in mode ξ in the one component polyatomic gas can be derived by using the results of the previous section. In this case we have, instead of (1.12),

$$\frac{d\varepsilon_\xi}{dt} = \frac{1}{2} Z_{AA} P_{AA} \begin{Bmatrix} l_i \to 0 \\ 0 \to l_j \end{Bmatrix} l_\xi \prod_{i=1}^{k} \binom{l_i + 2r_i - 1}{l_i} [r_i(r_i + \varepsilon_{0i})]^{-l_i} \prod_{j=k+1}^{L} (r_j \varepsilon_{0j})^{-l_j} \times$$
$$\times \left\{ \prod_{i=1}^{k} [\varepsilon_{0i}(r_i + \varepsilon_i)]^{l_i} \prod_{j=k+1}^{L} [\varepsilon_j(r_j + \varepsilon_{0j})]^{l_j} - \prod_{i=1}^{k} [\varepsilon_i(r_i + \varepsilon_{0i})]^{l_i} \prod_{j=k+1}^{L} [\varepsilon_{0j}(r_j + \varepsilon_j)]^{l_j} \right\} \tag{2.1}$$

The symbols here are as in Section 1, while the probabilities are [15] defined by

$$P_{AA}\begin{Bmatrix} l_i \to 0 \\ 0 \to l_j \end{Bmatrix} = P_{AA}^{SSH}\begin{Bmatrix} l_i \to 0 \\ 0 \to l_j \end{Bmatrix} \prod_{i=1}^{k} (2r_i)^{l_i} \prod_{j=k+1}^{L} (2r_j)^{l_j} \left[\prod_{i=1}^{k} \binom{l_i + 2r_i - 1}{l_i} \right]^{-1} \tag{2.2}$$

We substitute (2.2) into (2.1) to get an equation analogous to (1.14):

$$\frac{d\varepsilon_\xi}{dt} = \frac{1}{2} \prod_{i=1}^{k} 2^{l_i} \prod_{j=k+1}^{L} 2^{l_j} Z_{AA} P_{AA}^{SSH} \begin{Bmatrix} l_i \to 0 \\ 0 \to l_j \end{Bmatrix} l_\xi \prod_{i=1}^{k} (r_i + \varepsilon_{0i})^{-l_i} \prod_{j=k+1}^{L} \varepsilon_{0j}^{-l_j} \left\{ \prod_{i=1}^{k} [\varepsilon_{0i}(r_i + \varepsilon_i)]^{l_i} \prod_{j=k+1}^{L} [\varepsilon_j(r_j + \varepsilon_{0j})]^{l_j} - \right.$$
$$\left. - \prod_{i=1}^{k} [\varepsilon_i(r_i + \varepsilon_{0i})]^{l_i} \prod_{j=k+1}^{L} [\varepsilon_{0j}(r_j + \varepsilon_j)]^{l_j} \right\} \tag{2.3}$$
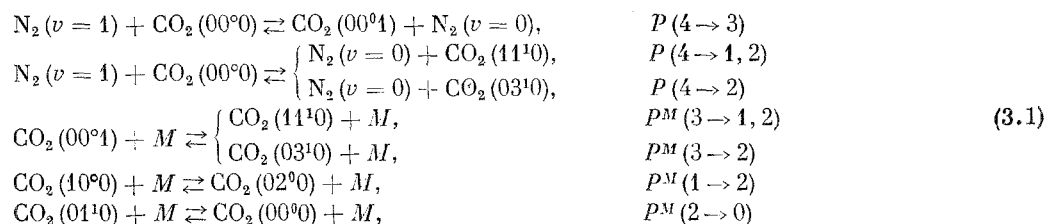
Comparison of (1.14) and (2.3) shows that the relaxation equations for ε_ξ in the A + B mixture take the same form as for a one-component gas; in the latter case, however, under otherwise similar conditions we get the additional factor $2l_1 + l_2 + \ldots + l_k + l_{k+1} + \ldots + l_L^{-1}$, which increases the relaxation rate, and the presence of this is related to the additional relaxation channels for mode ξ in A + A collisions on account of the different possible ways of redistributing the vibrational energy between identical molecules before and after collision. Therefore (2.3) can be obtained directly by summing (1.14) as written for each possible relaxation channel with the participation of two identical modes from groups i and j belonging to different molecules. These channels differ in that the jumps in transitions in identical molecules can be different and can vary within limits from 0 to l_1 or l_j, but the sum of the jumps in these modes must always be equal to l_1 or l_j for a given energy transition.

3. Equations for Vibrational Relaxation for a $CO_2 - N_2$ Mixture. We use the general expressions derived in Secs.1 and 2 to describe the vibrational relaxation in a $CO_2 - N_2$ mixture; very detailed studies have recently been made [7-14] on relaxation in CO_2 and in mixtures such as $CO_2 - N_2$, $CO_2 - N_2 - He$, etc., which is due to the production of high power infrared radiation at 10.6 μ in the $00^01 - 10^00$ transition and CO_2.

We number from 1 to 4 the symmetrical, bending, and antisymmetrical modes of CO_2 and the vibration of N_2:

$$(hv_1 / k) = 2000° \text{ K}, \quad (hv_2 / k) = 960° \text{ K},$$
$$(hv_3 / k) = 3380° \text{ K}, \quad (hv_4 / k) = 3353° \text{ K}.$$

Here $r_1 = r_3 = r_4 = 1$, $r_2 = 2$ (the bending mode is doubly degenerate), and the main relaxation channels in modes 1-4 are due to the following processes (the corresponding probabilities are shown on the right):

$$
\begin{aligned}
&N_2 (v = 1) + CO_2 (00^00) \rightleftarrows CO_2 (00^01) + N_2 (v = 0), && P(4 \to 3) \\
&N_2 (v = 1) + CO_2 (00^00) \rightleftarrows \begin{cases} N_2 (v = 0) + CO_2 (11^10), & P(4 \to 1, 2) \\ N_2 (v = 0) + CO_2 (03^10), & P(4 \to 2) \end{cases} \\
&CO_2 (00^01) + M \rightleftarrows \begin{cases} CO_2 (11^10) + M, & P^M(3 \to 1, 2) \\ CO_2 (03^10) + M, & P^M(3 \to 2) \end{cases} \\
&CO_2 (10^00) + M \rightleftarrows CO_2 (02^00) + M, && P^M(1 \to 2) \\
&CO_2 (01^10) + M \rightleftarrows CO_2 (00^00) + M, && P^M(2 \to 0)
\end{aligned}
\tag{3.1}
$$

Here $M = CO_2$ or N_2. Note that in (3.1) we have written for clarity only the transitions between the lowest levels; we have also made the simplifying assumptions

$$hv_3 = hv_4, \quad hv_1 = 2hv_2, \quad x_2 \ll 1, \quad T_2 = T_1$$

(the last assumption is usually justified in view of the rapid exchange of vibrational quanta between the symmetrical and bending modes, since $P^M(1 \to 2)$ is much larger than the other probabilities). Subject to these assumptions, we use (3.1) with (1.12) and (2.1) to write the relaxation equations for $CO_2 - N_2$ in the form

$$
\frac{d\varepsilon_4}{dt} = Z_{N_2, CO_2} \Big\{ P(4 \to 3)(\varepsilon_3 - \varepsilon_4) + P(4 \to \Sigma) \times
$$
$$
\times \Big[\exp\Big(-\frac{500}{T}\Big)\Big(\frac{\varepsilon_2}{2}\Big)^3 (1 + \varepsilon_4) - \varepsilon_4\Big(1 + \frac{\varepsilon_2}{2}\Big)^3\Big] \Big\}
$$
$$
\frac{d\varepsilon_3}{dt} = \Big\{ -Z_{CO_2, N_2} P(4 \to 3)(\varepsilon_3 - \varepsilon_4) + [Z_{CO_2, CO_2} P^{CO_2}(3 \to \Sigma) +
$$
$$
+ Z_{CO_2, N_2} P^{N_2}(3 \to \Sigma)]\Big[\exp\Big(-\frac{500}{T}\Big)\Big(\frac{\varepsilon_2}{2}\Big)^3 (1 + \varepsilon_3) - \varepsilon_3\Big(1 + \frac{\varepsilon_2}{2}\Big)^3\Big] \Big\}
\tag{3.2}
$$
$$
\frac{d(\varepsilon_2 + 2\varepsilon_1)}{dt} = \Big\{ -3 [Z_{CO_2, CO_2} P^{CO_2}(3 \to \Sigma) + Z_{CO_2, N_2} P^{N_2}(3 \to \Sigma)] \times
$$
$$
\times \Big[\exp\Big(-\frac{500}{T}\Big)\Big(\frac{\varepsilon_2}{2}\Big)^3 (1 + \varepsilon_3) - \varepsilon_3\Big(1 + \frac{\varepsilon_2}{2}\Big)^3\Big] - 3 Z_{CO_2, N_2} P(4 \to \Sigma) \times
$$
$$
\times \Big[\exp\Big(-\frac{500}{T}\Big)\Big(\frac{\varepsilon_2}{2}\Big)^3 (1 + \varepsilon_4) - \varepsilon_4\Big(1 + \frac{\varepsilon_2}{2}\Big)^3\Big] + [Z_{CO_2, CO_2} P^{CO_2}(2 \to 0) +
$$
$$
+ Z_{CO_2, N_2} P^{N_2}(2 \to 0)] (1 - \beta_2)(\varepsilon_{02} - \varepsilon_2) \Big\}
\tag{2.1}
$$

Here for simplicity we have introduced the symbols

$$P(4 \to \Sigma) = P(4 \to 2) + P(4 \to 1, 2)$$
$$P^M(3 \to \Sigma) = P^M(3 \to 2) + P^M(3 \to 1, 2)$$

The solution to (3.2) gives fairly accurate results when one uses the observed probabilities; one can write also equations resembling (3.2) by using (1.14) and (2.3), but then one needs calculated probabilities, which at present are less accurate than the observed ones

4. The Quasistationary Energy Distribution in a Mixture of Polyatomic Gases.

Such a distribution can arise when the vibrational energy exchange rate as between different modes substantially exceeds the rate of vibrational–translational relaxation. Here, although there is a general nonequilibrium in the vibrational energy of the system, the T_s for the individual modes are strongly linked and their values are determined only by this general nonequilibrium energy reserve and by the gas temperature T; it is found [1-6] that the coupling between the vibrational temperatures in the quasistationary distribution can be found by considering the steady-state ($d\varepsilon_\xi/dt = 0$) relaxation equations for the mean store of vibrational quanta in the various modes, eliminating from these terms that describe the vibrational–translational relaxation channel. We start from this basis and restrict consideration to vibrational exchange occurring for each mode only via one channel, and then from (1.14) and (2.3) we find that for the quasistationary distribution.

$$\prod_{i=1}^{k} [\varepsilon_{0i}(r_i + \varepsilon_i)]^{l_i} \prod_{j=k+1}^{L} [\varepsilon_j(r_j + \varepsilon_{0j})]^{l_j} = \prod_{i=1}^{k} [\varepsilon_i(r_i + \varepsilon_{0i})]^{l_i} \prod_{j=k+1}^{L} [\varepsilon_{0j}(r_j + \varepsilon_j)]^{l_j} \tag{4.1}$$

Then we get a relationship between the vibrational temperatures:

$$\sum_{i=1}^{k} \frac{l_i h\nu_i}{T_i} - \sum_{j=k+1}^{L} \frac{l_j h\nu_j}{T_j} = \left(\sum_{i=1}^{k} l_i h\nu_i - \sum_{j=k+1}^{L} l_j h\nu_j \right) T^{-1} \tag{4.2}$$

Expression (4.2) extends the results of [1-6] for rapid multiquantum vibrational exchange via one channel to the case of an arbitrary number of modes involved in the exchange; (4.2) has been derived from the condition $d\varepsilon_\xi/dt = 0$ for a single arbitrarily selected mode ξ. Analogous expressions (of course with other l_i and l_j) apply for all the other modes in this system. The resulting L equations of (4.2) type may be considered as a system of L linear equations relative to the L unknowns T_i^{-1}, T_j^{-1}; if the determinant of this system differs from zero, there is the unique trivial solution $T_i = T_j = T$, which means that one cannot establish a nonequilibrium quasistationary distribution.

If the number Q of independent equations is less than L, there is always a solution with T_i, $T_j \neq T$; this case corresponds to a quasistationary distribution, and the value of Q determines the strength of the coupling between the vibrational temperatures. For instance, with a $Q = L-1$, the temperatures of all modes may be expressed in terms of the temperature of one, and the value of this temperature is determined by the general nonequilibrium vibrational energy reserve of the system. If $Q = L-2$, the coupling is reduced, and the temperatures of two modes become independent. Therefore, with $Q \leq L-2$ we can speak only of partial quasiequilibrium.

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