

Calculation of Vibrational Relaxation Times in Gases

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Vibrational relaxation times in gases are calculated with the method of Zener using an exponential repulsion in a one-dimensional model. The constants of the interaction potential are determined by fitting it to the data of Hirschfelder, *et al.* The great effect which some impurities have is accounted for either by their low mass and resultant high velocity or by "near resonance" transfers in which the vibrational quantum of the substratum is used partly to excite the vibration of the impurity, only the difference being transferred to translation. However, there are other impurities, the action of which cannot be explained in this manner. The theoretical values for the relaxation times are 10 to 30 times shorter than the experimental ones, which difference may be accounted for by the use of the one-dimensional model. Macroscopic equations governing the more complex relaxation processes in polyatomic gases and gas mixtures are developed.

INTRODUCTION

CONTINUED interest in the study of relaxation phenomena in gases over the last 20 years has resulted in the accumulation of a large body of experimental data concerning the relaxation time of pure gases as well as gas mixtures. The dependence of the relaxation time on density over moderate ranges is now well known; the dependence on the temperature not as well known. The only theoretical calculation on the vibrational relaxation time of gases that has found any general acceptance to date was made by Landau and Teller¹ in 1936. This was refined somewhat by Bethe and Teller² in 1940. These calculations give the general character of dependence of the relaxation time of a pure diatomic gas on the density and temperature. No calculation of the effect of mixing different gases has been attempted.

With the advance in our knowledge of the force constants between molecules, it becomes possible to attempt a more quantitative calculation of the relaxation time and to even extend the calculations to mixtures of gases. The objective of this paper will be to make a quantitative calculation of the relaxation time in gases. The method of calculation given here is generally applicable to diatomic gases, to chemically nonreactive gas mixtures, and gas molecules with several normal vibrational modes. The theory of the macroscopic behavior of gases with relaxation times, such as sound dispersion and absorption, is then extended to include the cases of gas mixtures and polyatomic gases.

The behavior of a material volume of gas in a sound field or gas flow can be described by the standard equations: (1) equation of state of the gas; (2) law of conservation of mass; (3) momentum equation; and (4) energy equation. With relaxation phenomena present in the gas flow, these equations are not sufficient.

The internal energy of the gas can no longer be expressed as a function of a single temperature. It is customary to write for a perfect gas the internal energy as the sum of energies of translation, rotation, vibration, etc.,

$$E = E_{\text{trans}}(T) + E_{\text{rot}}(T_r) + E_{\text{vib}}(T_v) + \cdots, \quad (1)$$

where T , T_r , T_v , etc., are "temperatures," but not necessarily equal to one another.

For a pure diatomic gas the lack of adjustment of the vibrational degrees of freedom may be described by the equation derived by Landau and Teller:¹

$$\frac{dE_{\text{vib}}(T_v)}{dt} = -\frac{1}{\tau} \{E_{\text{vib}}(T) - E_{\text{vib}}(T_v)\}, \quad (2)$$

where T is the temperature of the translational degrees of freedom, T_v is the temperature of the vibrational degrees of freedom, and τ is called the relaxation time of the gas. As energy is transferred between degrees of freedom only during a molecular collision, the rate of energy transfer is inversely proportional to the number of collisions a molecule experiences per second, $M_{a,a}$, and thus to density. Furthermore, not every collision is effective in transferring a quantum of vibrational energy to translation or vice versa, so that the relaxation time must also be proportional to the probability of such an energy exchange, denoted by P . For the relaxation time we may write

$$\tau = 1/M_{a,a}P.$$

Here, P is, roughly speaking, the probability that upon a collision, a quantum of vibrational energy is removed from the vibrating system and converted to translational energy. For a gas composed of polyatomic molecules or mixtures of different types of molecules, there arises the possibility of energy exchange between the different vibrational degrees of freedom during a collision as well as exchanges with the translational degrees of freedom. A separate relaxation time must now be ascribed to each of these energy transfers.

¹ L. Landau and E. Teller, *Phys. Z. Sowjetunion* **10**, 34 (1936).

² H. A. Bethe and E. Teller, Aberdeen Proving Ground Report X-117.

Additional equations more complicated than Eq. (2) must be used to describe the behavior of the gas system.

GENERAL THEORY OF COLLISION PROCESS

We will first develop formulas for the numerical computation of the probability of a vibrational energy jump taking place during a molecular collision. Let $p^{i \rightarrow f}(v_0)$ denote the probability that the system made up of a pair of colliding molecules, originally of relative velocity v_0 and vibrational states i_1, i_2, \dots, i_n , will, after a collision, arrive at vibrational states f_1, f_2, \dots, f_n . The method of calculating $p^{i \rightarrow f}(v_0)$ given by Zener³ will be applied here. Zener assumed that the problem may be treated one-dimensionally. The molecules are taken as rotationless and approach each other along a straight line. This motion can be described in terms of the coordinate r , the distance between centers of gravity of the collision pair, and the normal vibrational coordinates s_1, s_2, \dots, s_n . It is further assumed that the zero-order wave functions describing the collision are separable in these coordinates. Then, if the interaction potential between the molecules is also approximated by a product of functions of the coordinates,

$$V = V_0 \cdot V_r(r) \cdot V_1(s_1) \cdots V_n(s_n), \quad (3)$$

it becomes possible to express the probability $p^{i \rightarrow f}(v_0)$ in a product form. Here V_0 is a constant with dimensions of energy.

$$p^{i \rightarrow f}(v_0) = \frac{16\pi^2 V_0^2}{v_0 v_F h^2} [V(i_1 \rightarrow f_1) \cdots V(i_n \rightarrow f_n) R]^2, \quad (4)$$

where $R, V(i_1 \rightarrow f_1), \dots, V(i_n \rightarrow f_n)$ are defined as follows:

$$R \equiv \int_{-\infty}^{\infty} F_0 F_F V_r dr, \quad (5)$$

where F_0, F_F are solutions of the Schrödinger equation for the motion of a free particle in the potential field V_r .

$$\frac{d^2}{dr^2} F_F + \frac{8\pi^2 \mu}{h^2} \left(\frac{\mu v_F^2}{2} - V_0 V_r \right) F_F = 0.$$

μ is the reduced mass of the molecules. The matrix elements $V(i_n \rightarrow f_n)$ are defined

$$V(i_n \rightarrow f_n) \equiv \int_{-\infty}^{\infty} \psi_{i_n}(s_n) V_n(s_n) \psi_{f_n}(s_n) ds_n, \quad (6)$$

where $\psi_{i_n}(s_n), \psi_{f_n}(s_n)$ are normalized oscillator wave functions for the s_n th normal vibrational coordinate. v_0 is the relative velocity of the molecules before collision, v_F the velocity after collision.

³ C. Zener, Phys. Rev. **37**, 556 (1931). Since this paper was finished C. F. Curtiss and F. T. Adler, J. Chem. Phys. **20**, 249 (1952), have applied group theoretical arguments to extend Zener's method of approximation to the three-dimensional collision of a nonspherical molecule and an atom. No actual evaluation of probabilities was carried out.

Jackson and Mott⁴ evaluated the integral R in a closed form for a potential $V_r = e^{-\alpha r}$. Making use of their results, $p^{i \rightarrow f}$ assumes the form

$$p^{i \rightarrow f} = V^2(i_1 \rightarrow f_1) \cdots V^2(i_n \rightarrow f_n) \frac{1}{16\pi^2} (\theta_0^2 - \theta_F^2)^2 \times \frac{(e^{\theta_0} - e^{-\theta_0})(e^{\theta_F} - e^{-\theta_F})}{(e^{\theta_0} + e^{-\theta_0} - e^{\theta_F} - e^{-\theta_F})^2}, \quad (7)$$

where $\theta_0 \equiv 4\pi^2 \mu v_0 / \alpha h$. Here v_0 and v_F are related by the fact that the total energy of the collision system is conserved in the collision, i.e.,

$$\mu/2 v_0^2 - v_F^2 = \Delta E, \quad (8)$$

where ΔE is the total energy exchanged between vibration and translation during a collision. Those energy exchanges for which $\Delta E = 0$ are called resonance exchanges; such occur when one molecule loses a quantum of vibrational energy to another molecule without changing their translational energies.

Equation (7) tells us that the probability of an energy exchange during collision depends on the linear momentum gained or lost in the collision. The probability is largest for a resonant exchange but may become exceedingly small for a typical nonresonant exchange in which the linear momentum is changed by a large fraction. Equation (7) may be simplified under these two limiting conditions of resonance or large non-resonance.

The probability $p^{i \rightarrow f}$, given in Eq. (7) is dependent on the initial velocity v_0 . We must therefore average over all initial velocities to arrive at a probability, $P^{i \rightarrow f}$. Assuming the velocities are distributed according to Maxwell's law at a temperature T ,

$$P^{i \rightarrow f} = 2 \left(\frac{\mu}{2kT} \right)^2 \int_0^\infty v_0^3 p^{i \rightarrow f} \exp(-\mu v_0^2 / 2kT) dv_0. \quad (9)$$

This integral may be evaluated in the limiting cases mentioned in the paragraph above. For a nonresonant energy exchange, in Appendix A we evaluated Eq. (9) to yield

$$P^{i \rightarrow f} = V^2(i_1 \rightarrow f_1) \cdots V^2(i_n \rightarrow f_n) 0.39 \times \left[\frac{8\pi^3 \mu \Delta E}{(\alpha^*)^2 h^2} \right]^2 \frac{\sigma^{\frac{1}{2}} e^{-\sigma}}{1 - e^{-\frac{1}{2}\sigma}}, \quad (A7)$$

where

$$\sigma \equiv 3 \left(\frac{2\pi^4 (\Delta E)^2 \mu}{(\alpha^*)^2 h^2 kT} \right)^{\frac{1}{2}} \pm \frac{\Delta E}{2kT},$$

and $V(i_n \rightarrow f_n)$ is defined by Eq. (6) and evaluated in Appendix A; α^* , further specified in the following paragraphs, is the reciprocal of a length, the measure of the "hardness" of the molecule on impact. The upper

⁴ J. M. Jackson and N. F. Mott, Proc. Roy. Soc. (London) **A137**, 703 (1932).

sign appearing in σ applies if the total vibrational energy decreases during collision, the lower if the vibrational energy increases.

Equation (A7) is valid as long as we limit ourselves to those molecular excitations and temperatures for which

$$\exp\left(-\frac{4\pi^2\Delta E}{\alpha^*h v_0^*}\right) \ll 1,$$

$$\Delta E \ll \frac{\mu}{2}(v_0^*)^2,$$

$$\Delta E \ll \frac{\mu}{2}(v_F^*)^2,$$

[as shown in Appendix A, Eqs. (A3) and (A6)], where v_0^* is a "most favorable" velocity for bringing about the excitation and is further specified in Appendix A. It is interesting to note that the classical estimate made by Landau and Teller gave a result

$$P \sim \exp\left(\frac{\pi^2(\Delta E)^2\mu}{2\alpha^2 h^2 kT}\right)^{\frac{1}{2}},$$

which agrees with the quantum-mechanical calculations of the dependence of $P^{i \rightarrow f}$ on ΔE , μ , α , and T but misses a factor of $(4\pi^2)^{\frac{1}{2}}$ in the exponents. The Eq. (A7) may be used for numerical computation of P once α^* is given. There is nothing in the development which restricts us to simple diatomic gases. Polyatomic gases and gas mixtures may be treated. As the quantum-mechanical development is one-dimensional, values of $P^{i \rightarrow f}$ so determined would be for molecular collisions in which the molecules are "pre-oriented" in a most favorable manner for the excitation to occur; $P^{i \rightarrow f}$ should be multiplied by a geometrical factor less than unity. This factor, denoted by $C^{i \rightarrow f}$, can be expected to be fairly constant from molecule to molecule and over a wide range of temperatures.

A number of general conclusions as to relaxation phenomena can be drawn from a brief examination of Eq. (A7). The probability of an excitation is seen to be $\exp(-\Delta E/kT)$ of the reverse process as demanded by general statistical principles. If a number of gases and gas mixtures are compared at the same temperature, the only factors in Eq. (A7) causing large variation in the calculated $P^{i \rightarrow f}$ from gas to gas are μ and ΔE . Since $P^{i \rightarrow f}$ decreases very rapidly with an increase in σ , small energy jumps, ΔE , and small masses, μ (i.e., high translational velocities), are favorable to energy transfer. As ΔE becomes small, however, condition (A6) mentioned above is not satisfied. Under conditions of exact resonance, $\Delta E=0$, $P^{i \rightarrow f}$ reduces to a simple expression and $P^{i \rightarrow f}$ is given:

$$P^{i \rightarrow f} = V^2(i_1 \rightarrow f_1) \cdots V^2(i_n \rightarrow f_n) \frac{8\pi^2 \mu kT}{(\alpha^*)^2 h^2}$$

(see (A9) in Appendix A).

THE POTENTIAL FIELD BETWEEN MOLECULES

It is customary to represent the field by the Lennard-Jones function:⁵

$$V = 4\epsilon\left\{\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^6\right\}. \quad (10)$$

This is made up of an attractive component as well as a short-range, repulsive component. For reasons already given by Landau and Teller,⁶ only short-range forces are of importance in energy transfer. Since Mott and Jackson have solved the Schrödinger equation for an exponential repulsive potential, we approximate the interaction between the individual atoms of different molecules by a similar function:

$$V = Ce^{-\alpha\chi}. \quad (11)$$

Here, χ is the distance between atoms A and A' , and $\alpha\chi$ may be taken as a measure of the effective extent of their mutual repulsive force field. In practice, the extent of the repulsive field is much smaller than the distance between the atoms in a molecule, i.e.,

$$\alpha\chi^{-1} \ll d, \quad (12)$$

so that influence of molecules B and B' (Fig. 1) on the collision may be neglected. Equation (11), therefore, may be used to approximate the intermolecular field for a collision such as illustrated by Fig. 1.

THE EVALUATION OF THE CONSTANTS IN

$$V = V_0 e^{-\alpha(r+A_1s_1+\cdots)}$$

In general, we may write the distance of separation of the nearest atoms of the two molecules, χ , in terms of the distance of separation of the centers of gravity of the molecules, r , and the normal coordinates of vibration, $s_1, s_2, s_3 + \cdots s_n$:

$$\chi = r + A_0 + A_1s_1 + A_2s_2 + \cdots$$

The potential function may be written as

$$V = V_0 e^{-\alpha(r+A_1s_1+\cdots+A_ns_n)}, \quad (13)$$

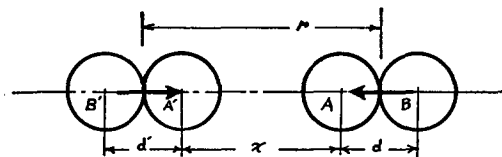


FIG. 1. Schematic drawing of the one-dimensional collision.

⁵ R. H. Fowler, *Statistical Mechanics* (The Cambridge University Press, New York, 1936), Chap. X; Hirschfelder, Bird, and Spotz, *Transport Properties of Gases* (University of Wisconsin Press, Madison, Wisconsin, 1948), II' CM-508, contain a compilation of constants ϵ and r_0 for many gases from viscosity and diffusion data.

⁶ In general, long-range forces distort, adiabatically, the internal and external wave functions without inducing transitions. (See Appendix.) For a discussion of the role of certain long-range forces, see Slawsky, De Wette, and De Groot, *Supplemento Al Volume VII, Serie IX Del Nuovo cimento*, N. 2 (1950). The effect of the centrifugal term appearing in a three-dimensional treatment is being evaluated as a long-range interaction.

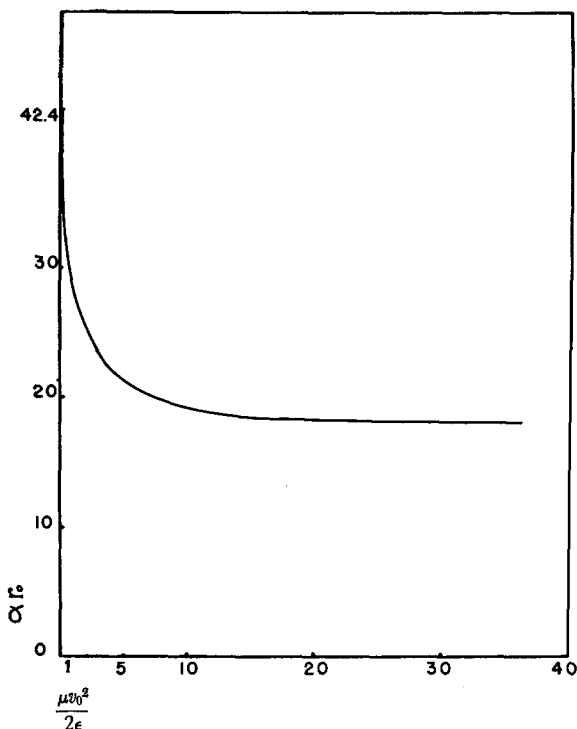


FIG. 2. The reciprocal of the effective extent of the repulsive molecular field, α^{-1} , as a function of the initial translational energy of the colliding molecules. ϵ and r_0 are constants for a given molecule appearing in the Lennard-Jones potential, Eq. (10).

which is of the form of Eq. (3). In order to determine α , the first term of Eq. (13),

$$V \cong V_0 e^{-\alpha r}, \quad (14)$$

is fitted to the Lennard-Jones potential curve (Eq. (10)) at the point $r=r_1$. This is done by setting V and dV/dr of Eqs. (10) and (14) equal and adding the condition $V \rightarrow -\epsilon$ as $r \rightarrow \infty$. The point $r=r_1$ is somewhat arbitrary. We have taken r_1 as the classical point of closest approach of the two molecules moving towards each other with relative velocity v_0 . Then,

$$\alpha = \frac{12}{r_0 D} \left[\frac{1}{2} + \frac{1}{2}(1+D)^{\frac{1}{2}} \right]^{1/6} [1 + (1+D)^{\frac{1}{2}} + D], \quad (15)$$

$$r_1 = r_0 \left[\frac{1}{2} + \frac{1}{2}(1+D)^{\frac{1}{2}} \right]^{-1/6},$$

where

$$D \equiv \frac{(\mu/2)v_0^2 + \epsilon}{\epsilon}.$$

The function αr_0 is plotted as a function of D in Fig. 2.

In treating unlike molecules, the effective values of α and r_0 used in Eq. (15) are approximated by

$$\begin{aligned} r_0(1, 2) &\cong \frac{1}{2}(r_0(1) + r_0(2)), \\ \epsilon(1, 2) &\cong (\epsilon(1)\epsilon(2))^{\frac{1}{2}}, \end{aligned} \quad (16)$$

for those cases in which experimental values of $r_0(1, 2)$ and $\epsilon(1, 2)$ are not available.

Two points of interest will be pointed out before closing the discussion of the molecular field. One is that from Fig. (2), it can be seen that, for molecules whose value of ϵ is not too great, we can make the approximate generalization that $\alpha \cong 17.5/r_0$. Secondly, that in the rather arbitrary manner we have chosen to compute α , the numerical value of α is slightly dependent on initial molecular velocities and consequently on temperature. In Eqs. (A7) and (A9), the value of α at $v_0 = v_0^*$ is used.

DIATOMIC MOLECULES

Landau and Teller¹ have shown that the P appearing in Eq. (3) when applied to diatomic molecules is

$$P = P^{1 \rightarrow 0}(1 - e^{-h\nu/kT}). \quad (17)$$

Numerical results from (A7) are given in Table I as $P^{1 \rightarrow 0}(a, a)$.

POLYATOMIC MOLECULES AND GAS MIXTURES

In these cases, two problems have to be considered: The numerical value of $P^{i \rightarrow f}$ as given by (A7), and the equation connecting P and $P^{i \rightarrow f}$, which will replace (17).

It is clear from the form of $P^{i \rightarrow f}$ that it makes no difference whether the gas is composed of molecules with several normal modes (CO_2 , COS , etc.) or a mixture of diatomic gases. It becomes possible, therefore, to calculate the adjustment rate of the vibrational energy for these complex situations and the acoustical relaxation times that should be assigned to them. The form of (A7) explains the great effect some impurities may have on the relaxation time. The addition of hydrogen to a heavier gas will decrease μ and thus increase $P^{i \rightarrow f}$. This may be termed a *mass effect* and further illustrations of it will be given later. This effect has been experimentally verified. On the other hand, an impurity, which permits the exchange of vibrational energy among two or more vibrational degrees of freedom with a consequent decrease in the amount of energy, ΔE , exchanged with translation, will again increase the probability $P^{i \rightarrow f}$. We will call this effect the *near resonance effect*; examples of such an effect will be given later. The existence of such an effect in ultrasonics has not been pointed out previously.⁷

THE MACROSCOPIC EQUATIONS

In the calculation of the resultant P of Eq. (3) from the $P^{i \rightarrow f}$ as computed above, we have to write differential equations which express the change of internal energy as a difference between the effect of deactivating and of exciting collisions for all possible transitions.

Our attention shall be limited to a gas whose molecules display but two different, active frequencies of internal vibration ν_a and ν_b ; the internal energy is the sum of energies $E_{\text{vib } 1}$ and $E_{\text{vib } 2}$, hereafter written E_a

⁷ It was pointed out by E. Patat and E. Bartholome, *Z. physik. Chem.* **32**, 396 (1936), that in the study of reaction kinetics, gas mixtures, for which a transfer of energy between vibrational degrees of freedom is easy, promote the reaction. However, they concluded that in ultrasonics, only the translational to vibrational energy transfer was important.

and E_b . We will further limit ourselves to cases where a change of two or more quanta in either vibrational mode during a collision is so improbable as to be negligible. This is most often the case. An exception, wherein a jump of two quanta in a particular mode must be considered will be treated separately.

In the following, we may picture the gas as being made up of two kinds of molecules, molecules a with frequency ν_a , and molecules b of frequency ν_b , a being the fraction of kind a and b the fraction of kind b .

Energy is being fed into the ν_a vibration of molecules a by collision with other molecules a (number per second $M_{a,a}$) and also by collision with molecules b (number per sec $M_{a,b}$). Each effective collision feeds in an amount $h\nu_a$. The fraction of effective collisions with other molecules a , is given by a sum of terms of transition probabilities, $P^{\lambda \rightarrow \lambda+1}(a, a)$, each weighted by the relative population of states λ . Similarly, the fraction of effective collisions with molecules b is given by a double sum of terms $P_{l \rightarrow l-1}^{\lambda \rightarrow \lambda+1}(a, b)$ weighted by the product of the relative populations of states λ (molecules a) and l (molecules b). The total change of energy in vibration is then

$$\begin{aligned} \frac{daE_a}{dt} = & N h \nu_a \left\{ M_{a,a} \left(P^{0 \rightarrow 1}(a, a) \frac{n_0}{N} + P^{1 \rightarrow 2}(a, a) \frac{n_1}{N} \right. \right. \\ & + \dots - P^{1 \rightarrow 0}(a, a) \frac{n_1}{N} - \dots \left. \right) \\ & + M_{a,b} \left(P_{0 \rightarrow 0}^{0 \rightarrow 1}(a, b) \frac{n_0 m_0}{N N} \right. \\ & + \dots + P_{1 \rightarrow 0}^{0 \rightarrow 1}(a, b) \frac{n_0 m_1}{N N} + \dots \left. \right) \left. \right\} \\ & + \text{terms involving } 2h\nu_a \text{ changes which are} \\ & \text{not considered at the moment.} \quad (18) \end{aligned}$$

The probability functions $P^{0 \rightarrow 1}(a, a) \dots, P_{1 \rightarrow 0}^{0 \rightarrow 1}(a, b)$, etc., have already been defined. The transition indicated by the superscript will refer to change in ν_a vibration, the subscript to the simultaneous transition in ν_b vibration. $n_0/N, n_1/N, \dots, n_k/N$ are the fractions of all molecules that are in the zeroth, first, etc., quantum levels of the ν_a vibration. $m_0/N, m_1/N, \dots$ are fractions in the quantum levels of the ν_b vibration.

Equation (18) can be considerably simplified by the use of relation (A11). It follows that

$$\begin{aligned} P^{\lambda \rightarrow \lambda-1}(a, a) &= \lambda P^{1 \rightarrow 0}(a, a), \\ P_{l \rightarrow l}^{\lambda \rightarrow \lambda-1}(a, b) &= \lambda P_{0 \rightarrow 0}^{1 \rightarrow 0}(a, b), \\ P_{l \rightarrow l-1}^{\lambda \rightarrow \lambda+1}(a, b) &= (\lambda+1) l P_{1 \rightarrow 0}^{0 \rightarrow 1}(a, b). \end{aligned} \quad (19)$$

Furthermore, the relationship (A7) tells us that

$$P_{1 \rightarrow 0}^{0 \rightarrow 1}(a, b) = P_{0 \rightarrow 1}^{1 \rightarrow 0} \exp \left[-\frac{h(\nu_a - \nu_b)}{kT} \right].$$

When the above relations are introduced into Eq. (18), it becomes

$$\begin{aligned} \frac{daE_a}{dt} = & N h \nu_a \left\{ M_{a,a} \sum_{\lambda=0}^{\infty} \frac{n_{\lambda}}{N} \left(P^{0 \rightarrow 1}(a, a) \sum_{\lambda=0}^{\infty} (\lambda+1) \frac{n_{\lambda}}{N} \right. \right. \\ & - P^{1 \rightarrow 0}(a, a) \sum_{\lambda=0}^{\infty} \frac{\lambda n_{\lambda}}{N} \left. \right) + M_{a,b} \sum_{l=0}^{\infty} \frac{m_l}{N} \\ & \times \left(P_{0 \rightarrow 0}^{0 \rightarrow 1}(a, b) \sum_{\lambda=0}^{\infty} (\lambda+1) \frac{n_{\lambda}}{N} \right. \\ & - P_{0 \rightarrow 0}^{1 \rightarrow 0}(a, b) \sum_{\lambda=0}^{\infty} \frac{\lambda n_{\lambda}}{N} \left. \right) \\ & + M_{a,b} \left(P_{1 \rightarrow 0}^{0 \rightarrow 1}(a, b) \sum_{\lambda=0}^{\infty} (\lambda+1) \frac{n_{\lambda}}{N} \sum_{l=0}^{\infty} \frac{m_l}{N} \right. \\ & \left. \left. - P_{0 \rightarrow 1}^{1 \rightarrow 0}(a, b) \sum_{\lambda=0}^{\infty} \sum_{l=0}^{\infty} \frac{n_{\lambda}}{N} \frac{m_l}{N} (l+1) \frac{m_l}{N} \right) \right\}. \quad (20) \end{aligned}$$

In this form the expression can readily be applied to the calculation of the adjustment rate of pure polyatomic gases or gas mixtures.

When a mixture of two gases is considered, the following relations hold

$$\begin{aligned} N &= \sum_{\lambda=0}^{\infty} n_{\lambda} + \sum_{l=0}^{\infty} m_l \quad h\nu_a \sum_{\lambda=0}^{\infty} \lambda n_{\lambda} = aE_a \\ \sum_{\lambda=0}^{\infty} n_{\lambda} &= aN \quad h\nu_b \sum_{l=0}^{\infty} l m_l = bE_b, \\ \sum_{l=0}^{\infty} m_l &= bN \end{aligned} \quad (21)$$

and reduce Eq. (20) to

$$\begin{aligned} \frac{dE_a}{dt} = & [aM_{a,a}P^{1 \rightarrow 0}(a, a) + bM_{a,b}P_{0 \rightarrow 0}^{1 \rightarrow 0}(a, b)] \\ & \times [E_a(T) - E_a] + M_{a,b}abP_{0 \rightarrow 1}^{1 \rightarrow 0}(a, b) \\ & \times \left[\frac{E_a(T) - E_a}{E_b(T)} \left\{ \frac{1 - e^{-h\nu_a/kT}}{1 - e^{-h\nu_b/kT}} \right\} \right. \\ & \left. - E_a \frac{E_b(T) - E_b}{E_b(T)} \right]. \quad (22) \end{aligned}$$

TABLE I. Probability of the simple excitation of vibration in a pure gas and a gas mixture.

Gases		T	$P^{1 \rightarrow 0}(a, a)$		$P_{1 \rightarrow 0}^{1 \rightarrow 0}(a, b)$	
a	b		Exp.	Theory	Exp.	Theory
Cl ₂	N ₂	288°A	3×10^{-5}	10^{-4}	2.3×10^{-5}	6×10^{-4}
Cl ₂	H ₂	288°A	3×10^{-5}	10^{-4}	1.3×10^{-3}	1.7×10^{-2}
CO ₂	N ₂	288°A	2×10^{-5}	4×10^{-4}	...	7.5×10^{-4}
CO ₂	H ₂	288°A	2×10^{-5}	4×10^{-4}	2×10^{-3}	4.5×10^{-2}
N ₂	A	600°A	3×10^{-8}	7×10^{-9}	...	3×10^{-8}
N ₂	H ₂	600°A	3×10^{-8}	7×10^{-9}	...	9×10^{-4}

a A. Eucken and R. Becker, Z. physik. Chem. **27**(B), 235 (1934).

b P. W. Huber and A. Kantrowitz, J. Chem. Phys. **15**, 275 (1947).

TABLE II. Probability of a complex excitation of vibration in a gas mixture.

Gases		T	$P^{1 \rightarrow 0}(a, a)$		$P_{1 \rightarrow 0}(b, b)$		$P_{0 \rightarrow 1}^{1 \rightarrow 0}(a, b)$	
a	b		Exp.	Theory	Exp.	Theory	Exp.	Theory
O ₂	N ₂	288°K	4×10^{-8}	8.5×10^{-8}	0	0	3×10^{-6}	3×10^{-7}
CO	N ₂	600°K	...	6×10^{-8}	3×10^{-8}	7×10^{-9}	...	1.5×10^{-3}
O ₂	CO	288°K	4×10^{-8}	8.5×10^{-8}	...	7×10^{-10}	1.2×10^{-4}	2×10^{-6}

* P. W. Huber and A. Kantrowitz, J. Chem. Phys. 15, 275 (1947).

Here $E_a(T)$ is the well-known Einstein function for the energy of a harmonic oscillator at temp. (T):

$$E_a(T) = \frac{Nh\nu_a}{e^{h\nu_a/kT} - 1}.$$

A similar expression may be given for dE_b/dt . The first terms of Eq. (22) describes the adjustment of E_a by a simple excitation process and was originally proved by Landau and Teller.¹ One finds that the effective relaxation time of the simple process is

$$\frac{1}{\tau_a(\text{eff.})} = \frac{a}{\tau_a(a, a)} + \frac{b}{\tau_a(a, b)},$$

where

$$\begin{aligned} [\tau_a(a, a)]^{-1} &\equiv M_{a,a} P^{1 \rightarrow 0}(a, a) (1 - e^{-h\nu_a/kT}) \\ [\tau_a(a, b)]^{-1} &\equiv M_{a,b} P_{0 \rightarrow 1}^{1 \rightarrow 0}(a, b) (1 - e^{-h\nu_a/kT}). \end{aligned}$$

The complex excitation process, one in which two degrees of freedom are involved, will have its own relaxation time,

$$(\tau_{a,b})^{-1} = ab M_{a,b} P_{0 \rightarrow 1}^{1 \rightarrow 0}(a, b),$$

and is described by the second term of Eq. (22).

In treating a pure polyatomic gas instead of a mixture as above, we substitute the following in Eq. (20) in place of relationships (21):

$$N = \sum_{\lambda=0}^{\infty} n_{\lambda} = \sum_{l=0}^{\infty} m_l,$$

$$E_a = K_a h\nu_a \sum_{\lambda=0}^{\infty} \lambda n_{\lambda}, \quad (23)$$

$$E_b = K_b h\nu_b \sum_{l=0}^{\infty} l m_l,$$

where K_i is the degree of degeneracy of i th degree of freedom. The resulting expression is similar to Eq. (20) except that here

$$\begin{aligned} a &= b = 1 \\ M_{a,b} &= M \\ M_{a,a} &= 0. \end{aligned} \quad (24)$$

APPLICATION OF THE RELAXATION EQUATIONS TO ACOUSTICS

As the measurements of relaxation times in gases have usually been made by acoustical methods, an approximate equation applicable to these measurements

will be given. In a sound field, we may write

$$\begin{aligned} T &\cong T_0 + \Delta T + \dots \\ T_a &\cong T_0 + \Delta T_a + \dots \\ T_b &\cong T_0 + \Delta T_b + \dots \\ \Delta E_a &\cong C_a \Delta T_a. \end{aligned}$$

Then, making use of the equation for the energy of an oscillator, the more general Eq. (22) reduces to⁸

$$\begin{aligned} \frac{d\Delta T_a}{dt} &= \frac{1}{\tau_a(\text{eff.})} (\Delta T - \Delta T_a) + \frac{1}{\tau_{a,b}} \frac{1 - e^{-h\nu_a/kT}}{1 - e^{-h\nu_b/kT}} \\ &\quad \times \left\{ (\Delta T - \Delta T_a) - \frac{h\nu_b}{h\nu_a} (\Delta T - \Delta T_b) \right\}, \quad (25) \end{aligned}$$

and a similar equation for ΔT_b . $\tau_{a,b}$ and $\tau_a(\text{eff.})$ have been defined already.

SOME SPECIFIC EXAMPLES

Cl₂—He Type Mixture

From Table I it can be seen that in mixtures in which the reduced mass μ of the two kinds of molecules is much smaller than for the pure gas, the effective relaxation time corresponding to the simple adjustment is markedly changed by the addition of the second gas. An excellent example of this "mass effect" is afforded by the addition of helium to chlorine gas. Equation (20) (without the second term describing a complex adjustment) may be used to describe the relaxation process.

CO—N₂ Type Mixture

This mixture should be an example of a mixture exhibiting the "resonance" effect mentioned in an earlier paragraph and should have a very short relaxation time because the vibrational frequencies of CO and N₂ are very close to one another. The frequencies are $\nu = 6.50 \times 10^{13}$ /sec for CO and 7.05×10^{13} /sec for N₂. These frequencies are quite large and the probability of a simple vibrational excitation of either CO or N₂ is small.⁹ On the other hand, the energy exchange involved in a complex process is small. That process whereby a N₂ molecule is de-excited simultaneously with each

⁸ This equation differs from each of the systems of equations proposed by Schafer, Z. physik. Chem. B46, 212 (1940) for a polyatomic gas with two active vibrational degrees of freedom.

⁹ At room temperature, there is no appreciable excitation of either CO or N₂. However, at 600°K, the temperature of the experiments, the effect is measurable.

excitation of a CO molecule will dominate the energy adjustment. Table II shows that for every adjustment involving a CO or N₂ singly, there will be 25,000 adjustments of energy between vibration and translation which involve simultaneous changes in CO and N₂. This means that for nearly equal amounts of the two gases, the second term in Eq. (20) is the dominant term and only the complex relaxation time will be observable. Where only small amounts of one gas are contained in the other, i.e., a or b small, the effective relaxation times of the simple and complex adjustment processes may be of the same order of magnitude, and two independent relaxation times should be observable in the gas.

Air is another case where the measured relaxation time can be attributed to a complex process. At room temperature the E_v of N₂ is essentially zero; the E_v of O₂ very small. Calling O₂ the a component of the gas, and N₂ the b component, we set E_b in Eq. (22) equal to zero. Then the vibrational adjustment of O₂ in air is given by

$$\frac{dE_a}{dt} = \frac{1}{\tau_a(\text{eff.})} (E_a(T) - E_a), \quad (26)$$

where now

$$[\tau_a(\text{eff.})]^{-1} = aM_{a,a}P_{1 \rightarrow 0}(a, a) + bM_{a,b}(P_{0 \rightarrow 1}^{1 \rightarrow 0}(a, b) + P_{0 \rightarrow 1}^{1 \rightarrow 0}(a, b)e^{\Delta E/kT}).$$

The most effective process of deactivating an O₂ molecule consists in exciting an N₂ molecule and supplying the difference of the quanta of N₂ and O₂ from translational energy. The value of $\tau_a(\text{eff.})$ of Eq. (26) is smaller than for pure O₂. The calculated values of these probabilities are given in Table II.

COS Type Gas

Equation (20), as modified by relations (24), is applicable to a polyatomic gas such as COS. In COS, there are three fundamental frequencies, only two of which are active at temperatures of a few hundred degrees centigrade. The active frequencies are $\nu_1 = 2.57 \times 10^{13}/\text{sec}$ and $\nu_2 = 1.576 \times 10^{13}/\text{sec}$. The ν_2 vibration is doubly degenerate. As ν_2 is much lower than ν_1 , the probability of the simple process $P_{1 \rightarrow 0}(\nu_1)$ is much smaller than $P_{1 \rightarrow 0}(\nu_2)$, and so, not observable. But the difference $(\nu_1 - \nu_2)$ is much less than ν_2 and the probability $P_{0 \rightarrow 1}^{1 \rightarrow 0}(\nu_1, \nu_2)$ (for which the ΔE of Eq. (A7) is $h(\nu_1 - \nu_2)$) cannot be neglected. A computation of $P_{0 \rightarrow 1}^{1 \rightarrow 0}(\nu_1, \nu_2)$ shows it to be somewhat less than $P_{1 \rightarrow 0}(\nu_2)$. Values of these probabilities are given in Table III. The experiments of Schafer seem to indicate two observable relaxation times. This is in keeping with the present analysis which identifies these two times as that of the simple ν_2 -adjustment and a complex adjustment of the ν_1 - and ν_2 -frequencies (see Table III).

CO₂ Type Gas

Whenever a harmonic of one of the fundamental frequencies lies close to another fundamental, we might suspect a "resonance" transfer of energy between degrees of freedom in which the probability of a jump of two quantum levels in one vibrational mode may be relatively high. An extreme example is CO₂, a gas which has been extensively studied. In CO₂, the ν_1 - and ν_2 -vibrations are accidentally degenerate, i.e., $2\nu_2 - \nu_1 = 0$. A resonant exchange between the ν_1 - and ν_2 -vibrations during a collision is very probable. It seems not unlikely that two competing excitation processes may be observed in CO₂. These are the simple excitation of the ν_2 -vibration and the resonant exchange between the ν_1 - and ν_2 -vibrations. The direct excitation of ν_1 -vibration is much less probable than these. Thus, for the case of CO₂, the variation in E_1 (which then receives its energy from E_2 and not from translation) is given by

$$\begin{aligned} \frac{dE_1}{dt} = 2MNh\nu_2 \left[\left(P_{2 \rightarrow 0}^{0 \rightarrow 1} \frac{n_0 m_2}{N N} + \dots \right. \right. \\ \left. \left. + P_{l \rightarrow l-2}^{\lambda \rightarrow \lambda+1} \frac{n_\lambda m_l}{N N} + \dots \right) - \left(P_{0 \rightarrow 2}^{1 \rightarrow 0} \frac{n_1 m_0}{N N} \right. \right. \\ \left. \left. + \dots P_{l \rightarrow l+2}^{\lambda \rightarrow \lambda-1} \frac{n_\lambda m_l}{N N} + \dots \right) \right], \quad (27) \end{aligned}$$

and

$$\frac{dE_2}{dt} = MP_{1 \rightarrow 0}(\nu_2)(1 - e^{-h\nu_2/kT})(E_2(T) - E_2) - 2 \frac{dE_1}{dt}.$$

The various terms have the same meaning as in Eq. (20), except that both modes now reside in the same molecule. The fractions n_0/N , n_1/N , etc., and subscripts λ refer to the ν_1 -vibration, and m_0/N , etc., and subscripts l refer to the ν_2 -vibration. Since here $E=0$ for the resonance transition,

$$P_{0 \rightarrow 2}^{1 \rightarrow 0} = P_{2 \rightarrow 0}^{0 \rightarrow 1},$$

and

$$P_{l \rightarrow l+2}^{\lambda \rightarrow \lambda-1} = (l+2)(l+1)\lambda P_{0 \rightarrow 2}^{1 \rightarrow 0}.$$

TABLE III. Probability of a complex excitation in a polyatomic gas.

Gas	T	Quantum change in ν_1 -vib.	Quantum change in ν_2 -vib.	Theory	Observed
COS	288°K	+1	0	10^{-7}	Not observed
COS	288°K	0	+1	10^{-3}	10^{-4} ^b
COS	288°K	-1	+1	6×10^{-2}	10^{-4}
CO ₂	288°K	0	1	4×10^{-4}	2×10^{-5} ^a
CO ₂	288°K	1	0	10^{-9}	Not observed
CO ₂	288°K	-1	+1	10^{-7}	Not observed
CO ₂	288°K	± 1	∓ 2	1.5×10^{-3}	10^{-5} ^a

^a K. F. Buschmann and K. Schafer, Z. physik. Chem. (B)50, 73-99 (1941).
^b K. Schafer, Z. physik. Chem. (B)46, 212 (1940).

Equation (27) is reduced to

$$\frac{dE_1}{dt} = 2MP_{2 \rightarrow 0}^{0 \rightarrow 1} N h \nu_2 \left[\sum_{l=0}^{\infty} l(l-1) \frac{m_l}{N} \sum_{\lambda=0}^{\infty} \frac{n_{\lambda}}{N} - \sum_{l=0}^{\infty} l(l+1) \frac{m_l}{N} \sum_{\lambda=0}^{\infty} \frac{n_{\lambda}}{N} \right]. \quad (28)$$

Assuming the ν_2 -vibration can exchange energy freely among its own vibrational levels, and making use of the accidental degeneracy between ν_1 - and ν_2 -vibrations, we have

$$E_1(T_2) = 2 \frac{N h \nu_2 e^{-2h\nu_2/kT_2}}{1 - e^{-2h\nu_2/kT_2}},$$

$$= \frac{e^{-h\nu_2/kT_2}}{1 + e^{-h\nu_2/kT_2}} E_2(T_2).$$

So that we can write Eq. (28) finally as

$$\frac{dE_1}{dt} = 2P_{2 \rightarrow 0}^{0 \rightarrow 1} M \frac{E_2(T_2)}{E_2(T_2) - 2E_1(T_2)} (E_1(T_2) - E_1). \quad (29)$$

Equation (29) describes the adjustment of the ν_1 -vibration with the ν_2 -vibration. The effective relaxation time is given as

$$(\tau_{1,2})^{-1} \equiv 2P_{2 \rightarrow 0}^{0 \rightarrow 1} M \frac{E_2(T_2)}{E_2(T_2) - 2E_1(T_2)}.$$

Under the approximation permissible in the applications of these equations to an acoustic field, we obtain for CO_2 ,¹⁰

$$\frac{d\Delta T_2}{dt} = \frac{1}{\tau_2} (\Delta T - \Delta T_2) - \frac{2}{\tau_{1,2}} \frac{C_1}{C_2} (\Delta T_2 - \Delta T_1),$$

$$\frac{d\Delta T_1}{dt} = \frac{1}{\tau_{1,2}} (\Delta T_2 - \Delta T_1),$$

where τ_2 is defined as above and $\tau_{1,2}$ is given by

$$(\tau_{1,2})^{-1} = 2MP_{2 \rightarrow 0}^{0 \rightarrow 1} \frac{1 + e^{-h\nu_2/kT}}{1 - e^{-h\nu_2/kT}}.$$

AGREEMENT OF THEORY AND EXPERIMENT

The authors have presented a method for calculating relaxation times in gases which has been applied to pure gases, mixtures, and polyatomic gases. A comparison of some results of these calculations and experiments are shown in Tables I-III. The agreement of calculated

¹⁰ These equations are similar in form to one of two proposed sets of equations given by Schafer, see reference 8.

and experimental results are considered better than expected. The predicted probability $P^{1 \rightarrow 0}$ for N_2 and for a Cl_2 - H_2 mixture differ by a factor of 10^6 and yet they each check with experiment within a factor of 25. The Tables I-III were computed assuming the geometrical factor $C^{i \rightarrow f}$ mentioned above to be unity, while in reality, this factor may be expected to be $1/3$ and perhaps as small as $1/30$ in particular cases. Gas mixtures which react chemically as CO and Cl_2 , as well as gases such as HCl and Cl_2 where the rotation-vibration interaction is important, cannot be treated by these methods.

APPENDIX A

Nonresonant Energy Exchanges

The contribution of low speed particles to the overall probability integral Eq. (9) is small for typical nonresonant energy exchanges, since $p^{i \rightarrow f}(v_0)$ will be extremely small. While only molecules of appreciable velocity have any reasonable value for $p^{i \rightarrow f}(v_0)$, the number of molecules having these velocities diminish sharply with increasing velocity, due to the Boltzmann factor $\exp(-\mu v_0^2/2kT)$. Thus, the integrand is expected to go through a maximum value at some velocity v_0^* . Assume for the moment: (a) That the factor appearing in Eq. (7) evaluated at $v_0 = v_0^*$

$$\exp\left(\frac{4\pi^2 \mu v_0^*}{\alpha h}\right) \gg 1. \quad (\text{A1})$$

Then Eq. (9) becomes approximately

$$p^{i \rightarrow f} = V^2(i_1 \rightarrow f_1) \cdots \frac{\pi^2}{16} \left(\left[\frac{4\pi \mu v_0}{\alpha h} \right]^2 - \left[\frac{4\pi \mu v_F}{\alpha h} \right]^2 \right)$$

$$\times \frac{\exp\left[\pm \frac{4\pi^2 \mu (v_0 - v_F)}{\alpha h} \right]}{\left\{ 1 - \exp\left[\frac{-4\pi^2 \mu (v_0 - v_F)}{\alpha h} \right] \right\}^2}, \quad (\text{A2})$$

in the neighborhood of $v_0 = v_0^*$. In this paragraph the upper sign applies if $v_F > v_0$; the lower sign applies if $v_0 > v_F$. (b) That the translational energies $(\mu/2)v_0^{*2}$ and $(\mu/2)v_F^{*2}$ are much greater than ΔE , i.e.,

$$(\mu/2)v_0^{*2} \gg \Delta E,$$

$$(\mu/2)v_F^{*2} \gg \Delta E. \quad (\text{A3})$$

Then Eq. (10) may be approximated by a series

$$v_F \cong v_0 \pm \frac{\Delta E}{\mu v_0} - \frac{1}{2} \frac{(\Delta E)^2}{\mu^2 v_0^3} + \cdots,$$

and the complete exponent appearing in Eq. (9), when the expression for $p^{i \rightarrow f}$ given by Eq. (A2) is inserted in

Eq. (4), becomes

$$\frac{\mu}{2kT}v_0^2 - \frac{4\pi^2\Delta E}{\alpha h v_0} \pm \frac{2\pi^2(\Delta E)^2}{\alpha h \mu v_0^3} + \dots \quad (\text{A4})$$

The maximum value of this expression and thus approximately the maximum of the integrand of Eq. (9) occurs at

$$v_0^* = \left(\frac{4\pi^2 kT \Delta E}{\alpha^* h \mu} \right)^{\frac{1}{3}} \mp \frac{\Delta E}{2\mu} \left(\frac{4\pi^2 kT \Delta E}{\alpha^* h \mu} \right)^{-\frac{1}{3}} + \dots \quad (\text{A5})$$

and has the value

$$\sigma = \frac{3\mu}{2kT}v_0^{*2} \pm \frac{\Delta E}{2kT} + \dots$$

Here α^* denotes the value of α at $v_0 = v_0^*$. As long as the denominator in Eq. (A2) is nearly equal 1, i.e.,

$$\exp\left[-\frac{4\pi^2\mu}{\alpha h}(v_F - v_0)\right] \approx 0, \quad (\text{A6})$$

the major contribution to the total probability $P^{i \rightarrow f}$ comes from the neighborhood of $v_0 = v_0^*$. $P^{i \rightarrow f}$ may be approximated by substituting the approximate $p^{i \rightarrow f}$ of Eq. (A2) into Eq. (9). Using the saddlepoint method of evaluating the integral,¹¹ $P^{i \rightarrow f}$ then becomes

$$P^{i \rightarrow f} = 0.394 V^2(i_1 \rightarrow f_1) \dots \left[\frac{8\pi^3 \mu \Delta E}{\alpha^* h^2} \right]^2 \sigma^{\frac{1}{2}} e^{-\sigma}, \quad (\text{A7})$$

where

$$\sigma = \frac{3\mu}{2kT}v_0^{*2} \pm \frac{\Delta E}{2kT} = 3 \left[\frac{2\pi^4 (\Delta E)^2 \mu}{\alpha^* h^2 kT} \right]^{\frac{1}{2}} \pm \frac{\Delta E}{2kT}.$$

Assuming realistic values of α^* , μ , and ΔE for specific cases, inequalities (A1) and (A3) are indeed satisfied and Eq. (A5) may be used to find v_0^* .

Likewise the assumed inequality (A1) is usually well satisfied. The deBroglie wavelength of the oncoming beam of particles for v_0^* is

$$\lambda^* = h/2\pi\mu v_0^*.$$

The inequality (A1) then means that we are dealing with the case for which $(\alpha^*)^{-1}$ is at least several times the deBroglie wavelength λ^* . A collision for which the extent of the intermolecular force field is large compared to λ^* would be "adiabatic" in nature and an energy "jump" unlikely. We see now that this is nearly the case

¹¹ H. Jeffreys and B. C. Jeffreys, *Methods of Mathematical Physics* (The Cambridge University Press, New York, 1950), p. 504, Eq. (12).

even for the relatively short-range, repulsive field we have chosen. The near "adiabatic" nature of the collision is the cause of the very low probability of energy transfer for vibration.¹² The conditions placed upon Eq. (A7) are not independent. If the conditions

$$\exp\left(-\frac{4\pi^2\Delta E}{\alpha^* h v_0^*}\right) \ll 1 \quad (\text{A6})$$

and

$$(\mu/2)(v_0^*)^2 \gg \Delta E \quad (\text{A3})$$

are satisfied, then inequality (A1) is automatically satisfied.

Resonant Energy Exchanges

From Eq. (19) it can be seen that the above development fails as $\Delta E \rightarrow 0$. Under conditions of exact resonance, Eq. (7) takes the form

$$p^{i \rightarrow f} = V^2(i_1 \rightarrow f_1) \dots \left(\frac{2\pi\mu v_0}{\alpha h} \right)^2 \quad (\text{A8})$$

and Eq. (9) may be integrated immediately to yield

$$P^{i \rightarrow f} = V^2(i_1 \rightarrow f_1) \dots \frac{8\pi^2 \mu kT}{\alpha^2 h^2}. \quad (\text{A9})$$

Evaluation of the $V(i_n \rightarrow f_n)$ for an Exponential Field

If $V_n = e^{-\alpha A_n s_n}$ is expanded in an infinite series, $V(i_n \rightarrow f_n)$ may be written

$$V(i_n \rightarrow f_n) = \int_{-\infty}^{\infty} \psi_i^{(n)} \left(1 - \alpha A_n s_n + \left(\frac{\alpha A_n s_n}{2!} \right)^2 + \dots \right) \psi_f^{(n)} ds_n. \quad (\text{A10})$$

This integral is well known and has been evaluated in standard textbooks on quantum mechanics:

$$V(i_n \rightarrow i_n) = 1;$$

$$V(i_n \rightarrow i_n \pm 1) = -\alpha A \left[\frac{h(i_n + \frac{1}{2} \pm \frac{1}{2})}{8\pi^2 M_n \nu_n} \right]^{\frac{1}{2}}, \quad (\text{A11})$$

where M_n is the reduced mass of the oscillator vibrating at the frequency ν_n . Similarly

$$V(i_n \rightarrow i_n \pm 2) = \alpha^2 A^2 \left[\frac{(i_n + 1 \pm 1)(i_n \pm 1)h}{16\pi^2 M_n \nu_n} \right]^{\frac{1}{2}}. \quad (\text{A12})$$

¹² This point was made by J. M. Jackson and N. F. Mott, *Proc. Roy. Soc. (London)* **A137**, 703 (1932).