# FREQUENCY FACTORS AND ISOTOPE EFFECTS IN SOLID STATE RATE PROCESSES*

GEORGE H. VINEYARD

Brookhaven National Laboratory, Upton, New York

*(Received 8 February 1957)*

**Abstract**—The movement of defects in solids on the basis of classical absolute rate theory is re-examined with special attention to many-body aspects. The effective frequency in the Arrhenius expression governing these processes is shown to be, in harmonic approximation, the ratio of the product of the $N$ normal frequencies of the entire crystal at the starting point of a transition to the product of the $N$-1 normal frequencies of the crystal when it is constrained in a saddle point configuration. The influence of the masses of the various atoms on the effective frequency is investigated. It is shown that an effective mass which depends on the direction of the path through the saddle point in configuration space determines this frequency. In the case of chemical diffusion by the vacancy mechanism the effective mass is approximately the same as the mass of the solute atom, and must always lie between the mass of the solute and the mass of the solvent. It is finally shown that the classical rate theory, even with many-body considerations, is unable to explain the recent observations of LAZARUS and OKKERSE on the isotope effect in the diffusion of iron in silver.

## 1. INTRODUCTION

THE rate of movement of defects in solids by thermal activation can be calculated on the absolute rate theory.[1–6] In general one finds that individual defect jump rates $\Gamma$ are given by the equation

$$\Gamma = \tilde{\nu} e^{-\Delta F/kT}. \tag{1}$$

Here $\Delta F$ is the free energy needed to carry the defect from an initial equilibrium position to a saddle point, $T$ is the absolute temperature, $k$ is Boltzmann's constant, and $\tilde{\nu}$ is an effective frequency associated with vibration of the defect in the direction of the saddle point. Even though only one atom jumps in the elementary process, the problem is essentially one of many bodies because the jumping atom is surrounded by other atoms with which it interacts. This fact is readily incorporated in the absolute rate theory in its general form; nevertheless all of the actual discussions of solid state processes with which the writer is acquainted oversimplify the problem by reducing it to a one-body model at some stage in the calculations. After this the frequency either

remains loosely defined, which is unnecessary, or is reduced to an Einstein frequency (frequency of the jumping atom when all other atoms are fixed at equilibrium points), which is inaccurate.

The recent discovery of an isotope effect in solid state diffusion,[7] an effect which appears to be anomalously large, focusses attention on the exact meaning of the terms in eq. (1). The purpose of this note is to show that, by a generalization of all the usual arguments $\tilde{\nu}$ and $\Delta F$ can be completely defined, within the area of approximation that is appropriate to rate theory, and to derive more complete expressions for these quantities. The approximations inherent in any rate theory are that well defined states exist for the original system (atom near its starting point) and the transition system (atom near the saddle point). This requires any interactions that are not a part of the phase space under consideration to be sufficiently weak. For usefulness the calculations will be simplified by two further assumptions: (a) At all stages quantum effects will be neglected. (b) At a later stage motions near the saddle point will be treated by the theory of small oscillations—i.e., the vibrations will be assumed to be nearly simple harmonic.

---

*Work performed under the auspices of the U.S. Atomic Energy Commission.

## 2. FREQUENCY FACTORS IN SOLID STATE RATE PROCESSES

Various atomic jump processes may be of interest, but the principles are best illustrated by treating a particular case. Consider a crystal containing a vacant lattice site and let $\Gamma$ be the average rate at which a specific atom adjacent to the vacancy jumps into the vacant site. Let the entire crystal contain $N/3$ atoms, so there are $N$ degrees of freedom, $x_1\ x_2 \dots x_N$. Let the mass associated with $x_j$ be $m_j$, and define new coordinates $y_j = \sqrt{m_j}\ x_j$. Let the potential energy of the entire crystal be $\Phi(y_1 \dots y_N)$. Consider the configuration space of the crystal ($N$ dimensional). $\Phi$ possesses a minimum at a point $A$ in this space, corresponding to the atom on its original site, the vacancy on its adjoining site, and every other
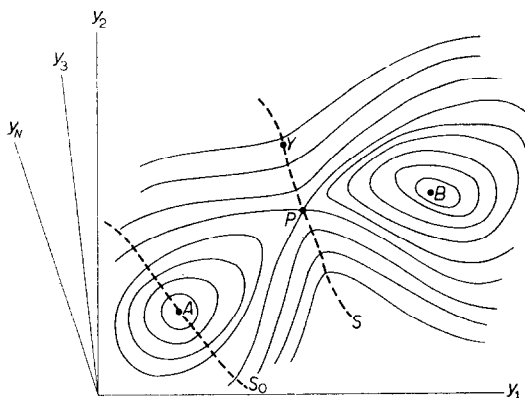


FIG. 1. Configuration space of $N$ dimensions showing, schematically, hyper-surfaces of constant potential energy (solid lines) and imaginary constraining hyper-surfaces (dotted lines).

atom at an equilibrium position (Fig. 1). $\Phi$ possesses another minimum at $B$, which corresponds to the atom and the vacancy interchanged in the crystal and other atoms relaxed again. By topological arguments it is seen that there must be at least one saddle point somewhere between $A$ and $B$. Also, only one saddle point would be expected for the likely transitions from $A$ to $B$. Label it $P$. Two dimensional contours of constant $\Phi$ are shown in the figure; it must be remembered that these actually represent $N-1$ dimensional hyper-surfaces.

There now exists a unique hyper-surface $S$, of dimensionality $N-1$, defined as follows: $S$ passes through $P$ and is perpendicular to the contours of constant $\Phi$ everywhere else. $S$ thus separates the region around $A$ from that around $B$, and any representative point reaching $S$ with finite velocity crosses over into the region around $B$.

In a system in thermal equilibrium there is a definite number of representative points, $Q_A$, in the region to the "left" of $S$, and a definite number, $I$, crossing $S$ from "left" to "right" per second. The average lifetime, $\tau$, of representative points in region $A$, and the rate, $\Gamma$, of transition from $A$ to $B$ are related as follows:

$$\Gamma = \frac{1}{\tau} = \frac{I}{Q_A}. \tag{2}$$

This $\Gamma$, of course, is assumed equal to the desired average jump rate already defined.

In classical systems in equilibrium the position and velocity of a representative point in configuration space are independently distributed, and the density in configuration space, $\rho$, can be written

$$\rho = \rho_0 e^{-\Phi/kT}, \tag{3}$$

where $\rho_0$ is a normalizing constant. Then

$$Q_A = \rho_0 \int_A e^{-\Phi/kT}\, dv, \tag{4}$$

where the integration is over the portion of configuration space to the "left" of $S$.

To calculate $I$, observe that the number of representative points at any point $Y$ of $S$, per unit volume, with hyper-velocity $V = \{\dot{y}_1 \dots \dot{y}_N\}$, within range $dV = d\dot{y}_1 \dots d\dot{y}_N$ is

$$\rho(Y, V)\, dV = \rho_1 e^{-\Phi(Y)/kT} e^{-V^2/2kT}\, d\dot{y}_1 \dots d\dot{y}_N, \tag{5}$$

where the normalizing constant is

$$\rho_1 = \rho_0 (2\pi kT)^{-N/2}.$$

If an element of $S$ at $Y$ is represented by the vector $dS = \{dS_1 \dots dS_N\}$ the current of velocity $V$ crossing $dS$ is expression (5) multiplied by $dS \cdot V$, and the total current crossing $dS$ is

$$dI = dS \cdot \int V\rho(Y, V)\, dV. \tag{6}$$

Here the integration is over all $V$ such that

$$dS \cdot V > 0. \qquad (7)$$

To allow for condition (7) the axes may be rotated so that one, say $y_1$, is parallel to $dS$ at $Y$, and then we find

$$dI = \rho_0 (2\pi kT)^{-N/2} e^{-\Phi(Y)/kT} \, dS_1 \times$$

$$\times \int_0^\infty \dot{y}_1 e^{-\dot{y}_1{}^2/2kT} \, d\dot{y}_1 \prod_{j=2}^N \int_{-\infty}^\infty e^{-\dot{y}_j{}^2/2kT} \, d\dot{y}_j \qquad (8)$$

$$= \rho_0 \sqrt{kT/2\pi} \, e^{-\Phi(Y)/kT} \, dS_1,$$

where now $dS \equiv |dS| = dS_1$.
Finally,

$$I = \int dI = \rho_0 \sqrt{(kT/2\pi)} \int_S e^{-\Phi(Y)/kT} \, dS, \qquad (9)$$

where the integration is over the hyper-surface $S$. Equations (2), (4), and (9) give

$$\Gamma = \sqrt{\frac{kT}{2\pi}} \, \frac{\int_S e^{-\Phi/kT} \, dS}{\int_A e^{-\Phi/kT} \, dv}. \qquad (10)$$

This is in an essentially familiar form—the ratio of two configurational partition functions. The generalization over the usual presentations at this stage is that the configuration space is specifically a many-body space so that the influence of *all* bodies and *all* degrees of freedom is accounted for in principle.

The theory of small vibrations can now be employed to approximate expression (10) in a useful way. Near point $A$ the function $\Phi$ may be expanded in Taylor series to second order. By an axis transformation this may be put in the form

$$\Phi \cong \Phi(A) + \sum_{j=1}^N \tfrac{1}{2}(2\pi \nu_j)^2 q_j{}^2, \qquad (11)$$

where $q_1 \dots q_N$ are the normal co-ordinates and $\nu_1 \dots \nu_N$ are the normal frequencies for vibrations about point $A$.* Similarly the potential may be

---

* Without loss of generality it may be supposed that the crystal is macroscopically constrained. Consequently there are no free translational or rotational modes and none of the frequencies is zero.

expanded about the saddle point $P$ *within the constraining surface $S$*

$$\Phi \cong \Phi(P) + \sum_{j=1}^{N-1} \tfrac{1}{2}(2\pi \nu_j')^2 q_j{}'^2, \qquad (12)$$

where $q_1' \dots q_{N-1}'$ and $\nu_1' \dots \nu_{N-1}'$ are the normal co-ordinates and frequencies for vibrations about $P$ with the constraint $S$.

With (11) and (12) the partition functions in (10) can be evaluated to give

$$\prod_{j=1}^{N-1} \left( \frac{\sqrt{(2\pi kT)}}{2\pi \nu_j'} \right) e^{-\Phi(P)/kT}, \qquad (13)$$

and

$$\prod_{j=1}^{N} \left( \frac{\sqrt{(2\pi kT)}}{2\pi \nu_j} \right) e^{-\Phi(A)/kT}, \qquad (14)$$

for the numerator and denominator, respectively. Finally, one finds

$$\Gamma = \left( \frac{\prod_{j=1}^N \nu_j}{\prod_{j=1}^{N-1} \nu_j'} \right) e^{-[\Phi(P)-\Phi(A)]/kT}. \qquad (15)$$

In this form the transition rate is displayed as a product of an effective frequency,

$$\nu^* = \left( \prod_{j=1}^N \nu_j \right) \Big/ \left( \prod_{j=1}^{N-1} \nu_j' \right) \qquad (16)$$

and an activation exponential. The activation energy is $\Phi(P) - \Phi(A)$, which is self-explanatory. The effective frequency is very different from a simple Einstein frequency, or any single frequency exhibited in physical space. *It is the ratio of the product of the $N$ normal frequencies of the entire system at the starting point of the transition to the $N-1$ normal frequencies of the system constrained in the saddle point configuration.*

A crude approximation to a normal frequency is found by constraining every $x_i$ but one and allowing this to vibrate. This process provides a set of Einstein frequencies, $\nu_j{}^E$, and $\nu_j{}^E$ is proportional to $1/\sqrt{m_j}$. If, on this model, the frequencies in the saddle point are the same as those at $A$, except

that the mode for motion of the jumping atom in the saddle point direction is missing, $\nu^*$ immediately reduces to $\nu_k{}^E$, the frequency of the moving atom when it was on its original site. This, as noted is proportional to $1/\sqrt{m_k}$ where $m_k$ is the mass of the jumping atom. In this approximation, a simple isotope effect in diffusion would be predicted. On the more complete model, the effect on $\nu^*$ of altering the mass of the jumping atom must be estimated in a more sophisticated way. In principle *all* of the normal mode frequencies would be altered and the dependence of each on $m_k$ is complicated. This question is taken up in the next section and a fairly simple answer is shown to exist.

Another dress may be put on the result (10) to make closer contact with the formulation of WERT and ZENER.[3, 4, 6] Let a hyper-surface $S_0$ be defined passing through $A$. The choice of $S_0$ is somewhat arbitrary, but the simplest would appear to be the following: Let $S_0$ be of the same shape as $S$ with the point corresponding to $P$ located at $A$, and oriented so that the normal to $S_0$ at $A$ is along the line of force leading to $P$. (Fig. 1). Define the constrained configurational partition functions $Q_0$ and $Q_s$, as follows:

$$Q_0 = \rho_0 \int_{S_0} e^{-\Phi/kT} dS_0, \qquad (17)$$

$$Q_s = \rho_0 \int_S e^{-\Phi/kT} dS. \qquad (18)$$

Here $\int_{S_0}$ means integration over the hyper-surface $S_0$, $\int_S$ means integration over the hyper-surface $S$. Recognizing that the numerator in (10) is $Q_S$, and multiplying and dividing the latter by $Q_0$, one gets

$$\Gamma = \sqrt{\left(\frac{kT}{2\pi}\right)} \frac{Q_0}{Q_A} \frac{Q_S}{Q_0}. \qquad (19)$$

$Q_S/Q_0$ is now precisely the exponential of minus $1/kT$ times the free energy change when the system, constrained to lie on the hyper-surface, is carried from $A$ to $P$ by reversible motion of the constraining hyper-surface. Calling this $\Delta F = \Delta U - T\Delta S$, one has

$$\frac{Q_S}{Q_0} = e^{-\Delta F/kT} = e^{\Delta S/k} e^{-\Delta U/kT}. \qquad (20)$$

This displays the activation free energy, entropy, and energy. The effective frequency, $\tilde{\nu}$, comes from the remaining factors in (19),

$$\tilde{\nu} = \sqrt{\left(\frac{kT}{2\pi}\right)} \frac{Q_0}{Q_A}. \qquad (21)$$

This again is a ratio of partition functions, the denominator referring to a system of dimensionality one less than the numerator. The previously defined effective frequency, $\nu^*$ is related to the present one by

$$\nu^* = \tilde{\nu} e^{\Delta S/k}. \qquad (22)$$

For the small vibration approximation

$$\Delta S = k \ln \left( \frac{\prod_{j=1}^{N-1} \nu_j{}^0}{\prod_{j=1}^{N-1} \nu_j{}'} \right), \qquad (23)$$

where $\nu_j{}^0$ is the frequency of the $j$th normal mode for the system constrained to lie on surface $S_0$. Since, in this approximation,

$$\frac{Q_0}{Q_A} = \sqrt{\frac{2\pi}{kT}} \left( \frac{\prod_{j=1}^{N} \nu_j}{\prod_{j=1}^{N-1} \nu_j{}^0} \right),$$

this gives

$$\nu^* = \frac{\prod_{j=1}^{N} \nu_j}{\prod_{j=1}^{N-1} \nu_j{}'},$$

in agreement with the previous result (16).

## 3. ISOTOPE EFFECT IN ACTIVATED PROCESSES (CLASSICAL TREATMENT)

The preceding analysis has shown that rate processes in a purely classical system undergoing small vibrations depend on products of frequencies of normal modes. We now consider these frequencies in a general way. With the origin taken at an equilibrium point in configuration space, the potential energy of the system can be written, (for small oscillations)

$$\Phi = \Phi_0 + \sum_{i,j=1}^{N} \frac{1}{2} \frac{\beta_{ij}}{\sqrt{m_i}, \sqrt{m_j}} y_i y_j, \qquad (24)$$

where $\beta_{ij}$ is the usual force constant relating the $i$th cartesian co-ordinate of the system to the $j$th and has the symmetry $\beta_{ij} = \beta_{ji}$. In the usual way it is shown that the normal frequencies are the roots of the characteristic equation

$$\det[X - (2\pi\nu)^2 I] = 0, \qquad (25)$$

where $I$ is the unit matrix and the $ij^{\text{th}}$ element of $X$ is $\beta_{ij}/\sqrt{(m_i m_j)}$.) By familiar theorems the product of the roots of (25), and hence $\prod\limits_{j=1}^{N} (2\pi\nu_j)^2$ is $\det(X)$. Considering the form of this determinant one sees that $1/\sqrt{m_i}$ factors out of the $i$th row $(i = 1, 2, ... N)$ and a similar factor comes out of each column, giving the theorem

$$\prod_{j=1}^{N} \nu_j = \frac{\sqrt{(\det[\beta_{ij}])}}{(2\pi)^N} \prod_{j=1}^{N} \frac{1}{\sqrt{m_j}}, \qquad (26)$$

(which is known as the product rule in molecular spectroscopy). The mass dependence of the frequency product is here exhibited explicitly, assuming that the $\beta_{ij}$ are all independent of mass. From this the numerator in (15) is seen at once to vary as the minus 3/2 power of the mass of the diffusing atom in case of isotopic substitution. The result is general and independent of restrictive assumptions such as an Einstein model.

The denominator in (15) requires more attention. Imposing the stipulated one dimensional constraint at a saddle point reduces the system to a stable one of $N-1$ degrees of freedom, and it is necessary to know which mass has essentially been removed. The constraint is in general not flat, but since $P$ is an equilibrium point, the expansion of $\Phi$ to second order about $P$ requires only first order knowledge of the constraining surface. Now consider the saddle point in $x_1 ... x_N$ configuration space. $S$ has a normal at $P$ (one dimensional). Let the cosine of the angle between this direction and the axis $x_j$ be $c_j$. If the representative point moves in this direction a distance $d\xi$ from $P$, $dx_j = c_j \, d\xi$, and the kinetic energy associated with this direction can be written $\frac{1}{2}m^*\dot\xi^2$, where $m^*$ is the effective mass for the direction. Also, the kinetic energy is

$$\sum_{j=1}^{N} \tfrac{1}{2}m_j\dot{x}_j^2 = \sum_{j=1}^{N} \tfrac{1}{2}m_j c_j^2 \dot\xi^2,$$

and equating the first and third expressions of kinetic energy one finds

$$m^* = \sum_{j=1}^{N} m_j c_j^2. \qquad (27)$$

By the properties of direction cosines $\sum\limits_{j=1}^{N} c_j^2 = 1$, and so $m^*$ is bounded by the smallest and largest masses $m_j$ in the system. Also if the normal to $S$ is parallel to an axis, say $x_i$, $m^* = m_i$, and if $S$ is nearly parallel to that axis $m^* \cong m_i$, the approximation being generally good because $\sum\limits_{j} m_j c_j^2$ is an extremum at each axial direction.

Now, without the constraint $S$, vibration about $P$ has $N$ normal modes (one of imaginary frequency), and the preceding discussion of the product of frequencies applies. Letting $\beta'_{ij}$ be the force constants in the vicinity of configuration. $P$, equation (26) gives

$$\prod_{j=1}^{N} \nu_j' = \frac{\sqrt{(\det[\beta'_{ij}])}}{(2\pi)^N} \prod_{j=1}^{N} \frac{1}{\sqrt{m_j}}. \qquad (28)$$

Since the normal to $S$ at $P$ is the direction directly across the saddle point, this is also the direction of motion of the normal co-ordinate of the problem that has imaginary frequency. We have labeled this the $N$th mode. Introducing the constraint $S$ removes this normal mode without disturbing the others. Thus

$$\prod_{j=1}^{N-1} \nu_j' = \frac{1}{\nu_N'} \frac{\sqrt{(\det[\beta'_{ij}])}}{(2\pi)^N} \prod_{j=1}^{N} \frac{1}{\sqrt{m_j}}. \qquad (29)$$

Finally, $\nu_N' = C/\sqrt{m^*}$, where $C$ depends only on the force constants $\beta'_{ij}$ and $m^*$ is the effective mass for motion in the $N$th mode, given by (27). Lumping all the terms that depend on force constants but not on the masses into a new constant $C'$, (29) can be written

$$\prod_{j=1}^{N-1} \nu_j' = \frac{\sqrt{m^*}}{C'} \prod_{j=1}^{N} \frac{1}{\sqrt{m_j}}. \qquad (30)$$

If moving through the saddle point along the normal to $S$ means that, at $P$, only the jumping

atom is in motion in physical space, then the normal to $S$ is along a co-ordinate direction associated with this atom, and $m^*$ equals precisely the mass of the jumping atom. In some crystalline symmetries this might be the true state of affairs, although the displacement of neighbors when an atom is at the saddle point would generally be expected to destroy such symmetry. In any case the jumping atom must have a large share of the motion, hence the approximation $m^* =$ mass of jumping atom should not be bad. If the jumping atom has mass $m_1$ and all the other atoms have mass $m_2 > m_1$ it is necessary from (27) that $m_1 \leqslant m^* < m_2$. In fact, cartesian axes in physical space can always be chosen such that

$$m^* = c_1{}^2 m_1 + (1 - c_1{}^2)m_2, \qquad (31)$$

where $c_1$ is the cosine of the angle between the normal of $S$ and axis 1 and is independent of isotopic substitution in $m_1$.

Combining (30) with (26) in (15) gives

$$\Gamma = \frac{C''}{\sqrt{m^*}} e^{-[\Phi(P) - \Phi(A)]/kT}, \qquad (32)$$

where $C''$ depends on the force constants $\beta_{ij}$ and $\beta'_{ij}$, but does not depend on any of the masses.

To a very good approximation then, it appears that $\Gamma$ should be inversely proportional to the square root of the isotopic mass of the jumping atom, and to the extent that $c_1$ is less than 1 the dependence on isotopic mass must be even slower than the square root.

The experiments of LAZARUS and OKKERSE[7] show that the diffusion coefficients of $Fe^{55}$ and $Fe^{59}$ in single crystals of silver at 1156°K are in the ratio of 1·15 to 1. The diffusion coefficients are proportional to the jump frequencies $\Gamma$ of the impurity atoms, and thus the foregoing analysis leads to the expectation that the ratio of the diffusion coefficients must lie between 1 and the square root of the isotope mass ratio, and would generally be expected to be close to the latter extreme. In the present instance the square root of the mass ratio is 1·035. The experimental results are thus inexplicable by classical rate theory, even when the many body feature of the diffusion process is taken into account. In view of the high temperature and large masses involved the usual quantum

corrections to classical rate theory [8–10] would not be expected to make an appreciable difference, although LAZARUS and OKKERSE speculate that an anomalously large tunneling effect might exist in this system. In seeking to explain these results it should be remembered that the diffusion coefficient is also proportional to the concentration of vacancies on sites adjacent to the diffusing atom, and any vibrationally dependent binding between a vacancy and an impurity will increase the concentration around one isotope compared to that around the other. An extra binding of about 0·01 eV around the light isotope as compared with the heavy seems to be required. The work of MONTROLL and POTTS [11] predicts a differential binding at low temperatures of this sign and of roughly this order of magnitude (although their formulas must be pushed beyond their strict domain of validity). At the temperature of this experiment the effect would be very much reduced and no valid calculation of its magnitude exists. The true meaning of the LAZARUS-OKKERSE results thus remains obscure.

One final remark is in order. The preceding discussion of $\Gamma$ commenced with the assumption that only one atom acquired a new lattice site during the jump, but this restriction is not essential. Two, three, or more atoms might be co-operatively involved in jumping to new sites, and, as long as the topology of the energy contours in configuration space is that of Fig. 1, the discussion through equation (30) remains valid. In a ring mechanism for self diffusion, for example, the effective mass $m^*$ is given by equation (27) and is seen to be identical with the common atomic mass. This has been pointed out before by ZENER.[6] The effect of an isotope in the ring is to alter the jump frequency. If the common mass is $m_2$ and a single isotope of mass $m_1$ occurs in a symmetrical ring of $n$ atoms, equations (15), (27), and (30) show that the frequency $\tilde{\nu}$ should be altered, in first approximation, by the factor

$$\frac{\sqrt{m_2}}{\sqrt{[m_1/n + m_2(1 - 1/n)]}}. \qquad (33)$$

## REFERENCES

1. GLASSTONE S., LAIDLER K. J., and EYRING H. *The Theory of Rate Processes* McGraw-Hill, New York (1941).
2. SEITZ F. *Phase Transformations in Solids* Chap 4. (Edited by R. SMOLUCHOWSKI) John Wiley, New York (1951).
3. WERT C. A., and ZENER C. *Phys. Rev.* **76,** 1169 (1949).
4. WERT C. A. *Phys. Rev.* **79,** 601 (1950).
5. SEEGER A. *Encyclopedia of Physics* Vol. VII, Part 1. Springer-Verlag, Berlin (1955).

6. ZENER C. *Imperfections in Nearly Perfect Crystals* p. 295. (Edited by W. SHOCKLEY, J. H. HOLLO-MAN, R. MAURER, and F. SEITZ) John Wiley, New York (1952).
7. LAZARUS D. and OKKERSE B. *Phys. Rev.* **105,** 1677 (1957).
8. BIGELEISEN J. *J. Chem. Phys.* **17,** 675 (1949).
9. BIGELEISEN J. and WOLFSBERG M. *J. Chem. Phys.* **21,** 1972 (1953).
10. BIGELEISEN J. and WOLFSBERG M. *J. Chem. Phys.* **22,** 1264 (1954).
11. MONTROLL E. W. and POTTS R. B. *Phys. Rev.* **102,** 72 (1956).