ADVANCES IN CHEMICAL PHYSICS

VOLUME I

ADVANCES IN CHEMICAL PHYSICS

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VOLUME I

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PREFACE

The literature concerned with what is now rightly called "Chemical Physics" is growing tremendously. I have often thought that it would be very convenient if, for every subject approached in, say, one of the new publications, which are mostly and very appropriately highly technical, I could find an expert who would be willing to tell me in simple words what it is all about. Of course, I would prefer an expert who is himself working in the special field of that publication, who really knows the whole background and who at the same time is not going to vulgarize the proceedings by making it too easy by hiding the subtle details of the newest findings. It seems to me that this is what we can expect of the articles which are going to be published in *Advances in Chemical Physics*, the series of which this is the first volume. Personally, I have had nothing to do with the preparation and the organization of this new venture. What I am saying here, therefore, is just my theory. I will be glad if it turns out to be right; I will be delighted when it has to be amended because of surprises which will make the articles still more useful and which were not anticipated.

P. DEBYE

INTRODUCTION TO THE SERIES

In the last decades, Chemical Physics has attracted an ever increasing amount of interest. The variety of problems, such as those of chemical kinetics, molecular physics, molecular spectroscopy, transport processes, thermodynamics, the study of the state of matter, and the variety of experimental methods used, makes the great development of this field understandable. But the consequence of this breadth of subject matter has been the scattering of the relevant literature in a great number of publications.

Despite this variety and the implicit difficulty of exactly defining the topic of Chemical Physics, there are a certain number of basic problems that concern the properties of individual molecules and atoms as well as the behavior of statistical ensembles of molecules and atoms. This new series is devoted to this group of problems which are characteristic of modern Chemical Physics.

As a consequence of the enormous growth in the amount of information to be transmitted, the original papers, as published in the leading scientific journals, have of necessity been made as short as is compatible with a minimum of scientific clarity. They have, therefore, become increasingly difficult to follow for anyone who is not an expert in this specific field. In order to alleviate this situation, numerous publications have recently appeared which are devoted to review articles and which contain a more or less critical survey of the literature in a specific field.

An alternative way to improve the situation, however, is to ask an expert to write a comprehensive article in which he explains his view on a subject freely and without limitation of space. The emphasis in this case would be on the personal ideas of the author. This is the approach that has been attempted in this new series. We hope that as a consequence of this approach, the series may become especially stimulating for new research.

Finally, we hope that the style of this series will develop into something more personal and less academic than what has become the standard scientific style. Such a hope, however, is not likely to be completely realized until a certain degree of maturity has been attained — a process which normally requires a few years.

At present, we intend to publish one volume a year, but this schedule may be revised in the future.

I. PRIGOGINE

CONTENTS

STATISTICAL-MECHANICAL THEORY OF TRANSPORT PROCESSES. X. THE HEAT OF TRANSPORT IN BINARY LIQUID SOLUTIONS*

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CONTENTS

I. INTRODUCTION

Denbigh[2] Drickamer and collaborators,[3, 9, 10] Wirtz,[11] Wirtz and Hiby,[12] and Prigogine and co-workers[8] have written numerous papers containing molecular interpretations of the heat of transport and the related Soret coefficient in liquids. These have proceeded on the basis of special assumptions concerning the molecular structure of the liquid and the mechanism of the diffusion process, and have assumed the validity of the equilibrium statistical-mechanical distribution in the nonequilibrium case. In the present paper we remove the special assumptions and show from general statistical mechanics that the heat of transport consists not only of an equilibrium term but also a term which arises from the non-equilibrium perturbation to the distribution function. In the special case of a regular solution, the expression for the equilibrium

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contribution reduces to a thermodynamic equation that is similar to expressions obtained previously.

In this article we shall not utilize the generalized Fokker-Planck equations[6] which have been successfully used to calculate coefficients of viscosity and thermal conductivity.[13, 14] Rather, we shall find it more convenient to proceed directly from the Liouville equation. To obtain an expression for the contribution of the intermolecular forces to the heat flux, we shall postulate a plausible generalization of the usual phenomenological equations of the thermodynamics of irreversible processes to the space of molecular pairs. Although we shall not prove it here, it may be shown that the same results can also be obtained (with greater labor) from the Fokker-Planck equations.

II. PHENOMONENOLOGICAL THEORY

The mass flux $\mathbf{j}_1$ of component 1 and heat flux $\mathbf{q}$ in a system of two components at uniform pressure are related to the gradient of the mole fraction of component 1 and the gradient of temperature by the phenomenological relations

$$-\mathbf{j}_1 = \frac{\Omega_{11}}{x_2}\frac{\partial \mu_1}{\partial x_1}\nabla x_1 + \Omega_{10}\nabla \ln T \tag{II.1}$$

$$-\mathbf{q} = \frac{\Omega_{01}}{x_2}\frac{\partial \mu_1}{\partial x_1}\nabla x_1 + \Omega_{00}\nabla \ln T \tag{II.2}$$

where x_α is the mole fraction of component α, μ_1 is the chemical potential of component 1, T is the absolute temperature, and Ω_{11}, Ω_{10}, Ω_{01} and Ω_{00} are the phenomenological coefficients.[1] The mass flux $\mathbf{j}_1$ is expressed as molecules per unit area per unit time relative to the local center of mass.

The heat of transport Q_1^* is defined by the equation

$$\mathbf{j}_1 Q_1^* = \mathbf{q} \tag{II.3}$$

when $\nabla T = 0$.

From Eqs. II.1, II.2, and II.3 it follows that

$$Q_1{}^* = \frac{\Omega_{01}}{\Omega_{11}}$$

If the Onsager reciprocal relation $\Omega_{01} = \Omega_{10}$ is valid, then the heat of transport is related to the stationary state of the Soret effect, as may be seen readily by setting $\mathbf{j}_1 = 0$ in Eq. II.1. Our calculation of the heat of transport will be based on Eq. II.3 and the statistical-mechanical expression for $\mathbf{q}$, and so we shall nowhere require the reciprocal relation.

The value of $Q_1{}^*$ (which depends only upon the local state), must be independent of the velocity of the center of mass, and in our equations below we have set this velocity equal to zero in order to facilitate the calculation.

III. STATISTICAL-MECHANICAL EXPRESSIONS FOR THE DENSITIES AND FLUXES

The single phase, two-component fluid system under consideration contains N molecules of which N_1 are of species 1 and N_2 are of species 2. The molecules of each species are labeled separately, so that the molecules of species α are numbered 1, 2, . . . N_α. For simplicity, we suppose that each molecule contains three degrees of translational freedom and no other degrees of freedom. The positions of the molecules of species α are denoted by the sequence of three vectors $\mathbf{R}_{\alpha_1}, \mathbf{R}_{\alpha_2}, \ldots \mathbf{R}_{\alpha_{N_\alpha}}$, and their momenta by $\mathbf{P}_{\alpha_1}, \mathbf{P}_{\alpha_2}, \ldots \mathbf{P}_{\alpha_{N_\alpha}}$.

We denote the time-smoothed probability distribution function at a time t in a statistical ensemble of identical systems containing the N molecules by $f(\mathbf{R}_{1_1} \ldots \mathbf{R}_{2_{N_2}}, \mathbf{P}_{1_1} \ldots \mathbf{P}_{2_{N_2}}; t)$. It obeys the Liouville equation

$$\frac{\partial f}{\partial t} + \sum_{\gamma=1}^{2} \sum_{i=1}^{N_\gamma} \frac{\mathbf{P}_{\gamma_i}}{m_\gamma} \cdot \nabla_{R_{\gamma_i}} f + \sum_{\gamma=1}^{2} \sum_{i=1}^{N_\gamma} \mathbf{F}_{\gamma_i} \cdot \nabla_{P_{\gamma_i}} f = 0 \qquad \text{(III.1)}$$

where $\mathbf{F}_{\gamma_i}$ is the force on molecule i of species γ, and m_γ is the mass of a molecule of species γ.

The expectation value at a time t of any dynamical variable a is

$$< a;f > = \int a(\mathbf{R}_{1_1} \ldots \mathbf{R}_{2_{N_2}}, \mathbf{P}_{1_1} \ldots \mathbf{P}_{2_{N_2}}) f d\mathbf{R}_{1_1} \ldots d\mathbf{R}_{2_{N_2}} d\mathbf{P}_{1_1} \ldots d\mathbf{P}_{2_{N_2}}$$

Using this notation, the concentration $c_\alpha(\mathbf{r}_1)$ of molecules α at time t at a point $\mathbf{r}_1$ in the system is

$$c_\alpha(\mathbf{r}_1) = \int \varphi_\alpha{}^{(1)}(\mathbf{r}_1, \mathbf{p}_1) d^3\mathbf{p}_1$$

where

$$\varphi_\alpha{}^{(1)} = < \nu_\alpha{}^{(1)}; f >$$

$$\nu_\alpha{}^{(1)} = \sum_{i=1}^{N\alpha} \delta(\mathbf{R}_{\alpha_i} - \mathbf{r}_1)\, \delta(\mathbf{P}_{\alpha_i} - \mathbf{p}_1)$$

and $\delta(\mathbf{R}_{\alpha_i} - \mathbf{r}_1)$ and $\delta(\mathbf{P}_{\alpha_i} - \mathbf{p}_1)$ are Dirac delta functions.

The particle current density $\mathbf{j}_\alpha(\mathbf{r}_1)$ of species α at point $\mathbf{r}_1$ is

$$\mathbf{j}_\alpha(\mathbf{r}_1) = c_\alpha(\mathbf{r}_1)\mathbf{u}_\alpha(\mathbf{r}_1) = \int \frac{\mathbf{p}_1}{m_\alpha} \varphi_\alpha{}^{(1)}(\mathbf{r}_1, \mathbf{p}_1) d^3\mathbf{p}_1$$

where $\mathbf{u}_\alpha(\mathbf{r}_1)$ is the local velocity of species α.

In the space of ordered pairs of molecules of species α at a point $\mathbf{r}_1$ and species β at $\mathbf{r}_2$, the average number density $c_{\alpha\beta}{}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ may be expressed as

$$c_{\alpha\beta}{}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \int \varphi_{\alpha\beta}{}^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2) d^3\mathbf{p}_1 d^3\mathbf{p}_2$$

where

$$\varphi_{\alpha\beta}{}^{(2)} = < \nu_{\alpha\beta}{}^{(2)}; f >$$

and*

$$\nu_{\alpha\beta}{}^{(2)} = \sum_{\substack{j=1 \\ \alpha_i \neq \beta_j}}^{N\beta} \sum_{i=1}^{N\alpha} \delta(\mathbf{R}_{\alpha_i} - \mathbf{r}_1)\, \delta(\mathbf{R}_{\beta_j} - \mathbf{r}_2)\, \delta(\mathbf{P}_{\alpha_i} - \mathbf{p}_1)\, \delta(\mathbf{P}_{\beta_j} - \mathbf{p}_2)$$

The particle current density in pair space $\mathbf{j}_{\alpha\beta}{}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ is given by the six-component vector

$$\begin{aligned} \mathbf{j}_{\alpha\beta}{}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) &= c_{\alpha\beta}{}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\mathbf{u}_{\alpha\beta}{}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \\ &= \int \left(\frac{\mathbf{p}_1}{m_\alpha} \oplus \frac{\mathbf{p}_2}{m_\beta} \right) \varphi_{\alpha\beta}{}^{(2)}\, d^3\mathbf{p}_1 d^3\mathbf{p}_2 \qquad \text{(III.2)} \end{aligned}$$

where $\mathbf{u}_{\alpha\beta}{}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ is the mean local velocity in pair space and the vector $\mathbf{p}_1/m_\alpha \oplus \mathbf{p}_2/m_\beta$ in six space is the direct sum of $\mathbf{p}_1/m_\alpha$ which lies in the three-dimensional momentum subspace of one molecule located at $\mathbf{r}_1$ and $\mathbf{p}_2/m_\beta$ which lies in the momentum

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* The symbolic notation $\alpha_i \neq \beta_j$ indicates that there is no term corresponding to $i = j$ when $\alpha = \beta$.

subspace of the other molecule located at $\mathbf{r}_2$. The symbol $\oplus$ is used to generate vectors in six space from vectors in three space. The symbol $+$ will be used to denote sums of six-component vectors as well as three-component vectors.

$\mathbf{j}_{\alpha\beta}^{(2)}$ may be written as the sum (in the six-dimensional configuration space of a molecular pair) of its projections onto the spaces of its first argument, $\mathbf{r}_1$, and its second argument, $\mathbf{r}_2$. Thus

$$\begin{aligned}
\mathbf{j}_{\alpha\beta}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) &= \mathbf{j}_{\alpha\beta,1}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \oplus \mathbf{j}_{\alpha\beta,2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \\
\mathbf{j}_{\alpha\beta,1}^{(2)} &= \int \frac{\mathbf{p}_1}{m_\alpha} \varphi_{\alpha\beta}^{(2)} \, d^3\mathbf{p}_1 \, d^3\mathbf{p}_2 \\
\mathbf{j}_{\alpha\beta,2}^{(2)} &= \int \frac{\mathbf{p}_2}{m_\beta} \varphi_{\alpha\beta}^{(2)} \, d^3\mathbf{p}_1 \, d^3\mathbf{p}_2
\end{aligned} \tag{III.3}$$

We now assume that the molecules interact with central forces only, the intermolecular potential V is the sum of pair potentials, and that external fields of force are absent. Therefore

$$V = \tfrac{1}{2} \sum_{\beta=1}^{2} \sum_{\substack{\alpha=1 \\ \alpha_i \neq \beta_j}}^{2} \sum_{j=1}^{N\beta} \sum_{i=1}^{N\alpha} V_{\alpha\beta}(R_{\alpha_i \beta_j})$$

where

$$R_{\alpha_i \beta_j} = |\mathbf{R}_{\beta_j} - \mathbf{R}_{\alpha_i}|$$

The force exerted on molecule i of species α by molecule j of species β is

$$\mathbf{F}_{\beta_j \alpha_i} = -\nabla_{R_{\alpha_i}} V_{\alpha\beta}$$

and the total force, $\mathbf{F}_{\alpha_i}$, on molecule i of species α, is then

$$\mathbf{F}_{\alpha_i} = \sum_{\substack{\beta=1 \\ \alpha_i \neq \beta_j}}^{2} \sum_{j=1}^{N_\beta} \mathbf{F}_{\beta_j \alpha_i}$$

Under the above assumptions, the expression found by Irving and Kirkwood[5] for the heat flux $\mathbf{q}$ in a one component system may be generalized readily to the two-component case, leading to the relations

$$\mathbf{q} = \mathbf{q}_k + \mathbf{q}_v - \sum_{\alpha=1}^{2} \mathbf{j}_\alpha \bar{H}_\alpha \tag{III.4}$$

$$\mathbf{q}_k(\mathbf{r}_1) = \sum_{\alpha=1}^{2} \int \frac{m_\alpha}{2} \left| \frac{\mathbf{p}_1}{m_\alpha} - \mathbf{u} \right|^2 \left(\frac{\mathbf{p}_1}{m_\alpha} - \mathbf{u} \right) \varphi_\alpha^{(1)} \, d^3\mathbf{p}_1 \tag{III.5}$$

$$\mathbf{q}_v(\mathbf{r}_1) = \tfrac{1}{2} \sum_{\beta=1}^{2} \sum_{\alpha=1}^{2} \int \left[V_{\alpha\beta}(r)\, \mathbf{1} - V'_{\alpha\beta}(r) \frac{\mathbf{r}\mathbf{r}}{r} \right] \cdot \left[\mathbf{j}_{\alpha\beta,1}(\mathbf{r}_1, \mathbf{r}_1+\mathbf{r}) - \mathbf{u}(\mathbf{r}_1) c_{\alpha\beta}^{(2)}(\mathbf{r}_1, \mathbf{r}_1+\mathbf{r}) \right] d^3\mathbf{r} \tag{III.6}$$

where $\bar{H}_\alpha$ is the partial molecular enthalpy, $\mathbf{u}$ is the mean velocity of the local center of mass (zero in the present calculations), $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$, and $\mathbf{1}$ is the unit tensor of second rank. The term $\sum_{\alpha=1}^{2} \mathbf{j}_\alpha \bar{H}_\alpha$ which is zero in the one-component system arises in the macroscopic equations of transport for multicomponent systems.[7]*

IV. THE GENERAL EXPRESSION FOR THE HEAT OF TRANSPORT

To evaluate $\mathbf{q}_k$, we shall employ the zero-order approximation to $\varphi_\alpha^{(1)}$, with Maxwellian distribution around the mean particle velocities $\mathbf{u}_\alpha$, and linearized with respect to $\mathbf{u}_\alpha$,

$$\varphi_\alpha^{(1)}(\mathbf{r}_1, \mathbf{p}_1) = \frac{c_\alpha}{(2\pi m_\alpha kT)^{3/2}} e^{-p_1^2/2m_\alpha kT} \left(1 + \frac{\mathbf{u}_\alpha \cdot \mathbf{p}_1}{kT} \right) \tag{IV.1}$$

where k is Boltzmann's constant. Substituting Eq. IV.1 into Eq. III.5 and carrying out the integration yields

$$\mathbf{q}_k = \frac{5}{2} kT \sum_{\alpha=1}^{2} c_\alpha \mathbf{u}_\alpha \tag{IV.2}$$

The use of Eq. IV.1 in Eq. III.5 neglects quantities (negligible in liquids) of the order of the nonequilibrium terms in the kinetic contribution to the stress tensor.[13] More exact calculations using the generalized Fokker-Planck equations show that the neglected terms are actually equal to zero.

To evaluate $\mathbf{q}_v$ we must express $\mathbf{j}_{\alpha\beta,1}^{(2)}$ as a function of the local velocities. In order to do this we shall postulate the validity in pair space of quasi-phenomenological relations strictly analogous

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* It should be noted that our $\mathbf{q}$ is denoted by $\mathbf{q}'$ in the Kirkwood and Crawford paper.

to the phenomenological relations of the thermodynamics of irreversible processes. We find it convenient first to obtain expressions for the mean forces in the singlet and pair spaces.

The mean force $\overline{\mathbf{F}}_\alpha^{(1)}(\mathbf{r}_1)$ on a molecule of type α located at $\mathbf{r}_1$ is

$$c_\alpha(\mathbf{r}_1)\overline{\mathbf{F}}_\alpha^{(1)}(\mathbf{r}_1) = < \sum_{i=1}^{N_\alpha} \mathbf{F}_{\alpha_i}\delta(\mathbf{R}_{\alpha_i}-\mathbf{r}_1); f > \tag{IV.3}$$

Similarly, the mean force $\mathbf{F}_{\alpha\beta}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ in pair space, when a molecule of type α is at $\mathbf{r}_1$ and a molecule of type β is at $\mathbf{r}_2$, is

$$c_{\alpha\beta}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\overline{\mathbf{F}}_{\alpha\beta}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = < \sum_{\substack{j=1\\ \alpha_i\neq\beta_j}}^{N_\beta} \sum_{i=1}^{N_\alpha} (\mathbf{F}_{\alpha_i} \oplus \mathbf{F}_{\beta_j})\delta(\mathbf{R}_{\alpha_i}-\mathbf{r}_1)\delta(\mathbf{R}_{\beta_j}-\mathbf{r}_2); f > \tag{IV.4}$$

Multiplying Eq. III.1 by $\mathbf{P}_{\alpha_j}\delta(\mathbf{R}_{\alpha_j}-\mathbf{r}_1)$ and integrating over all coordinates and momenta yields, upon neglecting inertial terms and terms of the order of the nonequilibrium terms in the kinetic contribution to the stress tensor,

$$kT\nabla_{\mathbf{r}_1}c_\alpha(\mathbf{r}_1) - c_\alpha(\mathbf{r}_1)\overline{\mathbf{F}}_\alpha^{(1)}(\mathbf{r}_1) = 0 \tag{IV.5}$$

The nonequilibrium temperature is defined in terms of the kinetic energy per molecule averaged over all species, and this has been supposed equal to the kinetic energy per molecule averaged over a single species. Similarly, multiplying Eq. III.1 by

$$(\mathbf{P}_{\alpha_j} \oplus \mathbf{P}_{\beta_k})\,\delta(\mathbf{R}_{\alpha_j}-\mathbf{r}_1)\delta(\mathbf{R}_{\beta_k}-\mathbf{r}_2)$$

and integrating gives

$$kT\nabla c_{\alpha\beta}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - c_{\alpha\beta}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\overline{\mathbf{F}}_{\alpha\beta}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = 0 \tag{IV.6}$$

where $\nabla = \nabla_{\mathbf{r}_1} \oplus \nabla_{\mathbf{r}_2}$, and $\oplus$ denotes a direct sum in the six-dimensional configuration space of a molecular pair.* To derive Eq. IV.6, we have assumed that the mean kinetic energy of a species averaged in pair space is the same as the average in singlet space.† From the thermodynamics of isothermal systems in

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* This use of the symbol ∇ is not to be confused with that in the phenomenological theory.

† Calculations using the Fokker-Planck equations show that this assumption is not exact to terms of order $\mathbf{u}_\alpha$. However, the additional terms do not contribute appreciably to the heat of transport.

external fields of force, we know that if the gradient of chemical potential at a point is equal to the external force, the system is at equilibrium. By imposing suitable external fields we may obtain an equilibrium state of our system in which the concentration distribution (in singlet space but not in pair space) is the same as in the diffusing system. From Eq. III.1 we find the following equations analogous to Eqs. IV.5 and IV.6 and valid in the system at equilibrium under these conditions

$$kT\nabla_{r_1} c_\alpha(\mathbf{r}_1) - c_\alpha(\mathbf{r}_1)\overline{\mathbf{F}}_\alpha^{(1,0)}(\mathbf{r}_1) = c_\alpha(\mathbf{r}_1)\nabla_{r_1}\mu_\alpha(\mathbf{r}_1) \qquad \text{(IV.7)}$$

$$\begin{aligned} kT\nabla c_{\alpha\beta}^{(2,0)}(\mathbf{r}_1, \mathbf{r}_2) - c_{\alpha\beta}^{(2,0)}(\mathbf{r}_1, \mathbf{r}_2)\overline{\mathbf{F}}_{\alpha\beta}^{(2,0)}(\mathbf{r}_1, \mathbf{r}_2) \\ = c_{\alpha\beta}^{(2,0)}(\mathbf{r}_1, \mathbf{r}_2)[\nabla_{r_1}\mu_\alpha(\mathbf{r}_1) \oplus \nabla_{r_2}\mu_\beta(\mathbf{r}_2)] \qquad \text{(IV.8)} \end{aligned}$$

$\overline{\mathbf{F}}_\alpha^{(1,0)}$ and $\overline{\mathbf{F}}_{\alpha\beta}^{(2,0)}$ are the mean intermolecular forces in singlet space and pair space in this equilibrium state. Equations IV.7 and IV.8 are exact since the averages are performed in a canonical ensemble.

Subtracting Eq. IV.5 from Eq. IV.7 we find that

$$\overline{\mathbf{F}}_\alpha^{(1)}(\mathbf{r}_1) - \overline{\mathbf{F}}_\alpha^{(1,0)}(\mathbf{r}_1) = \nabla_{r_1}\mu_\alpha(\mathbf{r}_1)$$

The phenomenological relations may be inverted to express the gradients of chemical potential as linear functions of the velocities, and therefore

$$\overline{\mathbf{F}}_\alpha^{(1)}(\mathbf{r}_1) - \overline{\mathbf{F}}_\alpha^{(1,0)}(\mathbf{r}_1) = \sum_\gamma N_\gamma \zeta_{\alpha\gamma}(\mathbf{r}_1)[\mathbf{u}_\gamma(\mathbf{r}_1) - \mathbf{u}_\alpha(\mathbf{r}_1)] \qquad \text{(IV.9)}$$

The friction coefficients $\zeta_{\alpha\gamma}$ defined by this equation may be expressed as functions of the phenomenological coefficients.*

We now postulate that the following equation in pair space, analogous to Eq. IV.9 in singlet space, is valid:

$$\begin{aligned} \overline{\mathbf{F}}_{\alpha\beta}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \overline{\mathbf{F}}_{\alpha\beta}^{(2,0)}(\mathbf{r}_1, \mathbf{r}_2) \\ = \sum_{\gamma=1}^{2}\sum_{\sigma=1}^{2} \tfrac{1}{2}\zeta_{\alpha\beta;\gamma\sigma} \cdot \{(\mathbf{u}_\gamma(\mathbf{r}_1) \oplus \mathbf{u}_\sigma(\mathbf{r}_2)) - \mathbf{u}_{\alpha\beta}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\} \qquad \text{(IV.10)} \end{aligned}$$

A heuristic justification for Eq. IV.10 is that it reduces to the sum of two equations of the form of Eq. IV.9 at large distances

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* The coefficient ζ_{11} (or ζ_{22}) is defined by applying Eq. IV.9 to a three-component system in which the third component is tracer component 1 (or 2) present in vanishingly small quantity.

between $\mathbf{r}_1$ and $\mathbf{r}_2$ when the force and velocity in pair space approach the sums of the forces and velocities, respectively, in singlet space. Equation IV.10 is not the only conceivable equation with this correct limiting property. Further justification is to be found in the fact that it is derivable from the generalized Fokker-Planck equations.

By comparing Eq. IV.10 with Eq. IV.9 at large distances, we see that an asymptotic value of the tensor $\zeta_{\alpha\beta;\gamma\sigma}$ is $N_\gamma \zeta_{\alpha\gamma}(\mathbf{r}_1)\mathbf{1}_1 \oplus N_\sigma \zeta_{\beta\sigma}(\mathbf{r}_2)\mathbf{1}_2$ where $\mathbf{1}_1$ is the unit tensor at $\mathbf{r}_1$ and $\mathbf{1}_2$ is the unit tensor at $\mathbf{r}_2$. In the remainder of this paper we shall make the approximation that

$$\zeta_{\alpha\beta;\gamma\sigma} = N_\gamma \zeta_{\alpha\gamma} \mathbf{1}_1 \oplus N_\sigma \zeta_{\beta\sigma} \mathbf{1}_2 \tag{IV.11}$$

for all distances between $\mathbf{r}_1$ and $\mathbf{r}_2$.

Subtracting Eq. IV.8 from the sum in six-dimensional space of Eq. IV.7 for species α and species β, we have

$$\overline{\mathbf{F}}_{\alpha\beta}^{(2,0)}(\mathbf{r}_1, \mathbf{r}_2) - (\overline{\mathbf{F}}_\alpha^{(1,0)}(\mathbf{r}_1) \oplus \overline{\mathbf{F}}_\beta^{(1,0)}(\mathbf{r}_2)) = kT\nabla \ln g_{\alpha\beta}^{(2,0)}(\mathbf{r}_1, \mathbf{r}_2) \tag{IV. 12}$$

where the radial distribution function $g_{\alpha\beta}^{(2,0)}(\mathbf{r}_1, \mathbf{r}_2)$ is defined by

$$g_{\alpha\beta}^{(2,0)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{c_{\alpha\beta}^{(2,0)}(\mathbf{r}_1, \mathbf{r}_2)}{c_\alpha(\mathbf{r}_1)c_\beta(\mathbf{r}_2)}$$

Substituting Eqs. IV.5, IV.6, IV.9, IV.11, and IV.12 into Eq. IV.10 yields upon neglecting terms of order u_α^2

$$\mathbf{j}_{\alpha\beta,1}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$$
$$= c_{\alpha\beta}^{(2,0)}(\mathbf{r}_1, \mathbf{r}_2)\,\mathbf{u}_\alpha(\mathbf{r}_1) - c_{\alpha\beta}^{(2,0)}(\mathbf{r}_1, \mathbf{r}_2)\,D_\alpha(\mathbf{r}_1)\,\nabla_{r_1} \frac{g_{\alpha\beta}^{(2,1)}(\mathbf{r}_1, \mathbf{r}_2)}{g_{\alpha\beta}^{(2,0)}(\mathbf{r}_1, \mathbf{r}_2)}$$

or

$$\mathbf{j}_{\alpha\beta,1}^{(2)} = c_\alpha c_\beta g_{\alpha\beta}^{(2,0)} \mathbf{u}_\alpha - c_\alpha c_\beta D_\alpha [\nabla_{r_1} g_{\alpha\beta}^{(2,1)} - g_{\alpha\beta}^{(2,1)} \nabla_{r_1} \ln g_{\alpha\beta}^{(2,0)}] \tag{IV.13}$$

where

$$g_{\alpha\beta}^{(2,1)} = g_{\alpha\beta}^{(2)} - g_{\alpha\beta}^{(2,0)}$$

and

$$g_{\alpha\beta}^{(2)} = \frac{c_{\alpha\beta}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{c_\alpha(\mathbf{r}_1)\, c_\beta(\mathbf{r}_2)}$$

and the self-diffusion coefficient D_α of species α in the mixture is defined by

$$D_\alpha(\mathbf{r}_1) = \frac{kT}{\zeta_\alpha(\mathbf{r}_1)}$$

where

$$\zeta_\alpha(\mathbf{r}_1) = \sum_{\gamma=1}^{2} N_\gamma \zeta_{\alpha\gamma}(\mathbf{r}_1)$$

We shall now find an expression for $g_{\alpha\beta}^{(2,1)}/g_{\alpha\beta}^{(2,0)}$ for substitution into Eq. IV.13. Multiplying Eq. III.1 by $\delta(\mathbf{R}_{\alpha_j}-\mathbf{r}_1)\,\delta(\mathbf{R}_{\beta_k}-\mathbf{r}_2)$, integrating over coordinates and momenta, and neglecting inertial terms gives

$$\nabla_{r_1}\cdot \mathbf{j}_{\alpha\beta,1}^{(2)}+\nabla_{r_2}\cdot \mathbf{j}_{\alpha\beta,2}^{(2)} = 0$$

Substituting Eq. IV.13 for $\mathbf{j}_{\alpha\beta,1}^{(2)}$ and a similar equation for $\mathbf{j}_{\alpha\beta,2}^{(2)}$ into this differential equation yields when terms of order u_α^2 and ∇u_α are neglected

$$\frac{\mathbf{u}_\beta-\mathbf{u}_\alpha}{D_\alpha+D_\beta}\cdot \nabla_r g_{\alpha\beta}^{(2,0)}-\nabla_r\cdot\left\{\nabla_r g_{\alpha\beta}^{(2,1)}-g_{\alpha\beta}^{(2,1)}\nabla_r \ln g_{\alpha\beta}^{(2,0)}\right\} = 0 \tag{IV.14}$$

Equation IV.14 provides differential equations for the coefficients of the spherical harmonic expansion of $g_{\alpha\beta}^{(2,1)}/g_{\alpha\beta}^{(2,0)}$ when $\mathbf{u}_\beta-\mathbf{u}_\alpha$ is chosen as the polar axis in spherical coordinates. When the expansion is substituted into Eq. IV.13 and thence into Eq. IV.6 and an integration is carried out over all angles, only the term, A_1, involving the first Legendre polynomial, P_1, contributes to $\mathbf{q}_v$. This term may be written in the form

$$A_1 = \frac{1}{D_\alpha+D_\beta}\,\psi_{\alpha\beta}(r)\{\mathbf{e}_r\cdot(\mathbf{u}_\beta-\mathbf{u}_\alpha)\} \tag{IV.15}$$

where $\mathbf{e}_r$ is the unit vector in the $\mathbf{r}$-direction and, by Eq. IV.14, $\psi_{\alpha\beta}$ obeys the following differential equation:

$$g_{\alpha\beta}^{(2,0)}\frac{d^2\psi_{\alpha\beta}}{dr^2}+\left(\frac{dg_{\alpha\beta}^{(2,0)}}{dr}+\frac{2}{r}g_{\alpha\beta}^{(2,0)}\right)\frac{d\psi_{\alpha\beta}}{dr}-\frac{2g_{\alpha\beta}^{(2,0)}}{r^2}\psi_{\alpha\beta} = \frac{dg_{\alpha\beta}^{(2,0)}}{dr} \tag{IV.16}$$

In the linear approximation to $g_{\alpha\beta}^{(2,1)}/g_{\alpha\beta}^{(2,0)}$, $g_{\alpha\beta}^{(2,0)}$ is equal to the radial distribution function in the equilibrium state achieved by the naturally diffusing system in the absence of an external field. It depends only on r. Because both the perturbed and equilibrium radial distribution functions approach unity as r approaches infinity, one boundary condition on $\psi_{\alpha\beta}$ is that it approaches zero as r approaches infinity. The other boundary condition arises because the relative pair current density $\mathbf{j}_{\alpha\beta,2}{}^{(2)}-\mathbf{j}_{\alpha\beta,1}{}^{(2)}$ must have no sources or sinks. If the potential is infinite for $r \leqq b$, this leads to the boundary condition

$$\lim_{r\to b^+} \frac{d\psi_{\alpha\beta}}{dr} = 1$$

Substituting Eqs. IV.13 and IV.15 into Eq. III.6, integrating by parts, and using Eq. IV.16 results in the following linearized expression for $\mathbf{q}_v$:

$$\mathbf{q}_v = (\mathbf{q}_v)_1 + (\mathbf{q}_v)_2$$

$$(\mathbf{q}_v)_1 = \tfrac{1}{2}\sum_{\alpha=1}^{2}\sum_{\beta=1}^{2} c_\alpha(\mathbf{r}_1)c_\beta(\mathbf{r}_1)\mathbf{u}_\alpha(\mathbf{r}_1)\cdot\int\left(V_{\alpha\beta}(r)\mathbf{1}-V'_{\alpha\beta}(r)\,\frac{\mathbf{r}\,\mathbf{r}}{r}\right)g_{\alpha\beta}{}^{(2,0)}(r)\; a$$

$$(\mathbf{q}_\iota)_2 = \tfrac{1}{2}c_1c_2\frac{D_2-D_1}{D_2+D_1}\,[\mathbf{u}_1-\mathbf{u}_2]\int\left[V_{21}-\frac{r}{3}V''_{21}-\frac{2}{3}r\,V'_{21}\left(\frac{d\psi_{21}}{dr}-1\right)\right]g_{21}{}^{(2,0}$$

(IV.17)

Eliminating u_2 in favor of u_1 and inserting Eqs. III.4, IV.2, and IV.17 into Eq. II.3 gives the following expression for $Q_1{}^*$:

$$Q_1{}^* = Q_{11}{}^* + Q_{12}{}^*$$

$$Q_{11}{}^* = (h_1-\bar{H}_1)-(h_2-\bar{H}_2)\,\frac{m_1}{m_2}$$

$$Q_{12}{}^* = \frac{1}{2}\frac{D_2-D_1}{D_2+D_1}\left(c_2+c_1\frac{m_1}{m_2}\right)\left\{2h_{21}-\frac{2}{3}\int r\left(\frac{d\psi_{21}}{dr}-1\right)V'_{21}g_{21}{}^{(2,0)}\,d^3\mathbf{r}\right\}$$

(IV.18)

where

$$h_1 = c_1h_{11}+c_2h_{12}+\tfrac{5}{2}kT$$

$$h_2 = c_2h_{22}+c_1h_{21}+\tfrac{5}{2}kT$$

$$h_{\alpha\beta} = h_{\beta\alpha} = \tfrac{1}{2}\int\left(V_{\beta\alpha}-\frac{r}{3}V'_{\beta\alpha}\right)g_{\beta\alpha}{}^{(2,0)}\,d^3\mathbf{r}$$

h_1 and h_2 (which in general are *not* equal to $\bar{H}_1$ and $\bar{H}_2$ respectively) obey the following equation readily derivable from equilibrium statistical mechanics:

$$x_1 h_1 + x_2 h_2 = H \tag{IV.19}$$

where H is the mean molecular enthalpy.

Equation IV.18 splits the heat of transport into two terms, the first of which is quasi-thermodynamic in that it involves only averages over equilibrium ensembles, and the second of which arises from the deviation of the distribution function in pair space from the equilibrium distribution function. $Q_{11}{}^*$ corresponds to the expressions for the heat of transport found by previous authors who have neglected the nonequilibrium perturbation to the distribution function.

V. AN APPROXIMATE FORMULA FOR THE HEAT OF TRANSPORT

By introducing an approximation into Eq. IV.18, we can gain insight into the formula for the heat of transport. It suffices to use the assumption of regular solution theory that the radial distribution function is independent of composition.[4] Under this assumption we may differentiate Eq. IV.19 (using the definition of partial molecular enthalpy) to obtain expressions for $h_{\alpha\beta}$ in terms of thermodynamic quantities. Substituting these into Eq. IV.18 yields

$$\begin{aligned}
Q_{11}{}^* &= \frac{1}{2}\left(\frac{m_1 x_1}{m_2} + x_2\right)\frac{\bar{v}_1 \bar{v}_2}{v}\left(\frac{L_2}{\bar{v}_2} - \frac{L_1}{\bar{v}_1}\right) \\
Q_{12}{}^* &= \frac{1}{2v}\frac{D_2 - D_1}{D_2 + D_1}\left(\frac{m_1 x_1}{m_2} + x_2\right)\Bigg\{\bar{v}_1 \bar{v}_2\left(\frac{L_1}{\bar{v}_1} + \frac{L_2}{\bar{v}_2}\right) \\
&\quad + 2x_1(L_1 \bar{v}_1 - L_1 v_1) + 2x_2(L_2 \bar{v}_2 - L_2 v_2) \\
&\quad - \frac{2}{3}\int r\left(\frac{d\psi_{21}}{dr} - 1\right) V'_{21} g_{21}{}^{(2,0)}\, d^3\mathbf{r}\Bigg\}
\end{aligned} \tag{V.1}$$

where v is the mean molecular volume, $\bar{v}_1$ and $\bar{v}_2$ are the partial molecular volumes of components 1 and 2, respectively, v_1 and v_2 are the molecular volumes of the pure components, $L_1 (= \bar{H}_1 - \frac{5}{2}kT)$ and L_2 $(= \bar{H}_2 - \frac{5}{2}\, kT)$ are the negatives of the latent heats of vaporization of components 1 and 2, respectively, from the solution to the ideal gas state, and L_1 and L_2 are the negatives of the latent heats of vaporization of the pure component to the ideal gas state. Although the derivation of Eq. V.1 does not require the use of all of the postulates of regular solution theory, the equation may be further reduced by introduction of the regular solution theory chemical potential and the assumption of additivity of volumes.

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THEORETICAL AND EXPERIMENTAL ASPECTS OF ISOTOPE EFFECTS IN CHEMICAL KINETICS *

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CONTENTS

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I. INTRODUCTION

The first definitive experimental demonstration of an isotope effect in chemical kinetics dates back to the discovery in 1932 by Washburn and Urey[61] that deuterium is enriched in the liquid phase in the electrolysis of water. This discovery came at a time when the transition state theory of reaction rates was in a stage of active development and was immediately explained by the zero-point energy difference between isotopic molecules.[23] The subsequent world-wide production of laboratory quantities of concentrated deuterium by the electrolytic method provided material for new experiments on kinetic hydrogen isotope effects in a multitudinous array of reactions. Many of these had an important bearing on the transition state theory (e.g., $H+H_2$).[26] In the succeeding years there was considerable interaction between experimental and theoretical progress on kinetic isotope effects and their application to the elucidation of reaction mechanisms.

Most of this work came to a virtual halt with the diversion of scientific effort to military problems during World War II. After the war, interest in the general problem of kinetic isotope effects was resumed, fortified by new interests, new experimental techniques, new theoretical developments in the statistical mechanics of isotopic molecules, and the widespread availability of radioisotopes and enriched stable isotopes. All these were materially advanced by the scientific war effort. The progress has been rapid along all lines. The initiation of the present series on *Advances in Chemical Physics* provides an opportune time for a recapitulation and reevaluation of the progress and status of our knowledge. It is not our intention to summarize the extensive literature in the field, but rather to point out the present status of theory and experiment, and through illustration, the areas of agreement and disagreement. A considerable amount of new material, which has not stood the test of critical review by experts in the field, has been incorporated. This material should be easily discernable and much of it is provocative of further experimental and theoretical work. We consider this sufficient justification for its inclusion.

It will be obvious to the reader that much remains to be done along all lines. We may confidently expect studies on kinetic isotope effects to continue to enrich and refine our understanding of rate theory and mechanisms.

II. THEORY OF THE ISOTOPE EFFECT ON REACTION RATES

A. Introduction

A starting point in the study of the effect of isotopic substitution on reaction rates must be furnished by a theoretical model of chemical reaction. The discovery by Arrhenius that experimental reaction rates may be expressed by $Ae^{-E/RT}$ forms the cornerstone of the modern understanding of chemical reactions. Here A and E are constants independent of the temperature, R is the gas constant, and T is the absolute temperature. The Arrhenius equation led to the formulation of the collision theory of reaction. In this approach, systems which possess at least an "activation energy" E react on collision. In discussing reaction rates, one must distinguish between bimolecular reactions in general, unimolecular reactions at high pressures, and unimolecular reactions at low pressures. The subsequent discussion is not applicable to unimolecular reactions at low pressure, and these reactions will be discussed in a separate section. Thus A becomes the collision number which, for gas phase reactions, may be calculated by the gas kinetic formula. It is found for many reactions that one thus obtains values of the temperature independent factor A which differ from the experimental values by many orders of magnitude. It may be also noted that, in this approach, A depends on the isotopic masses in a predictable way and that the dependence so predicted is not in general the one experimentally found. The difficulties with the simple collision theory led to the introduction of the steric factor Z, so that A becomes PZ, where P is the collision number. Z is then to be determined from experiment and is sometimes found to be larger than unity. Since Z is thus an empirical factor for making theory and experiment agree, the collision theory approach does not furnish a good model for studying isotope effects on reaction rates.

The transition state theory of Marcelin,[41] revised on the basis of quantum statistics by Wigner, Polanyi, Eyring, and others[29,66] forms the framework of most present-day interpretation of high-pressure reaction rates. In this formalism one assumes an activated state through which the reaction takes place. Molecules in the activated state are in thermal equilibrium with the normal reacting molecules (see, however, Refs. 24 and 25). The rate constant is then roughly equal to the concentration of molecules in the activated state times the rate of passage of the molecules through the activated state to the final product. Other quantum-mechanical approaches to the reaction rate problem have been developed by Golden and Peiser[30] and by Bauer and Wu.[1] The final expressions derived by these authors bear great similarity to the transition state theory results. However, no isotope effect calculations have been made by these authors, and one cannot say with certainty that the isotope effects calculated by these approaches will be exactly the same as those calculated by the transition state theory. The approach in this review will be to treat the kinetic isotope effects within the framework of the transition state theory.

B. Discussion of Isotope Effect in Transition State Theory

The transition state theory proceeds on the assumption that there is a single potential energy surface along which the reaction takes place. For the usual reaction there will be a barrier between the part of coordinate space corresponding to reactants and the part of space corresponding to products. The reaction will then take place over the path corresponding to the lowest barrier.

The transition state is located at the top of the barrier along the path of decomposition. Thus the transition state lies in a trough and in general will be stable along all degrees of freedom except along the path of decomposition. The transition state theory leads to the following well-known expression for the rate equation constant k,

$$k = \frac{kT}{h} \varkappa K' \tag{II.1}$$

where k is the Boltzmann constant, T is the absolute temperature, h is Planck's constant, $\varkappa$ is the transmission coefficient, and K' is the equilibrium constant between the activated state molecules and the reactants. The degree of freedom along the path of decomposition is missing for the activated state molecules. $\varkappa$ is a factor which takes into account the fact that if a system has the proper classical energy to surmount a barrier it may yet be reflected; on the other hand, a system which does not have the proper classical energy to surmount the barrier may tunnel through it quantum mechanically.[25] A knowledge of the potential energy surface enables one then to calculate K' by the methods of statistical mechanics in terms of the partition functions of the activated complex and of the reactants. Thus

$$K' = \frac{Q^{\ddagger}}{Q_A Q_B Q_C \cdots} \tag{II.2}$$

where the Q's are partition functions; $Q^{\ddagger}$ is the partition function of the activated complex omitting the degree of freedom along the path of decomposition, and $Q_A, Q_B, Q_C, \ldots$ are the partition functions of the reactants. Qualitatively the theory is able to predict reaction rates quite well. The quantitative application of the theory is always hindered by the lack of knowledge of a reliable potential energy surface and the corresponding inability to calculate $Q^{\ddagger}$ and $\varkappa$. The effect of isotopes on the various quantities can often be predicted with more reliability than the quantities themselves so that one might try to predict quantitative isotope effects for reactions so complex that quantitative predictions of k would not be attempted.

Denoting isotopic species by the subscripts 1 and 2, one finds[38, 43]

$$\frac{k_1}{k_2} = \frac{\varkappa_1}{\varkappa_2} \frac{Q_1^{\ddagger}}{Q_2^{\ddagger}} \frac{Q_{A_2}}{Q_{A_1}} \frac{Q_{B_2}}{Q_{B_1}} \frac{Q_{C_2}}{Q_{C_1}} \cdots \tag{II.3}$$

The initial assumption is made $\varkappa_1 = \varkappa_2$. This assumption will be discussed further subsequently. The problems of calculating ratios of rate constants become then a matter of calculation of ratios of isotopic partition functions. The latter is simplified by the fact that the potential energy surfaces for isotopic molecules are the same to a very high degree of approximation.

The theory of calculation of ratios of isotopic partition functions has been developed in detail for exchange equilibria in gases. The formulation of Bigeleisen and Goeppert-Mayer,[10] which writes everything in terms of the vibrational frequencies of the molecules, will be reviewed. Classically Q_{A_2}/Q_{A_1} is $\prod_j (m_{2j}/m_{1j})^{3/2}$, where the m_j's are the masses of the atoms composing the molecules. This is however not true for $Q_1^{\ddagger}/Q_2^{\ddagger}$ since here one degree of freedom is missing, so that k_1/k_2 does not go to unity in the classical limit. Except in the case of molecular hydrogen, where due account must be taken for the nonclassical behavior of the rotations, one may write for nonlinear gas molecules in the harmonic approximation

$$\frac{Q_2}{Q_1} = \frac{s_1}{s_2}\left(\frac{I_{A_2}I_{B_2}I_{C_2}}{I_{A_1}I_{B_1}I_{C_1}}\right)^{1/2}\left(\frac{M_2}{M_1}\right)^{3/2} \prod_i^{3n-6} e^{(\nu_{1i}-\nu_{2i})hc/2kT} \frac{(1-e^{-hc\nu_{1i}/kT})}{(1-e^{-hc\nu_{2i}/kT})} \tag{II.4}$$

where I_A, I_B, I_C are the moments of inertia about the three principal axes of the n-atomic molecule, the M's are the molecular weights, the ν's are the vibrational fundamentals of the molecules in wave numbers, and the s's are the symmetry numbers of the respective molecules. Use of the Teller-Redlich product rule or of the classical limit (equivalent to high temperature) of Q_2/Q_1 enables one to reduce equation II.4 to the following form

$$\prod_j^n \left(\frac{m_{1j}}{m_{2j}}\right)^{3/2} s_2Q_2/s_1Q_1 = \prod_i^{3n-6} \frac{u_{2i}}{u_{1i}} e^{(u_{1i}-u_{2i})/2} \frac{(1-e^{-u_{1i}})}{(1-e^{-u_{2i}})} \tag{II.5}$$

where the m's are the masses of the constituent atoms of the molecules and $u_i = hc\nu_i/kT$. Assuming that the subscript 1 refers to the lighter molecule, and defining $u_{1i} = u_{2i} + \Delta u_i$, one writes

$$(s_2/s_1)f = \prod_{j}^{n}\left(\frac{m_{1j}}{m_{2j}}\right)^{3/2}\frac{s_2 Q_2}{s_1 Q_1} = \prod_{i}^{3n-6}\frac{u_i}{u_i+\Delta u_i}e^{\Delta u_i/2}\frac{(1-e^{-(u_i+\Delta u_i)})}{(1-e^{-u_i})} \qquad \text{(II.6)}$$

where u_i now refers to the frequency of the heavier molecule. Since atoms always balance out in any chemical equilibrium, the product $\prod_j^n(m_{1j}/m_{2j})^{3/2}$ will cancel out in any equilibrium and one can just substitute the quantity f for the ratio of isotopic partition functions in an equilibrium expression. For linear molecules, $3n-6$ must be replaced by $3n-5$. For the case $\Delta u \ll 1$, which is true, except at low temperatures, for the isotopes of all elements except hydrogen

$$(s_2/s_1)f = \prod_{i}^{3n-6}(1+G(u_i)\Delta u_i) \cong 1+\sum_{i}^{3n-6}G(u_i)\Delta u_i \qquad \text{(II.7)}$$

where $G(u) = \frac{1}{2}-1/u+1/(e^u-1)$. $G(u)$ has been tabulated.[10] Expansion of $G(u)$ in powers of u yields $u/12$ as the leading term. Thus, for small u and small Δu,

$$(s_2/s_1)f = 1+\sum_{i}^{3n-6}\frac{u_i}{12}\Delta u_i \qquad \text{(II.8)}$$

or

$$(s_2/s_1)f = 1+\sum_{i}^{3n-6}(u_{1i}^2-u_{2i}^2)/24 \qquad \text{(II.9)}$$

Equation II.9 is especially useful in conjunction with the sum rule.[19, 59]

$$4\pi^2\sum_{i}^{3n-6}(\nu_{1i}^2-\nu_{2i}^2) = \sum_{j}^{3n}\left(\frac{1}{m_{1j}}-\frac{1}{m_{2j}}\right)a_{jj} \qquad \text{(II.10)}$$

where a_{jj} is the diagonal force constant, and m_j is the mass of the jth atom. The potential energy is expressed in terms of the Cartesian coordinates of the component atoms. Thus, one obtains[6]

$$(s_2/s_1)f = 1+\frac{1}{24}\left(\frac{\hbar c}{kT}\right)^2\sum_{j}^{3n}\left(\frac{1}{m_{1j}}-\frac{1}{m_{2j}}\right)a_{jj} \qquad \text{(II.11)}$$

We now define

$$\gamma_i = 12G(u_i)/u_i \qquad \text{(II.12)}$$

Equation II.7 can then be rewritten in the form

$$(s_2/s_1)f = 1 + \sum_i^{3n-6} \gamma_i \frac{u_i}{12} \Delta u_i \qquad \text{(II.13)}$$

$$= 1 + \sum_i^{3n-6} \gamma_i (u_{1i}^2 - u_{2i}^2)/24 \qquad \text{(II.14)}$$

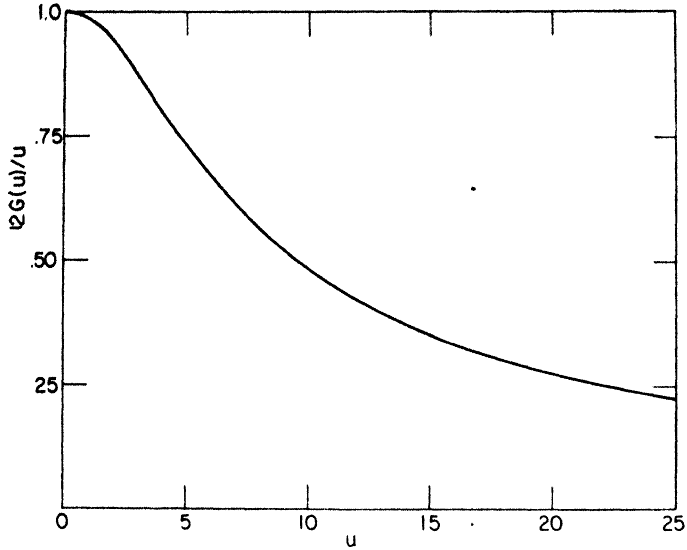

Fig. 1. Plot of the function $12G(u)/u$ vs. u.

It is seen from Fig. 1 that γ_i does not decrease very rapidly with u_i. Thus for $u_i = 5$ (a frequency of about 1000 cm^{-1} at 300°K), $\gamma_i = 0.73$. It is convenient, therefore, to define a $\bar{\gamma}$ such that

$$(s_2/s_1)f = 1 + \bar{\gamma} \sum_i^{3n-6} (u_{1i}^2 - u_{2i}^2)/24 \qquad \text{(II.15)}$$

The use of the correction term $\bar{\gamma}$ extends the method of the first quantum correction to values of u where the first quantum correction itself is inadequate. Equation II.11 becomes consequently

$$(s_2/s_1)f \simeq 1 + \frac{1}{24}\left(\frac{\hbar c}{kT}\right)^2 \bar{\gamma} \sum_j^{3n} \left(\frac{1}{m_{1j}} - \frac{1}{m_{2j}}\right) a_{jj} \qquad \text{(II.16)}$$

The usefulness of Eq. II.16 rests on the fact that γ_i does not vary rapidly with u so that $\bar{\gamma}$ can be guessed with good accuracy if one has some idea of the magnitude of the u's which make the major contribution to $\Sigma\Delta(u_i)^2$. Furthermore, magnitudes of a_{jj} may be well estimated so that Eq. II.16 enables one to calculate f without solving the potential problem.

In evaluating $Q_1^\ddagger/Q_2^\ddagger$ we recall that the vibrational degree of freedom along the path of decomposition is missing from the vibrational partition function. Similar to the derivation of Eq. II.5 one obtains

$$\prod_j^n \left(\frac{m_{1j}}{m_{2j}}\right)^{3/2} s_2^\ddagger Q_2^\ddagger/s_1^\ddagger Q_1^\ddagger = \prod_i^{3n-6} \frac{u_{2i}^\ddagger}{u_{1i}^\ddagger} \prod_i^{3n-7} e^{\Delta u_i^\ddagger/2} \frac{(1-e^{-u_{1i}^\ddagger})}{(1-e^{-u_{2i}^\ddagger})} \quad \text{(II.17)}$$

The degree of freedom along the decomposition path is missing in the second product. Solution of the equations of internal motion of the atoms in the activated complex by the theory of small vibrations leads to the $3n-6$ vibration frequencies indicated in the first product. One of these vibrations will be imaginary due to the fact that this degree of freedom does not correspond to binding but to a nongenuine vibration. This unique vibration will subsequently be referred to as the decomposition mode and the corresponding u will be designated $u_L^\ddagger$. Further discussion of $u_L^\ddagger$ will be the subject of one of the later sections. Then

$$\prod_j^n \left(\frac{m_{1j}}{m_{2j}}\right)^{3/2} s_2^\ddagger Q_2^\ddagger/s_1^\ddagger Q_1^\ddagger = \frac{\nu_{2L}^\ddagger}{\nu_{2L}^\ddagger} \prod_i^{3n-7} \frac{u_{2i}^\ddagger}{u_{1i}^\ddagger} e^{\Delta u_i^\ddagger/2} \frac{(1-e^{-u_{1i}^\ddagger})}{(1-e^{-u_{2i}^\ddagger})} \quad \text{(II.18)}$$

Now a part of this expression has the same form as Eq. II.6 for $3n-7$ degrees of freedom, so that we shall designate it as $f^\ddagger$. Thus

$$\prod_j^n \left(\frac{m_{1j}}{m_{2j}}\right)^{3/2} s_2^\ddagger Q_2^\ddagger/s_1^\ddagger Q_1^\ddagger = (\nu_{2L}^\ddagger/\nu_{1L}^\ddagger) f^\ddagger \qquad \text{(II.19)}$$

Then

$$\frac{k_1}{k_2} = \frac{\nu_{1L}^\ddagger}{\nu_{2L}^\ddagger} \frac{f_A f_B \cdots}{f^\ddagger} \qquad \text{(II.20)}$$

or for small Δu and with only one isotopic reactant

$$\frac{k_1 s_2 s_1^{\ddagger}}{k_2 s_1 s_2^{\ddagger}} = (\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger})(1+\sum_i^{3n-6} G(u_i)\Delta u_i) - \sum_i^{3n-7} G(u_i^{\ddagger})\Delta u_i^{\ddagger}) \qquad \text{(II.21)}$$

The problem of the transmission coefficient presents difficulty. One finds with model potential energy surfaces that transmission coefficients may depend strongly on the mass of the activated complex and its energy. The averaging over the thermal energy distribution may however destroy the isotope effect.[36] Further study is required here. "Tunneling" is frequently taken into account by a formulation due to Wigner.[65] If one approximates the potential along the reaction path through the activated complex by the parabola

$$V = V_0 - ax^2 \qquad \text{(II.22)}$$

the tunneling factor becomes to the first quantum approximation

$$\tau = 1 + \frac{1}{24}\left(\frac{\hbar}{kT}\sqrt{\frac{a}{M}}\right)^2 = 1 + \frac{1}{24}|u_L^{\ddagger}|^2 \qquad \text{(II.23)}$$

where M is the "effective mass" of the motion and $u_L^{\ddagger}$ has been associated with the motion along the decomposition path. Thus the isotope effect due to tunneling becomes

$$\tau_1/\tau_2 = 1 + \tfrac{1}{24}\Delta|u_L^{\ddagger}|^2 \qquad \text{(II.24)}$$

In the case of symmetric exchange reactions one must consider transmission coefficients as shown in Section VI, if there exists a potential basin in the potential surface between two equivalent activated complex sites.

It is seen that the ratio of isotopic rate constants is then given by

$$\frac{k_1}{k_2} = \frac{s_2^{\ddagger}\,\nu_{1L}^{\ddagger}}{s_1^{\ddagger}\,\nu_{2L}^{\ddagger}}(1+\tfrac{1}{24}\Delta\,|u_L^{\ddagger}|^2)\prod_K \prod_i^{3n-6} \frac{s_{1K}\,u_{2iK}}{s_{2K}\,u_{1iK}}\, e^{\Delta u_{iK}/2}\frac{(1-e^{-u_{1iK}})}{(1-e^{-u_{2iK}})} \Bigg/ \prod_i^{3n-7}\frac{u_{2i}^{\ddagger}}{u_{1i}^{\ddagger}}\, e^{\Delta u_i^{\ddagger}/2}\frac{(1-e^{-u_{1i}^{\ddagger}})}{(1-e^{-u_{2i}^{\ddagger}})} \qquad \text{(II.25)}$$

where the product $\prod_K$ runs over all the species of substrate molecules in the rate equation. It is clear from Eq. II.20, II.21, and II.25 that the ratio of rate constants of isotopic molecules is not simply the exponential of differences in zero-point energies. The latter, may in many cases, be a useful but insufficient approximation. The difference in experimental activation energies is obtained from a plot of log (k_1/k_2) vs. $1/T$. The theoretical difference involves the $H(u)$ function developed in connection with the statistical thermodynamics of isotopic molecules[5] as well as the temperature coefficient of the tunnel effect.[3]

The formal introduction of the tunnel correction has particular significance when Eq. II.25 is expressed in the $G(u)$ formalism Equation II.21 becomes

$$\frac{k_1}{k_2}\frac{s_2 s_1^{\ddagger}}{s_1 s_2^{\ddagger}} = (\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger})\Big(1 + \sum_i^{3n-6} G(u_i)\Delta u_i - \sum_i^{3n-7} G(u_i^{\ddagger})\,\Delta u_i^{\ddagger}\Big) \times \left(1 + \tfrac{1}{24}\Delta |u_L^{\ddagger}|^2\right). \qquad \text{(II.26)}$$

But, since $u_L^{\ddagger}$ is a pure imaginary and is sufficiently small that $u_L^{\ddagger}/12 = G(u_L^{\ddagger})$, we can write Eq. II.26 as

$$\frac{k_1}{k_2}\frac{s_2 s_1^{\ddagger}}{s_1 s_2^{\ddagger}} = (\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger})\Big(1 + \sum_i^{3n-6} G(u_i)\Delta u_i - \sum_i^{3n-6} G(u_i^{\ddagger})\Delta u_i^{\ddagger}\Big) \qquad \text{(II.27)}$$

Note that $G(u_L^{\ddagger})\ \Delta u_L^{\ddagger}$ is a negative number.

We now make use of the modified first quantum correction, Eq. II.15, and obtain

$$\frac{k_1}{k_2}\frac{s_2 s_1^{\ddagger}}{s_1 s_2^{\ddagger}} = (\nu_{1L}^{\ddagger}/\nu_{2Li}^{\ddagger})\Big[1 + (\bar{\gamma}/24)\sum_i^{3n-6}(u_{1i}^2 - u_{2i}^2) - (\bar{\gamma}^{\ddagger}/24)\sum_i^{3n-6}(u_{1i}^{\ddagger 2} - u_{2i}^{\ddagger 2})\Big] \qquad \text{(II.28)}$$

Equation II.28 is in a form to make use of the theorem of the trace, Eq. II.10, and gives

$$\frac{k_1}{k_2}\frac{s_2 s_1^{\ddagger}}{s_1 s_2^{\ddagger}} = (\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger})\left[1 + \frac{\bar{\gamma}}{24}\left(\frac{\hbar c}{kT}\right)^2 \sum_i^{3n}\left(\frac{1}{m_{1i}} - \frac{1}{m_{2i}}\right)a_{ii} - \frac{\gamma^{\ddagger}}{24}\left(\frac{\hbar c}{kT}\right)^2 \sum_i^{3n}\left(\frac{1}{m_{1i}} - \frac{1}{m_{2i}}\right)a_{ii}^{\ddagger}\right] \qquad \text{(II.29)}$$

If $\bar{\gamma} = \bar{\gamma}^{\ddagger}$, we get the simple and powerful formula

$$\frac{k_1}{k_2}\frac{s_2 s_1^{\ddagger}}{s_1 s_2^{\ddagger}} = (\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger})\left[1+\frac{\bar{\gamma}}{24}\left(\frac{\hbar c}{kT}\right)^2 \sum_{i}^{3n}\left(\frac{1}{m_{1i}}-\frac{1}{m_{2i}}\right)(a_{ii}-a_{ii}^{\ddagger})\right] \tag{II.30}$$

C. General Predictions on Kinetic Isotope Effects

Equation II.20 and simplified formulations like Eq. II.21 permit us to make some general predictions about isotope effects. Since f has been defined so that the subscripts 1 and 2 refer to the light and heavy isotopes, respectively, $\nu_{1L}^{\ddagger} \geqq \nu_{2L}^{\ddagger}$. Moreover $G(u)$ and Δu are positive. $G(u)$ increases with increasing u to the maximum value of $\frac{1}{2}$. Similarly $(s_2/s_1)f$ is always greater than unity. Since in general the binding is greater in the reacting molecule than in the transition complex, we would expect $k_1 > k_2$, apart from the classical statistical factor. In the case where the isotopic reactants are atoms, $G(u)\Delta(u)$ is zero and k_1/k_2 may well become less than unity. Cases in which the lighter isotope reacts more slowly than the heavy one are known as inverse isotope effects. The conditions necessary for such inverse isotope effects are

$$f^{\ddagger} > \frac{\nu_{1L}^{\ddagger}}{\nu_{2L}^{\ddagger}} f_A f_B \tag{II.31}$$

If the isotopic reactants are atoms, then $f_A = f_B = 1$ and the condition becomes

$$f^{\ddagger} > \nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger} \tag{II.32}$$

The latter requirement is easily satisfied by reactions involving hydrogen atoms.

Estimates of maximum regular and inverse isotope effects may be made quite simply. For simplicity of notation the classical symmetry number factors will be omitted. In order to arrive at maximal values of regular isotope effects, we assume no isotope effect in the activated complex, i.e., $f^{\ddagger} = 1$. This assumption is equivalent to no isotopic binding in the activated complex. The maximum value of $\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger}$ is $(m_2/m_1)^{1/2}$, where the m's are the masses of the isotopic atoms. Values of f for various isotopic species have been tabulated in the literature.[49] Using the values of f for strongly bonded species, one may then estimate maximum values of isotope effects. These are tabulated in Table I, which is

TABLE I. Estimated Maximum Ratios in Specific Rate Constants at 25° C.

Stable isotope	Tracer isotope	$k_1 s_2 s_1^{\ddagger}/k_2 s_1 s_2^{\ddagger}$
H^1	H^2	18
H^1	H^3	60
Li^6	Li^7	1.1
Be^9	Be^7	1.15
Be^9	Be^{10}	1.08
B^{10}	B^{11}	1.3
C^{12}	C^{13}	1.25
C^{12}	C^{14}	1.5
N^{14}	N^{15}	1.14
N^{14}	N^{13}	1.14
N^{14}	N^{16}	1.25
O^{16}	O^{18}	1.19
F^{19}	F^{18}	1.25
Na^{23}	Na^{22}	1.03
Na^{23}	Na^{24}	1.03
Mg^{24}	Mg^{27}	1.08
P^{31}	P^{32}	1.02
S^{32}	S^{35}	1.05
Cl (naturel abundance)	Cl^{36}	1.03
Cl (naturel abundance)	Cl^{38}	1.14
Ca^{40}	Ca^{45}	1.08
I^{127}	I^{131}	1.02

reproduced from Bigeleisen.[2] Maximum values for inverse isotope effects may be similarly calculated by setting f of the reactants equal to unity, which is indeed the case if the isotopic reactants are atoms. Now the value of $\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger}$ may be taken as unity which is the minimum value of this ratio. Maximal values of $f^{\ddagger}$ are estimated by taking the values for normal strongly bonded molecules. This maximum value of inverse effects may be obtained from the values in Table I by dividing by the square root of the ratio of masses of the heavier to the lighter isotope. It must be remembered that these values are very much maxima, since for normal reactions $f^{\ddagger}$ and f are not too different, while for atom reactions $f^{\ddagger}$ in general does not correspond to the stable molecule f-value.

It is [illegible] interest to comment at this point about the magnitude of secondary isotope effects. Secondary isotope effects occur when the isotopic atoms are not directly involved in the bond breaking and bond forming of a reaction. Examples of secondary isotope effects will be given in a subsequent section. From the definition of secondary isotope effect, $\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger} = 1$ should be valid to a high degree of approximation. Then one only calculates $f/f^{\ddagger}$ in order to compute secondary isotope effects. The major contributions to $f/f^{\ddagger}$ arise from large shifts in large frequencies. Magnitudes (probably upper limits) of secondary isotope effects will be calculated under the following assumptions: (1) we consider only the stretching frequencies, (2) the isotope shifts in these frequencies are calculated through the mass relationship of the frequency of a diatomic molecule, (3) for regular isotope effects it will be assumed that the stretching force constant decreases by a factor of two in the activated complex while for inverse isotope effects the force constant will be taken to increase by a factor of two. The results are tabulated in Table II. It is seen that under the present assumptions secondary isotope effects may be quite large. It must be remembered that if a compound is labeled in more than one position for a secondary isotope effect, the effect will be expected to be proportionally larger (e.g. $C-H_3$ *versus* $C-D_3$).

TABLE II. Magnitudes of Secondary Isotope Effects (25°C).

Isotopic substitution	Bond	Regular isotope effect	Inverse isotope effect
D, H	C—H	1.74	0.46
T, H	C—H	2.20	0.33
D, H	O—H	2.02	0.37
T, H	O—H	2.74	0.24
C^{13}, C^{12}	C—C	1.012	0.983
C^{14}, C^{12}	C—C	1.023	0.968

III. THE REACTION COORDINATE

As is seen from Eq. II.20, the high temperature limit of the isotope effect is given by $\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger}$, the ratio of the frequencies along the path of decomposition. We may note that, if the forward and backward reactions proceed through the same activated complex, the ratio $\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger}$ is the same for bond rupture and bond formation processes.[48] In the work of Eyring and co-workers,[29] the vibrational modes of the activated complex are usually found by solving the secular equation derived from the potential energy surface for $3n-6$ vibrations, one of which is usually an imaginary nongenuine vibration, corresponding to the fact that there is no binding along the corresponding "normal mode." Such a treatment corresponds to employing the $3n-7$ real vibrations in evaluating $f^{\ddagger}$ while the imaginary frequency is used to evaluate $\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger}$.

Slater[56] has carried out a classical investigation of unimolecular reaction rates at high pressures. The model used is that the molecule decomposes whenever a given coordinate q reaches a critical extension q_0. He obtains for the velocity constant

$$k = \nu e^{-E_0/kT} \tag{III.1}$$

where ν may be defined as the ratio of all $3n-6$ frequencies of the normal molecule to the $3n-7$ frequencies obtained when no motion is permitted to take place along q. For the case that the coordinate q is just the extension of a bond between two atoms A and B, which Slater defines as the coordinate q if the reaction involves only a single bond rupture, the isotope effect is found to be quite generally[57]

$$k_1/k_2 = (\mu_2/\mu_1)^{1/2} \tag{III.2}$$

where $\mu = m_A m_B/m_A+m_B$. Thus the frequency factor behaves isotopically as though one were just dealing with a diatomic molecule consisting of the two atoms, the bond between which is being broken.

Slater's result may now be compared with the high-temperature limit resulting from the calculations of the previous section,

$$\frac{k_1}{k_2} = \frac{\nu_{1L}^{\ddagger}}{\nu_{2L}^{\ddagger}} \tag{III.3}$$

The frequency $\nu_{1L}^{\ddagger}$ may be defined as the ratio of all $3n-6$ frequencies of the activated molecule to the $3n-7$ real frequencies which contribute to the zero-point energy. In the Eyring approximation described previously, $\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger}$ becomes just the ratio of the nongenuine vibrations, since the motion along the path of decomposition has been taken as the nongenuine normal mode which results from the solution of the potential problem. If the normal mode corresponding to the nongenuine vibration in the transition state involves motions solely of atoms A and B, between which the bond is ruptured or formed, the two methods become equivalent in the classical approximation. Considerable work has been carried out using such a formulation for the decomposition mode.[4] The process has even been extended to reactions which involve two bond extensions and/or contractions, i.e., three-center reactions.[11] The procedure for these three-center reactions again is based on the premise that the reaction coordinate involves only motions of those atoms whose internuclear separations have to reach certain critical values.

It seems worthwhile to examine critically this transcription of the Slater method into the standard absolute reaction rate theory. In the simple unimolecular bond break, it does appear reasonable that the coordinate q between the two atoms A and B must reach and go beyond a critical extension q_0 in order that decomposition takes place. In Slater's calculations account is taken of the different energies involved in stretching q to q_0. In regarding q as the mode of decomposition in the transition state method, one must, however, first look at the potential energy surface. The decomposition path involves passage over the lowest possible barrier between reactants and products. It does not seem reasonable to assume that this path necessarily only involves motion of the atoms A and B at the activated complex. Possibly, a more reasonable *a priori* formulation in a simple decomposition process would be to choose q as the coordinate which tears the two decomposition fragments apart. Such a coordinate would lead roughly to the relation

$$\frac{\nu_{1L}^{\ddagger}}{\nu_{2L}^{\ddagger}} = \left[\left(\frac{1}{M_{\alpha 1}} + \frac{1}{M_{\beta 1}}\right)\Big/\left(\frac{1}{M_{\alpha 2}} + \frac{1}{M_{\beta 2}}\right)\right]^{1/2} \qquad \text{(III.4)}$$

where M_α and M_β are the masses of the two fragments of the decomposition. It should not be surprising that such different results evolve from the Slater method and the Eyring potential method since, after all, the starting models are quite different.

The use of the Slater $(\mu_2/\mu_1)^{1/2}$ as the temperature independent factor does not obviously follow from a consideration of the potential energy surface, and thus its use must be regarded as an intermingling of the Eyring and the Slater approaches.

IV. UNIMOLECULAR REACTIONS

The formulation of reaction rate theory used in the previous sections applies to bimolecular and higher-order reactions in general, but to unimolecular reactions only at high pressures. We shall, therefore, reconsider the problem of isotope effects in unimolecular gas reactions. We start with the recent elaboration of the Lindemann hypothesis given by Marcus.[42]

The assumed reaction sequence is

$$A + N \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A^* + N \tag{IV.1}$$

$$A^* \xrightarrow{k_a} A^{\ddagger} \tag{IV.2}$$

$$A^{\ddagger} \xrightarrow{k_3} \text{products} \tag{IV.3}$$

where A^* denotes active molecule, $A^{\ddagger}$ denotes activated complex which is moving in the direction towards decomposition along the reaction coordinate, and N is all species of molecules which can cause activation or deactivation by collision. The steady-state assumption for A^* and $A^{\ddagger}$ leads to the following formulation of the "unimolecular rate constant"

$$k_{\text{uni}} = \int \frac{k_a d\,(k_1/k_2)}{1 + k_a/(k_2 p)} \tag{IV.4}$$

where p is the pressure. The integration takes account of the variation of the individual k's with energy.

Marcus computes the unimolecular rate constant after classifying the degrees of freedom in the active molecule as adiabatic, active, or inactive. Adiabatic degrees of freedom remain in the same quantum state throughout the decomposition process. Active degrees of freedom can transfer energy and contribute to the breaking of the bond. On the other hand, inactive degrees can transfer energy only when the molecule has essentially become an activated complex, and hence they do not contribute energy necessary for breaking the bond. Under the assumptions that the active and inactive degrees of freedom are vibrations and rotations and that the degree of motion along the decomposition path is a translation, a general formula is derived for k_{uni} as a function of pressure. At high pressure the formula becomes equivalent to the usual Eyring formula, which has been discussed in Section II.

Only one case of the formulation will be considered here. The three rotations of the molecule as a whole (as well as the three translations of the molecule, which make no contribution to the rate) will be considered to be adiabatic. All the internal degrees of freedom will be taken as active and as vibrations (except for the actual motion along the decomposition path in the activated complex). For this model, one finds

$$k_{\text{uni}} = k_{\infty} \int_0^{\infty} \frac{e^{-w}\, dw}{1 + a/p} \qquad \text{(IV.5)*}$$

where k_{∞} is the high pressure rate constant, w is a dimensionless integration variable, and

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* For all the assumptions leading to this final equation, the reader is referred to Marcus' original paper. Some of the assumptions could conceivably have an isotope effect. The assumptions necessary to arrive at the zero-pressure isotope effect ratio, Eqs. IV.7 to IV.9, are essentially the following:

(1) A semiclassical distribution function is substituted for the density of energy levels at energy E (including zero-point energy) of n harmonic oscillators (ν_i), i.e., $N(E) = (E)^{n-1}/(\Gamma(n)\Pi_{i=1}^{n} h\nu_i)$. The harmonic approximation is of course assumed even for high excitation.

(2) Having assumed the above semiclassical distribution, one makes the approximation

$$\int_{E_a + 1/2\Sigma h\nu_i^{\ddagger}}^{\infty} (E)^{s-1} e^{-E/kT}\, dE = (E_a + \tfrac{1}{2}\Sigma h\nu_i^{\ddagger})^{s-1} \int_{E_a + 1/2\Sigma h\nu_i^{\ddagger}}^{\infty} e^{-E/kT}\, dE$$

(3) The collision efficiency γ is taken to have no isotope effect. These approximations are currently under additional investigation.

$$a = \frac{Q^{\ddagger}\prod^{3n-6} h\nu_i \, e^{(E_a+E_0^{\ddagger})/kT}}{Q' hZ\gamma(E_a+E_0^{\ddagger})^{3n-7}} \Gamma(3n-6) \qquad \text{(IV.6)}$$

$Q^{\ddagger}$ is the usual partition function of the activated complex referred to the minimum in the potential of the normal molecule as the zero of energy, Q' is the partition function of the three rotations and three translations of the normal molecule, E_a is the activation energy of the reaction as measured from the minimum of the normal molecule potential energy surface to the minimum of the activated complex, $E_0^{\ddagger}$ is the zero-point energy of the activated complex, and the ν_i's are the vibrational frequencies of the normal molecule. Moreover, k_2, the rate of deactivation of active molecules to normal molecules, has been set equal to the collision number Z times an efficiency factor γ, assumed to be isotope independent.

At very low pressures

$$k_{\text{uni}} = k_{\infty} a^{-1} p \qquad \text{(IV.7)}$$

One obtains then for the limiting isotope effect at very low pressure for an activated complex with $3n-7$ real vibrations*

$$\frac{k_{\text{uni}_1}}{k_{\text{uni}_2}} = \frac{k_{\infty 1}}{k_{\infty 2}} \frac{a_2}{a_1} = \frac{Z_1}{Z_2} \frac{Q'_1}{Q'_2} \prod_i^{3n-6} \frac{u_{2i}}{u_{1i}} e^{-(E_{01}^{\ddagger}-E_{02}^{\ddagger})/kT}$$

$$\times \left(\frac{E_a+E_{01}^{\ddagger}}{E_a+E_{02}^{\ddagger}}\right)^{3n-7} \left(\frac{\nu_{1L}^{\ddagger}}{\nu_{2L}^{\ddagger}}\right) \frac{f}{f^{\ddagger}} \frac{Q_2^{\ddagger}}{Q_1^{\ddagger}} \qquad \text{(IV.8)}$$

Equation IV.8 can be rearranged through the use of Eq. II.5 and the Teller-Redlich product rule to give

$$\frac{k_{\text{uni}_1}}{k_{\text{uni}_2}} = \left(\frac{M_2}{M_1}\right)^{1/2} \left(\frac{E_a + \frac{1}{2}\sum_i^{3n-7} h\nu_{1i}^{\ddagger}}{E_a + \frac{1}{2}\sum_i^{3n-7} h\nu_{2i}^{\ddagger}}\right)^{3n-7} \frac{f}{f^{\ddagger}} \prod_i^{3n-7} \frac{u_{2i}^{\ddagger}}{u_{1i}^{\ddagger}} \frac{(1-e^{-u_{1i}^{\ddagger}})}{(1-e^{-u_{2i}^{\ddagger}})} \qquad \text{(IV.9)}$$

The collision diameters have been set equal for the isotopic species, and the assumption has been made that Z_1/Z_2 is just the square root of the inverse ratio of the molecular weights of the decomposing

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* Equation IV.8 may be derived from Eq. IV.4, $k_{\text{uni}} = \int k_2 p d(k_1/k_2)$, and the aforementioned assumptions.

molecules, $(M_2/M_1)^{1/2}$ (one-component systems). The functions f and u were defined in Section II.

Since in general $\nu_{1i} \geqq \nu_{2i}$, one would expect the isotope effect at lower pressures to be smaller than the high-pressure isotope effect. However, the temperature dependence of the isotope effect, which arises principally from the difference in differences of zero-point energies, should remain independent of pressure.

Only two experimental investigations have been carried out to study isotope effects in unimolecular reactions at low pressures. Weston[63] has studied the tritium isotope effect in the isomerization of cyclopropane to propylene, while Gray and Pritchard[31] have studied the individual rates of decomposition of octadeuterocyclobutane and unlabeled cyclobutane. Few details of the work by Gray and Pritchard are available. The isotope effect does not appear to change much with pressure. Strangly enough these authors find that the reaction exhibits an inverse isotope effect with $k_\infty(C_4H_8)/k_\infty(C_4D_8) = \frac{1}{2}$.

Weston's experiment was carried out with tritium at the tracer level and, therefore, in the labeled molecule only 1 hydrogen atom out of 6 equivalent ones is replaced. The reaction studied thus has both an intermolecular and an intramolecular isotope effect. Up to the approximation of no secondary isotope effects, the high-pressure rate of isomerization of a protium atom in the labeled molecule will not differ significantly from that of the unlabeled molecule. With these assumptions Weston obtains $(k_H/k_T)_{P=\infty} = 3.7 \pm 1.9$ at 775°K. The absolute error of the measurement is naturally magnified by the statistical correction for the intramolecular dilution. Because of this intramolecular dilution, a reliable temperature coefficient of the ratio of rate constants cannot be obtained by a least square treatment of the experimental data. As yet, the temperature dependence as a function of pressure has not been investigated.

At 775°K and 0.4 mm, the ratio k_H/k_T falls to unity and is independent of pressure. This may be taken as the ratio of unimolecular constants at this temperature. The combination of the product rule with Eq. IV.9, which is assumed to apply to the isomerization of cyclopropane, leads to

$$(k_H/k_T)_{P=\infty}/(k_H/k_T)_{P=0} = 4.8(I_A{}^{\ddagger} I_B{}^{\ddagger} I_C{}^{\ddagger})_H{}^{1/2}/(I_A{}^{\ddagger} I_B{}^{\ddagger} I_C{}^{\ddagger})_T{}^{1/2} \times \left[(E_a+\tfrac{1}{2}\sum_i h\nu_{Ti}{}^{\ddagger})/(E_a+\tfrac{1}{2}\sum_i h\nu_{Hi}{}^{\ddagger})\right]^{3n-7} \times \prod_i^{3n-7} (1-e^{-u_{Ti}\ddagger})/(1-e^{-u_{Hi}\ddagger})$$

The isotopic ratios multiplying the mass ratio factor, 4.8, are each less than, but probably close to unity. Thus the observed factor of 3.7±1.9 for the change of the isotope effect with pressure does not appear at all unreasonable. This theory predicts that the low-pressure isotope effect should change from unity with temperature.

We may utilize the experimental ratio $(k_H/k_T)_{P=\infty}/(k_H/k_T)_{P=\infty}$ to evaluate some of the factors in the high-pressure isotope effect. In addition we assume $[(E_a+\frac{1}{2}\sum h\nu_{Ti}{}^{\ddagger})/(E_a+\frac{1}{2}\sum h\nu_{Hi}{}^{\ddagger})]^{3n-7} \sim 1$ and $\prod^{3n-6} u_{Ti}/u_{Hi}$ is evaluated from molecular data and the product rule. One then obtains

$$(k_H/k_T)_{P=\infty} = 0.92 \prod_i^{3n-6} [1-\exp(-u_{Hi})]/[1-\exp(-u_{Ti})]e^{\Sigma(\Delta u_i-\Delta u_i{}^{\ddagger})/2}$$

The product of the excitation factors and the numerical factor of 0.92 may be assumed, with sufficient accuracy, to be unity. If the experimental data $(k_H/k_T)_{P=\infty}$ is put in the form $Ae^{B/T}$, one finds from the experimental value of 3.7 at 775°K that B is approximately 700 cm^{-1}. In agreement with Weston, one must conclude this to be a more reasonable value for the difference in activation energies than 2060 cm^{-1} obtained by least squares.

Certainly, additional experimental data on the pressure dependence of the isotope effect in unimolecular gas reactions are desirable.

V. EXPERIMENTAL METHODS

The theoretical calculations of the maximum isotopic effects on rate constants summarized in Table I lead one to expect differences in isotopic reaction rates ranging from a few per cent for most elements to orders of magnitude for the isotopes of hydrogen. Two methods can be used to measure the rates of chemical reactions: (1) measurement of absolute rates and (2) competitive methods. In a small number of favorable cases an accuracy of one-tenth of a per cent can be attained in the measurement of the rate constant by absolute methods. More generally, the accuracy is at best a few per cent. Therefore, the determination of isotope effects by the comparison of rate constants measured by the absolute method is practically limited to the isotopes of hydrogen.

A. Chemical *vs.* Isotopic Competitive Methods

Two types of competitive methods can and have been used. They are the chemical competitive and the isotopic fractionation techniques. In the chemical competitive method, the isotopic compounds A or A' compete with a chemically different species, B, for reaction with C. The method is, therefore, not applicable to unimolecular reactions and requires samples of A and A' of appreciable isotopic enrichment. Furthermore, the species B must react with C at a rate of similar order of magnitude as A or A' do. Consider for simplicity reactions first order in each of the reactants

$$A + C \xrightarrow{k} X \tag{V.1}$$

$$A' + C \xrightarrow{k'} X' \tag{V.2}$$

$$B + C \xrightarrow{k_B} Y \tag{V.3}$$

$$dx/dt = k(a_0 - x)(c_0 - (x+y)) \tag{V.4}$$

$$dx'/dt = k'(a_0' - x')(c_0 - (x'+y)) \tag{V.5}$$

$$dy/dt = k_B(b_0 - y)(c_0 - (y+x,\ x')) \tag{V.6}$$

Then

$$\frac{dx}{k(a_0 - x)} = \frac{dy}{k_B(b_0 - y)} \tag{V.7}$$

in the experiment where A and B are intercompared. Similarly,

$$\frac{dx'}{k'(a'_0 - x')} = \frac{dy}{k_B(b_0 - y)} \tag{5.8}$$

in the experiment where A' and B are intercompared. Integration and combination of Eq. V.7 and V.8 give

$$\frac{k'}{k}\frac{\ln(1-f_A)}{\ln(1-f_{A'})}=\frac{\ln(1-f_B)}{\ln(1-f_{B'})} \tag{V.9}$$

where $f_A, f_{A'}$, and f_B are the respective fractions of A, A', and B converted in the two competitive experiments. If the experiment is carried out under conditions such that A, A', and B are in considerable stoichiometric excess, then

$$\frac{k'}{k}=\frac{f_{A'}}{f_A}\cdot\frac{f_B}{f_{B'}} \tag{V.10}$$

Inasmuch as the fractional amounts of conversion can be determined with an accuracy of better than a half per cent only in a limited number of favorable cases, and because of the requirement of samples of high isotopic enrichment, the chemical competitive method is essentially limited to studies of the isotopes of hydrogen.

The isotopic competitive method is one of wide versatility and simplicity, especially when the isotopic pair have an abundance ratio of the order of 10^{-2} or less. For many of the stable isotopes, e.g. C^{13}, N^{15}, O^{18}, such studies have been carried out with material of natural abundance and many difficult synthetic problems are eliminated. However, in the use of this method, care must be exercised to eliminate effects due to isotopic exchange between reactants, intermediates, and products. In a number of cases the problem of isotopic homogeneity arises. We shall discuss the latter in connection with the problem of intramolecular isotope effects.

B. Kinetics of the Isotopic Competitive Method

We shall consider, first, the kinetics of a system undergoing an isotopic competitive intermolecular reaction, first order in the concentration of the isotopic species and of arbitrary order with respect to other reactants. Later we shall show that the results are applicable to intermolecular isotopic studies of any higher order in the isotopic molecular species if one isotope is present in dilute or tracer concentration.

(1) *Isotopic Analysis of the Substrate after a Known Amount of Reaction*

Consider the reactions

$$A + B + C + \ldots \xrightarrow{k} X + Y + \ldots \tag{V.11}$$

$$A' + B + C + \ldots \xrightarrow{k'} X' + Y + \ldots \tag{V.12}$$

From our assumption of reactions first order in A or A', it follows

$$-dA/dt = k(A)(B)^b(C)^c \ldots \tag{V.13}$$

$$-dA'/dt = k'(A')(B)^b(C)^c \ldots \tag{V.14}$$

Simultaneous solution of this set of differential equations with the boundary condition $A' = A'_0$ when $A = A_0$ yields

$$\left(\frac{k}{k'} - 1\right) \log (A'/A'_0) = \log \mathrm{R}_{af}/\mathrm{R}_{a0} \tag{V.15}$$

where $R_{af} = (A/A')$ after the fraction f of the substrate of chemical species A has reacted, and R_{a0} is the initial ratio $(A/A')_0$. Since the fraction reacted, f, is given by the stoichiometric relationship

$$1-f = \frac{A+A'}{A_0+A'_0} = \frac{A'(1+R_{af})}{A'_0(1+R_{a0})} \tag{V.16}$$

Eq. V.15 can be written

$$\left(\frac{k}{k'} - 1\right) = \frac{\log (R_{af}/R_{a0})}{\log [(1-f)(1+R_{a0})/(1+R_{af})]} \tag{V.17}$$

The method then consists of the determination of the isotopic ratios R_{a0} of the original substrate and R_{af} after a stoichiometrically measured fraction, f, has reacted. Apart from the isotopes of hydrogen $(k/k'-1)$ is of the order of -0.1, if the primed isotope is the light one and the reaction shows a normal isotope effect. If a precision of a few per cent in the quantity $\varepsilon = (k/k'-1)$ is desired and if the isotope ratios can be determined with a precision of a tenth per cent, it is necessary to carry the reaction to greater than fifty per cent of completion. The precision in ε increases with the amount of reaction and the absolute deviation in ε approaches the precision of the isotopic analysis when the fraction reacted is greater than 90 per cent. At higher amounts of conversion the precision drops as a result of errors in the determination of the fraction of the substrate unreacted.

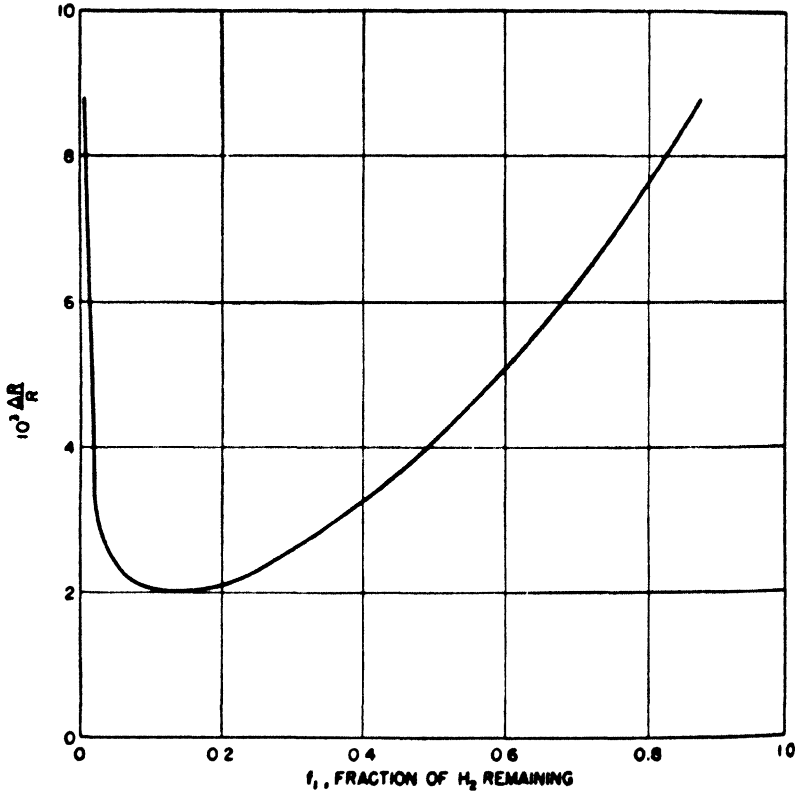


Fig. 2. Fractional error in k'/k, determined by isotopic analysis of unreacted substrate, as a function of the amount of reaction.

A similar but more detailed analysis of the effects of errors in the determination of k/k' by specific activity measurements of the unreacted substrate has been given by Jones.[37] Figure 2, taken from his paper, gives the per cent error in k'/k for the case where R_{af} and R_{a0} are measured with a precision of the order of 0.1 per cent, k'/k is 3, and the error in f, the fractional amount of reaction, is determined by the absolute error in measuring the amount of unreacted substrate. The curve is calculated for the case where f is determined by manometric measurements and $\delta p = 0.05$ mm, while the initial pressure is 150 mm.

(2) *Isotopic Analysis of the Product after a Known Amount of Reaction*

The kinetics of competitive isotopic reactions in terms of the isotopic composition of the product are developed in a manner similar to that in the preceding section. One rewrites Eq. V.13 and V.14 to read

$$dX/dt = k(A_0 - X)(B)^b(C)^c \ldots \tag{V.18}$$

$$dX'/dt = k'(A'_0 - X')(B)^b(C)^c \ldots \tag{V.19}$$

sets the boundary condition $X = 0$ when $X' = 0$, and writes the fraction of reaction as

$$f = \frac{X'}{A'_0}\frac{(1+R_{xf})}{(1+R_{a0})} \tag{V.20}$$

where $R_{xf} = X/X'$. These lead to the relationship for the ratio of rate constants in terms of R_{xf}, R_{a0}, and f

$$\left(\frac{k}{k'} - 1\right)\log\left[1 - f\frac{(1+R_{a0})}{(1+R_{xf})}\right] = \log\left[1 + \frac{R_{a0}-R_{xf}}{R_{a0}}\,\frac{f(1+R_{a0})/(1+R_{xf})}{1-f(1+R_{a0})/(1+R_{xf})}\right] \tag{V.21}$$

In the present case, where k'/k is determined by specific activity measurements on the product, it is most desirable to make the measurements on samples obtained from small amounts of conversion. A complete discussion of the errors involved has been given by Bigeleisen and Allen[7] for the following parameters: (1) tracer concentration of A_0, (2) $(k/k' - 1) = -0.10$, (3) the error in the ratio R_{xf}/R_{a0} is 10^{-3}, and (4) the fractional amount of reaction is determined with an accuracy of 0.5 per cent. Their results are shown in Fig. 3.

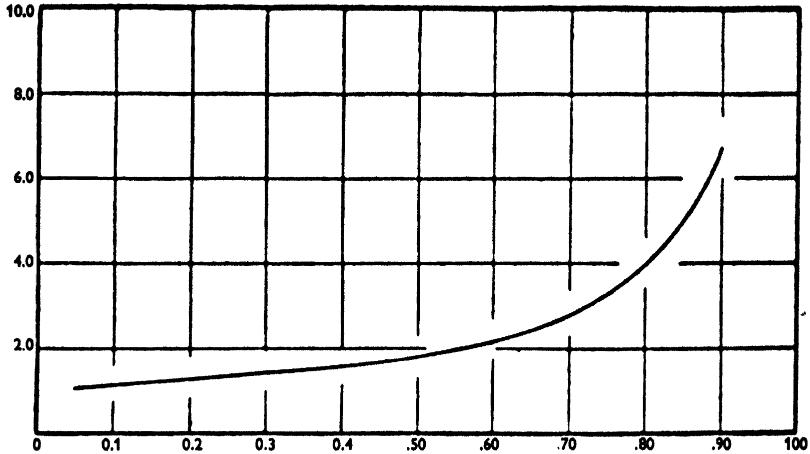


Fig. 3. Per cent error in $(k/k' - 1)$, determined by isotopic analysis of the product, as a function of the amount of reaction.

It is important to note that, apart from the correction factors to the amount of reaction $(1+R_{a0})/(1+R_{af,xf})$, the competitive isotopic method involves the determination of the ratio of two isotopic abundances and that absolute measurements of these quantities are avoided. This is the basis of the precision and accuracy of the method, since both mass spectrometric and nuclear radiation methods of determining the relative abundance are orders of magnitude greater than the accuracy of determination of the absolute abundance.

(3) *Application of the Isotopic Competitive Method to Systems at the Tracer Concentration Level*

When the isotopic ratio of the substrate A_0/A'_0 is small or the fractionation factor is sufficiently small so that $1+R_{a0} \cong 1+R_{af,xf}$ then Eqs. V.17 and V.21 reduce to

$$\left(\frac{k}{k'}-1\right)\log(1-f) = \log R_{af}/R_{a0} \qquad \text{(V.22)}$$

and

$$\left(\frac{k}{k'}-1\right)\log(1-f) = \log\left[1+\frac{R_{a0}-R_{xf}}{R_{a0}}\,\frac{f}{1-f}\right] \qquad \text{(V.23)}$$

respectively. There is no restriction to the effect that the heavy isotope be the one present at tracer level. These equations have been derived previously by Downes and Harris[22] and Bothner-By and Bigeleisen,[15] respectively, for the more general case of any order of reaction for A higher than zero. The differential equations for the rate of production of X and X', or disappearance of A and A', can be written as first order in A, if this is the isotope present at the tracer level, and $n-1$ order in A'. The relationships are[2]

$$\begin{aligned} dX/dt = -dA/dt &= k(A)(A')^{n-1}(B)^b(C)^c \\ &= k(A_0-X)(A')^{n-1}(B)^b(C)^c \qquad \text{(V.24)} \end{aligned}$$

$$\begin{aligned} dX'/dt = -dA'/dt &= k'(A')^n(B)^b(C)^c \\ &= k'(A'_0-X')(A')^{n-1}(B)^b(C)^c \qquad \text{(V.25)} \end{aligned}$$

which lead directly to the first-order Eqs. V.15 and V.21.

(4) *The Low Conversion Approximation*

When the fraction of conversion is sufficiently small such that

$$\ln(1-f) \cong -f \qquad \text{(V.26)}$$

then, Eqs. V.22 and V.23 become, respectively,[2]

$$f(1-k/k') = \ln R_{af}/R_{a0} \qquad \text{(V.27)}$$

and

$$k/k' = R_{xf}/R_{a0} \qquad \text{(V.28)}$$

Application of a simple error analysis to Eq. V.27 shows that the method of isotopic analysis of the substrate is a very poor one at small amounts of conversion. This conclusion has been reached in Section V.B-1 and shown in Fig. 2. Eq. V.28 is a simple and useful one.

(5) *The Method of Successive Product Fractions*

The methods of continuous isotopic analysis of the product or of successive product fractions have been applied to tracer systems, where $k/k'-1 \ll 1$, by Ropp, Weinberger, and Neville,[51] Downes,[21] and Schmitt, Myerson, and Daniels.[54] The expressions for $(k/k'-1)$ can be developed conveniently from Eqs. V.22 and V.23. Consider an experiment in which the reaction is allowed to proceed to an extent f_1 of completion. The product formed between f_1 and f_2 of completion is isolated for isotopic assay. From Eq. V.23 one obtains

$$\left(\frac{k}{k'}-1\right)\log\left(1-\frac{f_2-f_1}{1-f_1}\right)=\log\left[1+\frac{R_{af_1}-R_{xf_2}}{R_{af_1}}\,\frac{f_2-f_1}{1-f_2}\right] \qquad \text{(V.29)}$$

But

$$R_{af_1}=R_{a0}(1-f_1)^{k/k'-1} \qquad \text{(V.30)}$$

leading to

$$\left(\frac{k}{k'}-1\right)\log\left(\frac{1-f_2}{1-f_1}\right)=\log\left\{1+\frac{R_{a0}(1-f_1)^{k/k'-1}-R_{xf_2}}{R_{a0}(1-f_1)^{k/k'-1}}\,\frac{f_2-f_1}{1-f_2}\right\} \qquad \text{(V.31)}$$

For continuous isotopic analysis of the product or the removal of small samples, $(f_2-f_1)/(1-f_1) \ll 1$, we may limit the expansion of the logarithm to the first power and obtain the equation of Downes[21]

$$\frac{k}{k'}=\frac{R_{xf_2}}{R_{a0}}(1-f_1)^{1-k/k'} \qquad \text{(V.32)}$$

Since $R_{xf_2} \cong R_{xf_1}$ under the above conditions

$$\log R_{xf_1}/R_{a0}=\log k/k'+(k/k'-1)\log(1-f_1) \qquad \text{(V.33)}$$

A log-log plot of R_{xf_1} versus $(1-f_1)$ will give a straight line of slope $(k/k'-1)$. The method is entirely analogous to that of cumulative isolation of the product (cf. Section V.B-2). Any increase in precision results from the greater ease, in some cases, of increasing the number of experimental observations. Furthermore, a knowledge of R_{a0} is not required. The latter is mainly a matter of convenience, since it can usually be obtained experimentally either by extrapolation or by successive approximation in the cumulative product method. If R_{a0} is known in the successive fraction method, the intercept gives $(k/k'-1)$. This is the equivalent of an additional experiment in the cumulative product method.

For the case where (f_2-f_1) is appreciable one obtains the result given by Schmitt, Myerson, and Daniels,[54]

$$\frac{(f_4-f_3)R_{x(3-4)}}{(f_2-f_1)R_{x(1-2)}}=\frac{(1-f_3)^{k/k'}-(1-f_4)^{k/k'}}{(1-f_1)^{k/k'}-(1-f_2)^{k/k'}} \qquad \text{(V.34)}$$

which is valid only for small differences between $R_{x(3-4)}$ and $R_{x(1-2)}$ in addition to assumptions implicit in Eqs. V.22 and V.23. The method is a rather awkward one for systematic treatment of the experimental data, and it is equally convenient to sum R_{xf} from the values of R_{xfi} and use Eq. V.23, as Schmitt, Myerson, and Daniels did.

(6) *Intramolecular Isotope Effects — A Special Case of the Isotopic Competitive Method*

If a compound $A'BA'$ decomposes to form $A'B$ and A', then the decomposition of ABA' into AB and A' or into $A'B$ and A will show an intramolecular isotope effect or an intramolecular isotopic competition. The general solution to the kinetics of such a system involving the species $A'BA'$, ABA', and ABA all reacting at different rates to give the products $A'B$, AB, A', and A is rather unwieldy. We shall present several particular solutions to the kinetics of the system.

First we consider the case where ABA' is present at tracer concentration. The general formulation of the kinetics at the tracer level has been given by Bigeleisen.[2] The assumption made is that one neglects the contribution of A' from ABA' in comparison with its formation from $A'BA'$ and neglects the presence of ABA. The results are, in the present notation,

$$\frac{R_{xf}}{R_{a0}}=\frac{1-(1-f)^{\alpha}}{(m+nk_3/k_2)f/l} \qquad \text{(V.35)}$$

where

$$\alpha \equiv k_2(m+nk_3/k_2)/k_1l \tag{V.36}$$

$$R_{a0} = (A'BA/A'BA')_0 \tag{V.37}$$

and k_1, k_2, k_3, l, m, and n are defined by the equations

$$A'BA'+C+\ldots \xrightarrow{k_1} \frac{1}{l}\,(X'_{(1)}+Y'+\ldots) \tag{V.38}$$

$$A'BA+C+\ldots \xrightarrow{k_2} \frac{1}{m}\,(X+Y'+\ldots) \tag{V.39}$$

$$A'BA+C+\ldots \xrightarrow{k_3} \frac{1}{n}\,(X'_{(3)}+Y+\ldots) \tag{V.40}$$

$$A'BA' = A'BA'_0-lX'_{(1)} \tag{V.41}$$

$$A'BA = A'BA_0-mX-nX'_{(3)} \tag{V.42}$$

Equation V.35 can also be written in the form

$$(\alpha-1)\log(1-f) = \log\left[1+\frac{lR_{a0}-(m+nk_3/k_2)R_{xf}}{lR_{a0}}\,\frac{f}{1-f}\right] \tag{V.43}$$

If Y is isolated and analyzed, either instead of or in addition to X, one finds similarly

$$\frac{R_{yf}}{R_{a0}} = \frac{1-(1-f)^{\alpha}}{(mk_2/k_3+n)f/l} \tag{V.44}$$

and

$$(\alpha-1)\log(1-f) = \log\left[1+\frac{lR_{a0}-(mk_2/k_3+n)R_{yf}}{lR_{a0}}\,\frac{f}{1-f}\right] \tag{V.45}$$

From Eqs. V.35 and V.44 one finds directly

$$k_3/k_2 = R_{yf}/R_{xf} \tag{V.46}$$

Thus k_3/k_2 can be determined by measuring the ratios R_{yf} and R_{xf} without measurement of R_{a0}. The observed ratio R_{yf}/R_{xf} is independent of the amount of conversion and the coefficients l, m, and n.

If on the other hand R_{a0} is measured together with either R_{xf} or R_{yf}, then one obtains from Eqs. V.43 and V.45, respectively,

$$k_1/k_2 = R_{a0}/R_{xf} \tag{V.47}$$

TABLE III. Relative Yields of X, X', Y, and Y' from $A'BA'$, $A'BA$, and ABA According to Eqs. V.38–V.40 and V.57.

Species	Initial concentration	$f\to 0$				$f=1$			
		X'	X	Y'	Y	X'	X	Y'	Y
$A'BA'$	$(1-N_A)^2$	$k_1(1-N_A)^2$		$k_1(1-N_A)^2$		$(1-N_A^2)$		$(1-N_A)^2$	
$A'BA$	$2N_A(1-N_A)$	$2k_3N_A(1-N_A)$	$2k_2N_A(1-N_A)$	$2k_2N_A(1-N_A)$	$2k_3N_A(1-N_A)$	$\frac{2k_3}{k_2+k_3}N_A(1-N_A)$	$\frac{2k_2}{k_2+k_3}N_A(1-N_A)$	$\frac{2k_2}{k_2+k_3}N_A(1-N_A)$	$\frac{2k_3}{k_2+k_3}N_A(1-N_A)$
ABA	N_A^2		$k_4N_A^2$		$k_4N_A^2$		N_A^2		N_A^2

$$k_1/k_3 = R_{a0}/R_{yf} \qquad \text{(V.48)}$$

if the reaction is carried to a small fraction of completion. For complete conversion, Eq. V.35 gives

$$k_3/k_2 = lR_{a0}/nR_{x1}-m/n \qquad \text{(V.49)}$$

while Eq. V.44 gives

$$k_2/k_3 = lR_{a0}/mR_{y1}-n/m \qquad \text{(V.50)}$$

We now consider systems where the starting abundances of both isotopes A and A' are appreciable. Under these conditions one must take into consideration all three species $A'BA'$, $A'BA$, and ABA and the products X, Y, X', and Y' formed from each of them. The distribution of A and A' between these species is not necessarily given by classical statistics. For equilibrium distribution,

$$K = 4/(1+\delta) = (A'BA)^2/(A'BA')(ABA) \qquad \text{(V.51)}$$

$$N_A = (ABA'+2ABA)/2(A'BA'+A'BA+ABA) \qquad \text{(V.52)}$$

where N_A is the atom fraction of A. If the concentrations are expressed in mole fractions

expressed in mole fractions $ABA+C+\ldots\rightarrow X+Y+\ldots$ (V.57)

$$A'BA'+A'BA+ABA = 1 \qquad \text{(V.53)}$$

Solution of Eqs. V.51 to V.53 by expansion through the first power of δ and the second power of N_A, where A is assumed to be the minor constituent, gives

$$A'BA' = (1-N_A)^2(1+N_A{}^2\delta) \qquad \text{(V.54)}$$

$$A'BA = 2N_A(1-N_A)(1-N_A\delta) \qquad \text{(V.55)}$$

$$ABA = N_A{}^2(1+\delta) \qquad \text{(V.56)}$$

Apart from the molecular species H_2 or systems at very low temperatures, the values of δ for all chemical species is of the order of 10^{-2} or less.[6] Thus the correction for nonclassical equilibrium distribution to any species is at most one per cent. For dilute material, $N_A \sim 10^{-2}$, the correction is negligible. We shall, therefore, develop the kinetics in terms of the classical distribution. We assume kinetics either first order or pseudo first order in the substrate. In addition to the rate constants k_1, k_2, and k_3, defined by Eqs. V.38 to V.40, we define the rate constant k_4 through the reaction

$$ABA+C+\ldots \xrightarrow{k_4} X+Y+\ldots \qquad \text{(V.57)}$$

The relative yields of X, X', Y, and Y' from $A'BA'$, $A'BA$, and ABA as f, the fraction of substrate converted, approaches 0 or 1 are given in Table III. For simplicity we shall consider the case where $l = m = n$.

We now define a set of fractionation factors, ε_{ij}, such that

$$k_1/2k_3 = 1+\varepsilon_{13} \tag{V.58}$$

$$k_2/k_3 = 1+\varepsilon_{23} \tag{V.59}$$

etc.

Then in the approximation that $\varepsilon_{ij}N_A$ is small compared to unity, we obtain from the entries in Table III:

$$k_1/k_2 = R_{a0}/R_{x0} \tag{V.60}$$

$$k_1/k_3 = R_{a0}/R_{y0} \tag{V.61}$$

$$k_3/k_2 = (R_{a0}/R_{x1})-1 \tag{V.62}$$

$$k_2/k_3 = (R_{a0}/R_{y1})-1 \tag{V.63}$$

$$k_3/k_2 = R_{y0}/R_{x0} = R_{y1}/R_{x1} \tag{V.64}$$

R_{a0} is still defined by Eq. V.37. The approximation $\varepsilon_{ij}N_A \ll 1$ is valid for all concentrations of the isotopes of all elements except hydrogen. We note that, in the classical distribution approximation, one obtains the identical relations for the ratios k_i/k_j at $f = 0$ and 1 as we found previously for the tracer concentration. Plausible arguments can be advanced to show that, even if the original substrate is not in equilibrium according to Eq. V.51, the distribution of A and A', again excluding the isotopes of hydrogen, among the species $A'BA'$, $A'BA$, and ABA will not be sufficiently skewed to affect the distributions given in Table III.

(7) *The Determination of the Isotope Ratios and the Problem of Isotopic Homogeneity*

Two methods of measurement of isotope ratios have been developed to a sufficient degree of accuracy to make them useful for the determination of isotope effects on reaction rates. They are measurements of radioactivity and mass spectrometry. We shall not go into the details of these methods of measurement, but it suffices to point out that both methods have now been refined to yield isotope effect values $(k/k'-1)$ with an accuracy better than 5 per cent for isotopes of the light elements. The ratio of the specific activities of samples of carbon-14[18] and tritium[9,37,67] can be determined with an accuracy approaching 0.2 per cent. Relative isotope ratios can be made readily mass spectrometrically with an accuracy of 0.1 per cent and in some cases even one order of magnitude better.[60]

The isotopic competitive method, whether the analyses are made mass spectrometrically or by radioactivity measurements, is very sensitive to impurities. In the use of radioactive isotopes, the sample to be counted must be decontaminated of other chemical species containing the same radioactive nuclide and it must be chemically pure to avoid dilution. Both of these effects must be reduced to the order of 0.1 per cent, which is a very exacting restriction. In the mass spectrometric method one must avoid impurities which give ion peaks (m/q), either from the parent or from a fragment, at the same m/q as the product analyzed. A scan of the mass spectrum usually enables one to detect such impurities and provides the basis for further purification processes. The latter must all be isotopically nonfractionating.

In either the radioactive or the mass spectrometric determination only the relative isotope ratios need be determined for the isotopic competitive method, except for the correction factors of the form $(1+R_{a0})/(1+R_{xf})$.

In the mass spectrometric method it is usually most convenient to convert both the substrate and product to the same chemical species for isotopic analysis. This procedure, furthermore, eliminates the difficult corrections which would have to be applied for isotopic discrimination in the mass spectrometer. If the substrate or products contain the isotopes A and A' in groups or substituents other than the reaction center, there may be complications from isotopic homogeneity. This has been pointed out previously.[8] Recently Yankwich and Promislow[70] have shown that there is a 1 per cent difference in the C^{13} content of the methyl and aldehyde carbons of acetaldehyde derived from the air oxidation of propane and butane, while the similar compound produced commercially by successive oxidation of ethylene shows less than 0.1 per cent discrimination.

The isotopic inhomogeneity problem may arise in either intermolecular or intramolecular reactions even when working with isotope concentrations down to the tracer level. In general the corrections are small. We shall illustrate the nature of the corrections for the intramolecular isotope effect studied through Eq. V.62. Let A and A' be distributed on i different sites in the molecule, the number of equivalent sites be g_i and the atom fraction of A on the ith site be N_i. Then the average ratio of A/A' in the compound is

$$\bar{R} = \frac{A}{A'} = \sum_i g_i N_i \Big/ \sum_i g_i(1-N_i) \tag{V.65}$$

If the molecule ABA has one isotopic A atom per B group, then designating the terminal groups by the subscript 1 and the center group by 2, we have

$$g_1 = 2 \tag{V.66}$$

$$g_2 = 1 \tag{V.67}$$

$$R_{a0} = 2N_1/(1-N_1) \tag{V.68}$$

$$R_{b0} = N_2/(1-N_2) \tag{V.69}$$

Let

$$N_2/N_1 = 1+\delta \tag{V.70}$$

Then, for small δ

$$k_3/k_2 = R_{a0}/R_{x1}-1 = [2\bar{R}(1-\delta/3)/R_{x1}]-1 \tag{V.71}$$

We define

$$\bar{R}/R_{x1} = 1+\varepsilon \tag{V.72}$$

Then the fractional error in (k_3/k_2-1) is $\delta/3\varepsilon$.

(8) *Pre-equilibria*

It is well known that the rate controlling steps of many chemical reactions are preceded by rapid reversible equilibria. If the equilibrium concentration of the substrate differs by a negligible amount from the stoichiometric one and the thermodynamic equilibrium constant can be replaced by a concentration one, then it is convenient to write the rate law in terms of the stoichiometric concentration of substrate. The observed rate constant will be equal to the true rate constant multiplied by the equilibrium constant. In the other extreme the equilibrium concentration of substrate may be negligible compared to its stoichiometric concentration (e.g. complete dissociation or complexing). In this case it is convenient to write the rate law in terms of the concentration of the equilibrium species and the observed rate constant is the true one. If such a system is investigated for a kinetic intermolecular isotope effect, no correction is necessary. For the case of weak complexing, the observed ratio of rate constants will contain an isotopic exchange equilibrium constant in addition to the true ratio of rate constants. The situation becomes more complicated when one considers systems involving inter- and intramolecular isotope effects.

As an illustration of the method of treatment of such systems, we shall consider complexing as the rapid pre-equilibrium and tracer isotopic concentration of the substrate ABA'. The limiting cases of complete and of weak complexing will be considered. Analogous to Eqs. V.38 to V.40 we write

$$A'BA'+R = A'BA'R \xrightarrow{k_1} X'+Y'+\ldots \qquad (V.73)$$

$$ABA'+R = ABA'R \xrightarrow{k_2} X+Y'+\ldots \qquad (V.74)$$

$$ABA'+R = A'BAR \xrightarrow{k_3} X'+Y+\ldots \qquad (V.75)$$

One could also consider the case where $ABA'R$ leads to X' and Y while $A'BAR$ yields X and Y'. The kinetics of this system are entirely analogous to those illustrated by Eqs. V.73—V.75 and will not be given explicitly.

(a) Strong Complexing

We note that

$$A'BA'R = A'BA'_0 - X' \qquad (V.76)$$

There is a fractionation of ABA' in the complexing reaction which can be written in terms of the usual partition function ratios, $s/s' = f$ (cf. Section II), through the reactions

$$A'BA'R + ABA' = ABA'R + A'BA' \tag{V.77}$$

$$K = f_{AB}/f_{ABA'} \tag{V.78}$$

$$A'BA'R + ABA' = A'BAR + A'BA' \tag{V.79}$$

$$K = f_{AR}/f_{ABA'} \tag{V.80}$$

Then, at all times

$$ABA'R/A'BAR = f_{AB}/f_{AR} \tag{V.81}$$

and at $t = 0$

$$(ABA'R)_{te} = \frac{f_{AB}}{f_{AB}+f_{AR}}(ABA')_0 \tag{V.82}$$

$$(A'BAR)_{te} = \frac{f_{AR}}{f_{AB}+f_{AR}}(ABA')_0 \tag{V.83}$$

In a system in which $A'BA'$ and ABA' react to give products, the intermolecular isotope effect is most conveniently measured from the analysis of products obtained at small amounts of reaction (Eqs. V.47 and V.48). The intramolecular isotope effect can be obtained from any amount of reaction (Eq. V.46).

From the usual first-order equations implicit in Eqs. V.73—V.75 and Eqs. V.82 and V.83, one finds

$$\frac{k_1}{k_2} = \frac{R_{a0}}{R_{x0}} \frac{f_{AB}}{f_{AB}+f_{AR}} \tag{V.84}$$

$$\frac{k_1}{k_3} = \frac{R_{a0}}{R_{y0}} \frac{f_{AR}}{f_{AB}+f_{AR}} \tag{V.85}$$

Similarly, from Eq. V.81, one finds at all times

$$\frac{k_2}{k_3} = \frac{R_x}{R_y} \cdot \frac{f_{AR}}{f_{AB}} \tag{V.86}$$

The isotopic fractionation by the complexing equilibrium makes a more important contribution to the intramolecular than to the intermolecular isotope effect.

(b) Weak Complexing

We introduce the equilibrium constants

$$K_{A'BA'} = \frac{(A'BA'R)}{(A'BA')(R)} \tag{V.87}$$

$$K_{AB} = \frac{(ABA'R)}{(ABA')(R)} \tag{V.88}$$

$$K_{AR} = \frac{(A'BAR)}{(ABA')(R)} \tag{V.89}$$

and recall the symbolism for the partition function ratio

$$f_{ABA'} = (ABA')/(A'BA') \tag{V.90}$$

It follows again in a straightforward manner from the rate equations implicit in Eqs. V.73—V.75

$$\frac{k_1}{k_2} = \frac{R_{a0}}{R_{x0}} \frac{f_{AB}}{f_{ABA'}} \tag{V.91}$$

$$\frac{k_1}{k_3} = \frac{R_{a0}}{R_{y0}} \frac{f_{AR}}{f_{ABA'}} \tag{V.92}$$

$$\frac{k_2}{k_3} = \frac{R_x}{R_y} \frac{f_{AR}}{f_{AB}} \tag{V.93}$$

The ratio f_{AR}/f_{AB} is an isotopic isomerization equilibrium constant, while $f_{AR,\ AB}/f_{ABA'}$ is an isotopic exchange constant. The latter is usually larger than the isomerization constant[6] and for weak complexing a larger correction must be applied to the intermolecular than to the intramolecular reaction.

Equations V.84—V.86 and V.91—V.93 relate the true ratio of rate constants to the observed isotopic ratios.

VI. HYDROGEN ISOTOPE EFFECTS IN GAS REACTIONS

The isotopes of hydrogen have been used extensively in the study of kinetic isotope effects.[17] A theoretical discussion from first principles of such isotope effects requires accurate potential energy surfaces for the calculation of energies and frequencies. Moreover, for the isotopes of hydrogen both tunneling and transmission coefficients might be especially important and would conceivably lead to isotope effects. Attempts at such calculations have been made with approximate potential energy surfaces.

Farkas and Wigner[26] have discussed the $H+H_2$ reaction in a somewhat different manner. They employed the rates of the hydrogen reaction and those of the isotopes in order to compute satisfactory parameters for the activated complex. A similar procedure was employed by Bigeleisen and Wolfsberg[13] in studying the H_2+Cl reaction, which shall now be discussed in some detail in order to demonstrate the procedure.

In the photochemical reaction between hydrogen and chlorine, the slow step is usually assumed to be the reaction between hydrogen molecules and chlorine atoms. The experimental data used in obtaining information about the transition state are the relative rates of reactions of H_2 and HT with Cl atoms.[37] Experimentally one measures R, which is defined by the following relations:

$$H_2+Cl \overset{k_1}{\rightarrow} HCl+H \tag{VI.1}$$

$$HT+Cl \overset{k_{2a}}{\rightarrow} TCl+H \tag{VI.2}$$

$$HT+Cl \overset{k_{2b}}{\rightarrow} HCl+T \tag{VI.3}$$

$$R = \frac{k_1}{k_{2a}+k_{2b}} \tag{VI.4}$$

The isotopic rate equation from Section II is employed in the form

$$k_1/k_2 = (\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger})(f/f^{\ddagger})(1+\tfrac{1}{24}|u_{1L}^{\ddagger}|^2)/(1+\tfrac{1}{24}|u_{2L}^{\ddagger}|^2) \tag{VI.5}$$

The partition function ratio f for the isotopic hydrogen molecules, including a correction for nonclassical rotation, is known. For convenience a function $f_p^{\ddagger}$ is defined

$$\begin{aligned} f_p^{\ddagger} &= \nu_{2L}^{\ddagger}\, f^{\ddagger}/\nu_{1L}^{\ddagger} \\ &= (s_1^{\ddagger}/s_2^{\ddagger}) \prod_i^{3n-6} (\nu_{2i}^{\ddagger}/\nu_{1i}^{\ddagger}) \prod_i^{3n-7} e^{\Delta u_i^{\ddagger}/2} (1-e^{-u_{1i}^{\ddagger}})/(1-e^{-u_{2i}^{\ddagger}}) \end{aligned} \tag{VI.6}$$

The quantity $f_p^{\ddagger}$ will be evaluated for two models, a linear state and an isosceles triangular state. In the present calculations we utilize a prediction of Wheeler, Topley, and Eyring[64] that the ratio of the H—H to the H—Cl force constants in the transition state is a small negative number (about 10^{-1}). For the asymmetric linear model, the symmetry number ratio $s_1^{\ddagger}/s_2^{\ddagger}$ is equal to unity,

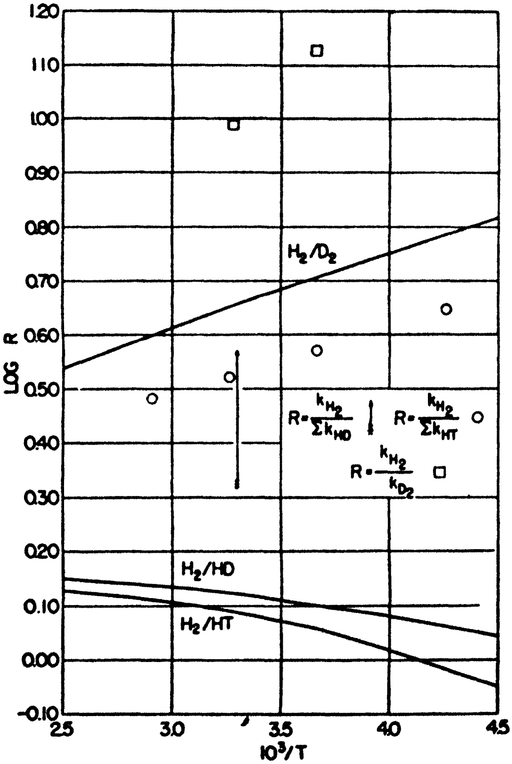


Fig. 4. Relative rates of reaction of the isotopic hydrogen molecules with chlorine atoms as a function of temperature. Solid lines calculated from the Wheeler, Topley, and Eyring potential for H_2Cl.

while for the isosceles triangular model, the ratio is two. This factor of two is, however, canceled since the symmetric H_2Cl complex has two different but equally probable methods of decomposition. In Eq. VI.6 two frequencies, one of which is a bending frequency, contribute to the zero-point energy and vibrational excitation terms for a triangular activated state, while for a linear activated state three frequencies, one of which is a doubly degenerate bending frequency, contribute to these terms.

Wheeler, Topley, and Eyring[64] carried out approximate calculations of the potential energy surface for the H_2+Cl reaction on the assumption that the activated state is linear. In Fig. 4, the results of their calculations are compared with the experimental data for the relative rates of H_2 and HT as well as some data available for H_2 and D_2 and H_2, HD, and D_2 mixtures. The fact that the slope of log R versus $1/T$ is found to be experimentally much larger than the theoretical slope indicates that the frequencies in the Wheeler, Topley, Eyring transition state are too large. These authors found 490 cm^{-1} for the bending frequency in the H_2Cl complex. The contribution of such a frequency to $f_p^{\ddagger}$ at 300°K may well be approximated by $1+\Delta(u_b^{\ddagger})^2/24$. The symmetrical stretching frequency should be of sufficient magnitude so that the term $[1-\exp(-u_1^{\ddagger}H_2)]/[1-\exp(-u_1^{\ddagger}D, T)]$ may be neglected. Thus Eq. VI.6 may be written

$$f_p^{\ddagger} = (\nu_1^{\ddagger}\, \nu_L^{\ddagger})_{D,T}/(\nu_1^{\ddagger}\, \nu_L^{\ddagger})_H\, e^{hc\Delta\nu_1^{\ddagger}/2kT}\, (1+\Delta(u_b^{\ddagger})^2/24)^g \quad (VI.7)$$

where $\nu_1^{\ddagger}$ is the symmetric stretching frequency, $\nu_L^{\ddagger}$ is the asymmetric stretching frequency, imaginary in value and corresponding to motion along the reaction path, and g is the degeneracy of the bending frequency.

Let us now investigate the effects which the two different models proposed for the activated state have upon the quantities k_1/k_{2a}, k_1/k_{2b}, and R. The difference in degeneracy between the two models will introduce a change of ten per cent at the most on account of the small magnitude of $1+\Delta(u_b^{\ddagger})^2/24$. In considering the contributions of the entropy terms to k_1/k_{2a} one finds, from Lechner's formulas[38] for the vibrations of a bent XYZ molecule, that the ratio $(\nu_1^{\ddagger}\, \nu_L^{\ddagger})_{HTCl}/(\nu_1^{\ddagger}\, \nu_L^{\ddagger})_{H_2Cl}$ is rather insensitive to large variations in the HTCl bond angle. Moreover the ratio $\nu_1^{\ddagger}{}_{HTCl}/\nu_1^{\ddagger}{}_{H_2Cl}$ is close to $1/\sqrt{3}$, while the ratio for the asymmetric stretching frequency is close to unity. For a given set of force constants $\nu_1^{\ddagger}{}_{H_2Cl}$ itself is also fairly independent of bond angle. Thus k_1/k_{2a} will not differ significantly for either a linear or a triangular model. On the other hand, significant differences are obtained for k_1/k_{2b} depending on the choice of model. For the linear model, the ratio of the symmetric stretching frequencies is close to unity while the ratio $\nu_L^{\ddagger}{}_{\mathrm{THCl}}/\nu_L^{\ddagger}{}_{\mathrm{H_2Cl}}$ is now close to $1/\sqrt{3}$. Thus for the linear model k_{2b} will be smaller than k_{2a} roughly by a factor exp $(-0.30\nu_1^{\ddagger}/T)$ where $\nu_1^{\ddagger}$ is expressed in cm^{-1}. On the other hand for an isosceles triangular model, with Cl at the apex, k_{2a}, and k_{2b} are equal. Therefore the differences in $\nu_1^{\ddagger}$ calculated from R for the two models will depend on the variation of the contribution of k_{2b}/k_{2a} to R.

The frequency ratios needed for the calculation are rather insensitive to force constants. For the linear model, ratios are calculated with the Wheeler, Topley, Eyring potential. For the triangular model the frequency ratios have been taken from the frequency values for HTO and H_2O, since the product rule value for the water molecule comes within the range of a number of triangular complexes and since the $\nu_1^{\ddagger}$ and $\nu_L^{\ddagger}$ ratios are practically the same as for HTCl, H_2Cl. Inasmuch as the bending frequency makes only a minor correction, this is not too important an approximation. The frequency ratios for the H_2Cl transition states are listed in Table IV. One also needs to estimate now $\nu_2^{\ddagger}$ and $\nu_L^{\ddagger}$ for H_2Cl. A value of 200 cm^{-1} has been chosen for $\nu_2^{\ddagger}$, a number which is smaller than 490 cm^{-1} which was calculated by Wheeler, Topley, and Eyring. Actually this difference in $\nu_2^{\ddagger}$ makes a difference of less than 10 per cent in the calculated value of $\nu_1^{\ddagger}$. For the imaginary frequency, $\nu_L^{\ddagger}{}_{\mathrm{H_2Cl}}$, the Wheeler, Topley, Eyring value of $720i$ has been used.

TABLE IV. Frequency Ratios for H_2Cl Complexes

	Linear HTCl/H_2Cl	Linear THCl/H_2Cl	Triangular HTCl/H_2Cl
$\nu_1^{\ddagger}$	0.597	0.998	0.618
$\nu_2^{\ddagger}$	0 680	0.938	0 831
$\nu_L^{\ddagger}$	0.993	0.595	0.986

One can now calculate $\nu_1^{\ddagger}$ for both the linear and triangular complexes by using the data for HT and H_2 at one temperature.

The results are summarized in Tables V and VI. For the triangular model, one arrives at a pre-exponential factor of 2.68 from the frequency ratios and statistical factors, in very good agreement with the experimental value 2(1.35±0.03). The choice of $\nu_1^{\ddagger}$ thus leads to very good agreement with experiment over the given temperature range. For the linear model the agreement between theory and experiment over the temperature range is not as good.

TABLE V. Frequency Assignment for Triangular H_2Cl Complex.

$\nu_1^{\ddagger}$	1002 cm^{-1}	calculated from HT experimental data at 273.16° K
$\nu_2^{\ddagger}$	200 cm^{-1}	approximated
$\nu_l^{\ddagger}$	720i cm^{-1}	calculated by WTE for a linear model

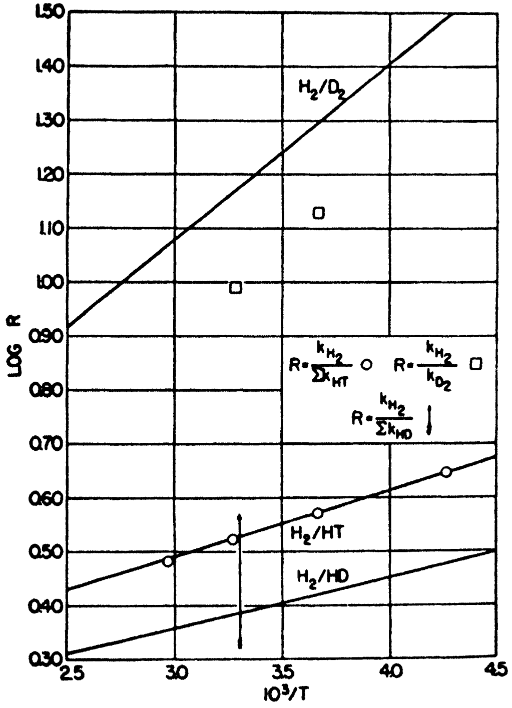


Fig. 5. Relative rates of reaction of the isotopic hydrogen molecules with chlorine atoms as a function of temperature. Solid lines calculated for an isosceles triangular H_2Cl complex, $\nu_1^{\ddagger} = 1002\ cm^{-1}$.

TABLE VI. Frequency Assignment for a Linear H_2Cl Complex.

$\nu_1^{\ddagger}$	1460 cm^{-1} calculated from HT experimental data at 273.16° K
$\nu_2^{\ddagger}$	200 cm^{-1} approximated
$\nu_L^{\ddagger}$	$720i$ cm^{-1} calculated by WTE

From the frequency assignments for H_2Cl given in Tables V and VI and the ratios analogous to those in Table IV, the theoretical ratios k_{H_2}/k_{D_2} and $R_{H_2/HD}$ are calculated as a function of temperature in Figs. 5 and 6. The agreement between theory and experiment appears good for both models, and more experimental data appears to be necessary before a choice can be made with regard to the models.

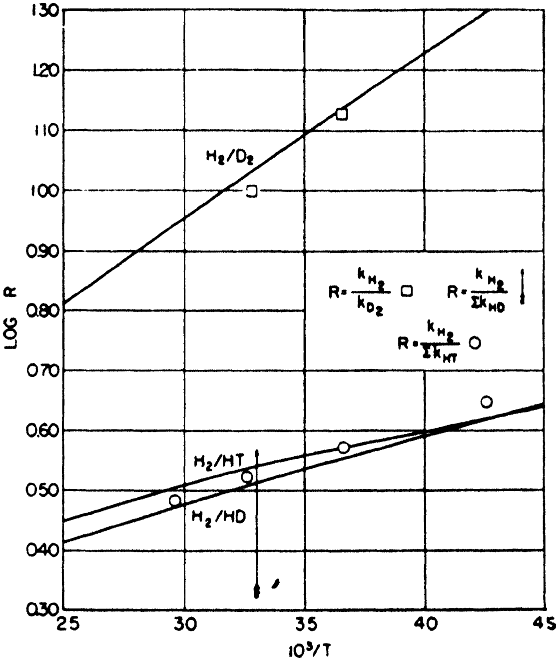


Fig. 6. Relative rates of reaction of the isotopic hydrogen molecules with chlorine atoms as a function of temperature. Solid lines calculated for a linear H_2Cl complex, $\nu_1^{\ddagger} = 1460$ cm^{-1}.

Polanyi[47] has recently carried out a theoretical investigation of the rates of eight isotopic reactions between methyl radical and hydrogen molecule, $CH_3 + H_2 \rightarrow CH_4 + H$. The potential energy surface was calculated semiempirically using the standard Eyring treatment. The system is treated as a three-electron problem. The energy was determined as a function of three parameters: r, the C—H separation; s, the H—H separation along the figure axis; and ω, the angle between the CH_3 umbrella and the axis. The potential surface so obtained leads to a metastable complex corresponding to a shallow potential energy basin and to a transition state which is fairly asymmetric in s and r. The results obtained with this surface after making a calibration for the activation energy are fairly unsatisfactory. A calculation was then carried out using a different semiempirical basis which removes the shallow energy basin and causes the transition complex to be close to symmetric in r and s. The isotope effects now obtained are in much better agreement with experimental data. These calculations point out some of the difficulties in the evaluation of isotope effects through the use of rough *a priori* potential energy surfaces.

Calculations have also been made on the isotopic reactions $H + H_2 \rightarrow H_2 + H$. As we have already stated, Farkas and Wigner[26] treated the theory of the isotope effect for this reaction by a semiempirical method similar to that discussed in connection with the $H_2 + Cl$ reaction. The effect of isotopic substitution on the transmission coefficient, to be discussed in the next paragraph, was taken into account. Boato, Careri, Cimino, Molinari, and Volpi[14] have recently repeated the experimental work for the reaction $H_2 + D_2 \rightarrow 2HD$ and found that the previous experimental work is somewhat in error because of the presence of oxygen in the systems. On the basis of their work, they deduce new values for the various isotopic reactions and also carry out a new Farkas-Wigner type of calculation. The agreement between theory and experiment is very good over a large range in temperature.

Hirschfelder, Eyring, and Topley[35] have calculated a semiempirical potential energy surface for this reaction. This potential energy surface has a shallow potential energy basin between two equally high potential energy barriers along the reaction path.

The existence of the basin leads then to two different activated states for the forward and the reverse reactions, respectively. The assumption is made that, once the system wanders around in the potential basin, its chances of decomposing in the two different ways are independent of the direction from which the system entered the basin. This is equivalent to setting the sum of the transmission coefficients, resulting from the basin in the surface, for the forward and backward reactions equal to unity, i.e., $\varkappa_f + \varkappa_r = 1$. Then

$$k_f = \varkappa_f G_f, \qquad k_r = \varkappa G_r \tag{VI.8}$$

where G_f and G_r are the rates in the forward and backward directions computed without transmission coefficients. One has, however, for the equilibrium constant K,

$$K = k_f/k_r = \varkappa_f G_f/\varkappa_r G_r \tag{VI.9}$$

or

$$\varkappa_f = \frac{G_r K}{G_f + G_r K}, \quad \varkappa_r = \frac{G_f K}{G_f + G_r K} \tag{VI.10}$$

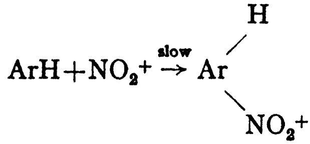
Equation VI.10 leads to transmission coefficients of one-half for symmetrical reactions but other factors for unsymmetrical reactions. These transmission coefficients must be taken into account in calculating isotope effects. The agreement between the values calculated by Hirschfelder, Eyring, and Topley[35] and the recently deduced experimental values of Boato, *et al.*[14] is fair.

VII. HYDROGEN ISOTOPE EFFECTS IN REACTIONS IN SOLUTION

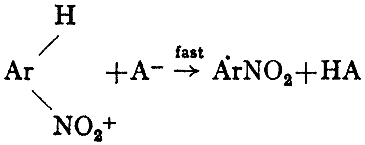
The literature on the effect of deuterium and tritium substitution on the rates of solution reactions is an extensive one[17] and beyond the scope of this chapter. We shall discuss briefly several different types of studies that have been made.

A. Isotope Effect in the Elucidation of Reaction Mechanism

Melander[43] has carried out a detailed and thorough investigation of the effect of tritium substitution at the aromatic nucleus on the mechanism of aromatic nitration. He has studied the dinitration of benzene, toluene, bromobenzene, and the nitration of naphthalene. He finds in all cases $k_H/k_T \simeq 1 \pm 0.25$ at 350°K. From these results one concludes that proton loss in the nitration is kinetically insignificant. The results confirm the hypothesis,[46] given in Eqs. VII.1 and VII.2, of an intermediate formed without loss of a proton.



$$\mathrm{ArH} + \mathrm{NO_2^+} \xrightarrow{\text{slow}} \mathrm{Ar}\begin{smallmatrix} \diagup \mathrm{H} \\ \diagdown \mathrm{NO_2^+} \end{smallmatrix} \qquad \text{(VII.1)}$$



$$\mathrm{Ar}\begin{smallmatrix} \diagup \mathrm{H} \\ \diagdown \mathrm{NO_2^+} \end{smallmatrix} + \mathrm{A^-} \xrightarrow{\text{fast}} \mathrm{ArNO_2} + \mathrm{HA} \qquad \text{(VII.2)}$$

This conclusion is in agreement with that arrived at on the basis of solvent effects on the rate.[28]

B. Location of Kinetically Significant Hydrogen

Westheimer and Nicolaides[62] have utilized the deuterium isotope effect to determine whether the C—H or O—H bond rupture is rate controlling in the oxidation of isopropanol by chromic acid. Isopropanol-2-d_1 was synthesized and found to react at approximately one-sixth the rate of the all protium compound. This is conclusive evidence that C—H rather than O—H bond rupture is rate determining.

C. Acid-Base Catalysis in H_2O—D_2O Solvents

It was an early hope that the comparison of acid and base catalyzed reactions in H_2O and D_2O would prove useful in understanding the general aspects of such reactions. This expectation has been realized only in part. One early observation was that many acid catalyzed reactions, e.g. ester hydrolysis, proceeded more rapidly in D_2O than in H_2O. The explanation of this result was immediately obvious from the mechanism of the reaction.[44] For specific acid catalyzed reactions, one finds

$$S + H^+ = SH^+ \rightarrow \text{products} \qquad \text{(VII.3)}$$

$$(k_H/k_D)_{\text{obs}} = (k_H/k_D)(K_D/K_H)_{\text{diss}} \qquad \text{(VII.4)}$$

where k_H is the rate constant for decomposition of SH^+, and K_H is its dissociation constant. In the ester hydrolysis there is at most a secondary isotope effect in k_H and the observed ratio of rate constants is essentially the inverse ratio of acid dissociation constants. Rule and La Mer[52] have summarized much of the work on the effect of deuterium substitution on acid dissociation constants. The ratio $(K_H/K_D)_{diss}$ varies between 2.74 and 4.16 for acids with K_{ion} from 10^{-3} to 10^{-11}. This explains the main feature of the results obtained since the values of $(k_D/k_H)_{obs}$ in hydrolysis reactions are about 2.

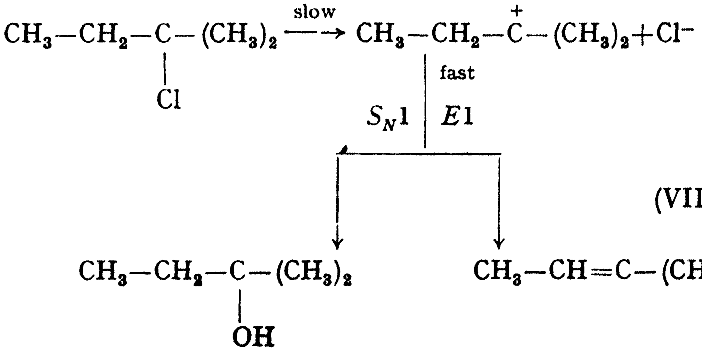
Similar studies have been carried out in H_2O–D_2O mixtures. The observed rate constant does not vary linearly with D_2O content. The dependence of the rate constant on the deuterium content of the solvent has been explained by Gross, Steiner, and Suess[33] in terms of the equilibrium

$$DH_2O^+ + D_2O = HD_2O^+ + HDO \tag{VII.5}$$

The distribution of protons and deuterons between the isotopic water molecules and hydronium ions is not random.[16]

D. Secondary Isotope Effects

Shiner[55] has studied the effect of β deuterium substitution on the solvolysis of tertiary amyl chlorides. The mechanism and classification of the reaction in the Ingold scheme is



(VII.6)

Over 80 per cent of the elimination reaction to give the olefin occurs via the methylene group.[20] The results obtained by β deuterium substitution are given in Table VII.

The results clearly show small secondary isotope effects in the formation of the intermediate carbonium ion. For the methylene hydrogen, the effect is 1.19 per deuterium atom, whereas it is 1.10 per deuterium atom for the methyl carbon calculated from experiments 1 and 2 and 1 and 3, respectively. The ratio k_1/k_2 differs from k_3/k_4 by a small, but definite amount. From the ratio of alcohol to olefin product in the various experiments, one concludes that there is no $D-CH_3$ isotope effect in the substitution or elimination reaction. Then, if we make the plausible assumption that there is no $D-CH_2$ isotope effect in the substitution reaction, one calculates from the experimental data a value of 1.80 for the ratio of proton to deuteron loss in the elimination reaction. This value is calculated by neglecting a possible secondary isotope effect in the elimination reaction.

TABLE VII. Effect of β Deuteration on the Solvolysis of Tertiary Amyl Chloride.
(80 per cent aqueous ethanol at 25° C.[55])

Experiment	1	2	3	4
Deuteration	none	CH_3-CD_2-C	$C(CD_3)_2$	$CD_2-C(CD_3)_2$
Relative k	15.72 ± 0.15	11.19 ± 0.12	8.83 ± 0.10	6.69 ± 0.07
Olefin fraction	0.36	0.25	0.37	0.23

The isotope effect in the ionization process results from a slight weakening of the β C—H bond in the transition state and has been interpreted in terms of hyperconjugation.[55] The isotope effect in the elimination reaction is a primary one and, therefore, rather small for C—H bond rupture, where factors of about 6 are usual. This has been interpreted to mean that there is appreciable solvation of the β methyl proton in the transition state leading to elimination. Since the zero-point energy of a normal OH bond is greater than that of a CH bond ($\nu_{OH} = 3400$; $\nu_{CH} = 2960$) there will be an appreciable cancellation of the zero-point energy differences between normal and transition states. If we neglect the entropy contributions from excitation of higher vibrational energy states, we can write the product of the translational and rotational entropy factors, and the rate of the crossing of the barrier in the form

$$\frac{A_{\mathrm{H}}}{A_{\mathrm{D}}}=\prod_{i}^{3n-6}(u_{\mathrm{D}i}/u_{\mathrm{H}i})/(u_{\mathrm{D}i}{}^{\ddagger}/u_{\mathrm{H}i}{}^{\ddagger}) \tag{VII.7}$$

where A is the pre-exponential in the Arrhenius equation. If the ratio of the products of inertia of the intermediate carbonium ion and its solvated transition complex is unity, then the zero-point energy contribution to $(k_{\mathrm{H}}/k_{\mathrm{D}})_{\text{elimination}}$ will be the observed factor of 1.8. One must expect the transition state to have a larger product of inertia than the carbonium ion because of the solvation. This will lead to a pre-exponential term $A_{\mathrm{H}}/A_{\mathrm{D}}$ greater than unity and its value will be in the range 1 to $\sqrt{2}$. The zero-point energy contribution is, therefore, not very significant in the present case.

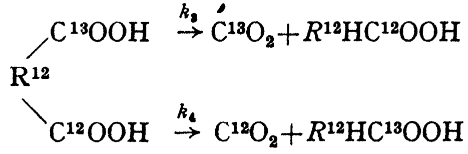
VIII. CARBON ISOTOPE EFFECTS IN DECARBOXYLATION REACTIONS

A. Intermolecular and Intramolecular Isotope Effects

In addition to hydrogen isotope effects on polyatomic molecules, there have been extensive investigations in complex systems using principally the isotopes of carbon, nitrogen, and oxygen. For such systems the theoretical analysis can be simplified through the use of the $G(u)$ formula and its approximation through the modified first quantum correction. Carbon isotope effects in decarboxylation may be taken as typical examples of such studies. The reactions and rate constants for the decarboxylation of mono- and dibasic acids may be defined by the set of equations:

$$\mathrm{R^{12}(C^{12}OOH)_2} \xrightarrow{k_1} \mathrm{C^{12}O_2}+R^{12}\mathrm{HC^{12}OOH} \tag{VIII.1}$$

$$\mathrm{R^{13}(C^{12}OOH)_2} \xrightarrow{k_2} \mathrm{C^{12}O_2}+R^{13}\mathrm{HC^{12}OOH} \tag{VIII.2}$$



$$\mathrm{R^{12}(C^{13}OOH)} \xrightarrow{k_3} \mathrm{C^{13}O_2}+R^{12}\mathrm{HC^{12}OOH} \tag{VIII.3}$$

$$\mathrm{R^{12}(C^{12}OOH)} \xrightarrow{k_4} \mathrm{C^{12}O_2}+R^{12}\mathrm{HC^{13}OOH} \tag{VIII.4}$$

Since the effect of the carbon isotope on vibrational frequencies is small, Eq. II.21 may be used.

$$\frac{k'}{k}=\frac{\nu_L{}^{\ddagger\prime}}{\nu_L{}^{\ddagger}}\left(1+\sum_{i}^{3n-6}G(u_i)\Delta u_i-\sum_{i}^{3n-7}G(u_i{}^{\ddagger})\,\Delta u_i{}^{\ddagger}\right) \tag{VIII.5}$$

Strictly speaking, Eq. VIII.5, which is derived for gas reactions, should be modified by a ratio of ratios of vapor pressures of reactants and transition states. The latter correction may be estimated to be two orders of magnitude smaller than the observed kinetic effects in gases, and is, therefore, neglected. The correction for quantum-mechanical tunneling is also neglected.

We shall first consider the isotope effects to be expected from an oversimplified model of the activated complex: namely, all frequencies in the activated complex are identical with those in the normal molecule except the C—C stretching frequency, which becomes a translation. The temperature independent factor $\nu_L^{\ddagger\prime}/\nu_L^{\ddagger}$ will, first, be calculated from the Slater coordinate. In addition we assume that the isotope shift in the C—C stretching frequency is again given by the diatomic reduced mass relationship.

$$\frac{k_1}{nk_3} = \left(\frac{\nu_{12}^{\ddagger}}{\nu_{13}^{\ddagger}}\right)_L (1+G(u_1)\Delta u_1) \qquad \text{(VIII.6)*}$$

$$\nu_{12} \simeq 900 \text{ cm}^{-1} \text{ (Ref. 34, p. 195)}$$

$$\left(\frac{\nu_{12}^{\ddagger}}{\nu_{13}^{\ddagger}}\right)_L = \left(\frac{\nu_{12}}{\nu_{13}}\right)_1 = \left(\frac{12\cdot 13}{25}\cdot\frac{24}{12\cdot 12}\right)^{1/2} = 1.020$$

At 400°K,

$$G(u_1) = G\left(\frac{hc\,\nu_1}{kT}\right) = G\left(\frac{(1.438)(900)}{400}\right) = 0.231$$

$$\Delta u_1 = \left(\frac{1.438}{400}\right) 18 = 0.065$$

$$k_1/nk_3 = 1.035 \qquad \text{(VIII.7)}$$

$$\frac{k_1}{nk_4} = \left(\frac{\nu_{12}^{\ddagger\prime}}{\nu_{12}^{\ddagger}}\right)_L (1+G(u_1)\Delta u_1) = 1$$

Therefore

$$k_4/k_3 = k_1/nk_3$$

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* The factor n is a statistical one, which is unity for the intermolecular decarboxylation of monobasic carboxylic acids but 2 for the dibasic acid (e.g. malonic acid). We use the subscripts 12 and 13 to refer to C^{12} and C^{13}, respectively.

We now consider the same model for the reaction but calculate the temperature independent factor from the considerations with regard to potential surfaces given in Section III. In addition, it is convenient to avoid the calculation of the frequency shift, $\Delta\nu_1$, and evaluate the quantum correction through an approximation (see Eq. II.30) based on the method of the first quantum correction. One obtains at 400°K

$$\frac{k_1}{nk_3} = \left(\frac{46 \cdot 59}{105} \cdot \frac{104}{45 \cdot 59}\right)^{1/2} \left[1 + \frac{1}{24}\left(\frac{1.438}{2\pi \cdot 400}\right)^2 \left(\frac{1}{12} - \frac{1}{13}\right) \frac{4.50 \times 10^5}{1.492 \times 10^{-3}} \frac{12G(u)}{u}\right.$$

where

$$12G(u)/u = 0.858 \quad (\text{using } \nu_1 = 900 \text{ cm}^{-1})$$
$$a_{11}(\text{C—C}) = 4.50 \times 10^5 \text{ dynes/cm}^*$$
$$c^2/N = 1.492 \times 10^{-3\dagger}$$

Then

$$k_1/nk_3 = 1.029$$
$$\frac{k_1}{nk_4} = \left(\frac{45 \cdot 60}{105} \cdot \frac{104}{45 \cdot 59}\right)^{1/2} = 1.004$$
$$k_4/k_3 = 1.025$$

This same quantum correction can be used with the Slater coordinate for the temperature independent factor. This would give $k_1/nk_3 = 1.045$ at 400°K, and would not change the conclusions to be reached.

These calculations may be compared with the rather extensive experimental data given in Tables VIII and IX. All the data in the literature have been corrected to the relations given in Section V and wherever possible the appropriate corrections have been made for isotopic inhomogeneity. The latter correction is unnecessary for the C^{14} experiments. Finally we have omitted several experiments where later work by the same authors repudiates their own earlier work. Despite the considerable amount of experimental work on malonic acid, the status of the experimental

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* This is the contribution of the C—C bonding to the sum of the Cartesian force constants of the carboxyl carbon atom (ref. 34, pg. 193).

† c is the velocity of light and N is Loschmidt's number.

TABLE VIII. C^{13} and C^{14} Isotope Effects in the Decarboxylation of Dibasic Acids.

Acid	Ratio	Isotope	T°C	100 ε[a]	Correction[b] for homogeneity	Ref.
Malonic	k_4/k_3	C^{13}	138	2.0		8
	$k_1/2k_3$	C^{13}	138	3.7 ±0.2		8
	k_4/k_3	C^{13}	138	2.6 ±0.4	H	39
	k_4/k_3	C^{13}	138	2.0		39
	k_4/k_3	C^{13}	151	2.0		39
	k_4/k_3	C^{13}	174	2.4		39
	k_4/k_3	C^{13}	199	2.0		39
	k_4/k_3	C^{14}	140	6 ±2		48
	$k_1/2k_3$	C^{13}	137	3.4		40
	$k_1/2k_3$	C^{13}	149(?)	4.1		40
	$k_1/2k_3$	C^{13}	173(?)	3.4		40
	$k_1/2k_3$	C^{13}	196(?)	3.6		40
	$k_1/2k_3$	C^{14}	154	6.4 ±0.6		50
	k_1/k_3	C^{14}	154	7.6 ±0.6		50
	k_4/k_3	C^{13}	140	2.8 ±0.2		72
Br Malonic	k_4/k_3	C^{13}	117	2.4 ±0.3		72
Malonic	k_4/k_3	C^{13}	140	2.99±0.05	H	71
	k_4/k_3	C^{13}	140	2.73±0.05	H	75
	k_4/k_3	C^{14}	140	5.47±0.36		75
	k_4/k_3	C^{14}	140	5.77±0.20		32
Br Malonic	k_4/k_3	C^{14}	118	6.46±0.24		32
Malonic (solution in H_2SO_4)	$k_1/2k_3$	C^{13}	56	4.69±0.06	H	74
			79	3.91±0.09	H	74
			100	3.63±0.04	H	74
			129	3.50±0.07	H	74

[a] $\varepsilon = (k_{12}/nk_{13, 14} - 1)$.

[b] H indicates a correction has been applied from experimental data.

measurements still leaves much to be desired. There is a significant discrepancy between the values reported for k_4/k_3 for C^{13} by Bigeleisen and Friedman,[8] Lindsay, Bourns, and Thode,[39] and Yankwich and co-workers.[71, 72, 75] Even different sets of experiments from the same laboratories (i.e., Lindsay, Bourns, and Thode and Yankwich and co-workers) show discrepancies beyond the statistical errors. Some of the discrepancy is undoubtedly

TABLE IX. C^{13} and C^{14} Isotope Effects in the Decarboxylation of Monobasic Acids.

Acid	Isotope	T°C	$100\left(\frac{k_1}{k_3} - 1\right)$	Ref.
Mestoic	C^{13}	61.2	3.7±0.3	15
	C^{13}	60	3.8 ±0.1	58
	C^{13}	92	3.2 ±0.1	15
	C^{14}	60	10.1 ±0.7	58
Trichloracetate	C^{13}	70.4	3.38±0.07	7

due to the necessary corrections for isotopic homogeneity. The data of Lindsay, Bourns, and Thode[39] do not have the precision necessary to look for a temperature coefficient of k_4/k_3 of the magnitude predicted by the model discussed above.

In spite of the limitations of the experimental data and the rough nature of the theoretical calculations, the agreement between theory and experiment is rather striking considering the magnitude of the effect under consideration. All the experimental data support the conclusion that $k_1/2k_3 > k_4/k_3$. This conclusion would remain unaltered even if a correction for isotopic homogeneity were applied to the experimental data. The conclusion from this observation is that the simple model discussed above utilizing the Slater decomposition coordinate is inadequate. In this model the zero-point energy contribution to k_4/k_3 arises from isotopic isomerism in the transition state, since $\sum^{3n-6} G(u_i)\Delta u_i$ is identically zero. The value of $k_1/2k_4$ calculated by the use of the fragment coordinate and the above model is again too low, and it is therefore reasonable to conclude that the failure of the model is due to an insufficient zero-point energy contribution to $k_1/2k_4$. It is rather easy to see how the model must be changed to increase the calculated value of $k_1/2k_4$.

$$\frac{k_1}{2k_3} = \frac{\nu_{12,L}^{\ddagger\prime}}{\nu_{13,L}^{\ddagger}}\left[1+\sum_i^{3n-6} G(u_i)(u_{12i}-u_{13i}) - \sum_i^{3n-7} G(u_i^{\ddagger})(u_{1i}^{\ddagger}-u_{3i}^{\ddagger})\right] \tag{VIII.8}$$

$$\frac{k_1}{2k_4} = \frac{\nu_{12,L}^{\ddagger\prime}}{\nu_{12,L}^{\ddagger}}\left[1+\sum_i^{3n-6} G(u_i)(u_{12i}-u_{13i}) - \sum_i^{3n-7} G(u_i^{\ddagger})(u_{1i}^{\ddagger}-u_{4i}^{\ddagger})\right] \tag{VIII.9}$$

$$\frac{k_4}{k_3} = \frac{\nu_{12,L}^{\ddagger}}{\nu_{13,L}^{\ddagger}}\left[1+\sum_{i}^{3n-7} G(u_i^{\ddagger})(u_{3i}^{\ddagger}-u_{4i}^{\ddagger})\right] \qquad \text{(VIII.10)}$$

where $(u_{3i}^{\ddagger}-u_{4i}^{\ddagger})$ is hc/kT times the difference between the ith frequency in the two isomeric transition states of $C^{12}OOHCH_2C^{13}OOH$ which lead to $C^{13}O_2$ and $C^{12}O_2$ respectively. The ratio $k_1/2k_4$ is increased by a decrease in the bonding in the transition state of the carboxyl group which remains intact and appears as acetic acid. One such model, which has been discussed previously,[3] and was the first one advanced for this reaction, is the loosening of both C—C bonds in the transition state. There may also be a contribution from hydrogen bonding. If the transition state is nearly symmetrical, k_4/k_3 contains no zero-point energy contribution. Such a model yields $k_4/k_3 = 1.020$ (independent of temperature) and $k_1/2k_3 = 1.035$ at 400°K,[3] if one uses the Slater coordinate. This model could not explain a value of $k_4/k_3 > 1.020$, which a considerable body of experimental data seems to support. Since the molecular fragment ratio of $\nu_{12,L}^{\ddagger}/\nu_{13,L}^{\ddagger}$ is much too small to account for the observed results, such a model might favor the Slater coordinate. An asymmetric decrease in the bonding of both carboxyl carbons in the transition state will raise $k_1/2k_4$ and may increase $k_1/2k_3$ in either calculation. If one takes into consideration the loss of the zero-point energy of the bending and twisting modes of the carboxyl group which gives CO_2, both $k_1/2k_3$ and k_4/k_3 will be increased, but $k_1/2k_4$ will remain relatively unchanged. Further calculations are too speculative at present and would be more meaningful if they were based on experimental data concerning the temperature coefficient of k_4/k_3.

Any of the models discussed above lead to the prediction that there should be little difference between k_1/k_2 and $k_1/2k_3$.[12] This result is true for both types of coordinates for the motion across the barrier and is supported by the experimental data of Ropp and Raaen.[50]

Figure 7 shows an intercomparison of the experimental data on the C^{13} isotope effect in intermolecular decarboxylation reactions with theoretical calculations based on the simple model of the loss of a C—C frequency in the transition state. The curve *S* is calculated using the Slater type formulation, while the curve *N* is based on the molecular fragment coordinate plus a modified first quantum correction. The solution data of malonic acid in 80 per cent H_2SO_4 join with those in the melt smoothly. The high-temperature data on the molten samples may not correspond to thermal equilibrium with the bath temperature. The dibasic acid (malonic acid) data seem to lie consistently above those of the monobasic acids. This may be a manifestation of the hydrogen bonding effect discussed previously in connection with the problem of $k_1/2k_4$. The present data on the intermolecular isotope effect alone do not favor either the Slater or the molecular fragment treatment over one another. It is significant to point out that a correction for the hydrogen bonding effect would lead to two new curves for the dibasic acid which may be somewhat higher and with slightly different slope than the ones shown in Fig. 7. The magnitude of the shift cannot be estimated with sufficient accuracy to draw any inferences.

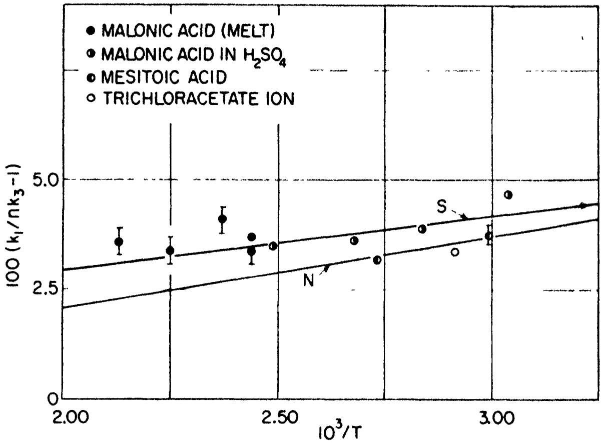

Fig. 7. C^{13} isotope effect in decarboxylation reactions Theoretical curves for transition state which has lost a C—C stretching frequency. Curve *S*—Slater decomposition coordinate, curve *N*—molecular fragment coordinate treatment

B. Catalyzed Decarboxylations

Quinoline and other bases catalyze the decomposition of β-keto acids.[45] The effect of one such catalyst, quinoline, on the inter- and intramolecular isotope effects in the decarboxylation of malonic acids has been investigated. The experimental data are summarized in Table X. Again the experimental data have been recalculated to conform with Eqs. V.60—V.64 and have been corrected for isotopic inhomogeneity. The true ratios of rate constants can be obtained from the data tabulated in Table X by multiplication by the appropriate equilibrium ratios, when these are known, through the use of Eqs. V.84—V.86 or V.91—V.93.

TABLE X. Carbon Isotope Effects in the Quinoline Catalyzed Decarboxylation of Malonic Acid.

Ratio	Isotope	T°C	100 s	Ref.
$k_1/2k_2$	C^{13}	34	5.83±0.11	68
		59	5.09±0.11	68
		79	4.53±0.02	68
		99	4.24±0.08	68
		118	3.94±0.09	68
k_4/k_3	C^{13}	86	4.45±0.08	69
		100	4.10±0.09	69
		110	3.73±0.01	69
		123	3.56±0.02	69
		138	3.17±0.06	69
$k_1/2k_2$ (monoanion)	C^{13}	67.5	4.21±0.06	73
		79	4.18±0.11	73
		98	3.95±0.07	73
		119	3.81±0.05	73
k_4/k_3	C^{14}	85	8.5	32
		95	8.1	32
		105	7,5	32
		115	7.0	32
		125	6.5	32
		135	6.0	32

It is reasonable to assume that the difference in the isotopic free energy function of the quinoline complex of malonic acid and its activated complex is the same as that of the uncomplexed molecule, i.e.,

$$(\Sigma\bar{\gamma}a_{ii})_{Q\,\mathrm{mal}} - (\Sigma\bar{\gamma}a_{ii})^{\ddagger}{}_{Q\,\mathrm{mal}} = (\Sigma\bar{\gamma}a_{ii})_{\mathrm{mal}} - (\Sigma\bar{\gamma}a_{ii})^{\ddagger}{}_{\mathrm{mal}} \qquad \text{(VIII.11)}$$

We may tentatively ascribe the difference in the observed fractionation factors observed in quinoline and in acid media to complexing. The differences are of the correct order of magnitude.[10] It is significant to note that the quinoline complexing has a larger effect on the intermolecular than the intramolecular isotope effect. This would argue in favor of weak complexing and is in agreement with the fact that the rate of decarboxylation of malonic acid in dioxane catalyzed by quinoline is first order in quinoline.[26a] The C^{14} data show the expected factor of 2 over the C^{13} data.[4]

C. C^{13} *versus* C^{14} Isotope Effects

At one time some workers gave serious consideration to the hypothesis that the C^{14} isotope effects in decarboxylation reactions are greater than twice the C^{13} ones.[72] A summary of the C^{14}/C^{13} ratios is given in Table XI. The data in Table XI provide little basis for the hypothesis that there are significant isotope dependent factors which have been neglected in Section II.

TABLE XI. Intercomparison of C^{14} and C^{13} Isotope Effects.

Reaction	$\varepsilon C^{14}/\varepsilon C^{13}$	Ref.
Decarboxylation of mesitoic acid	2.8 ± 0.3	58
Dehydration of oxalic acid	2.0 ± 0.2	27
Enzymatic hydrolysis of urea	3.2 ± 0.4	54
Hydrolysis of urea	1.8 ± 0.2	53
Decarboxylation of malonic acid (k_4/k_2)	2.0 ± 0.1	75
Decarboxylation of malonic acid in quinoline (k_4/k_2)	1.9 ± 0.1 (85° − 135°C)	32, 69
Decarboxylation of malonic acid melt ($k_1/2k_2$)	1.8 ± 0.2 at 150°C	8, 40, 50

IX. ACKNOWLEDGMENTS

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Table I is reproduced from *Science* through the courtesy of the AAAS. Figures 2, 3, 4, 5, and 6 and Tables IV, V, and VI are reproduced from the *J. Chem. Phys.* through the courtesy of the American Institute of Physics.

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DIELECTRIC PROPERTIES OF DILUTE POLYMER SOLUTIONS

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CONTENTS

I. GENERAL INTRODUCTION

Dielectric properties are essentially the dielectric constant ε' and the loss factor ε'', linked by the relation:

$$\varepsilon = \varepsilon' - i\varepsilon'' \tag{1}$$

The dielectric constant is related to the polarization due to the field, by the classical equation

$$(\varepsilon - 1)\mathbf{E} = 4\pi\mathbf{P} \tag{2}$$

where **P** is the polarization, **E** is the average macroscopic field. ε, ε', ε'' and the vector **P** are all *macroscopic* properties, related to the microscopic structure of the dielectric, since the polarization of the medium, as a whole, is obtained by summation of the polarization of the individual molecules.

Structural modifications brought about by an electric field can be of three kinds: (a) orientation polarization, which can only take place for molecules having a permanent dipole moment, (b) atomic deformation polarization, (c) electronic deformation polarization.

Dielectric constants and loss factors are generally independent of the intensity of the applied field, but may vary considerably with its frequency and with temperature. In particular, the orientation polarization is characterized by a relaxation, or decay time, so that it disappears for high enough frequencies. It generally decreases when the temperature is raised. The deformation polarizations depend on the density of the medium and become frequency dependent only in a region of much higher frequencies. The dielectric loss factor is negligible for sufficiently high and sufficiently low frequencies. It passes through a maximum value ε''_m for a critical frequency ν_c which is closely related to the relaxation time of the orientation polarization. At zero frequency, we have the static dielectric constant ε_0.

By measuring the static dielectric constant of solutions of polar polymers in nonpolar solvents, one may calculate a statistical mean dipole of the macromolecule. With polar solvents interesting information can be obtained concerning the interaction between polymer and solvent molecules. Finally the study of relaxation phenomena, including the accurate determination of the critical frequencies may lead us to a better knowledge of the statistical unit and of its interaction with its environment.

It therefore appears that a study of dielectric properties can be useful to the polymer chemist and physicist. This method should be used in conjunction with the more classical techniques of viscometry, osmometry, light scattering, etc.

Unfortunately, dielectric properties are not always easy to interpret, and accurate experimental data are lacking. For these reasons, we can only aim at qualitative conclusions.

A number of monographs and review articles have recently been published on this matter;[3, 11, 20, 37, 41, 47] in the present paper knowledge of the basic principles underlying the theory is assumed. The fundamental equations will only be recalled in so far as they are useful to us and particular stress will be laid on the validity of the approximations made.

II. THEORETICAL CONSIDERATIONS ON STATIC DIELECTRIC CONSTANTS

The problem can only be solved by the methods of statistical mechanics.

Let us consider a macroscopic volume V, containing N molecules. Let $\mathbf{E}_0$ be the mean macroscopic field due to electric charges situated outside the volume under consideration. The average moment $\langle \mathbf{M}_E \rangle$ of the volume, in the direction of the field is

$$\langle \mathbf{M}_E \rangle = \frac{\int \cdots \int \mathbf{M}_E \exp\left[-\frac{U(X, E_0)}{kT}\right] dX}{\int \cdots \int \exp\left[-\frac{U(X, E_0)}{kT}\right] dX} \tag{3}$$

where $\mathbf{M}_E$ is the moment associated with given values of E and X, $U(X, E_0)$ is the total potential energy of the N particles, and X is a set of coordinates allowing complete description of the system.

The energy U depends on all interactions of all particles one with another and also with the field E_0. All these interactions must be taken in consideration when calculating U and $\mathbf{M}$. This is obviously one of the major difficulties of the problem.

The moment $\mathbf{M}$ of the total volume is obtained by adding the moments of its N molecules, and this leads to the following value:

$$\mathbf{M} = \sum_{i=1}^{N} \mathbf{m}_i = \sum_{i=1}^{N} [\boldsymbol{\mu}_i + \alpha(\mathbf{E}_0 - \sum_{\substack{k=1 \\ k \neq i}}^{N} \mathsf{T}_{ik} \cdot \mathbf{m}_k)] \tag{4}$$

where $\boldsymbol{\mu}_i$ is the permanent dipole moment of the *isolated* molecule, that is in the absence not only of an electric field but also of the influence of electric charges situated in other molecules; α is the polarizability, taking care of both the atomic and the electronic deformation polarization.

The tensor product $\mathsf{T}_{ik} \cdot \mathbf{m}_k$ represents, in first approximation, the field created by molecule k in the region occupied by the molecule i. The tensor T is a symmetrical dyad defined by

$$\mathsf{T}_{ik} = \frac{1}{r_{ik}^3}\left[1 - 3\frac{\mathbf{r}_{ik}\,\mathbf{r}_{ik}}{r_{ik}^2}\right] \tag{5}$$

r_{ik} is the distance between molecules i and k; 1 is the unit tensor. This definition fulfils the condition

$$\mathsf{T}_{ii} = 0 \tag{6}$$

Equation 3 is valid for any volume. For a limited volume boundary conditions may be considered. Thus for a spherical volume surrounded by its own medium (spherical cavity in a dielectric), the field E_0 must be replaced by

$$\mathbf{G} = \frac{3\varepsilon_0}{2\varepsilon_0+1}\mathbf{E} \tag{7}$$

A general solution of our problem is hard to find, the main difficulty residing in the separation of orientation and deformation effects. In order to overcome this difficulty use is made of a *mean* effective, or internal field **F** defined by

$$\mathbf{F} = \mathbf{E}_0 - \sum_{k \neq i} \langle (\mathsf{T}_{ik} \cdot \mathbf{m}_k)_E \rangle \tag{8}$$

Combination of Eqs. 4 and 8 leads to

$$\langle \mathbf{M}_E \rangle = \sum_{i=1}^{N} [\langle (\boldsymbol{\mu}_i)_E \rangle + \alpha\, \mathbf{F}_i] \tag{9}$$

Sometimes, [42] the internal field may be split up into two parts: the cavity field **G** and the reaction field **R**.

The reaction field exists in the dielectric even when there is no externally applied field, and leads to an increase of the dipole moment as compared with that of the isolated molecule. Thus it is necessary to introduce at this stage the internal moment **p** given by the sum of the moment of the isolated molecule and the moment due to the reaction field.

In the earliest and crudest theories, those of Clausius-Mosotti and Debye,[12] the reaction field was completely ignored, so that theoretical predictions were not confirmed by the experimental facts except for gaseous dielectrics, and eventually for extremely dilute solutions of polar molecules in nonpolar solvents.

Onsager[42] has obtained better results by neglecting London-Van der Waals and other short-range orientation effects, but not the long-range electrostatic interactions between molecules.

A more general statistical treatment has been given by Kirkwood for two simplified cases. He has shown[30] that for nonpolar gases at low pressures Clausius-Mosotti's equation is a first approximation. Nevertheless, by refining Kirkwood's theory, several authors, among whom we wish to quote Mazur and Jansen,[40] have shown that even for nonpolar gases interaction effects must be considered and polarizability should be influenced by pressure.

Kirkwood[31] has also considered, and treated by statistical mechanics, the orientation polarization but not the deformation effects in a polar liquid. He considers a sphere *in vacuo* containing a set of nondeformable molecules characterized by an internal moment **p** (and not μ). The total potential energy U is divided in two parts: U_1, due to London-Van der Waals and dipole forces, is practically independent of the field; U_2 is due to electrostatic interactions of the dipoles with the external field. In Kirkwood's model, one finds:

$$U(X, E_0) = U_1(X) + U_2(X, E_0)$$

and

$$U_2(X, E_0) = -\sum_i \mathbf{p}_i \cdot \boldsymbol{E}_0 \tag{11}$$

If $p_i E_0/kT \ll 1$, the exponential in Eq. 3 may be expanded in a power series, and the field E factorized. The integration is carried out for the whole configurational volume, in two stages, the first considering all molecules except one, the second extending to all other configurations of this molecule. It is then shown that the total moment of the sample $\langle \mathbf{M}_E \rangle$ is related to the moment $\mathbf{M}_0$ of a sphere of radius r_0, surrounding a molecule in a given configuration. The radius r_0 is such that the orientation effect of the central molecule disappears outside the spherical cavity. The evaluation of $\mathbf{M}_0$ introduces a correlation factor g depending on the angle γ between a given molecule and its z nearest neighbors:

$$\mathbf{M}_0 = \mathbf{p}[1 + z\langle \cos \gamma \rangle] = \mathbf{p}g \tag{12}$$

Thus $\langle \mathbf{M}_E \rangle$ *can be expressed as a function of parameters which are independent of the applied field.*

In order to account for deformation polarization, Kirkwood writes

$$\frac{(\varepsilon_0 - 1)(2\varepsilon_0 + 1)}{3\varepsilon_0} = \frac{4\pi N}{V}\frac{p^2 g}{3kT} + \frac{4\pi N}{V}\alpha \tag{13}$$

It must be stressed that in this equation the first term is the only one which is calculated by statistical mechanics. The second term which takes care of deformation effects is introduced in a completely empirical manner. The internal moment **p** is simply taken from Onsager's theory.

More recently, Harris and Alder,[24] keeping the general principles of Kirkwood's theory, have tried to calculate the polarization effects more rigorously. Unfortunately their final equation does not coincide as it should, with Onsager's equation when it is assumed that there are no short-range interactions ($\langle\cos\gamma\rangle = 0$). This is because some of Kirkwood's equations are only valid when the assumptions of the author are justified, and cannot be used as was done by Harris and Alder, when a deformation polarization is superimposed on the orientation polarization. For instance, in presence of deformation effects boundary conditions cannot be introduced in the same manner as in Kirkwood's model (cf. Fröhlich[21]).

These difficulties have been avoided by Fröhlich[20] whose reasoning is very similar to Kirkwood's but who has chosen his model in such a manner that he need consider no boundary effect. He has treated the deformation polarization as a macroscopic phenomenon. Molecules are replaced by a set of nondeformable point dipoles, having a moment $\mathbf{p}'$ and placed in a continuous medium of dielectric constant n^2 (n = refractive index), accounting for deformation effects. The moment of a spherical molecule is given by

$$\mathbf{p}' = \left(\frac{n^2+2}{3}\right)\boldsymbol{\mu} \tag{14}$$

Fröhlich finally obtains the general relation

$$\frac{(\varepsilon_0-n^2)(2\varepsilon_0+n^2)}{3\varepsilon_0} = \frac{4\pi N_0 d}{3kT\mathscr{M}}\langle\mathbf{p}'\cdot\mathbf{M}^*\rangle \tag{15}$$

where N_0 is the Avogadro number; d is the density of the dielectric; $\mathscr{M}$ is the molecular weight; $\mathbf{p}'$ is the moment of a fundamental unit, which may be either a molecule, a fraction of a molecule, or a small set of molecules; and $\mathbf{M}^*$ is the moment of a spherical cavity placed in a continuous dielectric when the fundamental unit is fixed in a given configuration.

If the fundamental unit is the molecule itself,

$$\langle \mathbf{p}' \cdot \mathbf{M}^* \rangle = p'^2 g \tag{16}$$

and Eq. 15 reduces to Onsager's relation for $g = 1$. *Notwithstanding the crudeness of some of the approximations made, Fröhlich's treatment of deformation polarization is much less empirical than Kirkwood's, so that Eq.* 15 *is actually the best we have at present.*

Theoretical calculations of dielectric properties according to Kirkwood's or Fröhlich's theories can only be carried out if the correlation factor g is known from independent investigations on the structure of the dielectric. Conversely, as was shown by Fröhlich, experimental determinations of the dielectric properties may give us precious information as to the structure of condensed, and particularly of liquid phases. In particular data concerning the influence of temperature on the function

$$B(T) = \frac{(\varepsilon_0 - n^2)(2\varepsilon_0 + n^2)T}{3\varepsilon_0 d} = \frac{4\pi N_0}{3k\mathcal{M}} p'^2 g \tag{17}$$

should be very useful.

III. THEORETICAL CONSIDERATIONS ON DIELECTRIC RELAXATION

Experimental data on the frequency dependence of dielectric constants may be represented, in a very general manner, by the following relation:

$$(\varepsilon_\omega - \varepsilon_\infty) = y(\omega) \tag{18}$$

where ω is the angular frequency $2\pi\nu$ of the field, ν being the frequency in cps, ε_∞ is a constant, and $y(\omega)$ is a decreasing function of the frequency. The influence of frequency is only apparent in a restricted range, depending on the dielectric and the temperature. The function has two limiting values, $(\varepsilon_0 - \varepsilon_\infty)$ and zero, for low and high frequencies. Qualitatively the decrease in dielectric constant may be ascribed to the decrease and final disappearance of the orientation polarization, ε_∞ being due exclusively to the deformation polarization.

Static dielectric constants could be related to microscopic parameters through equations bearing on the equilibrium positions of dipole units. Relaxation phenomena can only be understood by considering the manner in which these equilibrium positions are reached. No general, rigorous and complete solution of this problem is available.

For time varying fields, Eq. 3 must be replaced by a more general relation

$$\langle \mathbf{M}_E(t) \rangle = C \int \ldots \int \mathbf{M}_E(t) f(X, E_\omega, t)\, dX \tag{19}$$

where the distribution function $f(X, E_\omega, t)$ depends explicitly, and implicitly through E_ω, on the time t.

The distribution function must be such that for $E_\omega = 0$, $\langle \mathbf{M}_E \rangle = 0$.

Since the field, even if fairly strong, causes only a slight perturbation to the statistical equilibrium distribution, a second boundary condition exists

$$\text{for } \omega = 0, \qquad \mathbf{E}_\omega = \mathbf{E}_0$$

$$f(X, E_0) = f_0(X)[1 + f_1(X)E_0 + \ldots] \tag{20}$$

$f_0(X)$ being the distribution function in the absence of an external field. Introducing these conditions in Eq. 19, we find that for $\omega = 0$ (static field)

$$\langle \mathbf{M}_E \rangle = C' E_0 \int \ldots \int \mathbf{M}_E f_0(X) f_1(X) dX \tag{21}$$

For a periodic field, we may write, in analogy to Eq. 20

$$f(X, E_\omega, t) = f_0(X)[1 + f_{1,\omega}(X) E_0 e^{i\omega t} + \ldots] \tag{22}$$

Only one problem remains: to find an explicit expression for $f_{1,\omega}$.

This has been attempted either by treating the problem as a diffusion problem, or by applying the superposition principle, that is by a macroscopical method. To understand the latter treatment, suppose that a static field is applied and suddenly cut off at $t = 0$. At a given moment t, the distribution function will be given by

$$f(X, t) = f_0(X)[1+f_1(X)E_0\,\varphi(t)+\ldots] \tag{23}$$

where $\varphi(t)$ is the decay function, characterizing the rate at which orientation polarization disappears.

Suppose now that a periodic field is equivalent to a continuous series of static fields, each being applied during an infinitely short time du between u and $u+du$. It is found by applying the superposition principle that the distribution function at a given moment is

$$f(X, E_{\omega,t}) = f_0(X)\left[1+f_1(X)\left(\int_0^\infty \varphi(x)e^{i\omega x}dx\right)E_0\,e^{i\omega t}+\ldots\right] \tag{24}$$

where $x = t-u$.

The problem would be solved if only $\varphi(t)$ were known. Unfortunately this decay function is probably quite complex, since the rate of disorientation must be influenced by interactions between dipoles and by the molecular field. Nevertheless it has often been assumed that this speed of decay is proportional to the orientation polarization itself, so that we have the well-known exponential law:

$$\varphi(t) \sim e^{-t/\tau} \tag{25}$$

where τ is the relaxation time of the *macroscopic* polarization. In that case, Eq. 24 may be replaced by

$$f(X, E_{\omega,t}) = f_0(X)\left[1+\frac{f_1(X)}{1+i\omega\tau}E_0\,e^{i\omega t}+\ldots\right] \tag{26}$$

leading to the classical relation

$$\varepsilon-\varepsilon_\infty = \frac{(\varepsilon_0-\varepsilon_\infty)}{1+\omega^2\tau^2} - i\,\frac{(\varepsilon_0-\varepsilon_\infty)\omega\tau}{1+\omega^2\tau^2} \tag{27}$$

in which the imaginary part

$$\varepsilon'' = \frac{(\varepsilon_0-\varepsilon_\infty)\omega\tau}{1+\omega^2\tau^2} \tag{28}$$

is related to the energy dissipated in the dielectric, that is the dielectric loss factor.

Debye's expressions, Eqs. 27 and 28, are in qualitative, but not in quantitative agreement with experimental data. For condensed systems, the dispersion curve $\varepsilon' - \log \omega$, are in general flatter and extend over a wider frequency range than predicted. The absorption curves are usually broader and the maximum value of the loss factor ε''_m is smaller than the calculated one, $(\varepsilon_0 - \varepsilon_\infty)/2$. However the curves generally remain symmetrical.

Discrepancies between theory and practice are explained by assuming that the very complex polarization phenomenon is characterized by a range of relaxation times rather than by a single one. $\varphi(t)$ in Eq. 23 must be written

$$\varphi(t) = \int_0^\infty e^{-t/\tau} F(\tau) \frac{d\tau}{\tau} \tag{29}$$

where $F(\tau)$ is the distribution function for relaxation times, leading to

$$f_{1,\omega} = f_1 \int_0^\infty \frac{F(\tau)d\tau}{1+i\omega\tau} \tag{30}$$

Equations 27 and 28 must be replaced by

$$\varepsilon' - \varepsilon_\infty = \int_0^\infty \frac{F(\tau)d\tau}{1+\omega^2\tau^2} \tag{31}$$

and

$$\varepsilon'' = \int_0^\infty \frac{F(\tau)\omega\tau d\tau}{1+\omega^2\tau^2} \tag{32}$$

The actual distribution function cannot be deduced from experimental data. However it may be characterized by an empirical or semiempirical coefficient.[10, 22]

Many attempts have been made in order to interpret the exponential decay function on a microscopic basis and to relate the macroscopic relaxation times to those of a single polar unit τ^*.

The earliest treatment of dielectric relaxation, on a molecular basis, is that of Debye.[12] He treated it as a diffusional process, assuming that spherical molecules were rotating in a continuous medium. Applying the Stokes law, he found

$$1/\tau^* = kT/4\pi r^3\eta \tag{33}$$

where r is the radius of the molecule, η is the viscosity of the medium.

Fuoss and Kirkwood[32] have obtained equations identical with Eqs. 31 and 32 without introducing, explicitly, the exponential decay function. Like Debye they reasoned as if the problem were mainly one of diffusion by Brownian motion under the influence of an external force. Treating this problem as a Sturm-Liouville equation, they developed $f_{1,\omega}$ into a complete set of orthogonal functions ψ_λ. A relaxation time τ_λ is associated with each of these functions.

At present[2,15,27,29] orientation polarization is generally treated as a rate process. It is assumed that the polar units jump from one equilibrium position to an other. The speed of orientation depends essentially on three factors: a frequency factor k' related to the number of collisions with neighboring molecules; an entropy factor ΔS^* describing the disturbance of the local structure of the medium during orientation; an energy factor, or heat of activation ΔH^* equal to the height of the potential barrier separating successive equilibrium positions. The classical relation between these factors is

$$\frac{1}{\tau^*} = k' \, e^{\Delta S^*/k} \, e^{-\Delta H^*/kT} \tag{34}$$

In fact Eqs. 33 and 34 are formally identical, since the viscosity itself can be treated as a rate process and related to temperature by

$$\frac{1}{\eta} = k'_v \, e^{\Delta Sv^*/k} \, e^{-\Delta Hv^*/kT} \tag{35}$$

Combining Eqs. 33 and 35,

$$\frac{1}{\tau^*} = \frac{kT}{4\pi r^3} k'_v \, e^{\Delta Sv^*/k} \, e^{-\Delta Hv^*/kT} \tag{36}$$

the subscript v signifies that the frequency factor and entropy and energy of activation are those characterizing viscous flow. For viscous flow, as well as for orientation in an electric field, ΔS^* and ΔH^* are associated with the breaking of bonds between neighboring molecules or submolecules. A polar unit can only move from one equilibrium position into another if this new position is vacant. A "hole" must be made in the liquid. The question arises as to whether the making of the hole or the rotating of the polar unit in the molecule is the rate determining factor.

It is often assumed, although without actual proof, that there exists a definite proportionality between the molecular and the macroscopic relaxation times. A relation between τ and τ^* could only be established if the actual field acting on the molecule were known. Equation 27 is obtained if this field is identified either with the external or with the Lorentz internal field. In the first case the macroscopic relaxation time is identical with the molecular one. In the second case τ is proportional to τ^*. If Onsager's model is used,[36] it may be shown that in first approximation, the cavity field **G** is itself subject to dispersion:

$$\mathbf{G}(\omega, t) = B(\omega)\mathbf{E}e^{i\omega t} \tag{37}$$

$$B(\omega) = \left(1 + \frac{B'_0 - 1}{1+\omega^2\tau'^2}\right) + i\frac{(B'_0-1)\omega\tau'}{1+\omega^2\tau'^2} \tag{38}$$

with

$$B'_0 = \frac{3\varepsilon_0}{2\varepsilon_0 + \varepsilon_\infty}.$$

τ' is the relaxation time of the cavity field, supposed to decay exponentially. Whether τ' is equal to the decay time of the macroscopic polarization τ or to that of the polar unit τ^* is difficult to forecast. If we accept $\tau' \simeq \tau^*$, we obtain a rather complicated expression which does not reduce easily to Eq. 27. On the other hand, this reduction is easy if we write $\tau' \simeq \tau$ and use the empirical relation[43]

$$\tau = B'_0\tau^*$$

The exact shape of the dispersion curves are as yet unknown since no calculations based on a really accurate expression for the decay function or for the internal field have even been attempted. A complete and general theory is difficult to establish, since the height of the potential barriers, depending as it does on local structures, may itself be a function of time.

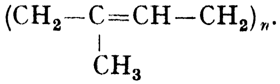
Although no convincing proof, either experimental or theoretical has been given for the exponential decay law, it is universally used, either in its simple form or in the more complex one corresponding to a spectrum of relaxation times.

It must always be born in mind that discrepancies between experimental and theoretical curves may be due to the inadequacy of the fundamental exponential law rather than to a distribution of relaxation times.

IV. THE DIPOLE MOMENT OF THE ISOLATED POLYMER CHAIN MOLECULE

Two classes of polymer chain molecules must be considered: the *homogeneous* and the *heterogeneous*.

Homogeneous chains consist of carbon atoms united by single bonds. The vinyl $(CH_2{-}CHR)_n$ and substituted vinyl $(CH_2{-}CR_1R_2)_n$ compounds are typical of this class.

Heterogeneous chains consist of different kinds of atoms as in the silicones $(SiR_1R_2{-}0)_n$, or of identical atoms united by bonds of different length as in natural rubber  $(CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CH_2)_n$.

All chain molecules, whether homogeneous or heterogeneous are able to assume an enormous array of configurations as a result of the considerable degree of rotational freedom about single bonds. In the simple polymethylene chains, for example, an almost limitless variety of irregular shapes may be realized by performing rotations about the bonds of the chain. But if bulky side-groups replace the hydrogen atoms, the number of possible configurations is considerably reduced by steric effects. This can easily be shown on molecular scale models.

Each configuration is characterized by a dipole moment $\boldsymbol{\mu}$ equal to the vectorial sum of the moments $\boldsymbol{\mu}_j$ of its N monomers

$$\boldsymbol{\mu} = \sum_{j=1}^{N} \boldsymbol{\mu}_j \tag{39}$$

An average square dipole moment $\langle \mu^2 \rangle$ is defined in the same manner as the average square displacement of the molecule:[18]

$$\langle \mu^2 \rangle = \langle \sum_{j=1}^{N} \boldsymbol{\mu}_j \cdot \sum_{k=1}^{N} \boldsymbol{\mu}_k \rangle = N \mu_{\mathrm{eff}}^2 \tag{40}$$

where μ_{eff} is the moment of each monomer in an imaginary chain, having the same moment as the real one but in which there is no correlation between the orientation of the different monomers (random flight). In general μ_{eff} is not equal to μ_0, the dipole moment of the monomer unit. $\bar{\mu} = \sqrt{\langle \mu^2 \rangle}$ will be called the mean statistical dipole. Equation 40 can be transformed into

$$\langle \mu^2 \rangle = \mu_0^2 [N + \sum_{\substack{j,k=1 \\ j \neq k}}^{N} \langle \cos \gamma_{j,k} \rangle] \tag{41}$$

where $\gamma_{j,k}$ is the angle between the dipole units of monomers j and k. Allowing that this angle depends on the *relative* positions, and not on the *absolute* positions of the units in the chain, and neglecting eventual end-group effects, we develop Eq. 41 into

$$\begin{aligned}\langle \mu^2 \rangle = \mu_0^2 [N + (N-1) \langle \cos \gamma_{1,2} \rangle + (N-2) \langle \cos \gamma_{1,3} \rangle \\ + \ldots 2 \langle \cos \gamma_{1,(N-1)} \rangle + \langle \cos \gamma_{1,N} \rangle]\end{aligned} \tag{42}$$

In order to obtain the average value of $\langle \cos \gamma_{1,j} \rangle$ all possible relative orientations of dipoles 1 and j must be considered, and each of the possible configurations must be given a statistical weight equal to its Boltzmann probability. The angle of the dipole and the main direction of the chain must also be considered.

Rigorous mathematical treatment will only be attempted for homogeneous molecules of the type $(CH_2{-}CXR)_n$, the dipole moment being localized in the side-groups. To an approximation which is adequate for all practical purposes, it is permissible to assume the length of the valence bonds in the chain, and the valence angle between successive bonds to be constant for a given polymer. Constancy of the angle between the dipole of X and the chain bond to which it is attached will also be assumed. It can be shown that the *general* conclusions reached in this manner may be extended to more complicated cases. For instance, these conclusions remain valid when the angle between the dipoles and the chain is not constant, as is the case for polyvinyl acetate studied in this laboratory,[6] or for heterogeneous polymers having their dipoles in the chain itself as in the polyoxyethylene glycols studied by Benoit and Marchal.[39]

As shown in Fig. 1, a unit vector $\mathbf{a}$ is chosen along each valence bond of the polymer chain, and a unit vector $\mathbf{b}$ along each dipole. It is obvious that vector $\mathbf{b}_1$ is preceded by vector $\mathbf{a}_1$ and followed by vector $\mathbf{a}_2$, that vector $\mathbf{b}_2$ is preceded by vector $\mathbf{a}_3$ and followed by $\mathbf{a}_4$, or in a general manner that vector $\mathbf{b}_j$ is preceded by vector $\mathbf{a}_{2j-1}$ and followed by vector $\mathbf{a}_{2j}$. The constant angle between successive valence bonds is represented by δ, and the constant angle between $\mathbf{b}_j$ and $\mathbf{a}_{2j}$ by β. ψ_j is the angle between $\mathbf{b}_j$ and the plane containing vectors $\mathbf{a}_{2j-1}$ and $\mathbf{a}_{2j}$,φ_{2j} is the angle between this plane and that containing vectors $\mathbf{a}_{2j-2}$ and $\mathbf{a}_{2j-1}$. Each vector $\mathbf{a}_j$ is included in a set of Cartesian reference axes $\mathbf{a}_j$, $\mathbf{a}'_j$, $\mathbf{a}''_j$, so that the plane defined by $\mathbf{a}_j$ and $\mathbf{a}'_j$ coincides with that of $\mathbf{a}_j$ and $\mathbf{a}_{j-1}$.

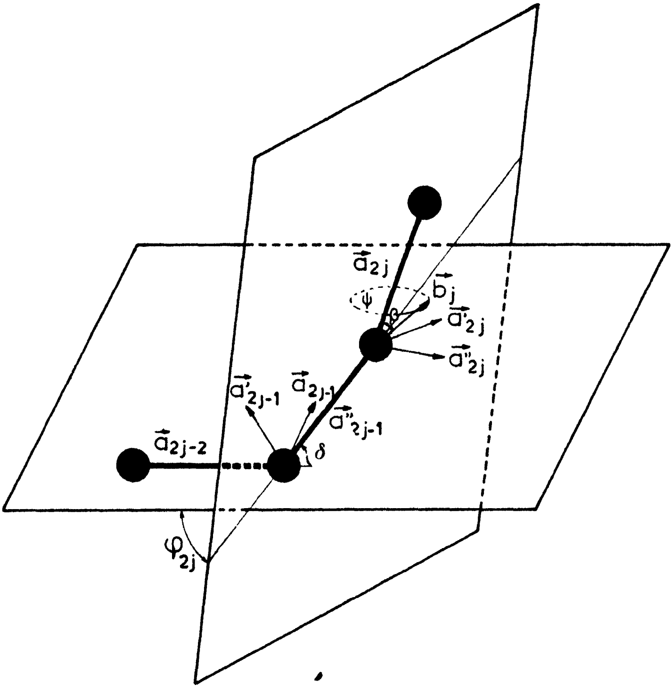


Fig. 1

We now write

$$\langle \cos \gamma_{1,j} \rangle = \langle \mathbf{b}_1 \cdot \mathbf{b}_j \rangle$$
$$= \langle \mathbf{b}_1 \cdot [\cos\beta \mathbf{a}_{2j} + (\cos^2 \psi_j - \cos^2 \beta)^{1/2} \mathbf{a}'_{2j} + \sin \psi_j \mathbf{a}''_{2j}] \rangle \qquad (43)$$

As the values ot $\langle \cos \gamma_{1,j} \rangle$ corresponding to different values of j will have to be included in a summation function, it seems appropriate to express them all as functions of the same unit vectors, for example $\mathbf{a}_2$, $\mathbf{a}'_2$, $\mathbf{a}''_2$, and $\mathbf{b}_1$.

In order to do this the three components of $\mathbf{b}_j$ will be projected; first on $\mathbf{a}_{2j-1}$, $\mathbf{a}'_{2j-1}$, $\mathbf{a}''_{2j-1}$; then on $\mathbf{a}_{2j-2}$, $\mathbf{a}'_{2j-2}$, $\mathbf{a}''_{2j-2}$, etc.; and finally on $\mathbf{a}_2$, $\mathbf{a}'_2$, $\mathbf{a}''_2$.

This is done with the aid of the projective matrix:

$$\begin{pmatrix} \cos \delta & \sin \delta \ \cos \varphi & \sin \delta \ \sin \varphi \\ \sin \delta & \cos \delta \ \cos \varphi & \cos \delta \ \sin \varphi \\ 0 & \sin \varphi & \cos \varphi \end{pmatrix}.$$

In this manner we find

$$\langle \cos \gamma_{1,j} \rangle = \langle \mathbf{b}_1 \cdot [\mathbf{a}_2 \cos\beta \cos^{2j-2}\delta + \mathbf{\Gamma}_{1,j}(\delta, \beta, \psi_j, \varphi_{2j}, \varphi_{2j-1} \cdots \varphi_2)] \rangle \qquad (44)$$

where $\mathbf{\Gamma}_{1,j}(\delta, \beta, \psi_j, \varphi_{2j-1}, \ldots \varphi_2)$ is a complicated function of all angles included in the brackets when expressed in components $\mathbf{a}_2$, $\mathbf{a}'_2$, $\mathbf{a}''_2$.

To reach the average values, integration must be extended to all possible values, not only of all angles ψ, but of all the angles φ. It must be remembered that the probability associated with a given ψ_j may depend on angles β and δ. The final equation is written

$$\langle \cos \gamma_{1,j} \rangle = \mathbf{b}_1 \cdot \mathbf{a}_2 (\cos \beta \cos^{2j-2} \delta)$$
$$+ \mathbf{b}_1 \cdot C'' \int_0^{2\pi} \cdots \int_0^{2\pi} \mathbf{\Gamma}_{1j}\, e^{-V(\psi_j, \varphi_{2j} \cdots \varphi_2)}\, kT \, d\psi_j \, d\varphi_{2j} \ldots \qquad (45)$$

where C'' is a normalization function and V the potential energy associated with a given configuration.

Thus even though we have limited ourselves to homogeneous chains and assumed the constancy of the angle β, our final expression can be given no general solution.

Various specific cases have been treated in the chemical literature, sometimes by very approximate methods.

The simplest case is that of completely free rotation. That is energies associated with all values of angles ψ and φ are supposed to be identical.

Assuming the equality of angles β and δ, Fuoss and Kirkwood[22] using a method proposed by Eyring[14] found the following value for the mean square dipole:

$$\langle \mu^2 \rangle = N\mu_0{}^2 \left[1 + \frac{2 \cos \delta}{1 + \cos^2 \delta} \right] \tag{46}$$

More recently Debye and Bueche[13] introducing an angle α between vector $\mathbf{b}_j$ and vector a_{2j-1} have obtained another value:

$$\langle \mu^2 \rangle = N\mu_0{}^2 \left[1 + \frac{2 \cos \delta \cos \beta \cos \alpha}{1 - \cos^2 \delta} \right] \tag{47}$$

Marchal and Benoit[39] have introduced a correction for steric hindrance. They represent $\langle \cos \varphi \rangle$ by a *constant* ζ assuming that this is the same for all bonds. They also assume that $\langle \sin \varphi \rangle = 0$, in other words that $V(\varphi)$ is a symmetrical function. Applying their calculations to the specific case of polyethylene glycols they suppose that the dipoles are associated with the C—O bonds, so that angle ψ is constantly equal to zero and that β is equal to half the valency angle δ. Taking the tetrahedral angle for δ they find, for high degrees of polymerization,

$$\langle \mu^2 \rangle = \frac{12}{13} N\mu_0{}^2 \frac{1 - \zeta^2}{1 + 0.08\,\zeta + \zeta^2} \tag{48}$$

This equation is interesting in so far as it shows that the maximum value of $\tilde{\mu}$ corresponds to $\zeta = 0$, as is the case for completely free rotation. Thus it appears that, in some cases at least, restricted rotation leads to a decrease in the mean statistical dipole, whilst it almost always causes an increase in the mean statistical displacement.[2] This is due to the fact that *trans* configurations are energetically more probable than *cis* configurations.

But it must be stressed that Eq. 48 is only valid when the dipole is in the polymer chain and not in the side-groups as is more generally the case. Even then some of the author's assumptions are rather crude. For instance it is almost certain that the average value of $\langle\cos\varphi_j\rangle$ is strongly dependent on $\langle\cos\varphi_{j-1}\rangle$ and that it is not constant along the chain. In the same manner, $V(\varphi)$ is certainly not always a symmetrical function as has been shown by Debye and Bueche[13] though this simplifying assumption is justified in the absence of bulky side-groups.

Equation 42 may be simplified in an entirely different way. Actually for sufficiently high values of s, $\langle\cos\gamma_{1,s+n}\rangle$ is constantly equal to zero, since the direction of a given bond is strongly influenced by the orientation of its predecessor in the chain, to a much less extent by the second, even less by the third, and so on. The value of s necessary to reach complete independence of orientation is minimum for completely free rotation, $\langle\cos\gamma_{1,2}\rangle = 0$. For a completely extended rigid chain, $s = N$. For intermediate cases, that is for all real polymer chains, having a considerable amount of flexibility and a high degree of polymerization, s is much smaller than N, so that we may accept with a reasonable degree of accuracy $N-s \simeq N$. Equation 42 simplifies to

$$\langle\mu^2\rangle = N\mu_0^2[1+\langle\cos\gamma_{1,2}\rangle+\langle\cos\gamma_{1,3}\rangle+\ldots\langle\cos\gamma_{1,s}\rangle] \tag{49}$$

$$\langle\mu^2\rangle = \left(\frac{N}{s}\right)s\mu_0^2\,[\sum_{j=1}^{s}\langle\mathbf{b}_1\cdot\mathbf{b}_j\rangle] \tag{50}$$

$$\langle\mu^2\rangle = N_\sigma\mu_\sigma^2 \tag{51}$$

Thus it appears, as shown by Kuhn,[34] that a real polymer chain is equivalent to a freely jointed chain in which monomer units are replaced by statistical units containing s monomer units. The number of statistical units in the molecule is

$$N_\sigma = N/s \tag{52}$$

and the moment of a unit is defined by

$$\mu_\sigma^2 = s\mu_0^2[\sum_{j=1}^{s}\langle\mathbf{b}_1\cdot\mathbf{b}_j\rangle] \tag{53}$$

It is extremely difficult to calculate μ_σ^2, as the different values of $\langle\mathbf{b}_1\cdot\mathbf{b}_j\rangle$ are not independent. They may even be of opposite signs so that an increase in s may cause a decrease in μ_σ. Even if μ_σ is increased by introducing more monomer units in the statistical element, this increase may not compensate the decrease in N/s, the number of statistical elements. In fact the average moment of the molecule is generally smaller for rigid chains than for flexible ones.

This is easy to understand, the *trans* positions of dipoles being energetically more favorable than the *cis* positions as was shown by Taylor.[48] In these favored positions, there is a certain amount of compensation of the individual dipoles, average values of $\cos \varphi$ are always positive, whilst average values of $\cos \psi$ tend to be alternatively positive and negative. In rigid *trans* molecules the dipole moment disappears completely.

In conclusion to this section, *we note that the statistical mean dipole moment of the molecule, as well as its mean displacement, should be proportional to the square root of the degree of polymerization. Hindrance to free rotation tends to decrease the mean statistical dipole moment and to increase the mean statistical displacement. Since hindrance to rotation must disappear at sufficiently high temperatures, the mean dipole moment of the isolated molecule should increase with temperature whilst the mean displacement should be a decreasing function of temperature.*

V. THE DIPOLE MOMENT OF POLYMER CHAINS IN DILUTE SOLUTIONS

As was recalled in the first part of this paper, the dipole moment of a given molecule, polymer or monomer, depends on its environment, since there is always some polarization by electric charges localized in the neighboring particles. In other words a reaction field exists even in the absence of external field, so that the internal moment p of a polymer chain in dilute solution may differ considerably from the moment μ of the same molecule *in vacuo*.

The total polarization of a small volume of solution as measured by the average moment $\langle \mathbf{M}_E \rangle$ depends on the total energy of interaction between molecules and between molecules and the field (Eq. 3). For polymer solutions three types of interaction between particles must be considered:

(a) Interaction between solvent molecules.

(b) Interaction between solvent molecules and monomer units.

(c) Interaction between remote monomer units of a given chain, or between monomer units belonging to different chains.

In this paper interactions between monomer units will be systematically neglected. This is permissible, since the number of contacts between monomer units is small as compared to the number of solvent-solvent or solvent-polymer contacts. This remains true even if there is a considerable amount of overlapping of the polymer clouds, as the density of segments in these clouds is always small.[18] Actually, the number of monomer-monomer contacts only becomes appreciable in the neighborhood of the precipitation point.

In the case of polymer solutions apart from this general polarization effect, the solvent may influence the statistical mean dipole moment by modifying the configuration of the molecule. This question has been treated thermodynamically by Flory[16] and, though his treatment is open to criticism,[25] his general conclusions are probably sound. Flory has shown that if the excess free energy of dilution is positive, as is the case for all real polymer solutions, the solvent favors the more extended configurations. Thus the solvent should cause an increase in the number of monomers contained in the statistical unit. Flory has also shown that the influence of solvent decreases when the temperature is lowered and disappears completely for a critical temperature θ which is very close to the precipitation point. *At θ the mean statistical dipole moment, corrected for polarization effects, should be the same for the dissolved and for the isolated molecule.* This value may be very different from the one calculated by the random flight approximation.

We may write

$$\langle\mu^2\rangle_D = \xi(T)\langle\mu^2\rangle_0 \tag{54}$$

where $\langle\mu^2\rangle_D$ is the mean square moment of the dissolved molecule, $\langle\mu^2\rangle_0$ is the mean square dipole moment of the isolated molecule, and $\xi(T)$ is an expansion or unwinding function, depending on temperature.

Equation 54 is somewhat similar to that proposed by Flory for the mean square displacement:

$$\langle h^2\rangle_D = \alpha(T)\langle h^2\rangle_0$$

But there is one important difference between the two: the expansion coefficient $\alpha(T)$ always increases as the chain unwinds, and is always equal to or greater than unity. On the other hand, $\xi(T)$ increases or decreases according to the positions favored by the solvent. If the *cis* positions of the dipoles are favored, as has recently been suggested for some ordinary isomeric molecules, $\xi(T)$ increases as the chain unwinds and is greater than unity. If the *trans* positions are favored, $\xi(T)$ is smaller than unity and decreases as the chain unwinds. If the *cis* positions of the dipoles are favored by the solvent, $\xi(T)$ increases with temperature. If the *trans* positions of the dipoles are favored, $\xi(T)$ decreases when the temperature is raised.

Equation 54 may be replaced by

$$\langle \mu^2\rangle_D = \xi(T)\frac{N}{s_0}(\mu_\sigma^2)_0 \tag{55}$$

where s_0 is the number of monomers in the statistical unit of the isolated molecule, and $(\mu_\sigma^2)_0$ the average square dipole unit of the statistical unit *in vacuo.*

We may further write

$$\langle \mu^2\rangle_D = \frac{N}{s_D}(\mu_\sigma^2)_D \tag{56}$$

where s_D and $(\mu_\sigma^2)_D$ are the number of monomers and the mean square dipole moment for the statistical unit in solution. Combining Eqs. 55 and 56, we find

$$(\mu_\sigma^2)_D = \frac{s_D}{s_0}\xi(T)(\mu_\sigma^2)_0 = \chi(T)(\mu_\sigma^2)_0 \tag{57}$$

where $\chi(T)$ is the expansion coefficient of the statistical unit.

Evaluation of the mean dipole moment from experimental data on dielectric constants is difficult and uncertain. Because of the strong polarization effects Debye's equation may not be used, even for dilute solutions in nonpolar solvents.[3] In this case, Eq. 58 derived from Onsager's theory is more appropriate:

$$\langle \mu^2 \rangle_D = \frac{900kT}{4\pi N_0} \frac{\mathcal{M}}{c} \frac{(2\varepsilon_0+n^2)^2(\varepsilon_0-\varepsilon_s)}{\varepsilon_0(2\varepsilon_0+\varepsilon_s)(n^2+2)^2} \tag{58}$$

where ε_s is the static dielectric constant of the solvent, n is the refractive index of the solute, $\mathcal{M}$ is the molecular weight of the polymer, c is the concentration in g/100 ml, and N_0 is the Avogadro number.

If ε_0 is a linear function of the concentration c, $(\varepsilon_0-\varepsilon_s)$ may be replaced by (ac) and if ε_0 and ε_s are sufficiently close to allow the approximation $(2\varepsilon_0+\varepsilon_s) = 3\varepsilon_0$, Eq. 58 is simplified to

$$\langle \mu^2 \rangle_D = a \frac{900kT\mathcal{M}}{4\pi N_0} \frac{(2\varepsilon_0+n^2)^2}{3\varepsilon_0^2(n^2+2)^2} \tag{59}$$

But it must be stressed that these equations rest on crude approximations. It is assumed that the polymer cloud is of spherical symmetry and that the actual dipole is located at the center of this equivalent particle.

Onsager's equation has been used for slightly polar solvents such as toluene. With strongly polar solvents, chloroform for instance, Kirkwood's or Fröhlich's theories must be resorted to, and no value of the dipole moment can be obtained unless the correlation factor g is known by independent data concerning the structure of the solution.

It has been shown in a number of cases, that for a wide range of molecular weights, the mean statistical dipole moment is proportional to the degree of polymerization. This conclusion is born out by experimental data concerning both heterogeneous[4, 39, 46] and homogeneous[5, 6, 13, 28] chains. It seems to indicate that the expansion coefficient $\xi(T)$ is independent of the chain length.

The influence of the solvent can best be seen by comparing values of $\sqrt{\langle \mu^2 \rangle_D}/N$ (Table I) for a given polymer in different solvents. The data given here will be published elsewhere in detail. They are the average of a considerable number of individual values for a wide range of concentrations and molecular weights. The moments were calculated by Eq. 58 extrapolated to infinite dilution. The dielectric constants were measured at 23°C at frequencies lower than or equal to 200 kc.

TABLE I. The Influence of Solvent on The Mean Dipole Moment of a Polymer Chain.

(Values of the ratio $\sqrt{\langle\mu^2\rangle_D/N}$.)

Solvent	Polymer	
	Polymethyl methacrylate	Polybutyl methacrylate
Carbon tetrachloride	—	1.48
Benzene	1 37	1.51
Toluene	—	1.39
Dioxane	1.50	1.65

It is seen that polybutyl methacrylate has practically the same moment in the two typically nonpolar solvents: carbon tetrachloride and benzene. The expansion coefficient therefore, has the same value in both cases, and it may reasonably be assumed, that for these two liquids, $\xi(T)$ is equal to unity. According to Flory the two solutions should then be in the neighborhood of their θ temperature. This does not seem to be the case for carbon tetrachloride at 23°, since it may be cooled to $-20°$ without precipitating.

The dipole moments calculated for solutions in toluene or dioxane are significantly different. This proves that there is some interaction between the solvent and the solute. The orientation interaction between polar toluene and polar polymethacrylates is easy to understand. In the case of dioxane it must be remembered that this is a nonpolar compound by *internal compensation* but that the strongly polar C—O groups must have considerable short-range interaction with the polar groups of the polymer. Because of these interactions, Onsager's formula is no longer valid, and the dipole moments given in Table I, for the solutions in toluene or dioxane, have no physical significance. They are given only in order to prove the existence of polymer solvent interactions.

In benzene, the dipole moment of the methyl compound is smaller than that of the butyl compound. Thus, if the monomers have practically similar moments, there is a better compensation of the individual dipoles in the methyl ester where they can more easily move into the energetically favored *trans* positions. The bulky butyl groups, by mere steric hindrance, introduce a certain amount of disorder, and the chain tends towards its random flight configuration.

The influence of temperature on the mean dipole moment of polybutyl methacrylate dissolved in carbon tetrachloride is shown in Table II. The average moments were calculated from Fröhlich's equation (see Section VI) taking unity as the most probable value of the correlation factor. Since the Onsager theory makes use of the refractive index of the solute, for which only approximate values can be found, results obtained by Onsager's and Fröhlich's theories for solutions are not identical even in a nonpolar solvent like carbon tetrachloride. The moments given in Table II are not comparable to those given in Table I, especially as they are not extrapolated to infinite dilution.

It is seen in Table II that the dipole moment of the polymer

TABLE II. Influence of Temperature on the Dipole Moment of Polybutyl Methacrylate.

(Solvent: CCl_4, concentration: 2.0 g/100 ml, DP : 789)

Temperature	$\langle\mu^2\rangle_D$ Debyes	$\tilde{\mu}_D$ Debyes
−20°C	1623	42
−10°C	2029	45
0°C	2439	49
+10°C	3039	55
+25°C	3610	60
+40°C	4015	64
+50°C	4007	65

chain increases steadily as the temperature is raised. If it is assumed that $\xi(T)$ remains equal to unity at all temperatures, this increase in $\tilde{\mu}_D$ is due to an increase in $\tilde{\mu}_0$.

It is our intention to measure the dipole moment and the mean displacement as a function of temperature on the same solutions. Considerations based on results of one type of experiment must not be extended too hastily to the other type. It is quite possible that the progressive liberation of rotation movements in lateral groups has a different effect on the mean dipole moment and the mean length of the molecule.

It would obviously be interesting to compare the actual experimental moments with those calculated by the random flight approximation. Unfortunately, this is almost impossible owing to our ignorance of the true dipole moment of the monomer unit. Moreover, experimental moments are calculated from very approximate formulas. They have a relative value and may be useful for comparison purposes, but their absolute values are probably grossly erroneous.

Nevertheless, the monomer moment calculated from the random flight model for polybutyl methacrylate in CCl_4 at 40°, is 1.90 D, a value which is very close to that of most aliphatic esters. This would seem to prove that, at temperatures higher than 40°, the moment has reached its highest possible value.

VI. INTERACTION BETWEEN POLYMER AND POLAR SOLVENTS IN DILUTE SOLUTIONS

An analysis of the previously defined function $B(T)$ for dilute solutions of polymers in polar solvents may be helpful for the understanding of the interaction between polymer and these solvents.[33] Applying Fröhlich's theory, in which deformation polarization is treated macroscopically, we consider the solution as a continuous medium containing polar units. The dielectric constant of the continuous medium is taken as equal to the square of the refractive index of the solution n_0. This value is very close to that of the solvent. Each polar unit is represented as a sphere of dielectric constant n_0^2, having a point dipole located at its center. It must be stressed that polar units may be either whole molecules, submolecules, or associations of several molecules. In a binary solution, two kinds of units have to be considered: those of the solvent characterized by the internal moment $\mathbf{p}'_1$, and those of the solute having a moment $\mathbf{p}'_2$. Equation 15 obtained by Fröhlich for pure liquids must therefore be replaced by

$$\frac{(\varepsilon_0-n_0^2)(2\varepsilon_0+n_0^2)T}{3\varepsilon_0}=\frac{4\pi}{3k}\left[\langle\mathbf{p}'_1\cdot\mathbf{M}_1^*\rangle N_1+\langle\mathbf{p}'_2\cdot\mathbf{M}_2^*\rangle N_2\right] \qquad (60)$$

where N_1 and N_2 are the number of polar units of solvent and solute per unit volume of solution. $\mathbf{M}_1^*$ and $\mathbf{M}_2^*$ are the total moments of a sphere having a polar unit of solvent or solute located at its center in a given configuration. $\mathbf{p}'_1$ and $\mathbf{p}'_2$ are the moments of the polar units of solvent and solute in this configuration.

Introducing weight fractions x_1 and x_2 in Eq. 60, we find

$$B(T)=\frac{(\varepsilon_0-n_0^2)(2\varepsilon_0+n_0^2)T}{3\varepsilon_0 d}$$

$$=\frac{4\pi N_0}{3k}\left[\langle\mathbf{p}'_1\cdot\mathbf{M}_1^*\rangle\frac{x_1}{\mathcal{M}_1}+\langle\mathbf{p}'_2\cdot\mathbf{M}_2^*\rangle\frac{x_2}{\mathcal{M}_2}\right] \qquad (61)$$

where d is the density of the solution, and $\mathcal{M}_1$ and $\mathcal{M}_2$, the molecular weights of solvent and solute.

In a dilute polymer solution there are many more solvent-solvent contacts than solvent-polymer contacts so that one may assume with a reasonable approximation that the value of $\langle\mathbf{p}'_1\cdot\mathbf{M}_1^*\rangle$ in the solution is practically equal to its value in the pure solvent. This is given by

$$B_s(T)=\frac{(\varepsilon_s-n_s^2)(2\varepsilon_s+n_s^2)T}{3\varepsilon_s d_s}\simeq\frac{4\pi N_0}{3k\mathcal{M}_1}\langle\mathbf{p}'_1\cdot\mathbf{M}_1^*\rangle \qquad (62)$$

where the subscript s refers to the pure solvent.

Combining Eqs. 61 and 62, we obtain

$$B(T)-x_1B_s(T)=\frac{4\pi N_0 x_2}{3k\mathcal{M}_2}\langle\mathbf{p}'_2\cdot\mathbf{M}_2^*\rangle \qquad (63)$$

The moments $\mathbf{p}'_2$ and $\mathbf{M}_2^*$, as well as their scalar product, depend on the mutual orientation of all the dipoles present in the macroscopic sphere under consideration. In a general manner, whatever the nature of the polar unit, we have:

$$\mathbf{M}_2{}^* = \mathbf{p}'_2 + z\langle \mathbf{p}'_1 \rangle \tag{64}$$

where z is the number of solvent molecules in direct contact with the polar unit of the solute. (We neglect interaction between solute units.) $\langle \mathbf{p}'_1 \rangle$ is the average moment of the solvent molecule in the direction of $\mathbf{p}'_2$.
Introducing the angle γ between the polar units of the solute and solvent molecules, Eq. 64 leads to

$$\langle \mathbf{p}'_2 \cdot \mathbf{M}_2{}^* \rangle = \langle p'^2_2 [1 + z \frac{p'_1}{p'_2} \langle \cos \gamma \rangle_2] \rangle = \langle p'^2_2 g \rangle \tag{65}$$

The average of the product must be taken over all coordinates describing configuration of the fixed polar unit. In a similar manner $\langle \cos \gamma \rangle_2$ is given by

$$\langle \cos \gamma \rangle_2 \sim \int \cos \gamma \, e^{-U/kT} d\omega_1 \tag{66}$$

where U is the total energy of interaction between polar unit 2 and the solvent, and ω_1 is the solid angle described by the rotation of polar unit 1.

The subscript 2 indicates that $\langle \cos \gamma \rangle_2$ is a function of the coordinates of unit 2. In fact, the energy U depends on the dipole p'_2 and on cos γ so that there is a different value of g for each value of p'_2. The average product $\langle p'^2_2 g \rangle$ is difficult to use, and for practical reasons we introduce a mean value g', defined by the two following equations:

$$\langle p'^2_2 g \rangle = \langle p'^2_2 \rangle g'$$

$$g' = 1 + z \frac{\langle p'_2 p'_1 \langle \cos \gamma \rangle_2 \rangle}{\langle p'^2_2 \rangle} \tag{67}$$

In this manner we may obtain numerical values of g' from which qualitative conclusions may be drawn as to the interaction between solute and solvent molecules.

Passing on to polymer solutions, let us first assume that the polar unit is identical to a statistical element. This unit is obviously attached to two other similar units but, by definition, each may be considered, as far as orientation is concerned, as completely independent of the other two.

From Eqs. 65 and 67, we find

$$\langle \mathbf{p}'_2 \cdot \mathbf{M}_2{}^* \rangle = \langle p_\sigma'^2 \rangle \left[1 + \frac{z\langle p'_\sigma p'_1 \langle \cos\gamma \rangle_2 \rangle}{\langle p_\sigma'^2 \rangle} \right] \tag{68}$$

In order to correct for the deformation polarization by the environment, we use Fröhlich's relation

$$\langle p_\sigma'^2 \rangle = \langle \mu_\sigma{}^2 \rangle_D \left(\frac{n_0{}^2+2}{3} \right)^2 \tag{69}$$

Combining Eqs. 57, 68 and 69,

$$\begin{aligned} \langle \mathbf{p}'_2 \cdot \mathbf{M}_2{}^* \rangle &= \langle \mu_\sigma{}^2 \rangle_0 \left(\frac{n_0{}^2+2}{3} \right)^2 \left[\chi(T) + \frac{z\langle (\mu_\sigma)_D \mu_1 \langle \cos\gamma \rangle_2 \rangle}{\langle \mu_\sigma{}^2 \rangle_0} \right] \\ &= g''_\sigma \langle \mu_\sigma{}^2 \rangle_0 \left(\frac{n_0{}^2+2}{3} \right)^2 \end{aligned} \tag{70}$$

On the other hand if the polar unit 2 is identified to the polymer molecule itself, we find:

$$\begin{aligned} \langle \mathbf{p}'_2 \cdot \mathbf{M}_2{}^* \rangle &= \langle \mu^2 \rangle_0 \left(\frac{n_0{}^2+2}{3} \right)^2 \left[\xi(T) + \frac{z'\langle \mu_{2D} \mu_1 \langle \cos\gamma \rangle_2 \rangle}{\langle \mu_2{}^2 \rangle_0} \right] \\ &= g'' \langle \mu_2{}^2 \rangle_0 \left(\frac{n_0{}^2+2}{3} \right)^2 \end{aligned} \tag{71}$$

In both cases, g'' depends simultaneously on the expansion factor $\chi(T)$ or $\xi(T)$ and on $\langle \cos\gamma \rangle_2$. The two effects are difficult to separate as very little is known about the expansion coefficients. Moreover if $\xi(T)$ is equal to unity in all nonpolar solvents as it seems to be the case for polybutyl methacrylate dissolved in benzene and in carbon tetrachloride, the expansion observed in polar solvents may be due entirely to an interaction effect, so that $\xi(T)$ and $\langle \cos\gamma \rangle_2$ are probably not independent of one another. More experimental work is necessary to confirm these views. As has already been said, comparison of the influence of various factors on the mean displacement and on the mean statistical dipole would be extremely useful.

Numerical values of g'' can be obtained by comparing values of $B(T)-x_1B_s(T)$ for a given polymer in polar and in nonpolar solvents.

For instance, in solutions of polybutyl methacrylate in carbon tetrachloride there is no orientation correlation either at solvent-solvent or at solvent-solute contacts, that is $\langle \cos\gamma\rangle_2 = 0$. Since in this case $\xi(T) = 1$, the correlation factor g'' is also equal to unity. From this we deduce:

$$B(T) = \frac{4\pi N_0 x_2}{3k\mathscr{M}_2}\langle p'^2_2\rangle = \frac{4\pi N_0 x_2}{27k\mathscr{M}_2}\langle \mu_2^2\rangle_0 (n_0^2+2)^2_{\mathrm{CCl_4}} \tag{72}$$

If μ_2 is identified to the dipole of the polymer chain as a whole, it may be calculated from Eq. 72. Values so obtained were given in Table II and are quite reasonable. As the molecular weight of the statistical unit is unknown, its dipole moment cannot be evaluated.

For polar toluene solutions, we have

$$B(T)-x_1B_s(T) = \frac{4\pi N_0 x_2}{27k\mathscr{M}_2}\langle \mu_2^2\rangle_0 g''(n_0^2+2)^2 \tag{73}$$

so that combining Eqs. 72 and 73, g'' for toluene solutions is finally given by

$$g'' = \frac{[B(T)]_{\mathrm{tol}} - [x_1B_s(T)]_{\mathrm{tol}}}{[B(T)]_{\mathrm{CCl_4}}}\;\frac{(n_0^2+2)^2_{\mathrm{CCl_4}}}{(n_0^2+2)^2_{\mathrm{tol}}} \tag{74}$$

Numerical values for different temperatures are assembled in Table III.

In order to interpret these results it must be remembered that $|\langle\cos\gamma\rangle_2|$ decreases when the temperature is raised, whether it is positive or negative.

If the *cis* positions of the dipoles are favored by the solvent, $\xi(T)$ and $\chi(T)$ are greater than unity and increase with temperature. In this case, the decrease in the observed values of g'' must be assigned solely to the decrease in $\langle\cos\gamma)_2$ and this cosine must be positive.

If the *trans* positions of the dipoles are favored and the polar

TABLE III. Correlation Factors g'' in Toluene Solutions of Polybutyl Methacrylate.

(Concentration: 2g/100 ml. Degree of polymerization: 789)

Temperature	$B(T)$ toluene solutions	$B(T)$ toluene	$B(T)$ CCl_4 solutions	g'' toluene solutions
−20°C	71.44	50.80	10.15	1.99
−10°C	78.15	51.04	12.59	2.09
0°C	84.17	51.40	15.02	2.11
+10°C	90.08	52.75	18.52	1.94
+25°C	92.05	53.40	21.82	1.71
+40°C	92.70	54.01	23.99	1.54

unit is identified with the entire molecule, values of g'' greater than unity can only be obtained if $\langle\cos\gamma\rangle_2$ is positive, as $\xi(T)$ is smaller than unity. If the statistical element is taken as a polar unit, $\chi(T)$ may be greater or smaller than unity and no definite conclusions may be drawn from the data in Table III. Nevertheless, when *trans* positions are favored $\xi(T)$ decreases with rising temperature and s/s_0 increases so that the product of the two, $\chi(T)$, is probably only slightly dependent on temperature. In that case the decrease in g'' must once again be attributed to a decrease in $\langle\cos\gamma\rangle_2$ and this cosine must be positive.

It therefore seems reasonable to suggest that in toluene solutions of polybutyl methacrylate there is a parallel orientation of the interacting dipoles.

In conclusion to this section we believe that a closer study of the correlation factor in polymer solutions may lead to a better understanding of the influence of the polymer molecule on the local structure of the solvent. This may be useful in interpreting anomalies of dilute solutions of high polymers.

VII. DIELECTRIC RELAXATION OF HIGH POLYMERS IN DILUTE SOLUTIONS

Experimental data concerning dielectric relaxation of dilute polymer solutions are relatively rare, and their accuracy is slight. The measured dielectric losses are small and uncertain as a great number of corrections for conductivity, for self-induction effects, and so on must be introduced. Nevertheless, it has been shown in a number of cases[5-7] that Eqs. 31 and 32 are in better agreement with the experimental curves than Eqs. 27 and 28. This means that if the exponential decay law is taken for granted, there is a spectrum of relaxation times. The flattening of the dispersion curve may be characterized by Fuoss and Kirkwood's factor,

$$\alpha = 2\frac{\varepsilon''_m}{(\varepsilon_0 - \varepsilon_\infty)} \tag{75}$$

ε''_m being the value given by the maximum of the loss curve. As shown in Table IV this factor α varies from 0.5 to 0.8 and is always smaller than unity, that is than its limiting value for a single relaxation time. This factor is larger than that observed for plasticized polymers which may be assimilated to concentrated solutions.[22]

It is also seen in Table IV that the relaxation time corresponding to the maximum of the loss curve τ_m is practically independent of the degree of polymerization. This empirical relaxation time is of the order of 10^{-8} sec and is determined to within 20 per cent. It is considerably lower than that calculated for the orientation of a whole polymer molecule (10^{-6}—10^{-3} sec according to the degree of polymerization) and much larger than that of a single monomer unit ($\tau \simeq 10^{-11}$ sec).

The relaxation time depends, as seen in Table IV, on the polymer, on the solvent, on temperature, and perhaps on the concentration of solute.

From the theoretical point of view, as has already been said in Section II, difficulties encountered are much greater than for the interpretation of dipole moments. At the present time, there is no hope of elaborating a complete theory based on the correct values of the internal field and accounting, in a rigorous manner, for all types of interaction. Even if one considers the individual polymer chains as independent of one another and of the solvent, the task of describing the movement of the resultant dipole is still quite overwhelming. In fact, consideration must be given to the simultaneous movements of the molecule as a whole, of the statistical elements, and of each dipole unit. In order to move, each molecule, submolecule, or dipole must overcome the viscous resistance of the

Polymer[b]	Degree of Polymerization	Temperatures[a]→		235° K		245° K		255° K		262° K		273° K		278° K	
		Solvent[c]	Conc. g/100 cm³	$\tau_m \cdot 10^8$	α	$\tau_m \cdot 10^8$	α	$\tau_m \cdot 10^8$	α	$\tau_m \cdot 10^8$	α	$\tau_m \cdot 10^8$	α	$\tau_m \cdot 10^8$	α
AV	2,500	TL	7.26	1.9	0.61	1.3	0.65	0.9	0.68						
	7,500	TL	6.92	2.7	0.60	1.7	0.77	1.2	0.77	0.8	0.77				
	11,500	TL	6.04	1.9	0.53	1.3	0.62	1.0	0.81						
	23,000	TL	5.56	2.0	0.64	1.3	0.68	0.9	0.73						
MM	140	TL	6.02	—	—	2.8	0.67	1.9	0.65	1.1	0.67				
	950	TL	5.82	—	—	2.8	0.72	2.0	0.67	1.3	0.77				
	2,100	TL	6.57	—	—	5.3	0.47	3 0	0.60	1.9	0.71				
	5,000	TL	6.10	—	—	4 4	0.59	2 3	0.62	1.6	0.71				
	9,000	TL	5.80	—	—	3.8	0.61	2.4	0.61	1.6	0.61				
	12,500	TL	5.14	—	—	3.5	0.61	2.4	0.61	1.5	0.61				
	17,500	TL	5.99	—	—	4.0	0.50	2.7	0.51	1.7	0.52				
MM	12,500	TL	4.23	—	—	4.7	0.60	2.6	0.70	2.0	0.70				
	17,500	TL	4.54	—	—	3.8	—	2.3	0.57	2.1	0.50	1.6	0.49		
MB	475	TL	4.54	—	—	—	—	2.1	0.62	1.6	0.62				
	725	TL	4.03	—	—	—	—	2.3	0.79	1.8	0.83				
	1,500	TL	4.57	—	—	—	—	—	—	2.2	0.61	1.3	0.58		
	2,750	TL	4.36	—	—	—	—	2.9	0.80	2.3	0.80				
MB	475	CT	4.23	—	—	—	—	5.0	0.54	—	—	—	—	1.6	0.57
	725	CT	4.72	—	—	—	—	—	—	4.2	0.70	—	—	2.3	0.74
	1,150	CT	3.92	—	—	—	—	5.3	0.68	—	—	—	—	2.0	0.72
	1,500	CT	4.13	—	—	—	—	—	—	4.8	0.68	—	—	2.1	0.70
	2,750	CT	4.29	—	—	—	—	—	—	3.6	0.65	2.8	0.65	1.9	0.70
VC	2,000	TH	4.6	0.8	0 70	0.7	0.70	0.4	0.70						
	2,000	TH	6.1	0.9	0.70	0.7	0.70	0.5	0 70	0.4	0.70				

+2° K. [b] PAV = polyvinylacetate; PMM = polymethyl methacrylate; PMB = polybutyl methacrylate; PVC = polymedium and the internal potential barrier opposing free rotation. If each of the single movements is characterized by a single, well-defined relaxation time, the superposition of these movements will lead to distribution of relaxation times for the macroscopic polarization.

Treating the problem as one of rotary Brownian movement, Kirkwood and Fuoss[32] were able to calculate the distribution functions $f_{1,\omega}$ and $F(\tau)$ of Eqs. 22 and 29. In their case $F(\tau)$ was a symmetrical function and they identified the average relaxation time with the value τ_m corresponding to the maximum in the loss curve. Unfortunately their theory is incompatible with existing experimental data on dilute solutions, since it specifies that τ_m should be proportional to the degree of polymerization.

More recently Kirkwood[33] has developed a general theory of irreversible processes in polymer solutions, which includes the dielectric relaxation as a particular case. He concluded that Oseen's hydrodynamic interaction between segments of the polymer chain could not be neglected in the calculation of the diffusion tensor. This lead Kirkwood and Hammerle[23] to recalculate Kirkwood and Fuoss' expression for the relaxation time τ_m. The influence of the molecular weight is less marked than in the original theory, τ_m being proportional to the square root of the degree of polymerization instead of to this degree itself. But the discrepancy between theory and experiment subsists. The theory also predicts that the heat of activation should be the same for the dielectric polarization and for the viscosity of the solvent, and that the distribution function of relaxation times should be independent of temperature. Neither of these conclusions is confirmed by experimental data, as is shown in Tables IV and V.

The most general treatment of dielectric relaxation in polymer solutions is that given by Kuhn.[35] He fixes the central chain element at the origin of coordinates with a permanent electric field along a given direction. If this field is suddenly withdrawn, the molecule drifts back to an equilibrium configuration by rotation of the various elements so that activation energies have to be introduced. From this starting point Kuhn derives the exponential decay law, which appears in the form:

$$\varphi(t) \backsim \sum_{i=1}^{N/2} e^{-D_i t} \tag{76}$$

where D_i is the rotary diffusion constant of the *i*th statistical element, D_i is obtained by superposition of the diffusion constant of the coil rotating as a whole, and of all the possible movements in the part of the chain extending from the origin to the *i*th element.

The interesting idea in this theory is that the statistical elements, which may be considered as completely independent units when the *equilibrium* distribution is investigated, are no longer *independent* from the kinetic point of view.

Unfortunately the computation of the D_i values is difficult and the final expression for the distribution function of relaxation times contains some rather arbitrary parameters.

Three principal times intervals appear in this function:

(1) ϑ_1 the time interval in which a chain element moving as a single particle covers a distance equal to half the mean displacement of the polymer molecule.

(2) ϑ_2 the time interval in which the end of the chain rotates over an angle of 116°.

(3) ϑ_3 the time interval in which the statistical coil as a whole rotates over an angle of 81°.

At sufficiently low molecular weights ϑ_3 is the smallest of these time intervals and determines the value of τ_m. This value should be proportional to the square of the degree of polymerization.

For higher molecular weights ϑ_3 and ϑ_2 become equal and $\tau_m \simeq 2\vartheta_2$ is independent of N.

Finally for very high molecular weights τ_m should be proportional to $N^{1/3}$.

Kuhn has shown that Kirkwood and Fuoss' 1941 theory is a particular case of this more general one.

Qualitative confirmation of Kuhn's theory appears in the fact that the relation between τ_m, the relaxation time for the maximum of the loss curve, and the degree of polymerization does, as predicted, depend on the range of molecular weights investigated. But even for $N = 140$, τ_m is definitely not proportional to N^2. For example, in the case of toluene solutions of polymethyl methacrylate at $-10°$ C, τ_m increases by about 50 to 80 per cent when the degree of polymerization rises from 140 to 2100 (from 1 to 15) and then remains practically constant up to $N = 17{,}500$.[5]

Comparison on a quantitative basis of Kuhn's theory with experiment is difficult because many factors are involved for which only a rough estimate can be made.

It should be pointed out that a distribution function such as that obtained by Kuhn $[M(\tau)]$ is not equivalent to $F(\tau)$ as defined by Eq. 29.

Kuhn himself suggests that other functions derived from $M(\tau)$ may be used. If $F(\tau) = \tau M(\tau)$ is taken, τ_m should be proportional to the degree of polymerization for high molecular weights.

Hermans and Van Beek[6, 26] have recently used the new model of polymer molecules suggested by Rouse.[45] At high frequencies the whole molecule cannot follow the field so it is divided into a number of submolecules small enough to follow the field and yet sufficiently large to have a Gaussian distribution. Dielectric relaxation for the case of dipoles parallel to the chain has been calculated by Fourrier sum transforms. The distribution of relaxation modes appears though the multiplicity of the mathematical solution for the diffusion equation.

A result similar to that of Van Beek's has been obtained by Zimm[51] applying Kirkwood's formalism to the Rouse model.

Both authors find that τ_m is equal to the relaxation time of a submolecule and should be quite independent of molecular weight. From this point of view the agreement between theory and practice is quite good, particularly for $N \geqq 1000$. Unfortunately the calculations have only been carried out for the case of dipoles parallel to the chain, and Rouse's model does not apply when the dipole is in the side-groups, as is the case for all polymers that have been studied in dilute solutions.

The three theories summarized in the foregoing have one point in common: the mathematics are very involved, whilst the physical assumptions are very crude and necessitate the introduction of undefined and arbitrary friction coefficients and diffusion constants. Under these circumstances one may question the usefulness of refining the theories by considering internal viscosities, friction forces, and other vague parameters.

Moreover it seems that a much simpler mathematical treatment leads to a *reasonable interpretation of all experimental data available.*

Taking Kuhn's original idea as a starting point, we fix the central unit of a molecule at the origin of coordinates and consider that the $N/2s$ units included in each of the half-molecules must overcome different energy barriers in order to resume their equilibrium positions when the field is suppressed.

Let v_0 be the energy associated with the hindrance to free rotation of element 1, element 0 being fixed. This energy should be very nearly independent of molecular weight. The total energy barrier characterizing the rotation of element 1 in solution is $(\Delta H_0^* + v_0)$, where ΔH_0^* is the activation energy necessary to permit a completely free unit to rotate from one equilibrium position to another.

The energy associated with the movement of unit i is $\Delta H_0^* + v_i$, the difference between v_i and v_0 results from the fact that the rotation of unit i is made easier by the superposition of all movements possible in that part of the chain extending from the center to the point considered.

For the end group $v \simeq 0$ and the total energy is ΔH_0^*.

Thus far we have only transcribed Kuhn's theory from the diffusional model to the energy barrier model.

We now consider our half-molecule as consisting of $N/2s$ units rotating more or less independently, the energy barriers being distributed regularly between ΔH_0^* and $\Delta H_0^* + v_0$. The distribution function for relaxation times may then be established by adapting equations given by Fröhlich[19, 20] for a somewhat similar case: that of dipoles, in a liquid or amorphous solid where the arrangement of the nearest neighbors may be different for each dipole. He supposed that in this case the energy barriers are also equally distributed over a range v_0.

Thus we find

$$F(\tau) = (\varepsilon_0 - \varepsilon_\infty)\frac{kT}{v_0}\frac{1}{\tau} \qquad \text{for} \qquad \tau_0 \leqq \tau \leqq \tau_1 \tag{77}$$

$$F(\tau) = 0 \qquad \text{for} \qquad \begin{cases} \tau < \tau_0 \\ \tau > \tau_1 \end{cases} \tag{78}$$

where the relaxation times are defined by

$$\tau_0 = k'' e^{\Delta H_0^*/kT} \tag{79}$$

$$\tau_1 = \tau_0 e^{v_0/kT} \tag{80}$$

$$\tau = \tau_0 e^{v/kT} \tag{81}$$

where $1/k''$ is a frequency factor containing an entropy contribution. Introducing Eq. 76 into Eqs. 31 and 32, we find

$$(\varepsilon'-\varepsilon_\infty) = (\varepsilon_0-\varepsilon_\infty)\left[1-\frac{kT}{2v_0}\ln\frac{1+\omega^2\tau_0^2 e^{2v_0/kT}}{1+\omega^2\tau_0^2}\right] \tag{82}$$

$$\varepsilon'' = (\varepsilon_0-\varepsilon_\infty)\frac{kT}{v_0}[\tan^{-1}\omega\tau_0 e^{v_0/kT} - \tan^{-1}\omega\tau_0] \tag{83}$$

The relaxation time associated with the maximum of the loss curve is equal to the geometrical mean of the two extreme values and

$$\tau_m = \sqrt{\tau_0\tau_1} \tag{84}$$

τ_0 is quite independent of the molecular weight of the polymer. τ_1 may be slightly dependent on N through v_0. It must be stressed that τ_1 and τ_m will be very sensitive to small changes in v_0 as they are exponential functions of this energy. It seems reasonable to suppose that the influence of N on v_0 disappears for high values of N, so that theoretical predictions agree, at least qualitatively with experimental data. It is our intention to study the dielectric dispersion of fairly small polymers ($N \simeq 10$) where the influence of the size of the molecule should be more apparent.

On the other hand, combination of Eqs. 75 and 83 leads to an explicit relation between α, the dispersion coefficient, and the energy v_0:

$$\alpha = 2\frac{\varepsilon''_m}{\varepsilon_0-\varepsilon_\infty} = 2\frac{kT}{v_0}[\tan^{-1}e^{v_0/2kT} - \tan^{-1}e^{-v_0/2kT}] \tag{85}$$

Using Eq. 85 we can obtain v_0 from experimental data, either by calculation or by interpolation on a curve $\alpha = \alpha(v_0/kT)$, published by Fröhlich.[19, 20] A set of values obtained in this manner is given in Table V.

It must be remembered that values of α are found by a graphical method based on the equation,

$$\log \omega = \log \omega_m - \alpha \text{ arc sech } (\varepsilon''/\varepsilon''_m) \qquad (86)$$

which is only approximately true and only in the immediate vicinity of the critical frequency. The values of α and v_0 are, therefore, relatively uncertain. Under those conditions it appears from Table V that the *internal energy barrier is of the same order of magnitude for all polymers investigated.* The average value of 2 kcal/mole is somewhat smaller than that of the energy barrier usually associated with the hindered rotation of carbon-carbon single bonds in a carbon chain, 3 kcal/mole.[48] This may be due to the fact that the rotation of dipoles in an electric field only covers a very small angle.

TABLE V. Activation Energies Calculated from Dielectric Dispersion Data.

Polymer	Solvent	Conc. g/100 cm^3	ΔH^* kcal/mole	ΔH_0^* kcal/mole	log $1/k''$	α mean value at 255° K	v_0 kcal/mole
PMB	CCl_4	4	6.3	5.1	27.3	0.6	2.5
PMB	toluene	4	6.2	5.3	27.8	0.7	1.9
PMM	toluene	4	6.8	5.7	29.0	0.65	2.2
PVC	tetrahydrofurane	4	2.2	1.3	29.0	0.7	1.9
PMM	toluene	6	4.5	3.3	24.6	0.6	2.5
PAV	toluene	6	4.4	3.6	25.3	0.75	1.6

It may be seen from Table IV that values of α found for solutions of polyvinyl acetate in toluene are systematically higher than for those for corresponding solutions of polymethyl methacrylate. This confirms the known fact that the polyvinyl chain has a greater mobility than the polymethacrylate chain.

From Eq. 85 it also appears that α.increases with temperature and tends towards unity when v_0/kT approaches zero. This is a complete agreement with experimental facts as can be seen from Table IV.

By studying the influence of temperature on relaxation time and using Eq. 82,

$$\tau_m = (\tau_0 \tau_1)^{1/2} = \tau_0 e^{v_0/2kT} = k'' e^{(\Delta H_0{}^* + v_0/2)/kT} \tag{87}$$

the frequency factor $1/k''$ and the energy $\Delta H_0{}^*$ can be calculated. Values so obtained are to be found in Table V. Various conclusions may be drawn from these results.

(a) The height of the energy barrier $\Delta H_0{}^*$ is different from that associated with the viscous flow of the pure solvent (which is about 2.1 kcal/mole for toluene and 2.5 kcal/mole for carbon tetrachloride). This might be explained by assuming that the hole which has to be made in the solvent, to receive a statistical unit, is much greater than that needed for a molecule of solvent.

(b) $\Delta H_0{}^*$ seems to decrease when the concentration of the polymer increases. This is probably due to the fact that the polymer destroys partially the local structure of the solvent and that this destruction is more marked in concentrated solutions than in dilute ones. Thus it would appear that it is easier to make a hole when the structure is already much perturbed.

(c) It must be remarked in comparing Eq. 87 with Eq. 34 that

$$\frac{1}{k''} = \frac{1}{k'} e^{\Delta S^*/k} \tag{88}$$

If the frequency factor $1/k'$ is nearly independent of solvent and solute, variations in $1/k''$ must be accounted for by variations in the entropy of activation. It results from Table V that this entropy of activation is a decreasing function of the concentration. This confirms the conclusion in (b). The structure of more concentrated solutions is already looser than in the dilute and less perturbation is needed to permit the rotation of a unit.

In conclusion we wish to point out that the relaxation properties of high polymer solutions seem to be determined both by the mobility of the polymer chain and by the structure of the solution. In this respect it would be interesting to investigate experimentally an eventual parallelism between the polymer-solvent interaction as revealed by the static dielectric properties and the influence of the structure of the solution on the dielectric dispersion.

VIII. CONCLUSIONS

In the foregoing pages, we have tried to show, among other things, that a study of dielectric properties of polymers in dilute solutions, combined with the more classical methods, might lead us to a better knowledge of solvent-polymer interactions.

From static dielectric constants measured at different temperatures in a set of nonpolar solvents, it seems possible to determine relative, if not absolute values of the "unwinding function" $\xi(T)$ which should be closely related to Flory's expansion coefficient $\alpha(T)$. With polar solvents, by calculating the factor g'', it may be possible to find evidence for a disturbance of the local structure due to the presence of the large solute molecule. Finally, a closer study of relaxation phenomena may give an opportunity to separate the energy of activation into two parts, one of which could be related to the solvent-polymer interactions.

Data obtained on this matter would undoubtedly be extremely useful for the elaboration of a general theory of polymer solutions and more particularly for predicting solubility relations.

In a quite different direction, Williams, Landel, and Ferry[9,50] have recently shown that from the point of view of mechanical relaxation, and to a lesser degree of dielectric relaxation, the glass transition temperatures of solid amorphous polymers are corresponding temperatures. In other words by a suitable adjustment of parameters, taking this temperature as a reference temperature, all relaxation curves could be interpreted by a single equation. Although the validity of this relation may be questioned, in particular for dielectric relaxation when the dipoles are located in the side chains, it would be interesting to find out if an analogous equation could be put forward for polymer solutions, the corresponding temperatures being related to a precipitation point, Flory's θ or a similar temperature. It must be stressed that for dilute solutions, polymer-solvent interaction should be the determining factor for such a relation.

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SOME PHYSICAL ASPECTS OF GASEOUS CHEMICAL KINETICS

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CONTENTS

I. INTRODUCTION

The most simple chemical reactions are the homogeneous gaseous reactions, and when they involve simple enough molecular species, they should be described fairly well by some simple treatments familiar to all graduate students in physics and chemistry, namely the collision theory and the activated state method. This attitude is shared among most people who are more interested in the practical results of these methods than in the physical pictures which are involved. However, a critical inspection of the grounds of these methods shows some obscure points which could invalidate to some extent the treatments themselves.

As Fowler and Guggenheim[8] realized, the main difficulty with the theories of chemical kinetics lay in the so-called equilibrium hypothesis, on which the treatments are grounded. As a matter of fact, in both the collision and activated state approaches, one uses a statistical method which is typical of the equilibrium phenomena and not of a real nonequilibrium process like a chemical change. At that time the only support for this procedure was the real success of these treatments in describing most of the simplest reactions, an *a posteriori* evidence as was emphasized by Fowler and Guggenheim.

In recent years many theoretical attempts have been made to evaluate the influence of the nonequilibrium distribution, and some experimental work has also shown the weakness in the supposed evidence of the successes of the current treatments. The object of this paper is to review some recent theoretical and experimental work concerned with grounding the theory of chemical change on sounder physical bases.

II. A DISCUSSION ON THE COLLISION THEORY

The usual way to check the simple collision theory was to choose some *ad hoc* values of the energy of activation E and of the reaction diameter D, and to fit the experimental data by the Arrhenius equation, or similar equations which can be deduced by taking into account the internal degrees of freedom of the reacting molecules. However, it is doubtful if these values of E and D are real physical quantities or whether they are only adjusted parameters. To answer this point, a critique of these quantities has been done by this author and is referred to hereafter.[2–4]

As far as the collision diameter D is concerned, the general use is to take the reaction diameter D as the average kinetic diameter between the two reacting molecules, as deduced from transport phenomena determinations.[17] This choice has no sound basis, and some improvements can be made if one considers the influence of the intermolecular field. Such an analysis shows that, if the reaction needs an activation energy E, then one must use an impact diameter D,

$$D = D_0(E/kT_0)^{-1/n} \tag{1}$$

where D_0 is the kinetic diameter determined from transport experiments in the dilute gas at the temperature T_0, and n is the exponent of the repulsive part of the intermolecular field assumed to be $W = A/r^n$. The effective diameter will be then smaller than the kinetic one.

On the other hand, if for the reaction to take place, it is only necessary that the two molecules get close together without any extra energy (for example, the deactivation process of the unimolecular reactions, the reactions between alkaline metals and halogen molecules, as $Na+Cl_2$, etc.), then the reaction diameter can be defined from inspection of the trajectories of the relative motion under the attractive field. As a matter of fact, for collisions which are not along the line of the centers, one may describe the collision as a head-on collision under an effective potential which is the normal intermolecular potential corrected by the centrifugal term. This effective potential happens to show a positive maximum, which must be overcome if one wants to bring the two centers together; therefore if one wants the reaction to take place, the two colliding molecules must meet with an impact parameter depending on the relative kinetic energy. One can then define the "collision diameter" as the value of the maximum impact parameter averaged over the Maxwellian distribution. One then finds an effective collision diameter larger than the kinetic one, even as much as a factor of three or four, and furthermore this collision diameter will be temperature dependent.

However the quantity which enters into the reaction rate expressions is not simply such an impact diameter, but a kind of cross section for the process, giving the probability for the reaction to occur when the energy conditions are fulfilled. It is, therefore, convenient to write the effective reaction cross section as the product of the area, calculated by the impact diameter defined in the foregoing, times a probability factor α, sometimes also called the steric factor. This quantity α can, in principle, be calculated by the quantum mechanics of the collision of the two atoms, but in practice must be regarded as an unknown.

The other important quantity E, the energy of activation, must be also regarded as an unknown, since the quantum-mechanical calculations of it are only very rough approximations. This quantity enters as an exponential factor in the rate expressions and makes impossible any reliable check.

However there is a class of reactions for which E is a well defined and known quantity. These are the dissociation reactions of the diatomic molecules, where the activation energy is the energy of dissociation, which is known from spectroscopic and calorimetric data

$$A_2 = A + A \tag{2}$$

Reactions of this kind have not been studied so far experimentally, but their rate can be deduced from the opposite recombination process, which is known to be a three-body process

$$A+A+N=A_2+N \tag{3}$$

Suppose now we are at equilibrium, when association and dissociation compensate each other. We may then apply the detailed balancing principle and say that the dissociation process must be a bimolecular reaction of the second order.[4] From a knowledge of the equilibrium constant and of the experimental association rate, we may then infer the pseudoexperimental dissociation rate at equilibrium. It is rather fortunate that the association process does not require an activation energy, since in this case, its rate is the same out of equilibrium, where the experiments have been carried out, as it is at equilibrium, where the values are interesting. We then understand that the dissociation reactions of a diatomic molecule by a bimolecular process offer the two interesting possibilities:

(a) From a comparison of the real experimental rates out of equilibrium with the pseudoexperimental value at equilibrium, one may check experimentally the influence of the nonequilibrium distribution.

(b) The activation energy being known, from a comparison of the rates calculated by the collision theory using suitable molecular models with the pseudoexperimental ones, one may deduce the pseudoexperimental value of α.

So far the first of the preceding possibilities has not been exploited, because of lack of experimental data. However, the second one has offered to some extent a check of the collision theory.

This comparison to find pseudoexperimental values of α, can be made only for 4 elements, for 3 of which (hydrogen, bromine, and iodine) there are good experimental data. The calculations have been made for six molecular models, the applicability of which is increasing in the following way:

(I). The colliding molecules are supposed to behave as rigid spheres, with no internal degrees of freedom. This is the well-known approximation called "the crude collision theory."

(II). The above model is corrected by using Eq. 1 for the collision diameter. This correction will also be made in the following models.

(III). We may allow the dissociation energy also to be supplied from the internal degrees of freedom, by simple additive combination with the translational energy along the centers. This internal energy is supposed to behave classically as two quadratic terms (namely as two rotational or one vibrational degrees of freedom).

(IV). The internal energy contribution to the dissociation energy is now due to four quadratic terms (namely two rotational plus one vibrational degrees of freedom, all classically excited).

(V). The vibrational degree of freedom of model IV is no longer classically excited, but now behaves as a quantum excited harmonic oscillator.

(VI). The harmonic oscillator of model VI is replaced by the Morse oscillator.

For sake of briefness, the rate expressions for these models are not quoted here, and we will limit ourselves to discuss the resulting pseudoexperimental values of α, which are given in Table I. The theoretical value of α is not known, but a simple glance at Table I allows one to say that the crude collision theory (models I and II) is wrong by a factor as large as 10^2 to 10^3. One may further notice that model III, which is a poor one, is also wrong, α still being larger than one. But as the molecular model is improved, the values are more and more consistent among themselves, in spite of the great difference of the properties of the elements involved, suggesting that α must probably be a geometrical factor. It is also worth noting the important contribution of the rotation to the

TABLE I. α-Values for Different Molecular Models.[a]

	I	II	III	IV	V	VI
H_2	77.5	209	1.09	0.0128	0.228	0.203
N_2	77.5	232	7.30	0.0510	0.576	0.464
Br_2	79.0	188	2.13	0.0517	0.114	0.090
I_2	137.0	310	4.50	0.1560	0.246	0.186

[a] From G. Careri *Nuovo cimento* 7, 155 (1950).

dissociation of the diatomic molecule; as a matter of fact the dissociation by rotation is a very familiar process in molecular spectroscopy.* It is too bad that so far there are no other sources of information concerning the α value, in order to allow a complete test of the rate expression.

As a conclusion of this section we may say that we know for sure that the crude collision theory can be much poorer than we thought, but improvements of the molecular models may improve it considerably. However this is obviously difficult to do for complex systems, where the activated state method may be sometimes easier to apply.

III. AN EXPERIMENTAL TEST OF THE ACTIVATED STATE METHOD

The applications of the activated state method generally have dealt with molecular systems which were too complex to enable one to investigate, both theoretically and experimentally, the validity of the approximations in the theory. The ambitious attitude to provide an "absolute" method to calculate the reaction rate, which in principle is, of course, correct, has made the check still more difficult.

If the equilibrium hypothesis is assumed to be correct and classical mechanics applies to all degrees of freedom, the activated or transition state method for calculating the absolute rate of a chemical reaction with an activation energy would be rigorously valid.[10] The extent of the limitations imposed by quantum mechanics has been considered by Wigner and others,[12,13] with the conclusion that on the whole these limitations invalidate the method to a much smaller extent than could be presumed, and it is only in the considerations of the relative rates of reaction between

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* It must be mentioned that Rice[16] has postulated a different mechanism for the dissociation of a diatomic molecule. He assumes that only ordinary thermal collisions of molecules excited into extremely high vibrational states are responsible for the dissociation. The effect of the rotation is then only to increase the density of these excited states. We[4] instead believe that the probability of the high-energy collisions and of the excited rotational states is comparable with that of the high vibrational excited states, and that all these probabilities must be added with the proper weight.

isotopes of light elements and reactions at very low temperature that these effects may be important.

An attempt to check the activated state method from the experimental side, has been recently made by this author and his co-workers,[1] and will be referred to in the following.

The most simple homogeneous exchange gas reactions were considered, such as

$$H+D_2 = HD+D \tag{4}$$

$$D+H_2 = HD+H \tag{5}$$

which were first studied experimentally in 1935 by A. and L. Farkas[6] in the range 740—600° C, and, more recently, by van Meersche[18] in the range 600—450° C. The interest in these reactions lies in the simplicity of the reacting system, which together with the ortho-para conversions of H_2 and D_2, are more amenable to theoretical treatments than any other chemical reactions. As is well known, these reactions were used as the first test of the activated state method developed by Polany, Wigner, and Eyring. Among the theoretical papers in which the *a priori* calculation of the rate of these reactions has been attempted, we may recall the one by Hirschfelder, Eyring, and Topley,[11] where, with an assumed percentage of ionic terms, the calculated values of the reaction constant fit the experimental results within a factor of two at 1000° K.

To check the activated state method independently from the details of the potential energy of the system, Farkas and Wigner[7] used the experimental ortho-para hydrogen conversion values at high temperature to obtain the unknown constants of the activated complex. With these constants so determined, the ortho-para hydrogen conversion at low temperature and the $H_2—D_2$ exchange reaction data were calculated. The experimental values of the exchange reaction were fairly consistent with this treatment, but, for the low temperature conversion, this procedure gave values differing by more than a factor of three from the experimental ones of Geib and Harteck.[9] It is worth remarking that the lack of agreement was no longer now due to possible errors in constructing the potential surface, bût either to the transition method itself or to the experimental values.

For this reason it seemed important to the author and his co-workers to repeat the experiments using a mass spectrometer for the analysis of the mixtures instead of the thermal conductivity method previously used. As a matter of fact, it was found that a serious systematic source of error must have vitiated the previous experimental work, in that a slight permeation of air through the quartz walls of the reaction vessel occurred at the high temperatures, so that the small amount of oxygen affected the exchange rate. When this perturbing factor was eliminated by the help of a quartz jacket connected to high vacuum, a much better reproducibility and lower values for the rate constants were obtained (Fig. 1). Since the oxygen was affecting the velocity of the exchange reaction, leaving the order and the energy of activation practically constant, the reaction mechanism is the same in the various cases, and the influence of a wall contaminated with

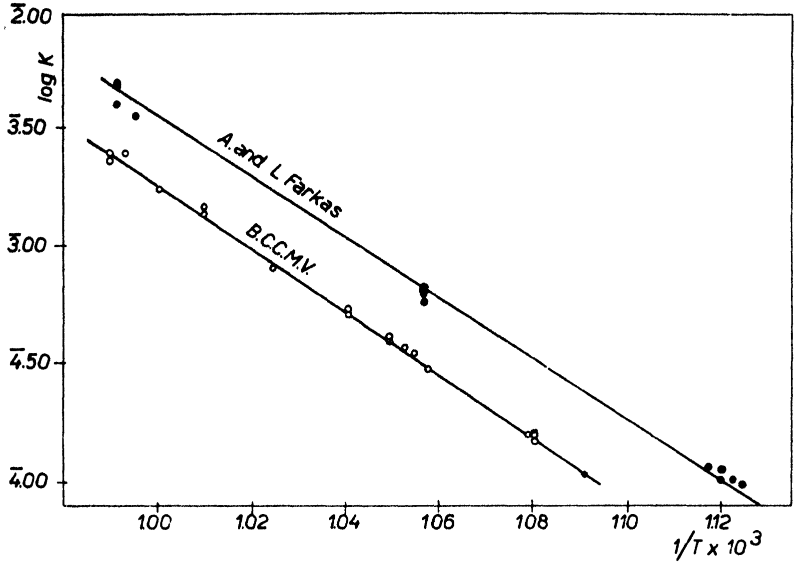

Fig. 1. The temperature dependence of the hydrogen-deuterium exchange. T is the absolute temperature, and K a quantity proportional to K_1K_2/K_1+K_2; K_1 and K_2 are the rate constants of Eqs. 3 and 4. (From Boato *et al.*, *J. Chem. Phys.* **24**, 783, 1956.)

air makes itself felt not through a heterogenous process of formation of HD molecules, but through an influence on the homogeneous reaction velocity. Actually, the factor which is modified by the presence of air is the stationary concentration of the free atoms, which was in the previous experiments larger than the equilibrium one. In the following it is not intended to refer to the details of the reaction mechanism and of the experimental technique of these measurements, but only to show how the validity of the activated state method has been verified.

The theoretical formula for the rate constant of the reactions for which the activated complex is linear and for which there is no change in the ortho-para ratio is given by

$$K = \gamma \frac{g_c}{g_a g_m} \left(\frac{M_a + M_m}{M_a M_m} \right)^{3/2} \frac{I_c \sigma_m}{I_m \sigma_c} \left(\frac{h}{2\pi} \right)^2 \left(\frac{2\pi}{kT} \right)^{1/2} \cdot e^{-Q/RT} \frac{N \sinh \beta \nu_m (1 + \frac{1}{6} \beta^2 \nu_t{}^2)}{4 (\sinh \beta \nu_D)^2 \sin h\, \beta \nu_s} \tag{6}$$

where γ is the transmission coefficient; g_c, g_a, and g_m are the numbers of electronic states of the activated complex of the atom and of the molecules; M_a and M_m are the masses of the colliding atoms and molecules; I_c and I_m are the moments of inertia of the complex and of the molecule; σ_m and σ_c are the symmetry numbers of the molecule and the complex; Q is the classical activation energy, $\beta = h/2kT$; ν_m is the vibration frequency of the molecule; ν_D is the deformational frequency of the complex; ν_s is the other stable frequency of the complex; and ν_t is the imaginary frequency.

The procedure adopted by Farkas and Wigner consists in determining from the experimental data at high temperature the values of Q, ν_s, and ν_D which are particularly dependent on the characteristics of the potential surface, and in calculating the values of the reaction rate constant at low temperature from Eq. 6 in which these quantities are now known. These values were then compared with the low-temperature experimental data of Geib and Harteck. If one applies this procedure to the new experimental results, the velocity constants given in Table II are obtained together with the observed values and with the theoretical reaction rates calculated by Hirschfelder, Eyring, and Topley.

For a comparison with the data of Geib and Harteck it is necessary to remember that their experimental conditions were such that in order to calculate the values of the velocity constant they had to admit two extreme hypotheses on the time spent by the hydrogen atoms in the reaction vessel. The real values of the velocity constants and activation energy must therefore lie between the ones calculated according to the two extreme hypotheses, which suppose a constant time of permanence (A) and a time varying between zero and infinity, respectively (B).

TABLE II. Rate Constants at 1000° K.[a]
(CC mole^{-1} sec^{-1} units × 10^{12})

		B.C.C.M.V. (Ref. 1)		H. E. & T. (Ref. 11)	F. & F. (Ref. 6)
Reaction		Obs.	Calc.		
H+H$_2$	H$_2$+H	1.1 [b]		1.5	2.2
D+D$_2$	D$_2$+D	0.57 [b]		0.76	1.1
D+H$_2$	HD+H	0.98	1.03	1.2	2.5
H+D$_2$	HD+D	0.61	0.67	0.74	1.2
H+HD	H$_2$+D	0.37	0.39	0.45	0.95
D+DH	D$_2$+H	0.40	0.44	0.50	0.79

[a] From Boato *et al.*, *J. Chem. Phys.* **24**, 783 (1956).

[b] The values of F. & F. divided by 2.

If one considers Table II and Fig. 1, one sees that the application of the semiempirical method proposed by Farkas and Wigner to these new experimental results brings the experimental velocity constants of Eqs. 3 and 4 to fit well with the calculated values (compare columns 1 and 2 of Table II). Furthermore, this method gives a fine agreement between the low-temperature measurements of Geib and Harteck and the extrapolated values (Fig. 2). Such an agreement is particularly significant in view of the large extrapolation interval ($\simeq$ 500°). If one compares also the experimental velocity constants at 1000° K with the theoretical values calculated by Hirschfelder, Eyring, and Topley, one sees that the agreement is rather good (columns 1 and 3 of Table II). The activation energy calculated by these authors is 8.60 kcal/mole as compared with the experimental value at low temperature of 7 7±0.4 kcal/mole. Therefore, the elimination of the catalyzing effect of air and the higher accuracy of the measurements have

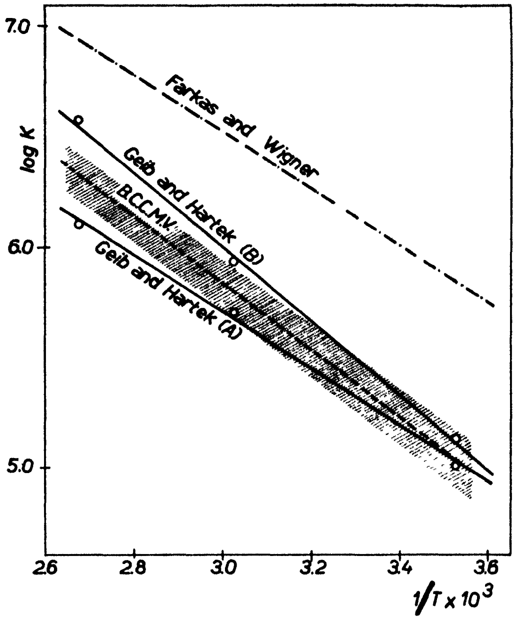

Fig. 2. Comparison of the extrapolated with the experimental values of the rate constants at low temperature. (From Boato *et al.*, *J. Chem. Phys.* **24**. 783, 1956.)

removed the inconsistency previously found between the experimental and the theoretical values of the velocity constants, and have given a satisfactory quantitative proof of the activated state method for this simple reacting system.

IV. SOME THEORETICAL INVESTIGATIONS OF THE EQUILIBRIUM HYPOTHESIS

The equilibrium hypothesis supports both the collision and the activated state methods. This hypothesis has been discussed theoretically on the basis of specific models, and the main results are quoted in the following.

The first important theoretical work on the subject seems to be by Kramers,[14] who tried to discuss the matter from the point of view of the activated state method by help of an ingenious model. A particle is considered, which moves in an external field of force and is also subjected to the irregular forces of a surrounding medium in temperature equilibrium, like a Brownian particle; the Brownian forces of the medium are the mechanism which strives to bring about temperature equilibrium.

The conditions are such that the particle is originally in a potential hole, but it may escape in the course of time by passing over a potential barrier. The analytical problem is to calculate the escape probability as a function of the temperature and of the viscosity of the medium, and then to compare the values so found with the ones of the activated state method. For sake of simplicity, Kramers studied only the one-dimensional model, and the calculation rests on the equation of diffusion obeyed by a density distribution of particles in the phase space. Definite results can be obtained in the limiting cases of small and large viscosity, and in both cases there is a close analogy with the Cristiansen treatment of chemical reactions as a diffusion problem. When the potential barrier corresponds to a rather smooth maximum, a reliable solution is obtained for any value of the viscosity, and, within a large range of values of the viscosity, the escape probability happens to be practically equal to that computed by the activated state method.

This result is quite general, but, unfortunately, it is of qualitative significance only. For instance, let us consider an homogeneous gas reaction. The Brownian forces will now represent the action of separate collisions between the molecules, and in order for the model to remain of some value, the change in the state of motion of the reactive molecule by the collision with another molecule must be small. Therefore the reacting molecule must be heavy, and the others colliding with it must be very light; for instance the dissociation of diatomic iodine by impact of helium atoms is a good example quoted by Kramers. But, in general, when the ratio of the masses is not small, the Kramers results are no more than qualitative.

The foregoing general conclusions of Kramers were first verified in a specific case by Eyring and Zwolinsky,[19] who took into account the quantized nature of the molecular levels in an elementary way. They compared the results of the exact integration of typical unimolecular kinetic equations to the results based on the assumption that equilibrium was maintained throughout the reaction. By making assumptions which are supposed to cover the extremes likely to be encountered, they found that the non-equilibrium rate may deviate by no more than 20 per cent from its equilibrium rate.

A more general but qualitative attempt was made soon after by Hulburt and Hirschfelder,[13] who treated a chemical reaction by the motion of a fluid in the configuration space of the reaction complex and derived the hydrodynamic equations for this compressible flow under a wide range of conditions out of equilibrium. They succeeded in showing that no change in the energy distribution can occur among the several degrees of freedom of a reaction complex before the activated state is reached, unless the complex suffers a collision with a third body. The rarity of this event, together with the low probability of collisional transfer of the vibration energy, support the application of the transition state method to processes not at equilibrium.

More quantitative results have been obtained by Prigogine[15] and co-workers, who adopted a kinetic method of approach and who treated this problem by the modern methods of the kinetic theory of gases. The integro-differential Maxwell-Boltzmann equation was extended to the case of inelastic collisions to get the velocity distribution functions f_γ, in terms of which the reaction rate may be written

$$K = \frac{1}{\nu_\gamma} \int \frac{df_\gamma}{dt} d\bar{c}_\gamma \tag{7}$$

$\bar{c}_\gamma$ is the velocity, and ν_γ the stochiometric coefficient of the γ-component. In the case of the simple reaction

$$A + A = B + C \tag{8}$$

if one neglects the $B-C$ collisions, as in the initial stage of the reaction, one can obtain the distribution function by integration of an integro-differential equation, in which the effect of the elastic collision is separated from the inelastic ones. If the probability of these latter collisions is assumed to depend on the relative impact velocity only, and then an activation energy ε is introduced as the energy for which this probability is close to 1, one can derive the following reaction rate

$$K = K_0\left(1 - \frac{1}{25}\frac{kT}{\varepsilon}\right) \tag{9}$$

where K_0 is the rate evaluated by the equilibrium assumption. From this expression one may see that the error introduced by using K instead of K_0 is usually quite small.

The same results have been obtained independently by Curtiss,[5] who used the same method of the kinetic theory to get an expression for the rate constant following the activated state picture, but without making the equilibrium assumption. The reaction rate is always given by the steady-state frequency of passage of points over the potential barrier, and is established in the following way. First an infinitely high potential barrier is placed at the potential maximum, and the steady-state distribution is set up. Then the potential barrier is removed, and the points in the configuration space begin to move over the barrier; the limiting frequency of passage at infinite time is taken as the reaction rate. In the case of a simple bimolecular reaction between two like molecules, it is shown that the rate constant can be written as the product of the well-known activated state method expression times a factor λ. The latter was evaluated for the two extreme cases in which either only the relative kinetic energy was available, or also all the internal energy of both molecules was effective in producing a reaction. Such an analysis shows that λ is almost the same in both the cases, and is close to 1 when the activation energy is large in comparison with kT. However when the activation energy is comparable with kT, large deviations can occur. This rather intuitive result was independently found by Prigogine and co-workers, as mentioned previously. It is also evident that a much larger deviation will occur if a positive heat of reaction is developed. The quantitative estimate of this deviation has also been made by Prigogine and co-workers.

V. CONCLUSIONS

We may say that the work which has been done after the war has somewhat changed our views about the physical grounds of chemical kinetics. We have learned that the old *a posteriori* experimental evidence of the collision theory has proved to be unsafe, being grounded upon ill-defined quantities, such as the diameter to be used in the rate expressions. This has been particulary evident for thermal dissociation reactions, where the knowledge of the activation energy makes possible a real test.

We have also seen that new experimental work on the hydrogen-deuterium exchange reaction has eliminated some previous discrepancies and has further confirmed the applicability of the activated state method. In the meantime, many theoretical attempts have been made to evaluate the influence of the non-equilibrium hypothesis on which that method is based. It is encouraging to see the generally optimistic results of these efforts, and we may conclude that we can now use with more confidence the familiar expressions of the rate processes.

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TRANSPORT PROCESSES IN LIQUIDS *

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CONTENTS

I. INTRODUCTION

Transport processes are concerned with the flow of mass, momentum, and energy in fluids in nonuniform states. For normal liquids near equilibrium, the transport rates are proportional to the gradients of concentration, mass velocity, and temperature; and the coefficients of diffusion, viscosity, and thermal conductivity are the respective proportionality constants. Various cross coefficients such as those of binary and thermal diffusion arise in reciprocal processes expressing the effects of combined gradients of concentration and temperature.

A primary aim of theoretical work in this field is to obtain the phenomenological transport coefficients in terms of molecular scale processes and in terms of molecular parameters such as the intermolecular pair potential energy. Most of the work prior to 1946 rested on rather crude pictures of the liquid state, and various arbitrary assumptions were made as to the nature of the molecular scale transport processes taking place. Born and Green[3, 20, 21] and

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Kirkwood and co-workers[22, 25, 27, 35, 36] have more recently presented molecular theories of transport processes in liquids making use of extensions of nonequilibrium statistical mechanics which were developed for the purpose. The assumed structure of the liquid state was quite general with the principal restriction that it be composed of spherical molecules. Some further simplifying assumptions were introduced at later stages in the treatments in order to render the mathematical derivations tractable.

Neither approach to the transport processes in liquids has been carried to final completion because of serious mathematical difficulties and considerable additional theoretical work is required before the problem can be regarded as essentially solved.

Before proceeding to the theoretical formulation, it is desirable to review briefly the characteristic features of transport processes in liquids from the experimental aspect. It is of immediate importance to note the radically different temperature coefficients of transport processes in gases and in liquids. For example, the viscosity coefficient of gases depends approximately on the square root of the absolute temperature,

$$\eta_{\text{gas}} \simeq AT^{1/2} \tag{1}$$

while that of liquids has an exponential dependence on the reciprocal of the absolute temperature,

$$\eta_{\text{liquid}} \simeq B \exp (C/T) \tag{2}$$

The temperature coefficient of the viscosity thus differs not only in magnitude but also in sign from that of gases.

The viscosity and the self-diffusion coefficient are functionally related through the Einstein-Stokes equation

$$D = kT/a\eta \tag{3}$$

where a is a length of the order of a molecular radius. The Einstein-Stokes equation is also approximately obeyed in the more complicated case of the binary-diffusion coefficient. Thus the temperature coefficient of the reciprocals of the self- and binary-diffusion coefficients are also of the form of Eq. 2. The exponential dependence of the viscosity and diffusion coefficients of liquids upon the temperature has been widely interpreted as implying that an activation energy is involved which is analogous to that of chemical reaction kinetics.[18]

The temperature dependence of the thermal conductivity of liquids is more complicated. At atmospheric pressure, the temperature coefficient of thermal conductivity of liquids, other than water, is negative. Bridgman[4] has shown, however, that the temperature coefficient changes sign at a pressure of around 3000 atm. The published data as to the magnitude of the temperature coefficient at atmospheric pressure are somewhat conflicting. Uhlir's[32] data for liquid argon in the range of 24 to 96 atm display a nearly linear negative dependence on the temperature T.

The elucidation of the temperature dependence of the transport coefficients of liquids is complicated by the fact that thermal expansion of the liquid takes place together with the rise in temperature, so that the pure temperature and the volumetric dependence of the transport processes are combined in isobaric observations of the temperature dependence.[1,7] Thus we have

$$\left(\frac{\partial \ln \eta}{\partial T}\right)_P = \left(\frac{\partial \ln \eta}{\partial T}\right)_V + \left(\frac{\partial \ln \eta}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \tag{4}$$

Unfortunately, there are relatively few data for transport coefficients measured under high pressure from which the coefficient $(\partial \ln \eta/\partial T)_V$ can be calculated. Table I compares the isobaric and isochoric temperature coefficients of viscosity and binary diffusion for a number of liquids. It will be seen that the isochoric temperature coefficients are considerably smaller than those observed at constant pressure. The data of Jobling and Lawrence[23] indicate that $(\partial \ln \eta/\partial T)_V$ is more nearly proportional to $(1/T^2)$ than is $(\partial \ln \eta/\partial T)_P$. This observation is confirmed in an analysis of viscosity data for a number of hydrocarbons made by Simha, Eirich, and Ullmann.[31] The small number of substances studied and the shortness of the temperature range covered, however, do not enable us to assume a logarithmic dependence of the isochoric viscosity as a generally valid relationship.

Table I illustrates the large variation of the transport coefficients, and their temperature coefficients, for liquids of comparable molecular weight. These variations are due to molecular shape and flexibility, as well as to dipole moment and hydrogen bonding. It is, of course, the final task of the fundamental theory of transport processes to take detailed account of these molecular complexities. However, any extended consideration of them would be premature before the simpler problem of molecules with spherical symmetry, such as argon, has been more completely resolved than is at present the case.

TABLE I. Viscosity Coefficients and their Isobaric and Isochoric Temperature Coefficients for a Number of Common Liquids at 30° C. and 1 atm. (The viscosity-pressure coefficient data are from Bridgman.[4])

Substance	Molecular weight	Viscosity coeff , cp.	$(\partial \ln \eta/\partial T)_P \times 10^2/°C$	$(\partial \ln \eta/\partial T)_V \times 10^2/°C$
Carbon tetrachloride	153.8	0.843	−1.39	−0.521
Chloroform	119.4	0.514	−1.09	−0.50
Benzene	78.1	0.564	−1.50	−0.534
n-Octane	114.2	0.483	−1.12	−0.41
Methanol	32.0	0.510	−1.29	−1.03
Mercury	200.6	1.516	−0 28	−0.18

The present review of the theory of transport processes in liquids is confined to considerations of the primary molecular mechanism involved in these processes. Thus the questions of irreversibility of nonequilibrium systems in general and of the reciprocal relations among the transport coefficients in coupled processes are not developed. Also in the interest of brevity, the special problems of binary and thermal diffusion are not dealt with in detail. This being a review of theory, there is no attempt to present the numerous experimental studies of transport processes in various liquid systems in the past decade.

Several good reviews of the theory of transport processes have been published previously to which the interested reader is referred.[2, 14, 19, 29] The literature concerning modern theories of the structure of the liquid state upon which the various molecular theories of transport processes are based is quite extensive. It is, however, comprehensively reviewed in the recent treatise of Hirschfelder, Curtiss, and Bird.[19]

II. STATISTICAL-MECHANICAL BACKGROUND

Viscosity, diffusion, and thermal conduction in liquids involve the dynamical and statistical properties of a large number of interdependent molecules, each of which exerts a force on the others. Discussion is here confined to the special case in which the force between two molecules is derivable from a potential which is a function of intermolecular distance alone. This corresponds to the case of monatomic liquids. It is further assumed that the force acting on any molecule is the sum of the gradients of separate pair potentials of its $N-1$ neighbors. Thus the force acting on the ith molecule can be written as the gradient of the total potential Φ

$$\frac{\partial \Phi}{\partial \mathbf{r}_i} = \sum_{\substack{j=1 \\ \neq i}}^{N} \frac{\partial \varphi_{ij}}{\partial \mathbf{r}_i} \tag{5}$$

where $\varphi_{ij} = \varphi(|\mathbf{r}_j - \mathbf{r}_i|)$ is the pair potential, $\mathbf{r}_i$ and $\mathbf{r}_j$ being vectors denoting the positions of the ith and jth molecules. The notation of Chapman and Cowling[6] is used throughout this paper. The vector derivative $(\partial f/\partial \mathbf{x})$ denotes the gradient in $\mathbf{x}$ of the scalar function f. The detailed behavior of the system may be represented by the motion of a point in a hyperspace of $6N$ coordinates, there being six coordinates for the position and velocity of each of the N molecules. The average behavior of the system may be deduced from the behavior of a large but finite number of identical systems, each of which may be represented by a point in the $6N$ hyperspace. Let us now consider the time dependence of the density $f^{(N)}$ of representative points in the volume element $\prod_i^N d\mathbf{c}_i d\mathbf{r}_i$ located at $(\{\mathbf{r}_i\}, \{\mathbf{c}_i\})$ where $\{\mathbf{r}_i\}$ and $\{\mathbf{c}_i\}$ denote the set of the N position and velocity vectors. The time derivative of the density is simply equal to the net flux of points into the fixed volume element and is given by the Liouville equation as

$$\begin{gathered} \frac{\partial f^{(N)}}{\partial t} + \sum_{i=1}^{N} \frac{\partial f^{(N)}}{\partial \mathbf{c}_i} \cdot \frac{d\mathbf{c}_i}{dt} + \sum_{i=1}^{N} \frac{\partial f^{(N)}}{\partial \mathbf{r}_i} \cdot \frac{d\mathbf{r}_i}{dt} = 0 \\ \frac{\partial f^{(N)}}{\partial t} - \frac{1}{m} \sum_{i=1}^{N} \frac{\partial f^{(N)}}{\partial \mathbf{c}_i} \cdot \frac{\partial \Phi}{\partial \mathbf{r}_i} + \sum_{i=1}^{N} \frac{\partial f^{(N)}}{\partial \mathbf{r}_i} \cdot \mathbf{c}_i = 0 \end{gathered} \tag{6}$$

As will be later developed, the transport processes may be expressed in terms of the behavior of single molecules and molecular pairs. Hence a continuity equation analogous to Eq. 6 is required for a subset of a small number of molecules, say h, in the system of N molecules. The density $f^{(h)}$ of representative points in the subspace of the positions and velocities of the molecules 1 to h may be formally obtained from the density $f^{(N)}$ as follows:

$$f^{(h)}(\{\mathbf{c}_j\}, \{\mathbf{r}_j\}; t) = [(N-h)!]^{-1} \int \ldots \int f^{(N)}(\{\mathbf{c}_i\}, \{\mathbf{r}_i\}; t) \prod_{k=h+1}^{N} d\mathbf{c}_k d\mathbf{r}_k \quad (7)$$

The normalization factor $[(N-h)!]^{-1}$ is that used by Born and Green[3] and takes account of the indistinguishability of the molecules h to N. Kirkwood[25] defines the density $f^{(N)}$ in a somewhat different way which permits the use of unity as the normalizing factor.

Equation 6 is integrated over all velocities and positions of the $N-h$ molecules with repeated use of Green's theorem. The latter is permissible because of the restriction of the system to the volume V and the absence of molecules with infinite velocities. We then obtain

$$\begin{aligned} \frac{\partial f^{(h)}}{\partial t} - \frac{1}{m} \sum_{j=1}^{h} \frac{\partial f^{(h)}}{\partial \mathbf{c}_j} \cdot \sum_{\substack{k=1 \\ \neq j}}^{h} \frac{\partial \varphi_{jk}}{\partial \mathbf{r}_j} + \sum_{j=1}^{h} \frac{\partial f^{(h)}}{\partial \mathbf{r}_j} \cdot \mathbf{c}_j \\ = \frac{1}{m(N-h)!} \sum_{j=1}^{h} \frac{\partial}{\partial \mathbf{c}_j} \cdot \int \ldots \int \sum_{k=h+1}^{N} \frac{\partial \varphi_{jk}}{\partial \mathbf{r}_j} f^{(N)} \prod_{i=h+1}^{N} d\mathbf{c}_i d\mathbf{r}_i \end{aligned} \quad (8)$$

The $(N-h)$-fold integration is unity except for $i = k$ and, remembering the indistinguishability of the molecules $h+1$ to N, we may write for the simplest case of $h = 1$:

$$\begin{aligned} \frac{\partial f^{(1)}}{\partial t} + \frac{\partial f^{(1)}}{\partial \mathbf{r}_1} \cdot \mathbf{c}_1 &= \frac{(N-2)!}{m(N-1)!} \frac{\partial}{\partial \mathbf{c}_1} \cdot \sum_{k=2}^{N} \int \int \frac{\partial \varphi_{1k}}{\partial \mathbf{r}_1} f^{(2)} d\mathbf{c}_k d\mathbf{r}_k \\ &= \frac{1}{m} \frac{\partial}{\partial \mathbf{c}_1} \cdot f^{(1)} \int \int \frac{\partial \varphi_{12}}{\partial \mathbf{r}_1} f^{(2/1)} d\mathbf{c}_2 d\mathbf{r}_2 \end{aligned} \quad (9)$$

where

$$f^{(2/1)} = f^{(2)}(\mathbf{c}_2, \mathbf{r}_2, \mathbf{c}_1, \mathbf{r}_1)/f^{(1)}(\mathbf{c}_1, \mathbf{r}_1) \quad (10)$$

denotes the relative pair probability density conditional upon the first molecule being at the point $(\mathbf{c}_1, \mathbf{r}_1)$.

In principle, Eq. 8 might be solved to yield the densities $f^{(1)}$ and $f^{(2)}$, corresponding to the various nonuniform states of the system such as those involved in steady-state transport processes. However, there is no requirement implicit in this equation which assures that the average forces acting will correspond to a drift of the system toward thermal equilibrium instead of a way from it, and no progress has been made in solving them in the absence of additional assumptions.

III. BROWNIAN MOTION THEORY

The most successful line of attack is due to Kirkwood[25] and eliminates detailed consideration of the other molecules of the system by the introduction of concepts taken from Brownian motion theory. The central idea of Kirkwood's theory is that the average force exerted by $N-h$ molecules on a subgroup of h molecules will be analogous to the average frictional force on a particle of colloid dimensions undergoing Brownian motion. Let us briefly consider the latter situation. The force $\mathbf{F}(t)$ acting on the colloid particle is a function of the positions of the neighboring molecules and fluctuates rapidly with these changing positions. The positions of the neighbors are influenced by the velocity $\mathbf{c}$ of the colloid particle so that the force $\mathbf{F}(t)$ is biased by the peculiar velocity $(\mathbf{c}-\mathbf{c}_0) = \mathbf{C}$, $\mathbf{c}_0$ being the local mass velocity of the liquid. The acceleration of the particle is customarily resolved into two parts:

$$\begin{aligned} \mathbf{F}(t)/m &= \mathbf{A}(t)-\zeta\mathbf{C} \\ \dot{\mathbf{c}}+\zeta\mathbf{C} &= \mathbf{A}(t) \end{aligned} \tag{11}$$

where $\zeta\mathbf{C}$ is a systematic frictional acceleration which is assumed to be proportional to the peculiar velocity, and the fluctuating acceleration $\mathbf{A}(t)$ is purely random. Equation 11 is the well-known equation of Brownian motion.

Let us now introduce a time τ long enough so that $\mathbf{A}(t)$ undergoes a substantial number of fluctuations but short enough so that the velocity $\mathbf{C}$ is almost unchanged. It is clear that a time τ can always be selected which is much shorter than the time required for observation of any macroscopic property of the colloid particle because of the extreme rapidity of molecular motion. Under these conditions Eq. 11 can be integrated over the time τ with $\mathbf{C}$ treated as constant in the integration. We then have

$$\varDelta\mathbf{C}+\zeta\mathbf{C}\tau = \mathbf{B}(\tau) \tag{12}$$

where

$$\mathbf{B}(\tau) = \int_t^{t+\tau}\mathbf{A}(s)\,ds \tag{13}$$

Now the fluctuations of $\mathbf{A}(t)$ may be assumed to be extremely irregular, so that $\mathbf{B}(\tau)$ is likewise a stochastic variable. Hence we may appropriately enquire as to the probability of occurrence of a given $\mathbf{B}(\tau)$ at t. Chandrasekhar[5] has shown that, if the probability distribution of $\mathbf{B}$ is given by

$$w(\mathbf{B}) = \left(\frac{m}{4\pi\zeta kT\tau}\right)^{3/2}\exp\left(-\frac{m\mathbf{B}^2}{4\zeta kT\tau}\right) \tag{14}$$

then the velocity $\mathbf{C}$ will tend to the equilibrium Maxwellian distribution after the lapse of sufficient time. The importance of Eq. 14 is that it demonstrates that the colloid particle executes a random walk in velocity space which is analogous to its random walk in physical space which obeys an analogous distribution function.

We now have a stochastic "equation of motion" for the colloid particle which will also govern the behavior of the phase density function f in time. If the probability of the particle being at $(\mathbf{C}-\varDelta\mathbf{C}, \mathbf{r})$ at t is $f(\mathbf{C}-\varDelta\mathbf{C}, \mathbf{r}; t)$, then its probability of being at $(\mathbf{C}, \mathbf{r}+\mathbf{C}\tau)$ at $t+\tau$ is

$$f(\mathbf{C}, \mathbf{r}+\mathbf{C}\tau; t+\tau) = \int f(\mathbf{C}-\varDelta\mathbf{C}, \mathbf{r}; t)w(\mathbf{C}-\varDelta\mathbf{C}, \mathbf{r}; \varDelta\mathbf{C})d(\varDelta\mathbf{C}) \tag{15}$$

where w is the probability of the transition $(\mathbf{C}-\varDelta\mathbf{C}, \mathbf{r})$ to $(\mathbf{C}, \mathbf{r}+\mathbf{C}\tau)$ occurring in the time τ. According to the starting postulates $\varDelta\mathbf{C}$ is small compared to $\mathbf{C}$, and the time τ is sufficiently short so that terms of order τ^2 and higher may be neglected. Expansion of both sides of Eq. 15 then yields

$$\begin{aligned} &f(\mathbf{C}, \mathbf{r}; t)+\frac{\partial f}{\partial t}\tau+\frac{\partial f}{\partial \mathbf{r}}\cdot\mathbf{C}\tau+\ldots \\ &=\int\left\{f(\mathbf{C}, \mathbf{r}; t)+\frac{\partial f}{\partial \mathbf{C}}\cdot\varDelta\mathbf{C}+\frac{1}{2}\frac{\partial^2 f}{\partial\mathbf{C}\partial\mathbf{C}}:\varDelta\mathbf{C}\varDelta\mathbf{C}+\ldots\right\}w\,d(\varDelta\mathbf{C}) \end{aligned} \tag{16}$$

where $\frac{1}{2}(\partial^2 f/\partial\mathbf{C}\partial\mathbf{C}):\Delta\mathbf{C}\Delta\mathbf{C} = \frac{1}{2}\sum_j^3\sum_i^3(\partial^2 f/\partial C_i\partial C_j)\Delta C_i\Delta C_j$, the subscripts indicating the space components of the velocity, and w is given in terms of $\mathbf{C}$ and $\Delta\mathbf{C}$ by Eqs. 12 and 14. Upon carrying out the indicated integration with respect to $\Delta\mathbf{C}$, it is noted that

$$\int \Delta\mathbf{C} w d(\Delta\mathbf{C}) = \zeta\mathbf{C}\tau \tag{17}$$

$$\left.\begin{aligned}\int (\Delta\mathbf{C})^2 w d(\Delta\mathbf{C}) &= \frac{2\zeta kT}{m}\tau \\ \int \Delta C_j \Delta C_i w d(\Delta\mathbf{C}) &= 0(\tau^2)\end{aligned}\right. \tag{18}$$

with Eq. 15 becoming

$$\frac{\partial\bar{f}}{\partial t} + \frac{\partial\bar{f}}{\partial\mathbf{r}}\cdot\mathbf{c} = \zeta\frac{\partial}{\partial\mathbf{c}}\cdot[\bar{f}(\mathbf{c}-\mathbf{c}_0)] + \frac{\zeta kT}{m}\frac{\partial^2}{\partial\mathbf{c}^2}\bar{f} \tag{19}$$

The phase density is now denoted by $\bar{f}$, the bar being added in recognition of the fact that Eq. 19 describes a time-smoothed density rather than the behavior of the instantaneous density of the particle subject to the fluctuations of the acceleration $\mathbf{A}(t)$. The smoothing time τ must be properly chosen in order that two assumptions in this analysis be fulfilled. It must be short enough so that the velocity of the particle does not change appreciably so that the indicated simple integration of Eq. 11 is possible. At the same time it must be long enough so that the accelerations $\mathbf{A}(t)$ and $\mathbf{A}(t+\tau)$ are not correlated, a prerequisite for the applicability of Eq. 14.

IV. BROWNIAN MOTION TREATMENT OF TRANSPORT PROCESSES

In extending the Brownian motion theory of colloids to the transport processes of liquids, it is desired to construct a continuity equation paralleling Eq. 19 of Chandrasekhar, but with the intermolecular forces introduced explicitly. For simplicity we will here deal with the case of a subset consisting of a single molecule with no external forces. The generalization of the treatment to subsets of larger numbers of molecules follows without essential difficulty. Equation 8 is first averaged over the smoothing time τ:

$$\frac{\partial \bar{f}^{(1)}}{\partial t}+\frac{\partial \bar{f}^{(1)}}{\partial \mathbf{r}_1}\cdot \mathbf{c}_1=\frac{1}{m}\frac{\partial}{\partial \mathbf{c}_1}\cdot \mathbf{\Omega}_1 \tag{20}$$

where

$$\bar{f}^{(1)}(\mathbf{c}_1, \mathbf{r}_1; t)=\frac{1}{\tau}\int_0^{\tau} f^{(1)}(\mathbf{c}_1, \mathbf{r}_1; t+s)\,\mathrm{d}s \tag{21}$$

and

$$\mathbf{\Omega}_1=-\int\ldots\int\frac{1}{\tau}\int_0^{\tau}\mathbf{F}_1(t+s)\,f^{(N)}(\{\mathbf{c}_i\}, \{\mathbf{r}_i\}; t+s)\,\mathrm{d}s\prod_{i=2}^{N}\mathrm{d}\mathbf{c}_i\,\mathrm{d}\mathbf{r}_i \tag{22}$$

The force $\mathbf{F}_1$ is assumed to be derivable from a potential such as that given by Eq. 5 and has only indirect dependence on the time. The time dependence of the integrand of Eq. 22 is obtained by Taylor's series expansions which will here be carried out in a somewhat more elementary manner than in the original presentation of Kirkwood. However, the assumptions introduced and the final results are the same.

If the N molecules have the velocities $\{\mathbf{c}'_i\}$ and positions $\{\mathbf{r}'_i\}$ at t and are carried into the velocities $\{\mathbf{c}_i\}$ and positions $\{\mathbf{r}_i\}$ at $t+s$ by the deterministic mechanics of the system, the probability of these events must be the same, so that

$$\begin{aligned} f^{(N)}(\{\mathbf{c}_i\}, \{\mathbf{r}_i\}; t+s) &= f^{(N)}(\{\mathbf{c}_i'\}, \{\mathbf{r}_i'\}; t) \\ &= f^{(N/1)}(\{\mathbf{c}'_j\}, \{\mathbf{r}'_j\}/\mathbf{c}'_1, \mathbf{r}'_1; t)f^{(1)}(\mathbf{c}'_1, \mathbf{r}'_1; t) \end{aligned} \tag{23}$$

where $f^{(N/1)}$ is the probability density of the velocities $\{\mathbf{c}'_j\}$ and positions $\{\mathbf{r}'_j\}$ subject to the first molecule being at $(\mathbf{c}'_1, \mathbf{r}'_1)$. It is assumed that the environment of the first molecule is close enough to equilibrium so that $f^{(N/1)}$ may be approximated by its equilibrium value

$$\begin{aligned} {}^0f^{(N/1)}(t) &= {}^0f^{(N)}/{}^0f^{(1)}(t) \\ &= {}^0f^{(N)}\Big/\left\{\left(\frac{m}{2\pi kT}\right)^{3/2} n_1 \exp\left[-\frac{1}{kT}\left(\tfrac{1}{2}m(\mathbf{c}'_1-\mathbf{c}'_{01})^2+\Phi_1(\mathbf{r}'_1)\right)\right]\right\} \end{aligned} \tag{24}$$

where $\Phi_1(\mathbf{r}'_1)$ is the potential of the mean force between the molecule at $\mathbf{r}'_1$ and the other molecules of the system, and $\mathbf{c}'_{01}$ is the mass velocity of the liquid at $\mathbf{r}'_1$. The conditional density

${}^0f^{(N/1)}$ is an implicit function of the time because of the time dependence of $\mathbf{c}'_1$ and $\mathbf{r}'_1$.

Expansion of Eq. 24 in Taylor's series about the values of $\mathbf{c}_1$ and $\mathbf{r}_1$ at the time $t+s$ gives

$$\begin{aligned}{}^0f^{(N/1)}(t) = {}^0f^{(N/1)}(t+s)\Big\{&1-\Delta\mathbf{c}_1\cdot\frac{m}{kT}(\mathbf{c}_1-\mathbf{c}_{01})\\ &+\Delta\mathbf{c}_1\Delta\mathbf{c}_1 : \left[\frac{1}{2}\left(\frac{m}{kT}\right)^2(\mathbf{c}_1-\mathbf{c}_{01})(\mathbf{c}_1-\mathbf{c}_{01})+\frac{m}{kT}\mathsf{U}\right]+\dots\\ &-\Delta\mathbf{r}_1\cdot\left[\frac{1}{kT}\frac{\partial\Phi_1}{\partial\mathbf{r}_1}-\frac{m}{kT}(\mathbf{c}_1-\mathbf{c}_{01})\cdot\frac{\partial\mathbf{c}_{01}}{\partial\mathbf{r}_1}\right]+\dots\Big\}\end{aligned} \tag{25}$$

where the negative signs have been introduced by defining the differences as follows

$$\Delta\mathbf{r}_1(s) = \mathbf{r}_1-\mathbf{r}'_1 = \mathbf{c}_1 s \tag{26}$$

$$\Delta\mathbf{c}_1(s) = \mathbf{c}_1-\mathbf{c}'_1 = \frac{1}{m}\int_0^s \mathbf{F}_1(t+s')ds' \tag{27}$$

Terms of order higher than second in $\Delta\mathbf{c}_1$ and higher than first in $\Delta\mathbf{r}_1$ have been dropped. In the subsequent ensemble averaging process, the lower-order terms are proportional to τ by Eqs. 17, 18, and 26 while it can be shown that the neglected higher-order terms are proportional to τ^2 and higher powers.

The singlet probability density is not assumed to be the equilibrium one; it may be an explicit function of the time. It is expanded over the small region of phase space $\Delta\mathbf{c}_1$, $\Delta\mathbf{r}_1$, with t constant,

$$\begin{aligned}f^{(1)}(\mathbf{c}'_1, \mathbf{r}_1'; t) = f^{(1)}(\mathbf{c}_1, \mathbf{r}_1; t)\Big\{&1-\Delta\mathbf{c}_1\cdot\frac{\partial \ln f^{(1)}}{\partial\mathbf{c}_1}\\ &+\tfrac{1}{2}\Delta\mathbf{c}_1\Delta\mathbf{c}_1 : \frac{\partial}{\partial\mathbf{c}_1}\frac{\partial}{\partial\mathbf{c}_1}\ln f^{(1)} - \dots - \Delta\mathbf{r}_1\frac{\partial \ln f^{(1)}}{\partial\mathbf{r}_1}+\dots\Big\}\end{aligned} \tag{28}$$

When the Eqs. 25 and 28 are substituted into Eq. 22, the integration over the time interval s may now be carried out in principle. The subsequent integration over the ensemble of $N-1$ molecules enables the application of Eqs. 17 and 18 with neglect of higher-order terms. The force $\mathbf{\Omega}_1$ may be written with these terms dropped:

$$\begin{aligned}\boldsymbol{\Omega}_1 &= \frac{f^{(1)}(\mathbf{c}_1, \mathbf{r}_1; t)}{\tau} \int \cdots \int\int_0^\tau \mathbf{F}_1(t+s)\, {}^0f^{(N/1)} \Bigg\{ -1 \\ &\quad + \left[\frac{(\mathbf{c}_1 - \mathbf{c}_{01})}{kT} + \frac{\partial \ln f^{(1)}}{m \partial \mathbf{c}_1} \right] \cdot \int_0^s \mathbf{F}_1(t+s')\, ds' \Bigg\} ds \prod_{j=2}^N d\mathbf{c}_j\, d\mathbf{r}_j \qquad (29) \\ &= -\langle \mathbf{F}_1 \rangle^0 f^{(1)}(\mathbf{c}_1, \mathbf{r}_1; t) + \boldsymbol{\zeta} \cdot \left[(\mathbf{c}_1 - \mathbf{c}_{01}) + \frac{kT}{m} \frac{\partial}{\partial \mathbf{c}_1} \right] f^{(1)}(\mathbf{c}_1, \mathbf{r}_1; t)\end{aligned}$$

where

$$\langle \mathbf{F}_1 \rangle^0 = \frac{1}{\tau} \int_0^\tau \int \cdots \int \mathbf{F}_1(t+s)\, {}^0f^{(N/1)} \prod_{j=2}^N d\mathbf{c}_j\, d\mathbf{r}_j\, ds \qquad (30)$$

Under equilibrium conditions, $\langle \mathbf{F}_1 \rangle^0 = 0$ and this term can be dropped under the assumptions which have been introduced concerning the environment of the first molecule. The friction tensor is given by

$$\boldsymbol{\zeta} = \frac{1}{kT\tau} \int_0^\tau \int_0^s \int \cdots \int \mathbf{F}_1(t+s) \mathbf{F}_1(t+s')\, {}^0f^{(N/1)} \prod_{j=2}^N d\mathbf{c}_j\, d\mathbf{r}_j\, ds'\, ds \qquad (31)$$

As the liquid is assumed to be isotropic,

$$\boldsymbol{\zeta} = \zeta \mathsf{U} \qquad (32)$$

where the scalar frictional coefficient is given by

$$\zeta = \frac{1}{3kT\tau} \int_0^\tau \int_0^s \int \cdots \int \mathbf{F}_1(t+s) \cdot \mathbf{F}_1(t+s')\, {}^0f^{(N/1)} \prod_{j=2}^N d\mathbf{c}_j\, d\mathbf{r}_j\, ds'\, ds \qquad (33)$$

Upon inserting these last equations into Eq. 20, the continuity equation becomes formally identical in form with Eq. 19 obtained by Chandrasekhar. However, it differs in that an expression for ζ has been obtained which is explicit in the intermolecular forces in contrast to the older Brownian motion theory in which ζ is a phenomenological constant only.

The generalization of Eq. 19 to the behavior of a molecular pair in phase space in a near-equilibrium state may be developed by the same methods and yields

$$\begin{aligned}\frac{\partial f^{(2)}}{\partial t} + \frac{\partial f^{(2)}}{\partial \mathbf{r}_1} \cdot \mathbf{c}_1 + \frac{\partial f^{(2)}}{\partial \mathbf{r}_2} \cdot \mathbf{c}_2 &= \frac{1}{m} \frac{\partial}{\partial \mathbf{c}_1} \cdot \boldsymbol{\zeta}_1 \cdot \left[(\mathbf{c}_1 - \mathbf{c}_{01}) + \frac{kT}{m} \frac{\partial}{\partial \mathbf{c}_1} \right] f^{(2)} \\ &\quad + \frac{1}{m} \frac{\partial}{\partial \mathbf{c}_2} \cdot \boldsymbol{\zeta}_2 \cdot \left[(\mathbf{c}_2 - \mathbf{c}_{02}) + \frac{kT}{m} \frac{\partial}{\partial \mathbf{c}_2} \right] f^{(2)}\end{aligned} \qquad (34)$$

where now there are two frictional tensors $\boldsymbol{\zeta}_1$ and $\boldsymbol{\zeta}_2$. Kirkwood, Buff, and Green[27] set both of these equal to $\zeta\mathsf{U}$ as in the singlet case. Eisenschitz[14] raises some question as to the validity of this identification. It will later appear that the coordinate of the pair which is significant in transport problems is that of relative motion of the pair rather than the independent motions with respect to inertial coordinates. The friction tensors for the two types of motion may be quite different from each other. The degree of approximation involved in making the pair friction tensors proportional to the unit tensor cannot be easily ascertained.

In using Eqs. 19 and 34 as starting points for the development of the theory of transport processes, several tasks remain. The first and perhaps simplest is to develop expressions for the transport coefficients in terms of the single and pair densities $f^{(1)}$ and $f^{(2)}$. Next the continuity equations must be solved to give explicit expressions for the densities when the system is perturbed from its equilibrium state by the transport process under consideration. Finally, it is required to obtain the frictional coefficient ζ in terms of the intermolecular potential energy function according to Eq. 33.

The transport coefficients have been obtained by Green[20] and by Irving and Kirkwood[22] in terms of the molecular densities and intermolecular potentials by methods which introduce no assumptions beyond those already discussed herein. A review of the derivation is presented in U.S. Air Force Note No. 56—255, Part 2.* As this aspect of the liquid transport processes is completely solved, the present discussion will be confined to a brief exposition of the transport coefficients.

The viscous properties of a liquid are defined in relation to the rate of distortion and dilatation of a local region R in response to stresses applied at the surface S which encloses it. In the analysis, we consider an element δS of the surface and construct a unit normal vector $\mathbf{n}$ directed outwardly from the surface. The applied stress can then be resolved into components tending to stretch the vector and components tending to rotate it. The force $\mathbf{F}$ per unit area can then be represented in terms of a tensor $\mathsf{P}(\mathbf{r})$ operating

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* Astia Document No. AD 110471, on public sale.

on the vector $\mathbf{n}$:

$$\mathbf{F}\delta S = \mathsf{P}(\mathbf{r}) \cdot \mathbf{n}\delta S \tag{35}$$

As the liquid is assumed to be isotropic, the tensor P is symmetric. The rate of shear tensor is also nondivergent, with the sum of its diagonal elements equal to zero.

It is customary to convert the nondivergent rate of shear tensor $(\partial\mathbf{c}_0/\partial\mathbf{r})^{\neq\circ}$ into the symmetric rate of strain tensor $(\partial\mathbf{c}_0/\partial\mathbf{r})^{\neq}$ by adding the sum of the diagonal terms thus

$$2\eta(\partial\mathbf{c}_0/\partial\mathbf{r})^{\neq} = 2\eta(\partial\mathbf{c}_0/\partial\mathbf{r})^{\neq\circ} + \tfrac{2}{3}\eta\frac{\partial}{\partial\mathbf{r}} \cdot \mathbf{c}_0\mathsf{U} \tag{36}$$

The factor 1/3 arises because $(\partial/\partial\mathbf{r}) \cdot \mathbf{c}_0$ is the scalar sum of the diagonal elements.

The macroscopic motion of the liquid at the point $\mathbf{r}$ can be identified with the mean molecular velocity $\mathbf{c}_0(\mathbf{r})$ at the given point. The components of the dilatation and distortion at $\mathbf{r}$ then are the space derivatives of $\mathbf{c}_0$. In the case of the Newtonian liquids, to which the present discussion is confined, the elements of the pressure tensor are proportional to the components of the rate of shear plus contributions from the hydrostatic pressure and the rate of dilatation. Thus we have

$$\mathsf{P} = \left(p - \phi\frac{\partial}{\partial\mathbf{r}} \cdot \mathbf{c}_0\right)\mathsf{U} - 2\eta(\partial\mathbf{c}_0/\partial\mathbf{r})^{\neq\circ} \tag{37}$$

where p is the hydrostatic pressure, U the unit tensor, $(\partial/\partial\mathbf{r}) \cdot \mathbf{c}_0$ the rate of dilatation, ϕ the volume viscosity, η the shear viscosity, and $(\partial\mathbf{c}_0/\partial\mathbf{r})^{\neq\circ}$ the nondivergent rate of pure shear tensor. The pressure tensor can then be written in the more usual form

$$\mathsf{P} = \left[p + \left(\frac{2\eta}{3} - \phi\right)\frac{\partial}{\partial\mathbf{r}} \cdot \mathbf{c}_0\right]\mathsf{U} - 2\eta(\partial\mathbf{c}_0/\partial\mathbf{r})^{\neq} \tag{38}$$

The force acting on the surface δS is evaluated in terms of molecular scale processes and leads to the following expression for the pressure tensor:

$$\mathsf{P} = m\int f^{(1)}[\mathbf{c}_1\mathbf{c}_1 - \mathbf{c}_0\mathbf{c}_0]\,d\mathbf{c}_1 - \frac{n^{(1)2}}{2}\int\frac{\mathbf{RR}}{R}g^2(\mathbf{r}, \mathbf{R})\frac{d\varphi_{12}}{dR}\,d\mathbf{R} \tag{39}$$

where $\mathbf{R}$ is the distance between the centers of the representative molecular pair. In the second integral, the pair number density function has been replaced by $n^{(1)2}g^{(2)}$, where $n^{(1)}$ is the singlet number density which is independent of position and $g^{(2)}$ is the radial distribution function. The first of the right-hand side terms represents the transport of momentum across the surface element δS by molecular motion. Although this is the dominant term in the case of transport properties of dilute gases, in the case of dense liquids it is well known to make but a small contribution to the stress on δS and consequently will not be examined in detail. It is the evaluation of the last term which constitutes the principal task of statistical mechanical theories of liquid viscosity.

The calculation of the perturbed radial distribution function $g^{(2)}$ for steady-state viscous flow is carried out using Eq. 34 for continuity in molecular pair phase space. The development is by no means simple but it is carried out without the introduction of additional assumptions beyond the formulation of appropriate boundary conditions. Those used by Kirkwood and co-workers[27, 36] make use of the following:

$$g^{(2)} = g_0^{(2)}(R)\left\{1 + \frac{\zeta}{2kT}\left[\frac{\mathbf{RR}}{R^2} : \frac{\partial \mathbf{c}_0}{\partial \mathbf{R}} - \frac{1}{3}\frac{\partial}{\partial \mathbf{R}} \cdot \mathbf{c}_0\right]\psi_2(R) + \frac{\zeta}{6kT}\frac{\partial}{\partial \mathbf{R}} \cdot \mathbf{c}_0\psi_0(R)\right\} \tag{40}$$

where $g_0^{(2)}(R)$ is the equilibrium radial distribution function, and ψ_2 and ψ_0 are perturbation functions. The latter functions have been evaluated numerically and the reader is referred to the original papers for details of the derivation and numerical tabulations of the functions.

Eisenschitz[13, 15] has suggested other boundary conditions in configuration space under conditions of viscous shear. Using these alternative boundary conditions in an approximate solution to Eq. 34, Eisenschitz obtained the perturbation function ψ_2 in terms of an algebraic expression. It differs significantly from the function derived by Kirkwood's group in having a singularity at the origin. It is, however, of interest because it has explicit dependence on the temperature,

$$\psi_2(R) = u_0(R) \exp\left[-\Phi_1(R)/2kT\right] \tag{41}$$

where $\Phi_1(R)$ is again the potential of mean force acting on a given molecule. The results were not, however, carried through to a comparison with experiment.

Upon introducing the Kirkwood Eq. 40 into Eq. 39, and comparing with like terms in the phenomenological pressure tensor, the shear and volume viscosity coefficients are immediately obtained:

$$\eta = \frac{n^{(1)}mkT}{2\zeta} + \frac{\pi\zeta}{15kT} n^{(1)2} \int_0^\infty R^3 \frac{d\varphi_{12}}{dR} g_0^{(2)}(R)\psi_2(R)\,dR \tag{42}$$

$$\phi = \frac{n^{(1)}mkT}{3\zeta} + \frac{\pi\zeta}{9kT} n^{(1)2} \int_0^\infty R^3 \frac{d\varphi_{12}}{dR} g_0^{(2)}(R)\psi_0(R)\,\mathrm{d}R \tag{43}$$

An integration over all orientations of the vector **R** has been effected in these equations. The first term arises from momentum transport from mass motion and can be neglected in comparison with the second term. The indicated integration of Eq. 42 has been carried out numerically. That of Eq. 43 proved to be too sensitive to variation in the radial distribution function $g_0^{(2)}$ to yield reliable results. In order to obtain the shear viscosity η, it is now necessary to evaluate the frictional coefficient ζ. A solution in series was obtained by Kirkwood[25] but its numerical evaluation is too unwieldy for practical calculations. The analysis, however, suggests the following estimate for the frictional coefficient:

$$\zeta = \left(\frac{m}{3kT}\right)^{1/2} \langle F^2 \rangle^{1/2} \tag{44}$$

where the ensemble average square force $\langle F^2 \rangle$ is given by

$$\begin{aligned} \langle F^2 \rangle &= \int \dots \int F^2 \, {}_0f^{(N)} \prod_{j=1}^{N} d\mathbf{c}_j d\mathbf{r}_j \\ &= n^{(1)2} \int_0^\infty \left[\frac{d^2\varphi_{12}}{dR^2} + \frac{2}{R}\frac{d\varphi_{12}}{dR} \right] g_0^{(2)}(R)\, 4\pi R^2 dR \end{aligned} \tag{45}$$

It is now possible to calculate a shear viscosity coefficient for actual liquids composed of spherical molecules. By assuming an explicit function $\varphi_{12}(R)$ for the intermolecular potential, the equilibrium radial distribution function $g_0^{(2)}(R)$ at densities corresponding to the liquid state may be calculated using the methods of Born and Green[3] and Kirkwood and Boggs.[26] The intermolecular potential for argon is fairly accurately known from second virial coefficient data for the imperfect gas. Using an estimated value of 4.84×10^{-10} g/sec for the frictional coefficient ζ, Kirkwood, Buff, and Green[27] obtained a shear viscosity coefficient of 1.27×10^{-3} poise for the viscosity of liquid argon at its boiling point which compares moderately well with the experimental value of 2.39×10^{-3} poise. A revised calculation of the viscosity coefficient of liquid argon with Eqs. 40 and 42 was subsequently made by Zwanzig, Kirkwood, Stripp, and Oppenheim[36] which, in addition, used a new estimate for ζ of 2.85×10^{-10} g/sec. The revised viscosity coefficient agreed less well with experiment, being only 0.73×10^{-3} poise. More recently Corbett and Wang[10] have experimentally determined the self-diffusion coefficient of argon at a temperature near its normal boiling point, thus enabling the frictional coefficient ζ to be directly calculated from the Einstein equation

$$D = kT/\zeta \tag{46}$$

The experimentally determined frictional coefficient was 5.93×10^{-10} g/sec and leads to some minor improvement in the above calculated viscosity coefficients.

The thermal conductivity coefficient has been derived from Brownian motion theory by Irving and Kirkwood[22] in terms of the equilibrium singlet and pair distribution functions ${}^0f^{(1)}$ and ${}^0f^{(2)}$. Thermal conduction under a macroscopic temperature difference involves a gradient in the mean square molecular velocity rather than in the mean molecular velocity. The steady-state radial distribution function then remains spherically symmetric except for a small correction arising from the number density variation with the temperature. As the analysis introduces no new assumptions and is somewhat lengthy, it will not be reproduced here. The resulting equation for the thermal conductivity coefficient $\varkappa$ is

$$
\begin{aligned}
\varkappa = {} & \frac{k^2T}{2\zeta}n^{(1)} - \frac{k^2T^2}{6\zeta}\left(\frac{\partial n^{(1)}}{\partial T}\right) \\
& + \frac{\pi kT}{3\zeta}n^{(1)2}\int_0^\infty R^3\left(R\frac{d\varphi_{12}}{dR}-\varphi_{12}\right)g_0^{(2)}(R)\,\frac{d}{dR}\left[\frac{\partial}{\partial T}\ln g_0^{(2)}(R)\right]dR \qquad (47) \\
& + \frac{\pi kT}{\zeta}n^{(1)2}\left[\frac{\partial}{\partial T}\int_0^\infty\left(R^2\varphi_{12}-R^3\frac{d\varphi_{12}}{dR}\right)g_0^{(2)}(R)\,dR\right].
\end{aligned}
$$

The first two terms of the above expression arise from kinetic energy transport by molecular motion across an arbitrary surface δS moving with the local mass velocity $\mathbf{c}_0(\mathbf{r})$ and are ordinarily negligible. The last two terms represent the contribution of the intermolecular energy. This is divided into two parts: that due to the transport of potential energy by motion of the molecular pair and containing the function $\varphi_{12}(R)$, and that representing the work dissipated by the molecular motion and involving the derivative $d\varphi_{12}/dR$.

It will be noted that a function analogous to ψ_2 which arises in the shear viscosity, does not appear in the thermal conductivity. Its absence, of course, is due to the lack of second order surface harmonic perturbation of the radial distribution function $g_0^{(2)}$ in the case of heat conduction. It may be anticipated that this difference in the form of the number density perturbation might lead to the thermal conductivity coefficient leaving a functional dependence on the temperature which is quite different from that of the shear viscosity coefficient. However, the exact temperature dependence of the two coefficients (Eqs. 42 and 47) has not yet been explored.

Zwanzig, Kirkwood, Oppenheim, and Alder[35] have numerically evaluated Eq. 47 for liquid argon at its normal boiling point, using the same Born-Green radial distribution function $g_0^{(2)}$ and the same numerical values for the frictional coefficient ζ and for the constants in the intermolecular potential function $\varphi_{12}(R)$ as previously employed in the evaluation of the shear viscosity coefficient for the same substance. The value obtained was $\varkappa = 4.1\times10^{-4}$ cal/g—sec—°K which is in reasonable agreement with the experimental value of 2.9×10^{-4}.

A precise determination of the frictional coefficient ζ in terms of the intermolecular potential and the radial distribution function at present constitutes the principal unresolved problem of the Brownian motion approach to liquid transport processes. It has been suggested by Kirkwood that an analysis of the molecular basis of self-diffusion might be a fruitful approach. The diffusion constant so calculated would be related to the frictional coefficient through the Einstein equation, Eq. 46.

Yang[34] has suggested an approximate mean-free-path treatment which might possibly be suitable for this purpose. It involves a calculation of the diffusion constant for the relative motion of two molecules in terms of their time-smoothed average trajectory. Yang proposes the assumption that the dynamics of the molecular pair are governed by the ensemble, when the pair is within a distance R_0. Beyond this distance it is assumed that the motions of the molecular pair are independent of each other, so that the pair density function for $R > R_0$ may be written as the product of the two singlet densities, thus achieving desired mathematical simplification.

V. TRANSPORT PROCESSES AND THE SUPERPOSITION HYPOTHESIS

In the foregoing discussion of the Brownian motion method, the ensemble averages are all constructed from an ensemble of replica systems of the subset of h molecules, the behavior of each replica having been time-smoothed over the interval τ. However, in a steady-state transport process $\partial f^{(N)}/\partial t = 0$ at every point in phase space, where $f^{(N)}$ is the instantaneous phase density of the N molecules. In principle, at least, it should thus be possible to express the steady-state pressure tensor and the mass and heat currents in terms of ensemble averages constructed without preliminary time-averaging in the replica systems. Thus it is desirable to examine the possibility of obtaining solutions to the reduced Liouville equation, Eq. 8, without preliminary time-averaging.

For the discussion of transport processes in terms of molecular pairs, Eq. 8 may be put into the form

$$\frac{\partial f^{(2)}}{\partial t}+\sum_{i=1}^{2}\frac{\partial f^{(2)}}{\partial \mathbf{r}_i}\cdot \mathbf{c}_i=\sum_{i=1}^{2}\frac{1}{m}\frac{\partial}{\partial \mathbf{c}_i}\cdot\iint\frac{\partial \varphi_{i3}}{\partial \mathbf{r}_i}f^{(3)}\,d\mathbf{c}_3\,d\mathbf{r}_3 \tag{48}$$

The introduction of Eq. 34 with time-smoothing in the Kirkwood method eliminates detailed consideration of the higher-order distributions such as $f^{(3)}$ in the continuity equation for $f^{(2)}$. In a sense, however, they implicitly reappear in the evaluation of the frictional coefficients. Kirkwood avoids the reintroduction of the triplet density $f^{(3)}$ by the assumption that the pair frictional tensors $\boldsymbol{\zeta}_1$ and $\boldsymbol{\zeta}_2$ may be equated to the singlet friction tensor $\zeta\mathbf{U}$ which is evaluated in terms of the pair densities $f^{(2)}$.

Born and Green[3] proposed that the higher-order density functions might be reduced by means of the superposition hypothesis which for the triplet density may be written

$$f^{(3)}=\frac{f^{(2)}(\mathbf{c}_2,\mathbf{r}_2,\mathbf{c}_1,\mathbf{r}_1)}{f^{(1)}(\mathbf{c}_1,\mathbf{r}_1)}\cdot\frac{f^{(2)}(\mathbf{c}_3,\mathbf{r}_3,\mathbf{c}_2,\mathbf{r}_2)}{f^{(1)}(\mathbf{c}_2,\mathbf{r}_2)}\cdot\frac{f^{(2)}(\mathbf{c}_1,\mathbf{r}_1,\mathbf{c}_3,\mathbf{r}_3)}{f^{(1)}(\mathbf{c}_3,\mathbf{r}_3)} \tag{49}$$

This assumes the independence of the three relative second-order densities $f^{(2/1)}$. By combining the last two equations, a closed continuity equation for the pair density is obtained. Unfortunately, the superposition hypothesis is not valid when extended to nonequilibrium states of the system. Klein and Prigogine[24] have carried out a rigorous development of Eqs 48 and 49 for a one-dimensional system with nearest neighbor interactions only. Their results show that, while the superposition hypothesis is valid for equilibrium systems, it cannot be used to describe transport processes and fails badly for the case of thermal conduction. While the treatment presented is limited to a one-dimensional system, it can be generalized to three dimensions with equivalent results. The essential difficulty of Eq. 48 is that, like the Liouville equation for N molecules, it is completely reversible in time so that it is intrinsically incapable of treating unidirectional dissipative processes.

VI. RIGID SPHERE MODEL

In view of the difficulties of the rigorous development of the transport properties of liquids with spherically symmetric intermolecular potential functions, it is desirable to explore simpler models of the liquid state. Some progress has been made in the statistical-mechanical treatment of the transport properties of liquids idealized as collections of rigid spheres. The method extends the well-known approximate calculation of the transport properties of dilute gases to include the transport of momentum and energy across the bodies of molecules which occurs upon collision.

As might be expected, the model leads to a great simplification over the calculations required for molecules with a continuous potential energy function, as it enables the analysis to be confined to binary collisions and permits the definition of a collision frequency. Because there is no molecular interaction between collisions, the velocity distributions of two colliding molecules may be assumed to be re-established by the time a second collision occurs between them. Thus a Maxwellian distribution around the local mass velocity may be postulated for the calculation of the mean frequency of collision and the average momentum and energy transported per collision in the nonuniform state of the liquid.

The calculations were first made by Van der Waals[33] for liquids, and Enskog[16] for dense gases. The resulting equations were equivalent but involved parameters which were not completely evaluated in terms of molecular properties. More recently, Collins and Raffel[9] and Longuet-Higgins and Pople[30] have extended these calculations using differing approaches. Longuet-Higgins and Pople's calculation of the transport coefficients introduced the radial distribution function for rigid spheres thus establishing a correspondence with the more rigorous calculations which involve the corresponding distribution for molecules with a Lennard-Jones type of potential function. Collins and Raffel's calculation made use of the uniform potential free-volume theory[17] and led to equations for the viscosity and hydrodynamic frictional coefficients which contained only the apparent molecular diameter as an unknown parameter. This parameter may be evaluated in terms of macroscopic equilibrium properties of the liquid at the given temperature and density by use of the same form of the free volume theory.[8] Thus the artificiality of the model was in part overcome and a partial correlation obtained between the transport and equilibrium properties of the liquid.

The parallelism of the above four papers was pointed out by Dahler[11] and the following discussion is based on his analysis.

As in the kinetic theory of gases, a selected molecule is represented as a collision sphere of radius equal to the sum of the radii of the colliding molecules. The neighbors with which it collides are mass points. The uncorrected frequency of collision is given by the usual equation of the kinetic theory of gases:

$$dZ_0 = \sigma^2 \mathbf{g} \cdot \mathbf{k} f^{(2)}(\mathbf{c}_1, \mathbf{c}_2, \mathbf{r}_1, \mathbf{r}_2; t)\, d\mathbf{k}\, d\mathbf{c}_1 d\mathbf{c}_2 \tag{50}$$

where the relative velocity $\mathbf{g} = \mathbf{c}_2 - \mathbf{c}_1$, and $\mathbf{k}$ is a unit vector along the line of centers of the molecules at collision.

In liquids as contrasted with gases there is a nonnegligible probability that the collision of the two molecules is prevented by the intervention of a third molecule. In the papers under discussion here, this "shielding effect" is taken into account by the introduction of a correction factor A which depends only on the local number density and the collision radius σ.

The flux $\mathbf{J}$ of a quantity ψ such as the momentum or the kinetic energy is calculated as follows: If the flux is to be across the arbitrary surface element δS, the center of the first molecule must lie in the parallelopiped $\sigma(\mathbf{k} \cdot \mathbf{n})\delta S$, where $\mathbf{n}$ is the unit normal to the surface element, and the vector $\mathbf{k}$ must intersect the surface element. The flux in the direction of positive $\mathbf{n}$ is then given by

$$\begin{aligned} \mathbf{J} &= \mathsf{J} \cdot \mathbf{n} \\ &= A\sigma^3 \iiint (\psi' - \psi) f^{(2)}\left(\mathbf{c}_1, \mathbf{c}_2, \mathbf{r} - \frac{\sigma}{2}\mathbf{k}, \mathbf{r} + \frac{\sigma}{2}\mathbf{k}\right) \mathbf{g} \cdot \mathbf{k}\mathbf{k} \cdot \mathbf{n}\, d\mathbf{k}\, d\mathbf{c}_1 d\mathbf{c}_2 \end{aligned} \tag{51}$$

where A is the shielding correction factor in the preceding, and ψ' is the value of the quantity ψ possessed by the second molecule after the collision. The integrations are restricted by the conditions $\mathbf{k} \cdot \mathbf{g} \geqq 0$ and $\mathbf{k} \cdot \mathbf{n} \geqq 0$. The momentum and energy are conserved in the collision, so that the latter condition may be removed by interchanging the roles of the two molecules and taking half the resulting integral.

The radial distribution function is defined as before and is evaluated at the point $\sigma\mathbf{k}$ on the collision sphere:

$$
\begin{aligned}
f^{(2)}\left(\mathbf{c}_1, \mathbf{c}_2, \mathbf{r}-\frac{\sigma}{2}\mathbf{k}, \mathbf{r}+\frac{\sigma}{2}\mathbf{k}\right) \\
= g^{(2)}(\mathbf{r}, \mathbf{k}\sigma) f^{(1)}\left(\mathbf{c}_1, \mathbf{r}-\frac{\sigma}{2}\mathbf{k}\right) f^{(1)}\left(\mathbf{c}_2, \mathbf{r}+\frac{\sigma}{2}\mathbf{k}\right)
\end{aligned}
\tag{52}
$$

The radial distribution function implicitly takes account of the enhancement of the number density in the neighborhood of the collision sphere due to the excluded volume of the other molecules making up the system.

The flux tensor may now be written

$$
\mathsf{J} = \tfrac{1}{2} Y \sigma^3 \iiint\limits_{\mathbf{k}\cdot\mathbf{g} \geq 0} \mathbf{k}\mathbf{k}\cdot\mathbf{g}(\psi'-\psi) f^{(1)}\left(\mathbf{c}_1, \mathbf{r}-\frac{\sigma}{2}\mathbf{k}\right) f^{(1)}\left(\mathbf{c}_2, \mathbf{r}+\frac{\sigma}{2}\mathbf{k}\right) d\mathbf{k}\, d\mathbf{c}_1\, d\mathbf{c}_2 \tag{53}
$$

where $Y = Ag^{(2)}$ and is a function only of the local macroscopic variables $T(\mathbf{r})$, $n(\mathbf{r})$, and $\mathbf{c}_0(\mathbf{r})$. The assumption that $f^{(1)}$ is locally Maxwellian, is now made use of:

$$
f^{(1)}(\mathbf{r}, \mathbf{c}) = n(\mathbf{r}) \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left\{-\frac{m[\mathbf{c}-\mathbf{c}_0(\mathbf{r})]}{2kT}\right\} \tag{54}
$$

The product of the two singlet densities is expanded in a Taylor series in $\sigma\mathbf{k}$ about the point $\mathbf{r}$ with terms in $\sigma\mathbf{k}$ of order higher than first neglected:

$$
\begin{aligned}
f^{(1)}\left(\mathbf{c}_1, \mathbf{r}-\frac{\sigma}{2}\mathbf{k}\right) f^{(1)}\left(\mathbf{c}_2, \mathbf{r}+\frac{\sigma}{2}\mathbf{k}\right) = f^{(1)}(\mathbf{c}_1, \mathbf{r}) f^{(1)}(\mathbf{c}_2, \mathbf{r}) \\
\times\left\{1 - \frac{\sigma m}{2kT}\mathbf{k}\cdot\frac{\partial \ln T}{\partial \mathbf{r}}\mathbf{g}\cdot\mathbf{G} - \frac{\sigma m}{2kT}\mathbf{g}\mathbf{k} : \frac{\partial \mathbf{c}_0}{\partial \mathbf{r}} + \dots\right\}
\end{aligned}
\tag{55}
$$

where $2\mathbf{G} = [\mathbf{c}_1 - \mathbf{c}_0(\mathbf{r})] + [\mathbf{c}_2 - \mathbf{c}_0(\mathbf{r})]$ and the double dot product has been earlier defined. Further

$$
f^{(1)}(\mathbf{c}_1, \mathbf{r}) f^{(1)}(\mathbf{c}_2, \mathbf{r}) = n^2(\mathbf{r}) \left(\frac{m}{2\pi kT}\right)^3 \exp\left[-m(G^2+g^2/4)/kT\right]. \tag{56}
$$

Introduction of these into Eq. 53 yields

$$
\begin{aligned}
\mathsf{J} = \tfrac{1}{2} Y \sigma^3 n^2(\mathbf{r}) \left(\frac{m}{2\pi kT}\right)^3 \iiint\limits_{\mathbf{k}\cdot\mathbf{g}\geq 0} \mathbf{k}\mathbf{k}\cdot\mathbf{g}(\psi'-\psi) \exp\left[-m(G^2+g^2/4)/kT\right] \\
\times\left[1 + \frac{\sigma m}{2kT}\mathbf{g}\mathbf{k} : \left(\frac{\partial \mathbf{c}_0}{\partial \mathbf{r}} + \frac{\partial \ln T}{\partial \mathbf{r}}\mathbf{G}\right)\right] d\mathbf{k}\, d\mathbf{g}\, d\mathbf{G}
\end{aligned}
\tag{57}
$$

the Jacobian of the transformation of the integration variables being unity. To calculate the collisional transport contributions to the viscosity and thermal conductivity, the proper choice of the dynamical quantity ψ is inserted into Eq. 57.

The pressure tensor can be reduced to the following form, as $m(\mathbf{c}'_1-\mathbf{c}_1)=m\mathbf{kk}\cdot\mathbf{g}$ by the conditions of conservation of momentum and energy for rigid spheres:

$$\mathsf{P}_\varphi=\frac{m}{2}Y\sigma^3n^2(\mathbf{r})\left(\frac{m}{2\pi kT}\right)^3\left(\frac{\pi kT}{m}\right)^{3/2}\iint\limits_{\mathbf{k}\cdot\mathbf{g}\geq 0}\mathbf{kkkk}:\mathbf{gg}\exp\left(-\frac{mg^2}{4kT}\right)\times\left[1-\frac{\sigma m}{2kT}\mathbf{gk}:\frac{\partial\mathbf{c}_0}{\partial\mathbf{r}}\right]d\mathbf{g}\,d\mathbf{k} \tag{58}$$

The remaining integrations may be readily effected using the methods of Chapman and Cowling[6] and Collins and Raffel, yielding

$$\mathsf{P}_\varphi=Y\left\{\left[\tfrac{2}{3}\pi n^2\sigma^3kT-\tfrac{4}{9}n^2(\pi mkT)^{1/2}\sigma^4\frac{\partial}{\partial\mathbf{r}}\cdot\mathbf{c}_0\right]\mathsf{U}-\tfrac{8}{15}n^2(\pi mkT)^{1/2}\sigma^4(\partial\mathbf{c}_0/\partial\mathbf{r})^{\mp\circ}\right\} \tag{59}$$

where $(\partial\mathbf{c}_0/\partial\mathbf{r})^{\mp\circ}$ is again the nondivergent rate of shear tensor.

The complete pressure tensor includes a term arising from the motion of molecules across the surface element δS. This motion, of course, is impeded by the molecular collisions. The kinetic contribution according to Enskog is

$$\mathsf{P}_K=nkT\,\mathsf{U}-\frac{2}{Y}\left(1+\tfrac{4}{15}\pi n\sigma^3Y\right)\eta^0(\partial\mathbf{c}_0/\partial\mathbf{r})^{\mp\circ} \tag{60}$$

where η^0 is the coefficient of shear viscosity in the dilute gas limit. The complete pressure tensor $\mathsf{P}=\mathsf{P}_\varphi+\mathsf{P}_K$ is then

$$\mathsf{P}=\left[nkT\left(1+\tfrac{2}{3}\pi n\sigma^3Y\right)-\phi\left(\frac{\partial}{\partial\mathbf{r}}\cdot\mathbf{c}_0\right)\right]\mathsf{U}-\left[\frac{2}{Y}\left(1+\tfrac{4}{15}\pi n\sigma^3Y\right)\eta^0+\tfrac{6}{5}\phi\right](\partial\mathbf{c}_0/\partial\mathbf{r})^{\mp\circ} \tag{61}$$

where the coefficient of volume viscosity ϕ has been defined as

$$\phi=\tfrac{4}{9}n^2\sigma^4Y(\pi mkT)^{1/2} \tag{62}$$

The coefficient of $(\partial \mathbf{c}_0/\partial \mathbf{r})^{\ddagger\circ}$ has earlier been defined as -2η where the viscosity coefficient η is now the sum of the following collisional and kinetic contributions

$$\eta_\varphi = \tfrac{3}{5}\phi \tag{63}$$

and

$$\eta_K = \frac{1}{Y}\,(1+\tfrac{4}{15}\pi n\sigma^3 Y)\eta^0 \tag{64}$$

For the heat flux, we note that kinetic energy transported per collision is given by $\frac{1}{2}m\{[\mathbf{c}'-\mathbf{c}_0(\mathbf{r})]^2-[\mathbf{c}-\mathbf{c}_0(\mathbf{r})]^2\} = m\mathbf{k}\cdot\mathbf{g}\mathbf{k}\cdot\mathbf{G}$ so that the heat flux vector becomes

$$\mathbf{q}_\varphi = \tfrac{1}{2}m\sigma^3 Y\iiint \mathbf{k}(\mathbf{k}\cdot\mathbf{g})^2\mathbf{k}\cdot\mathbf{G}f^{(1)}\left(\mathbf{c}_1,\,\mathbf{r}-\frac{\sigma}{2}\mathbf{k}\right)f^{(1)}\left(\mathbf{c}_2,\,\mathbf{r}+\frac{\sigma}{2}\mathbf{k}\right)d\mathbf{k}\,d\mathbf{c}_1\,d\mathbf{c}_2 \tag{65}$$

This equation may be reduced by the same mathematical devices as before and leads to

$$\mathbf{q}_\varphi = -\varkappa_\varphi \frac{\partial T}{\partial \mathbf{r}} \tag{66}$$

with

$$\varkappa_\varphi = n^2\sigma^4\frac{2\pi k}{3}\left(\frac{kT}{\pi m}\right)^{1/2} Y \tag{67}$$

The foregoing equations are those obtained by Enskog using somewhat different methods. Let us examine the results of Longuet-Higgins and Pople. From Eq. 61, the equilibrium hydrostatic pressure is given by

$$p = nkT(1+\tfrac{2}{3}\pi n\sigma^3 Y) \tag{68}$$

which may be used as a definition for the factor Y. The various transport coefficients are then in the form given by Longuet-Higgins and Pople:

$$\eta_\varphi = \tfrac{2}{5}\sigma\left(\frac{mkT}{\pi}\right)^{1/2}\left(\frac{p}{kT}-n\right) \tag{69}$$

$$\phi = \tfrac{2}{3}\sigma\left(\frac{mkT}{\pi}\right)^{1/2}\left(\frac{p}{kT}-n\right) \tag{70}$$

$$\varkappa_\varphi = \sigma k\left(\frac{kT}{\pi m}\right)^{1/2}\left(\frac{p}{kT}-n\right) \tag{71}$$

The results of Collins and Raffel are obtained by making use of the uniform potential free-volume theory of Eyring and Hirschfelder[17] which gives the following equation of state for the liquid:

$$\left(\frac{p}{kT}-n\right)=\frac{1}{v}\left[\frac{1}{1-(v_0/v)^{1/3}}-1\right] \tag{72}$$

where v_0 is the "molecular incompressible volume." The ratio $(v_0/v)^{1/3}$ may be calculated[8] from the velocity of sound in the liquid and is of the order of 0.9 in the usual density range. However, the pressure p may be interpreted as the "internal pressure" of the liquid $(\partial E/\partial V)_T$ and may be directly obtained from the velocity of sound without resort to the free-volume theory by the thermodynamic relation:

$$\left(\frac{\partial E}{\partial V}\right)_T=\frac{T\alpha C_p M u_s^2}{TV\alpha^2 M u_s^2+VC_p} \tag{74}$$

where α is the expansion coefficient.

TABLE II. Comparison of Calculated Collisional Viscosities and Their Calculated Isobaric Temperature and Isothermal Volume Dependence with Experimental Values at 30° C and 1 atm.

Substance	η_c	η_c/η_{exp}	$(\partial \ln \eta_c/\partial T)_P \times 10^2/°\text{C}$	$(\partial \ln \eta_c/\partial \ln V)_T$	$(\partial \ln \eta_{\text{exp}}/\partial T)_P \times 10^2/°\text{C}$	$(\partial \ln \eta_{\text{exp}}/\partial \ln V)_T$
Carbon tetrachloride	0.256	0.304	−0.49	−4.10	−1.39	−7.04
Chloroform	0.234	0.456	−0.51	−3.85	−1.09	−4.31
Benzene	0.195	0.346	−0.54	−4.14	−1.50	−7.77
Chlorobenzene	0.260	0.364	−0.44	−4.81	−1.14	−6.87
Methanol	0.091	0.178	−0.44	−2.35	−1.29	−3.02
Argon [a]	0.106	0.401	−1.26	—	−2.84	—

[a] The data for argon are at a temperature of −187.2° C.

Table II presents a comparison of the values for the shear viscosity coefficients calculated from Eqs. 69 and 72 with those obtained experimentally for a few liquids. While the calculated results are of the correct order of magnitude, they are significantly lower than the experimental values. Further, it will be noted the isobaric temperature coefficients of the calculated viscosities are considerably lower than those given by experiment. The latter is scarcely surprising, as the calculated isochoric temperature coefficient is

$$\left(\frac{\partial \ln \eta}{\partial T}\right)_V = \frac{1}{2T} \tag{75}$$

which is that given by the kinetic theory of gases and thus is of incorrect algebraic sign. The calculated isothermal volume dependence turns out to be in moderately good agreement with experiment. Thus it may be anticipated that any improvement of the rigid sphere treatment of transport properties must introduce new considerations of energetic relationships.

VII. CELL THEORY AND TRANSPORT PROCESSES

In view of the failure of the rigid sphere model to yield the correct isochoric temperature coefficient of the viscosity, the investigation of other less approximate models of the liquid state becomes desirable. In particular, a study making use of the Lennard-Jones and Devonshire cell theory of liquids[28] would be of interest because it makes use of a realistic intermolecular potential function while retaining the essential simplicity of a single particle theory. The main task is to calculate the probability density of the molecule within its cell as perturbed by the steady-state transport process.

Eisenschitz[12] has calculated a cell probability density perturbation for viscous flow and thermal conduction using Brownian motion theory. The viscosity and thermal conductivity coefficients are then rewritten in terms of the displacement of the single molecule within the cell in place of intermolecular distances. The use of Brownian motion theory, however, leads to transport coefficients in terms of the frictional coefficient ζ which again is not easy to evaluate.

VIII. TRANSITION STATE THEORY OF TRANSPORT PROCESSES

The well-known viscosity and diffusion theory of Eyring[18] was originally based on a cell model of the liquid state. The theory is, however, compatible with several molecular mechanisms of viscous flow including that of partial rotation of molecular pairs.[2] Let us consider the special form of the theory described by Glasstone, Laidler, and Eyring.[18] The viscous flow process is here viewed as consisting in the transport of single molecules from one cell to an adjoining unoccupied one. The determination of the viscosity coefficient is then reduced to calculations of the frequency of transit of molecules into adjoining empty cells and of the probability of a given cell being empty. The frequency of molecular transit is obtained from the transition state theory of chemical reactions and assumes a single slow step. There are alternative methods for handling the calculation of the probability of a cell being empty. The one generally used leads to the following expression for the viscous flow of monatomic liquids:

$$\eta = (2\pi mkT)^{1/2} \frac{v_f^{1/3}}{v} \exp(\varepsilon_0/kT) \tag{76}$$

where v is the liquid volume per molecule and v_f the Eyring-Hirschfelder free volume.[17] The activation energy ε_0 is assumed to be made up of two parts: ε_1 corresponding to the activation energy for the molecular transit, and ε_2 the work of formation of an empty cell. This assumes that the probability of finding an empty cell is given by $\exp(-\varepsilon_2/kT)$.

The energy ε_0 is experimentally evaluated from the isobaric viscosity coefficient

$$\left(\frac{\partial \ln \eta}{\partial T}\right)_P = -\frac{\varepsilon_0}{kT^2} \tag{77}$$

It has been shown, however, that this determination of ε_0 is inconsistent with the assumptions involved in Eq. 76.[7]

The alternative form of the Eyring equation is free from this objection and is given by

$$\eta = (2\pi mkT)^{1/2} \frac{v_f^{1/3}}{v} \frac{v_k}{(v-v_s)} \exp(\varepsilon_1/kT) \tag{78}$$

where v_k is the volume of an empty cell, and v_s is the volume of the solid so that $v_k/(v-v_s)$ is the probability of finding a given cell to be empty. The activation energy is now explicitly to be evaluated from the isochoric viscosity coefficient. The viscosities calculated from Eq. 78 are in fair agreement with experiment. There is some question, nevertheless, whether the representation of the viscous flow process can be properly simplified to any molecular mechanism involving a single rate determining step which would enable the general theory of chemical reaction kinetics to be applicable.

IX. CONCLUSION

It may be concluded from this review that in spite of some of the excellent progress made to date, significant advances must be made before the molecular theory of transport processes can be considered to be satisfactorily resolved. While the Brownian motion theory method of Kirkwood is very attractive, no rigorous method has been yet devised for the calculation of the required frictional coefficient. The Born and Green method involving the partially integrated Liouville equation does not lead to useful results for dissipative processes because of the lack of irreversibility in the Liouville equation. The successfully developed rigid sphere model theory of transport processes fails to reproduce the experimental temperature dependence of the transport coefficients presumably because of the crudity of this model of the liquid state.
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THE RELATION BETWEEN STRUCTURE AND CHEMICAL REACTIVITY OF AROMATIC HYDROCARBONS WITH PARTICULAR REFERENCE TO CARCINOGENIC PROPERTIES

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CONTENTS

I. INTRODUCTION

In this article certain aspects of the relation between chemical reactivity and the structure of hydrocarbons will be discussed. In order to give an idea of the possible extent of the applications, we shall show that there are important applications in pathological biology.

It will be desirable to recall certain facts about the structure of hydrocarbons; but this presentation will not use only the concepts of classical chemistry. Recent developments in the study of the structure of atoms and molecules make it possible to discuss the nature of chemical bonds much more clearly than was previously possible.

The results of these new developments will be briefly reviewed, which will give us the opportunity to emphasize one of the important aims of quantum chemistry—to make it possible to understand the basic physical nature of the phenomena which govern molecular structure. Then we shall try to show that it is sometimes possible to establish very accurate relations between certain characteristic properties of the structure of hydrocarbons and their chemical reactivity. This has been developed to such a point that from these properties it is possible to calculate theoretically *a priori* the rate constant which will characterize the action of a reagent on a given hydrocarbon under certain experimental conditions when the rate constant of the same reagent acting on another hydrocarbon in the same experimental conditions is known.

The knowledge gained from these studies will then be applied to the study of the relations between the structure and carcinogenic properties of these hydrocarbons.*

II. GENERAL REMARKS

Before beginning the discussion of the subject proper of this article, it may be desirable to say a few words about the nature of the interactions which determine molecular structure. A number of rather misleading expressions like exchange energy tend to obscure the problem.

If Coulomb interactions between electrons and protons and attractions between electrons and protons are introduced by the methods of wave mechanics, then the other types of interactions can be neglected for chemical problems.

Since the virial theorem is still valid, the total energy of the particles which make up an atom or molecules has the form

$$E = \tfrac{1}{2}\int F dp$$

where F is the potential energy of the Coulomb interaction when the electrons occupy a certain set of positions in space, and dp is the probability of finding them in these positions.

It is clear that wave mechanics has not, strictly speaking, introduced a new energy as might be imagined when "exchange" energy is contrasted with "Coulomb" energy. In the present approximation all the energy can be considered to be Cou-

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* The problems which are discussed in this article have been given a detailed analysis in Daudel, R., Lefebvre, R., and Moser, C., *Introduction to Methods and Applications of Quantum Chemistry*, Interscience, New York, in press.

lombic. Wave mechanics only provides a procedure for calculating the probabilities dp, that is, it provides a means of studying the "movement" of the particles under the influence of the Coulomb interactions coming from the potential F. Exchange energy is only a name given to a noninvariant part of the total energy.[44] Exchange energy appears in certain very particular approximate calculations and never in rigorous calculations. Thus exchange energy has no physical meaning.

Language which is in common use today dates from the time of the old quantum mechanics and really is not adapted to the needs of wave mechanics. Thus (incorrectly) quantum numbers are often associated with the electrons of an atom, or electrons are given the designation K, L, M, etc. while, in fact, these numbers and these names can only be associated with functions which are used in some approximate representations of the total wave function. These functions are called orbitals.

Often as many orbitals as electrons are used in the representation of an atom or molecule, but the movement of a given electron at each instant is given by the whole set of orbitals. There is no direct one-to-one relationship between an electron and an orbital.

This is, furthermore, a consequence of the symmetry properties of the total wave function. These symmetry properties also, in effect, make each electron in an atom or molecule on the average strictly identical. Thus, for example, the average distance between a given electron and the nucleus of an atom is the same for all the electrons of the atom (see, e.g. 24).

It is thus clear that the words like shell, electron levels, and bond are no longer used in the sense today as they were a few years ago. In particular the geometrical implications of these words are not very clear, and this makes it difficult to establish a solid bridge between the notation of classical chemistry and of the new quantum chemistry.

These difficulties crop up in all structural studies and it will be wise to clarify this as much as possible before discussing the structure of the hydrocarbons. Along this line, it may be helpful to briefly review some of the recent results that have been obtained in studying the localizability of electrons in atoms and molecules.

III. ELECTRONIC ORGANIZATION OF ATOMS

In recent years, several different procedures have been used to study electronic organization. One of these consists in determining the most probable configuration of the electrons in an atom, that is, the set of positions of these electrons which has the highest probability density.[1, 46, 67, 75]

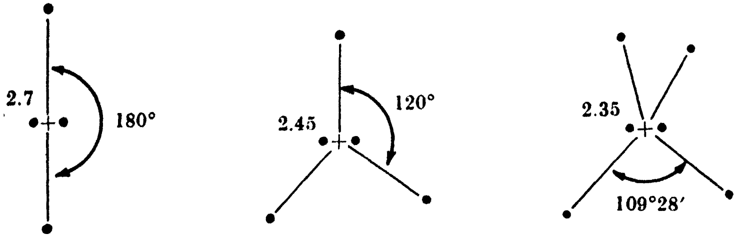


Fig 1

Figure 1 shows some of the results that have been obtained.[46] In this figure the nuclei are shown by a+sign, and the electrons by points. For the ^3P state of beryllium, which classically corresponds to a pair of electrons with opposite spins in the K-shell and to two electrons with the same spin in the L-shell, the most probable configuration corresponds to two electrons (with opposite spin) at 2.7 atomic units from an opposite side of the nucleus and to two electrons near the nucleus. The two electrons that are near the nucleus resemble the K-shell, and the two others the L-shell.

In boron, similarly, one pair of electrons is found near the nucleus and the three other electrons with the same spin form angles of 120° with respect to the nucleus.

In carbon (^5S state) as usual a pair of electrons is found near the nucleus. The number of electrons (of the same spin) that resemble the L-shell are four and are found at the vertices of a regular tetrahedron with the center at the nucleus.

The angle which two electrons of the same spin at the same distance from the nucleus form with this nucleus is as large as possible: 180° for two electrons, 120° for three electrons, 109° 28′ for four.

This seems to show that electrons of the same spin tend to be as far apart as possible from each other. This is not surprising if it is recalled that the wave function which describes a system of like particles and with half-integer spin must be antisymmetrical. This implies that the probability of finding two electrons with the same spin at the same point is zero. The probability of finding two electrons with the same spin close to each other should then be small, which would then readily explain why electrons tend to be as far apart as possible.

However, even in the most probable configuration, two electrons of opposite spin can be found together at the same point—at least in the approximation of Linnett and Poe[46] where the electrostatic repulsion between the electrons has been neglected. It is from this work that the interesting idea of electron pairs results. This does not, as is sometimes said, mean that two electrons of opposite spin attract each other, but that two electrons of opposite spin *can* be in the same small region of space at the same time, which is not possible if the two electrons have the same spin.

Another way of studying the electronic arrangement of atoms consists in dividing space into regions where there is a high probability of finding a certain given number of electrons.[23] Thus, if the space of the F^- ion in its ground state is divided by a sphere with its center at the nucleus and a radius of 0.35 atomic unit, there is a 90 per cent probability of finding only one electron of given spin in this sphere, and four electrons with this same spin outside the sphere.

Thus this sphere very often contains two electrons of paired spin, and the space outside this sphere contains four electrons with spin $+\frac{1}{2}h/2\pi$ and four electrons with spin $-\frac{1}{2}h/2\pi$. The central sphere thus resembles the K-shell, and the outside space the L-shell.

In general, spheres or concentric spherical rings can be found where there exists a high probability of finding a certain number of electrons, and these regions can be associated with the different shells of the atom. This makes it possible to again give to the idea of shell a certain geometrical character.[5, 25, 28, 55]

In addition, these rings correspond to a filled shell in the classical sense, as they can contain on the average a number of electrons very close to $2n^2$, where n is the quantum number associated with the shell.[52] The quotient of the volume of the ring by the average number of electrons gives some idea of the volume which an electron tends to occupy in the atom when it is in this ring. If V is the volume and F is the average electric potential which acts in the electron when it is in the ring, then

$$F^{3/2} \cdot V = \text{constant}$$

whatever the shell and the atom.[54]

In atomic structure there exists a kind of Mariotte's law: the power 3/2 of the electric potential playing here the role of pressure.

IV. ELECTRONIC ORGANIZATION AND THE CLASSIFICATION OF CHEMICAL BONDS

Parallel studies have been carried out to analyze the division of the electrons in molecules.

One of the procedures is to calculate a certain function $\delta(M)$ which is the difference between the electronic density at a point M of a molecule and the density at this point which would result from adding together the densities of the atoms which make up the molecule. This function makes clear the effect of the chemical bond on the electric organization. At a point where this function is positive, the chemical bond causes an increase in the number of electrons; if the function is negative, then there has been a decrease in the number of electrons.

Figure 2[63] gives the variation of the function along the line of two neighboring nuclei in several molecules. This figure clearly shows that for the homopolar bonds (the central bond of naphthalene, the hydrogen molecule, the lithium molecule) the result of the chemical bond is an increase of electrons "between" the nuclei, while for the heteropolar bond (LiH) there is a transfer of charge from one atom towards the others.

While these results are in agreement with what would seem reasonable from chemical intuition, they nonetheless deserve to be mentioned because they are so clear. Rather similar conclusions would be reached using another method due to Mulliken.[50]

Just as in atoms, it is possible to divide the space occupied by the electrons of a molecule into regions where there exists a strong

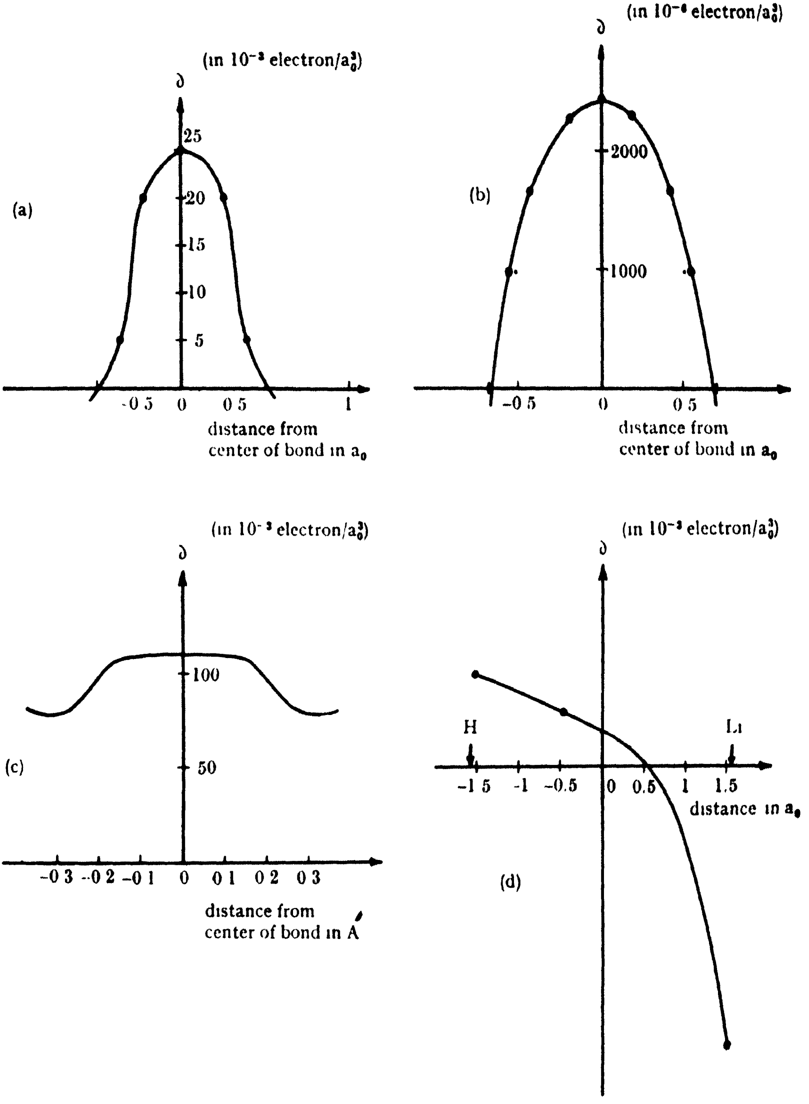


Fig. 2. (a) The central bond of naphthalene; (b) lithium molecule; (c) hydrogen molecule; and (d) the heteropolar bond, LiH.

probability of finding a given number of electrons with a certain spin organization.[6]

In general, it is possible to describe regions around the nuclei where the electronic organization is very similar to that in the same region of the corresponding free atoms, which is called the core zone, and there is a region where the electronic organization is different, which is called the bond zone.

In the ground state of the lithium molecule, Li_2, if each of the nuclei is surrounded by a concentric sphere of 1.53 atomic units radius, then it can be shown that there is a 96 per cent probability of finding only two electrons of paired spin in one of the spheres, and a 90 per cent probability of finding a pair between the spheres. The two spheres resemble the K-shell (the core zone) and the intermediate space corresponds to the bond zone. In this example, two electrons of opposite spin are localized between the cores with a high probability; this illustrates the idea of a two-electron bond.

In general there exists a localized bond of n electrons between two neighboring cores of a molecule when there is a region in the molecular space which only extends between the two cores and in which there is a high probability of finding only n electrons with a certain spin organization.

As a localized bond thus corresponds to finding with a high probability a given number of electrons between two cores, it is natural to suppose that the properties of this bond would not particularly depend on the other cores in the molecule. It would thus be of interest to divide the bond zone of a molecule into localized bonds, because then the properties of the molecule could be reduced to a set of values which, as a first approximation, only depends on a certain number of pairs of neighboring cores.

Unfortunately this division is not always possible. This often occurs when the number of electrons N, which is associated with the bond zone of a molecule, is either less than or greater than twice the number of pairs of neighboring bonds P.

An example is diborane. In this molecule there are twelve electrons which are associated with the bonds, and there are eight pairs of neighboring cores. Thus $N < 2P$.

Experimental evidence indicates that the four-end BH bonds have all the properties that would be expected of a two-electron bond. There remain only four electrons for the double central bridges. It is tempting to divide the space associated with this bridge into four bonds.

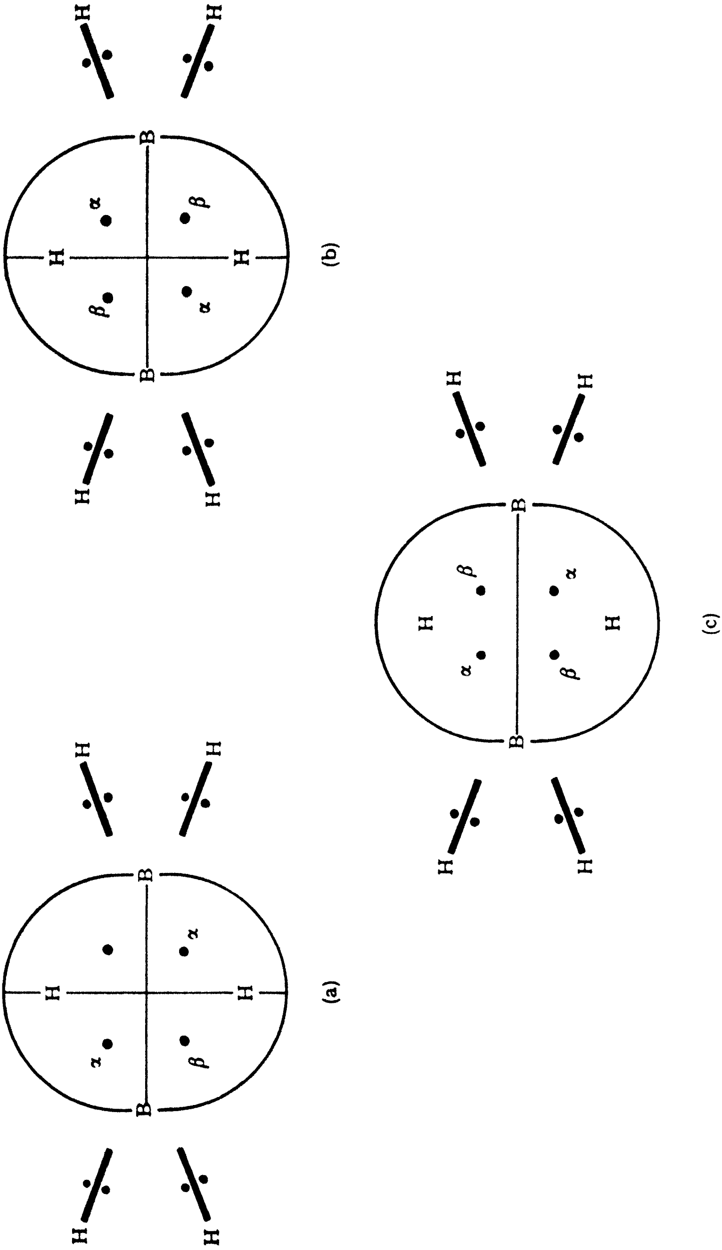
Part (a) of Fig. 3 gives a distribution of the electrons of this bridge corresponding to the presence of one electron in each of these bond regions. The letter α indicates spin of $+\frac{1}{2}h/2\pi$, β denotes spin of $-\frac{1}{2}h/2\pi$. The distribution indicated as (b) is equally probable from symmetry. As the sum of the probabilities for finding (a) and (b) cannot exceed 1, the probability of finding (a) cannot exceed 0.5. In fact the probability of finding only one electron of given spin in one of these BH regions is surely less than 0.5, which is not very high. These one-electron BH bonds appear not to be a very satisfactory representation of the molecule. The arrangement (c) in which there are two regions where two electrons are localized does not have the drawbacks of (a) and (b). However, these regions extend over more than two cores; it might be said that they correspond to delocalized bonds. Of course, the properties of bonds like these cannot only be given in terms of elements which are characteristic of only pairs of cores but depend on the geometry and the nature of all the cores over which they extend. This is the most important factor that is found in studying the structure of the aromatic hydrocarbons.

V. THE STRUCTURE OF AROMATIC HYDROCARBONS

A similar line of reasoning would show that it is very desirable to think of the conjugated hydrocarbons as containing a delocalized bond which extends over all the carbon cores of the molecule.

It is generally assumed today that each CH bond is a two-electron localized bond and between each pair of carbon cores there is a localized two-electron bond. These CC localized bonds "swim" in the delocalized bond to which there are associated as many electrons as there are carbon atoms in the molecule. Part (a) of Fig. 4 gives one such decomposition in naphthalene.

There is a serious objection in considering the structure of aromatic hydrocarbons only from the geometrical point of view. Coulson, March, and Altmann[21] have observed that the σ orbital



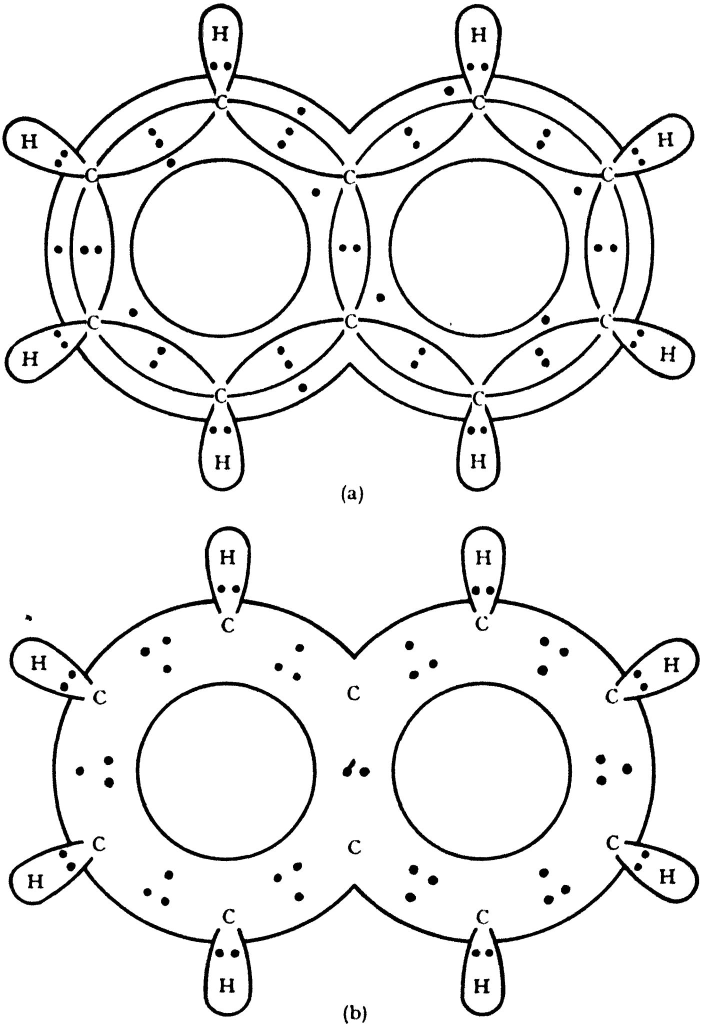
(a)

(b)

(c)

Fig 3.

which is generally associated with the CC localized bonds has large values in the regions where the π orbitals which characterize the delocalized bonds are themselves important. It could then be deduced that it should be difficult to define a region between two



(a)

(b)

Fig. 4.

carbon cores where only two electrons of paired spin can be localized with a very high probability. A calculation carried out along this line has confirmed this prediction.[6]

It is well known, of course, that the π and σ orbitals that are used in these calculations are built from atomic orbitals which are rough approximations to the accurate wave functions. Thus the electronic density calculated from the James and Coolidge function for the hydrogen molecule is very different from that obtained from the usual functions built from atomic orbitals.[63] It is thus at least possible that a very accurate wave function for an aromatic hydrocarbon would give an electronic density which could resemble Fig. 4a. If this should prove not to be the case, then scheme 4b could be used where the delocalized bond of naphthalene now contains 32 electrons.

The principal conclusion remains the same regardless of which of the two representations is used: the electronic organization between two carbon cores of an aromatic molecule does not correspond to a clearly differentiated bond. It is always part of a delocalized bond.

It would then be expected that the properties of a CC "bond" of a conjugated hydrocarbon depend on the geometrical organization of all the carbon cores of the molecule and in particular on its position in this set.

Hartmann[36] has introduced a useful notion to classify the CC bonds as a function of the organization of the neighboring carbon cores. He suggests calling the type of a CC bond in a conjugated hydrocarbon the number of CC bonds which are adjacent to it.

Thus in naphthalene the central CC bond is adjacent to 4 CC bonds; it is thus of type 4. The $\alpha\beta$ bond is of type 2 (Fig. 5). Vroelant and Daudel have extended this classification by in-

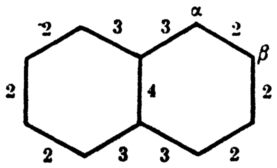


Fig. 5. Types of naphthalene bonds.

troducing a "notation" describing the set of types of CC bonds which are adjacent to a given CC bond. The $\alpha\beta$ bond of naphthalene which is between a bond of type 2 and a bond of type **3** is indicated (2,3), and the central bond of naphthalene is (3,3,3,3).

The notation of a bond gives a rather exact idea of how it participates in the delocalized bond. The notation describes the set of neighbors to a given bond. As a first approximation then the properties of a CC bond of a conjugated hydrocarbon should be a simple function of the notation of this bond. Table I shows that this is indeed so for interatomic distances.

TABLE I. The Variation of Interatomic Distance as a Function of the "Notation" of the Bond.

Notation	Length (in A)
(3,3)	1.367 ± 0.022
(2,3)	1.382 ± 0.019
(2,4,4)	1.390 ± 0.010
(3,4,4)	1.392 ± 0.012
(2,2)	1.397 ± 0.013
(3,3,3,3)	1.415 ± 0.021
(3,3,4,4)	1.42 ± 0.030
(2,3,4)	1.425 ± 0.025
(4,4,4,4)	1.444 ± 0.021

In order to determine these intervals, the distances in parentheses and those marked by an asterisk in Table II have been excluded for the reasons given at the foot of that table.

It is seen that the length of a given bond notation hardly deviates more than 0.025 A about a central value. As this is of the order of magnitude of experimental error, it can be said that, with the exception of these errors, bond length is a constant for a given notation.

This clearly shows that the properties of a CC bond depend on how it participates in the delocalized bond. The notation of the bonds takes into account a sufficient number of bonds which are neighbors to the CC bond being considered so as to describe accurately the situation.

In order to simplify the discussion we will say that in the condensed aromatic hydrocarbons there are three families of CC bonds: the short bonds (notation (3,3), (2,3), or (2,4,4)) with average length of 1.38 A, the average bonds ((3,4,4), (2,2), and (3,3,3,3)) of average length 1.40 A, and the long bonds ((3,3,4,4), (2,3,4), (4,4,4,4)) of average length 1.42 A.

The length of the bonds in aromatic hydrocarbons, does vary over a rather large range. In Table II the lengths go from 1.345 A to 1.50 A. As it is well known that the shorter a bond is, the stronger it is, it can be said that the force of a CC bond varies with its position in the delocalized bond. For a long time a mathematical quantity was sought which could represent this bond strength.

This quantity, which is called bond order[18, 56, 57, 59] is generally defined in such a way that it is directly linked to the not very precise idea of the bond energy which can be associated with a

TABLE II. Length of CC Bonds in Some Condensed Aromatic

otation	Benzene	Naphthalene	Anthracene	Coronene	Pyrene
,3)					
,3)		1.365	1.370	1.385	1.39
,4,4)					
,3,4)			1.396		
,2)	1.39	1.404			
,3,3,3)		1.393	1.436	1.430	
,3,4,4)					1.39
,3,4)		1.425	1.423	1.415	1.42 – 1.45
,4,4,4)				1.430	1.45

Notes

The distances given in this table are taken from G. W. Wheland, *Resonance in Organic Chemistry,* Wiley, New York, 1955, pp. 685–784.

The lengths in parentheses correspond to bonds which are probably somewhat extended due to steric interference coming from certain hydrogen atoms in the molecule.

The underlined distances are accurately known at least to 0.02 A. For the others the accuracy does not exceed 0.03 to 0.04 A. The two distances marked with asterisks may be in error.

pair of CC cores. For some time now it has been known that bond orders which can be calculated by wave mechanical methods are related in a simple way to interatomic distances.

Figure 6 (p. 180) shows the relation that has been obtained between the measurements and the calculations which have been carried out up to now. The curve gives the relation between the measured interatomic distances to the bond orders calculated by the molecular orbital method in what is called the L.C.A.O. or Hückel approximation.[39]

VI. THEORETICAL CALCULATION OF THE RELATIVE RATES OF REACTION OF AROMATIC HYDROCARBONS; COMPARISON WITH EXPERIMENTAL DATA

Consider a chemical reaction which takes place by a simple bimolecular process:

Hydrocarbons as a Function of the Notations of these Bonds.

Triphenylene	Perylene	1 12 - Benzoperylene	Dibenzanthracene	Ovalene
		1 38 – 1 38	1.38	1.345 – 1.38
1 375	1 38 – 1 45*		1 39 - 1.40	
1 39	1.38		1 40	
			1 38	1.404
1.385			1 41	
(1.47) – 1 435	1 45 – (1.50)	1.41 – 1.42 – 1.42 – 1.41	1 40 - 1.45	1.435 – 1.41
	1 38*	1 41 – 1 43 – 1.43 – 1 41	1 40	1.441 – 1.43
		1.40 – 1.40	1 44 – 1 40	– 1.40
		1 43 – 1 42 - 1 43		1.428 - 1.42 – 1 461 – 1.44

$$A+B\xrightarrow{k}C+D+\ldots$$

In the transition state theory[32, 34, 58] the rate constant k is given by the formula:

$$k=\frac{\varkappa T}{h}\frac{f_{M\ddagger}}{f_A f_B}e^{-U/RT}$$

In this expression $\varkappa$ is Boltzmann's constant, h is Planck's constant, T is the absolute temperature, f_A, f_B, $f_{M\ddagger}$ are the partition functions corresponding to molecules A and B and the transition state $M^{\ddagger}$ of the complex intermediate which is formed from the collision of molecule A with molecule B. These partition functions are related to the distribution of the different molecules among the different possible energy levels at the given temperature.

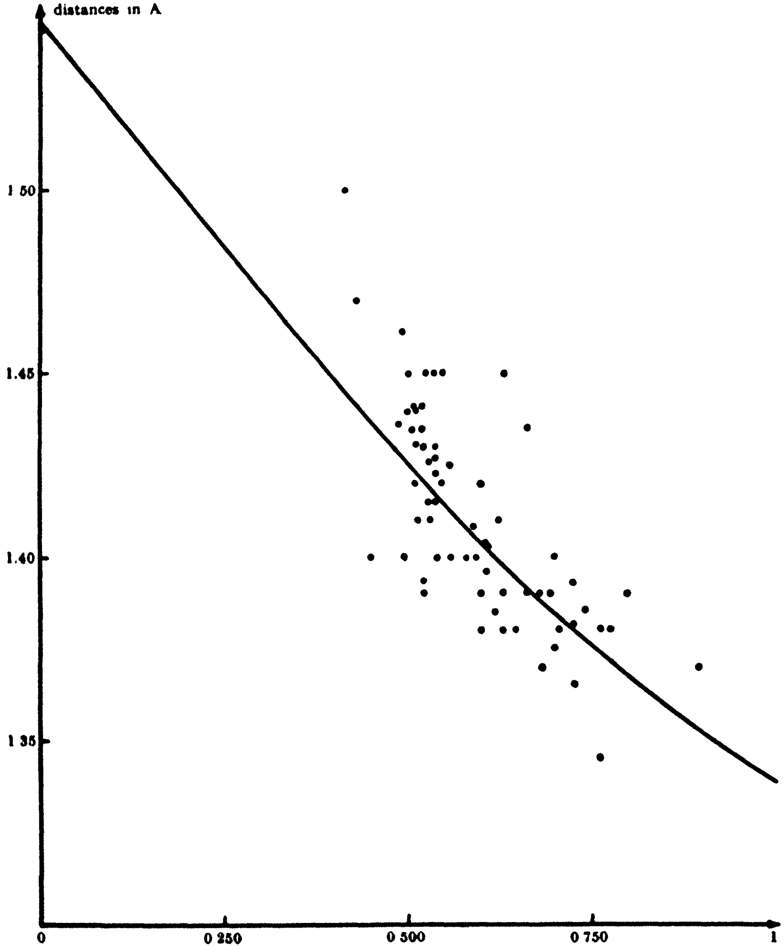


Fig. 6.

The quantity U is called the potential barrier which is the difference between the energy of the ground state of the transition state of the complex intermediate and the sum of energies of the two molecules A and B, each presumed to be in its ground state.

Let us study the action of a given reagent R under carefully defined experimental conditions on several hydrocarbons AH. For example, the rate constant k of the reaction:

$$\mathrm{R+AH} \xrightarrow{k} \mathrm{C+D+} \ldots$$

will be compared with the rate constant k' of the reaction:

$$\mathrm{R+A'H} \xrightarrow{k'} \mathrm{C'+D'+} \ldots$$

The ratio takes the form:

$$k'/k = \frac{f_{M\ddagger'}/f_{\mathrm{A'H}}}{f_{M\ddagger}/f_{\mathrm{AH}}} e^{-\frac{(U'-U)}{RT}}$$

In a series of condensed ring aromatic molecules, it often happens that the ratio of the partition functions,

$$\frac{f_{M\ddagger'}/f_{\mathrm{A'H}}}{f_{M\ddagger}/f_{\mathrm{AH}}}$$

is close to one.[27] Under these circumstances the ratio of rate constants becomes $k'/k = e^{-(U'-U)/RT}$

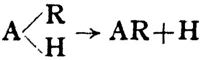
The calculation of relative rates is thus reduced to the calculation of the term $U'-U$. The calculation of this quantity is carried out in a way that depends on the type of reaction that is being studied.

First of all, substitution of aromatic hydrocarbons will be discussed. Two principal mechanisms have been proposed for these reactions.[47] The first, mechanism 1, proposes a one-step substitution:

$$\mathrm{AH+R} \rightarrow \mathrm{AR+H} \qquad (1)$$

The second mechanism takes place in two stages:

$$\mathrm{AH+R} \rightarrow \mathrm{A}\langle^{\mathrm{R}}_{\mathrm{H}} \qquad (2a)$$



$$\mathrm{A}\langle^{\mathrm{R}}_{\mathrm{H}} \rightarrow \mathrm{AR+H} \qquad (2b)$$

With the second mechanism either the first step (2a) or the second step (2b) can be rate-determining.

Since in mechanism 1, R is fixed to the molecule simultaneously as H leaves, the CH and CR bonds will be long bonds in the transition state $M^{\neq}$. With mechanisms 2 it can be assumed that only the CR bond is long. Figure 7 gives the corresponding reaction paths for benzene. With mechanisms 2 the assumption, originally introduced by Wheland,[70] can be made that the delocalized bond in the intermediate complex does not extend to the carbon which is the site of the reaction.

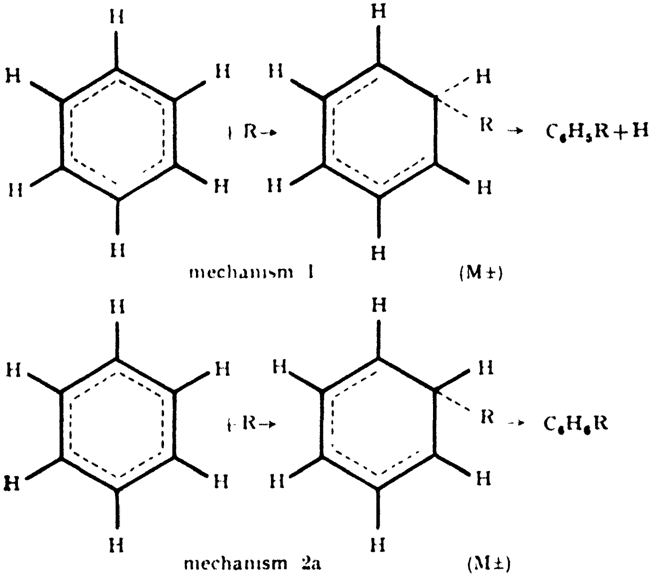


Fig. 7

Let U_π be the change in the energy associated with the delocalized bond in going from the hydrocarbon to the transition state. It can be shown [70] that as a first approximation the difference $U'-U$ for mechanisms 1 and 2a is equal to $U'_\pi - U_\pi$.

In comparing the rate of the nitration of benzene to that for tritio-benzene, Melander[47] showed that under particular experimental conditions the reaction follows mechanism 2a. There are reasons to believe that substitution by the free radicals CCl_3 and CH_3 follows the same course.[41, 45]

In these circumstances the calculation of k'/k is reduced to the calculation of $U'_\pi - U_\pi$ if, in addition, the partition functions are not important.

The U'_π's can in the molecular orbital method (Hückel approximation) be easily expressed in terms of Coulomb integrals α and resonance integrals β which characterize the C atoms and the CC bonds.[39]

The quantity U_π, which is often called the localization energy, is given by the following expression:

$$U_\pi = n\alpha + m\beta$$

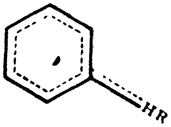
where n only depends on the reagent, and m on the hydrocarbon and the positions of reaction in the hydrocarbon.

In the example which is being considered here there is the simple expression:

$$U'_\pi - U_\pi = (m' - m)\beta$$

The coefficients m of U_π have been calculated for the different atoms of many hydrocarbons.*

In describing the complex intermediate, hyperconjugation can be introduced by the method of Muller, Pickett, and Mulliken.[49] In this procedure the first atom of the reagent R and the hydrogen atom of the carbon where reaction takes place form a "pseudo-atom." This complex can be represented in benzene as:



It can be shown that there is a linear relation between the m's calculated including and neglecting hyperconjugation.[27]

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* These values are listed in the *Dictionary of Theoretical Constants Descriptive of Molecules*, edited by the Mathematical Institute, Oxford, and the Centre de Chimie Théorique de France, Paris. The volumes of this dictionary are provided without charge on request as long as copies are available.

The localization energies are not a direct measure of molecular structure. In view of the purposes of this article it will be better to replace it by a more evidently structural quantity.

Free valence introduced by Daudel and Pullman[29] following a suggestion of Svartholm[65] in the valence bond approximation and then by Coulson[19] in the molecular orbital method will be more useful here.

Free valence is the counterpart in modern terminology to the residual affinity of classical chemistry. A fundamental assumption is that the sum of bond energies of the bonds about a given carbon atom cannot exceed a certain maximum.

If the bond orders are considered to be a measure of this energy, then the free valence of a carbon atom, say i, of an aromatic hydrocarbon is defined by the expression:

$$F_i = C - \sum_j p_{ij}$$

where C is the maximum energy and the summation is carried out over all the bond orders p_{ij} of CC bonds ending at atom i. A number of authors[9,30] have shown that the free valence of atoms of the same type in aromatic hydrocarbons which only contain even numbered rings vary linearly with m. Here

$$m = -aF + b$$

where a is a constant and thus

$$U'_\pi - U_\pi = -a\beta(F' - F)$$

In a series of aromatic molecules which do not contain odd numbered rings, the rate constants which are characteristic of the same type of substitution which follows mechanisms 1 or 2a and which take place at the same type of carbon atoms obey the relation:

$$\frac{k'}{k} = e^{+a\frac{\beta(F'-F)}{RT}}$$

when, as is often the case, the partition function terms are nearly constant.

Thus a precise relation between reactivity as represented by k and structure as represented by F has been established. It will be interesting to see if experimental facts confirm this relation.

We shall begin by a consideration of some semiquantitative observations for nitration. We have already mentioned that Melander has shown that this reaction, at least in a mixture of nitric and sulfuric acids, follows mechanism 2a. Dewar[31] has measured the ratios k'/k of the rates of reaction for the nitration of several aromatic hydrocarbons. Unfortunately Dewar's experimental conditions are not the same as those of Melander. He used acetic anhydride as solvent and nitrated with pure nitric acid in the presence of an excess of hydrocarbon in order to obtain only the mononitro derivative. It is not certain that Melander's conclusions would be valid in this particular way of carrying out the nitration. Still it is interesting to see if the constants k do vary in the same way as the free valence.

Table III gives some values of k'/k_B measured (where k_B is the constant for benzene) and the values of the free valence for atoms at the position of reaction.

TABLE III. Relative Rates of Nitration and Free Valence Values.

Molecule	Position	k'/k_B	F
Benzene		1	0.398
Naphthalene	β	50	0.404
Naphthalene	α	490	0.453
Pyrene	3	20000	0.468
Perylene	3	98000	0.474

As expected, the rate increases with increasing free valence and it is clearly seen that the free valence can be used either to predict the most reactive position in a molecule (here, for example, free valence indicates that the α position in naphthalene should be more reactive than the β position) or to compare the reactivity of two molecules.

A more quantitative discussion can be made concerning the fixation of the CCl_3 group which probably also follows mechanism 2a. Kooyman and Farenhorst[41] have studied this reaction in two different ways. In one, the addition of carbon tetrachloride to hexadecene-1 was initiated by the action of benzoyl peroxide. The $\cdot CCl_3$ radicals are fixed on the olefin by the reaction:

$$\cdot CCl_3+H_2C{=}CH{-}C_{14}H_{29} \xrightarrow{k_a} CCl_3{-}CH_2{-}\cdot CH{-}C_{14}H_{29}$$

If an aromatic hydrocarbon ArH is added to the reaction medium, this reaction slows down. This is interpreted by assuming that the following competitive reaction takes place:

$$CCl_3+ArH \xrightarrow{k_T} ArCCl_3H$$

$$ArCCl_3H \rightarrow ArCCl_3+H$$

The kinetic study makes it possible to measure the quantity

$$K = \frac{1}{2}\frac{k_T}{k_a}$$

In order to simplify the comparison between theory and experiment the authors have assumed that only the atoms with the highest free valence will be of appreciable importance for the reaction. If n is the number of these atoms in a molecule, the following quantity is introduced:

$$K_r = \frac{1}{2}\frac{k_T}{nk_a} = \frac{1}{2}\frac{k}{k_a}$$

where k represents the rate constant reduced to one of the most reactive atoms.

In comparing two constants K_r and K'_r corresponding to two hydrocarbons,

$$\frac{K'_r}{K_r} = \frac{k'}{k}$$

and it is of interest to see if

$$\frac{k'}{k} = e^{\alpha\beta\frac{(F'-F)}{RT}}$$

or

$$\ln k' = \frac{\alpha\beta F'}{RT} + \ln k - \frac{\alpha\beta F}{RT}$$

In other words a linear relation should exist (at constant temperature) between $\ln k'$ or $\ln K'_r$ and F'.

The curve corresponding to a temperature of 91° in Fig. 8 shows that this is found. This is at the same time a proof of the accuracy of the theoretical relation which has been given and the reasonableness of the mechanism which has been proposed for the reaction.

Some further refinement is possible with the fixation of the methyl group which has been carried out experimentally by Szwarc and Levy[45] in a very similar way to the experiment of Kooyman and Farenhorst.

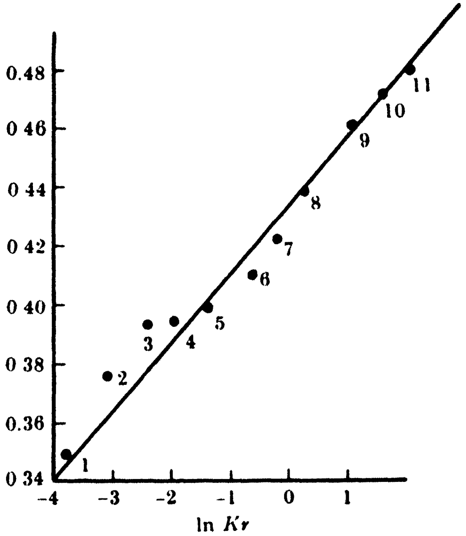

Fig 8 Relation between free valence values and reaction speed on CCl_3. 1, Benzene; 2, diphenyl; 3, phenanthrene; 4, naphthalene; 5, chrysene, 6, pyrene; 7, stilbene, 8, 1,2—5,6-dibenzanthracene; 9, anthracene; 10, naphthacene; 11, 1,2-benzanthracene.

Coulson has related rate reactions to localization energies.[20] We will reconsider this question here in somewhat greater detail. As was previously the case, measurements refer to total rates of reaction.

As all the six carbon atoms in benzene are equivalent, the total rate constant k_T can be written:

$$k_T = 6\frac{\varkappa T}{h}\frac{f_M{\ddagger}}{f_A f_B} e^{-U/RT}$$

For another molecule the rate constant would have the form:

$$k'_T = \frac{\varkappa T}{h} \frac{f_{M'}{}^{\ddagger}}{f_{A'} f_{B'}} \sum_i e^{-U_i/RT}$$

if it is assumed that the partition function term is the same whichever atom is the position of reaction in the molecule. Here U_i is the potential barrier of the ith atom.

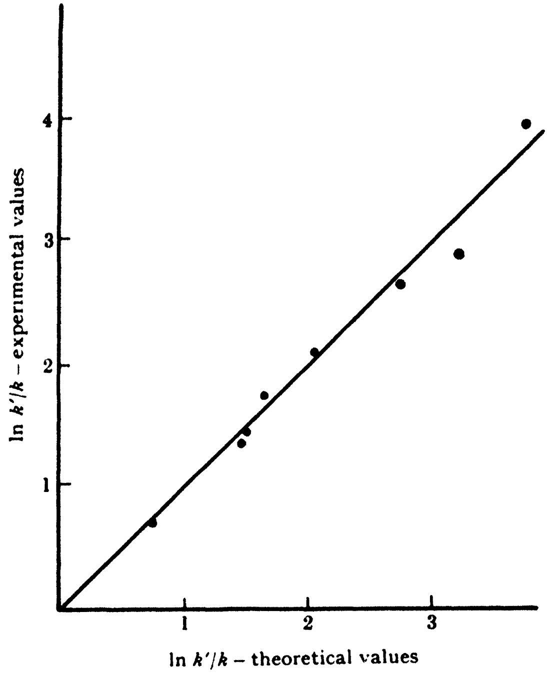

Fig 9

If the ratios of partition functions are equal, then the ratio of rate constants has the form:

$$\frac{k'_T}{k_T} = \frac{1}{6} \sum_i e^{-\frac{U_i - U}{RT}}$$

As all the atoms in a series of aromatic molecules that can react by substitution are of the same type (type 2), this equation can be rewritten:

$$\frac{k'_T}{k_T} = \frac{1}{6} \sum_i e^{+\alpha\beta\frac{(F_i - F)}{RT}}$$

Here a is a known coefficient but the value of the resonance integral is not very accurately known.

The value of this integral is thus generally determined empirically using this formula as an experimental value of k'_T/k_T. In taking $\lambda = a\beta/RT = 30$, the curve given in Fig. 9 has been obtained[27] which relates ln k'_T/k_T calculated theoretically to ln k'_T/k_T measured experimentally at 85°.

The agreement is remarkably good.

Free valence can be used for reactions which involve substituted hydrocarbons. Fierens, Hannaert, Van Rysselberge, and Martin[35] have studied the exchange of chlorine by iodine in the chloromethylated derivatives of aromatic hydrocarbons using potassium iodide in acetone solution. This is an S_N2 reaction. Figure 10 gives the reaction path which is assumed for a benzene derivative.

A careful study of this reaction has shown[27] that the partition function terms vary only a little bit so that it is possible to write:

$$\frac{k'}{k} = c^{-\frac{U'-U}{RT}}$$

Since here the reaction involves only a single atom it is not necessary to use the index T.

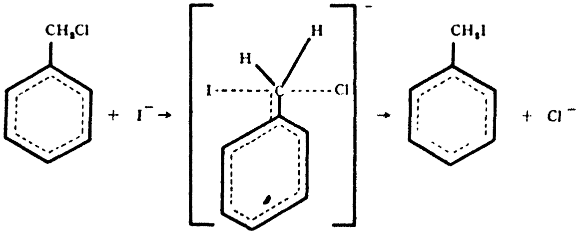

Fig. 10.

It can also be shown that

$$U'-U \backsim U'_\pi - U_\pi$$

where the π terms refer to the change in energy of the delocalized bonds of the aromatic molecules.

The π quantities can be calculated and the exponential relation between k' and U'_π has been verified.[26]

Free valence can also be used. There is a linear relation[26] between U'_π and the free valence of the atom to which the CH_2Cl group is attached and this explains why Fierens and his collaborators found a linear relation between ln k and free valence.

The same kind of discussion can be extended to cover some kinds of addition reactions which involve only aromatic hydrocarbons with even-numbered rings. For example, the diene synthesis is often considered to be a one-step reaction in which two carbons of the hydrocarbon simultaneously add to the dienophile.[2, 7, 33, 69]

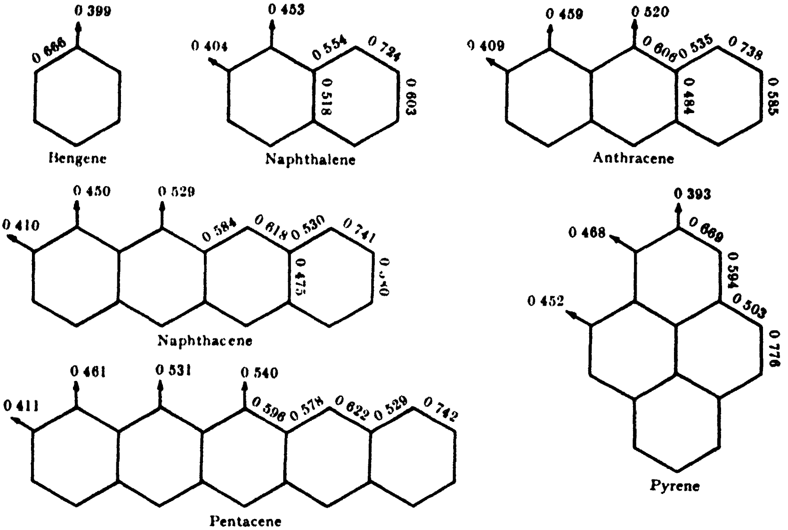

Fig. 11. Bond and free valence values, from the *Dictionary of Theoretical Constants Descriptive of Molecules* (quoted on p. 183)

Then there should be an exponential relation between the rate constant and the sum of the free valences of the atoms where reaction takes place.[16] The kinetic data which are available now are not sufficient for a quantitative consideration of this problem, but the qualitative agreement is very satisfactory. Figure 11 shows that, for example, in anthracene the sum of the free valences of the "meso" carbon atoms is greater than the sum of the free valences of other pairs of para positions. In fact, addition of maleic anhydride takes place at the meso position.[11, 13]

In going from benzene to pentacene the largest sum of the free valence of a pair of atoms in a para position increases as does the ease of the diene synthesis in this series. It is well known that maleic anhydride hardly reacts with benzene or naphthalene. A reaction takes place with anthracene and even more readily with naphthacene and pentacene.[12]

It can be shown that the one-step addition to the bonds of the same type in similar series of molecules takes place more readily, as the bond order of these bonds is large. Thus ozone adds first of all to the $\alpha\beta$ bonds in naphthalene and to the $1-2$ bonds of pyrene[40, 66, 71] where, as the diagrams in Fig. 11 show, the highest bond orders are found.

VII. APPLICATIONS TO THE STUDY OF THE CARCINOGENIC POWER OF AROMATIC HYDROCARBONS*

Schmidt[64] was the first to use wave mechanical methods to study the mechanism of the action of carcinogenic substances. He concluded that in order for an aromatic hydrocarbon to be carcinogenic, it was necessary that there exist in the molecule a region rich in π electrons the density of which exceeded a certain threshold value.

In the course of a similar investigation Svartholm[65] concluded that it was reasonable to associate the carcinogenic properties of hydrocarbons to their reactivity with respect to addition across one of their bonds.

In order to explain an antagonism phenomenon which they had observed Lacassagne, Buu-Hoi, Daudel, and Rudali[42] imagined that carcinogenic hydrocarbons must be capable of forming an addition complex with the substrate which determines cellular division and that this addition is only effective for the production of carcinomas if it takes place at certain definite points in the cell.

Several years later Miller and Miller[48] confirmed a part of this hypothesis. They have observed in the liver of rats treated with

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* An extended and excellent review of this question is given in A. Pullman and B. Pullman, *Cancérisation par les substances chimiques et structures moléculaires*, Masson, Paris, 1955.

p-dimethyl aminoazobenzene a complex formed by this molecule bound to cellular material.

Several theoretical studies[22] have shown that hydrocarbons or derivatives that are carcinogenic have a bond with high bond order. As we have seen that this property determines the rate of certain addition reactions to this bond, it is tempting to assume that the addition of the hydrocarbon through one of its bonds to certain cellular constituents is an important step in the production of cancer.

More recently it has been shown[60] that the ability to react by addition across a pair of opposite positions hinders, on the contrary, the appearance of carcinogenic activity.

Let k be the total rate constant for the addition of the hydrocarbon by one of its bonds and k' be the total rate constant for the addition of the same molecule across a pair of opposite atoms. The proportion of molecules which react by addition of a bond is

$$\frac{k}{k+k'}$$

The following quantity may be considered as giving an idea of the efficiency of the reaction:

$$I = \frac{k^2}{k+k'}$$

It would be interesting to compare this quantity to the carcinogenic power of hydrocarbons.

This cannot unfortunately be done, for *in vivo* measurement of this rate would be extremely difficult. It is, however, possible to calculate theoretically I, at least approximately. The discussions of the preceding paragraph suggest that the k's be replaced by quantities of the type $\sum_i e^{-U_{in}/RT}$ which would only differ from the k's by some constant factor. Table IV gives the results of one such calculation. The quantities U_{in} have been replaced by the corresponding quantities $m\beta$. The value of 40 $k$cal/mol has been used for β and 300° K for T. As the rate constants are valuated except for a constant factor we have arbitrarily taken $k = 1$ for $m = 1.15$ and $k' = 1$ for $m' = 3.67$.

For each of the substances in the table there is given, in addition to I, an indication of its carcinogenic power. From a study of the table it will be seen that in order for a substance to be clearly carcinogenic (+, ++, or ++++) the effective coefficient of addition by a bond must be greater than 40.

This necessary condition is not sufficient as anthanthrene (with $I = 8000$), for example, is not carcinogenic.

A similar idea has been studied experimentally to see if there exists a relation between the ability of hydrocarbons to add to cellular constituents and their carcinogenic activity. Wiest and Heidelberger[72] have shown with 1, 2—5, 6-dibenzanthracene marked with radio carbon that a high proportion is fixed to the soluble proteins of the animals painted with a solution of a carcinogenic substance.

However, Woodhouse[73] has observed that this same phenomenon occurs even with substances which are not carcinogenic, like perylene. More recently Heidelberger and Moldenhauer[38] have taken up the question again. They measured the amount of hydrocarbon fixed to the protein as a function of time after painting. They obtained curves which went through a maximum about two days after the experiment was started. The values of these maxima (in millimicrograms of hydrocarbon per milligram of protein) are given in Table IV.

There are not enough data to arrive at any definite conclusion. It may be that for a substance to be carcinogenic it is necessary that this maximum be high. This is certainly not a sufficient condition because of all the molecules studied 1, 2—3, 4-dibenzanthracene has the highest maxima and it is not carcinogenic.

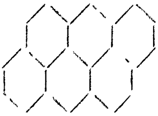
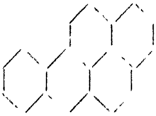
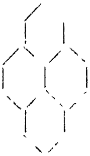
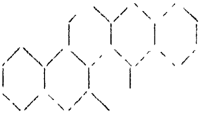
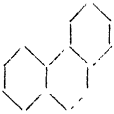
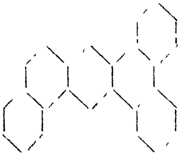
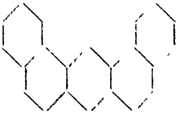
However, it is important to remember that experimental evidence does not indicate exactly how the hydrocarbon is fixed to the proteins. It is not certain whether addition takes place at a bond or across two opposite atoms or in both ways at the same time.

In order to try to get some information on this point the quantity

$$J = \frac{k'^2}{k+k'}$$

has been added to Table IV.

TABLE IV

	I	J	Carcinogenic power[a]	Amount of hydrocarbon fixed to protein
	8000	0	—	—
	4000	1.6×10^{-8}	++++	30
	1000	0	—	
	360	0.6×10^{-10}	++++	
	360	10^{-8}	—	2
	250	1000	—	
	230	6×10^{4}	+	

[a] —, Not carcinogenic; ±, hardly carcinogenic; +, slightly carcinogenic; ++, rather carcinogenic; ++++, very carcinogenic.

TABLE IV (Continued)

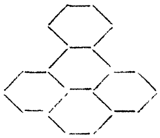
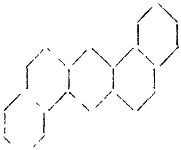
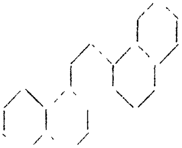
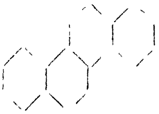
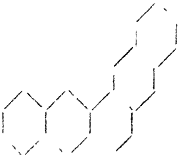
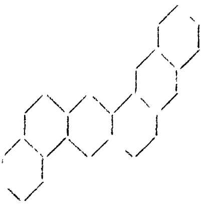
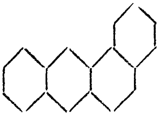
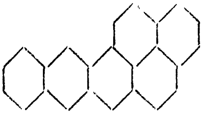
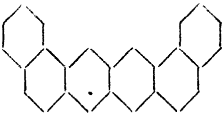
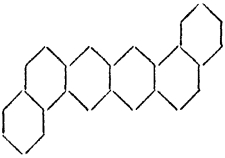
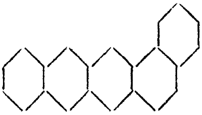
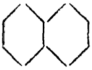
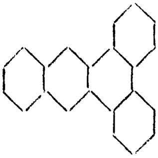
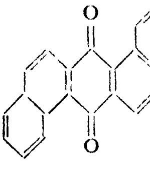
	I	J	Carcinogenic power[a]	Amount of hydrocarbon fixed to protein
	130	4×10^{-10}	—	
	120	64000	++	25
	16	4×10^{-6}	—	
	16	1.5×10^{-5}	—	
	40	8×10^{6}	—	
	2	8×10^{6}	—	

TABLE IV (Continued)

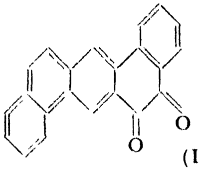
	I	*J*	Carcinogenic power*	Amount of hydrocarbon fixed to protein
	0.2	3×10^{7}	$\mp$	10
	10^{-1}	8×10^{9}	—	
	3×10^{-2}	2×10^{9}	—	
	3×10^{-2}	2×10^{9}	—	
	3×10^{-4}	10^{12}	—	
	10^{-5}	4×10^{-1}	—	
	6×10^{-11}	2.5×10^{5}	—	48
	5×10^{-12}	4×10^{-10}	—	
	2×10^{-13}	6×10^{10}	—	

The fact that the fixation maximum is of the same order of magnitude for benzopyrene ($I = 4000$, $J = 1.6 \times 10^{-8}$) and for 1, 2—5, 4-dibenzanthracene ($I = 6 \times 10^{-11}$, $J = 2.5 \times 10^{5}$) seems to show that the fixation takes place both by bonds and by a pair of opposite atoms. It would thus not be very surprising if the correlation between the fixation maximum and carcinogenic activity is not very good.

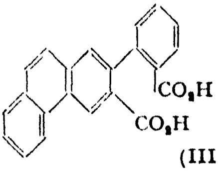
The discussion of nonsubstituted aromatic hydrocarbons will be terminated by a few words on the kinds of metabolites which are formed when these substances circulate in the animal organism.



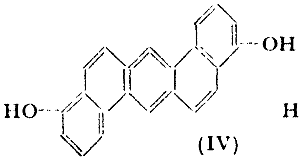
(I)



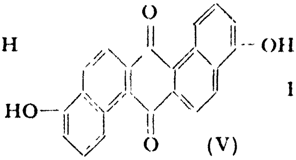
(II)



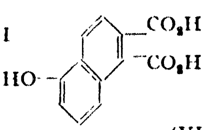
(III)



(IV)



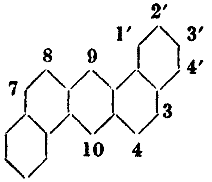
(V)



(VI)

Scheme 1 gives the principal metabolites which are formed from 1, 2—4, 6-dibenzanthracene.[3, 37] Finding (I), (II), and (III) seems very normal as the bonds of the dibenzanthracene most likely to react by addition are 3—4 and 7—8. The 9 and 10 atoms also are a pair of very active atoms. The formation of (IV) and (V) is much more difficult to understand as 4′ is not a normal center of reactivity.

Boyland and Weigert[4] have suggested that the metabolites



might be formed while the hydrocarbon is fixed on the tissue. In that case, hyperconjugation between the hydrocarbon and the part of the tissue which has reacted might well activate atoms such as 3′ and 4′.[22] A quantitative study of this problem, using slightly different methods but essentially the same type of calculation, by Pullman and Baudet[62] has confirmed that prediction.

The values of $m\beta$ used in the calculation of the I's and the J's of Table IV have been calculated neglecting hyperconjugation. We have said (p. 183) that this should not have an important effect on the results. Nagata, Fukui, Yonezawa, and Tagashira[51] have found, to the contrary, that introducing hyperconjugation completely changes the order of $m\beta$. This abnormal result is due to the fact that the Japanese workers have used some further approximations. When hyperconjugation is properly introduced, the results are exactly the same as when it is neglected.[15]

It would be very valuable to measure in a number of examples the percentage of each metabolite which is formed in order to see what relation exists between these percentages and the quantities I and J. If the approximation which is now accepted is correct, it seems likely that the proportion of substances like (I) should increase with $I/(I+J)$ while, on the contrary, substances like (II), (III), and (IV) should depend on $J/(I+J)$.

The relation between structure and carcinogenic activity of substituted and heteroatom conjugated hydrocarbons has also been extensively studied. Here, unfortunately, theoretical calculations are very much less well founded as the substituents and heteroatoms are represented by parameters which are not well defined. As an example, consider the methyl derivatives of the angular benzacridines. Using the suggestions of Schmidt, Pullman[61] has shown that in the valence bond approximation there is an increasing relation between carcinogenic power and electronic charge of the bond which in the unsubstituted hydrocarbon had the highest bond order.

In a similar way it was possible to predict[10] the carcinogenic activity of a number of molecules in this series when the experimental data were not available. The agreement between the predictions and the experimental results is satisfactory.[74]

As large electronic calculating machines are now available, it is possible to calculate the charge distribution in molecules[17] much more accurately. In addition, experimental data in 75 angular benzacridines is now available. The current conclusion of this work[43] is that the probability of finding a carcinogenic substance in this series increases with the charge of the bond which is most likely to react by addition.

In conclusion it seems that a necessary condition that a molecule be carcinogenic is that it has a high effective rate of addition across one of its bonds to an electrophilic center in the tissue. This shows how a quantum-chemical study can help one to understand certain aspects of the pathogenic properties of chemical substances.

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MOLECULAR THEORY OF SURFACE TENSION

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CONTENTS

I. INTRODUCTION

Attempts to calculate surface tension or surface energy from the knowledge of intermolecular potentials have been made since the time of Laplace. However, because the intermolecular potentials and the distribution functions of liquids, both of which are necessary for the study of surface tension, have only recently become known, the theory has remained undeveloped until recent years.

As a result of the clarification of the nature of intermolecular forces by quantum mechanics and of the investigation, both from the experimental and the theoretical points of view, of the distribution of atoms or molecules in liquids, the situation has become more favorable for the study of the theory of surface tension. Thus surface tensions or surface energies of some simple liquids have already been calculated in terms of intermolecular forces from theories which are based on some simplifying assumptions such as the cell model of liquid structure. The results are in good agreement with observed values.

As will be seen later, the expression of the surface tension in terms of the intermolecular forces and distribution functions has been obtained without resorting to any simplifying assumption. However, numerical calculation of the strict expression has not yet been successfully completed.

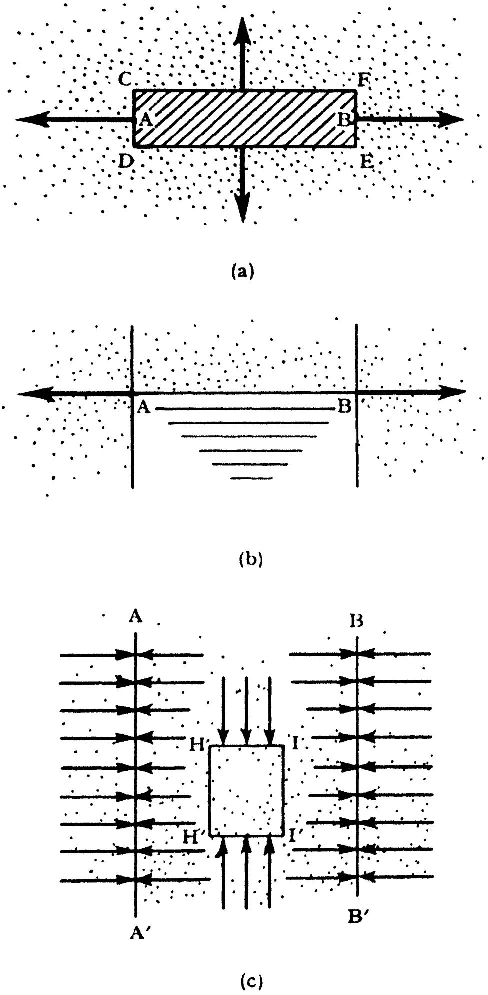
In this paper recent developments in the theory of surface tension will be reported with special reference to statistical mechanics, and problems which are to be solved in the future will be presented.

II. THERMODYNAMICS OF SURFACE TENSION

It will first be shown how surface tension can be expressed in terms of stresses in the transition layer between liquid and vapor phases by discussing the equilibrium of the sides of a rectangular vessel which contains the liquid under consideration.

The vessel is shown by CDEF in Fig. 1a.[3] The walls CD, DE, EF, and FC are assumed to be freely movable, but kept in the positions by forces on both sides of each of the walls. The pressure exerted by the liquid or the vapor on both sides of the walls is equal to the saturation pressure of the vapor except at the positions where the transition layer is in contact with the wall. In Fig. 1b, a macroscopic view near the surface of the liquid is shown. AB is the boundary between the liquid and the gas phases. In Fig. 1c a microscopic view is shown. Consider a portion between the two planes AA′ and BB′ in the vessel. The lower part of this portion is filled with liquid while the upper part is filled with the saturated vapor. The density varies continuously from the value appropriate to the liquid in bulk to the value of the saturated vapor. The pressure inside the walls varies continuously as the transition layer is traversed, being lower than the pressure of the saturated vapor in the transition zone. Thus it is necessary to exert tensions on the outer sides of AA′ and BB′ in order to maintain the shape of the vessel.

Let the saturated vapor pressure be p and the pressure exerted on the inside of the walls be p_T, which is a function of the height of the point at which the pressure is considered. As will be shown later, there is some ambiguity as to the definition of pressure when the pressure across a strip of atomic dimension is considered.



(a)

(b)

(c)

Fig. 1. Liquid-vapor interface. (a) Plane figure. (b) Side view (macroscopic). (c) Side view (microscopic).

For the present, however, it will be assumed that such a quantity as p can be defined in the usual manner at any point of the transition layer. If the height is denoted by z, the tension per unit length which must be applied on the outer sides of AA′ and BB′ is given by

$$\gamma = \int_{-\infty}^{\infty} [p - p_{\mathrm{T}}(z)]dz \tag{II.1}$$

This equation is then the surface tension of the liquid. One of the main purposes of this paper is to show how the pressure $p_{\mathrm{T}}(z)$ and hence the surface tension γ can be given in terms of intermolecular forces and statistical mechanical quantities such as the distribution functions.

Now, it is well known that in the inner part of a fluid the pressure across a plane is the same irrespective of the directions of the plane, that is, Pascal's law holds. But Eq. II.1 shows that surface tension arises from the circumstance that the law does not hold in the transition region of two homogeneous phases. Thus the pressure p_{T} (tangential pressure) across a plane perpendicular to the surface of the liquid is different from that across a plane parallel to the surface of the liquid. The latter may be called the normal pressure and denoted by p_{N}. Since p_{N} is shown to have the same value irrespective of position, it may be denoted simply by p as is done in Eq. II.1

The thermodynamics of the transition layer will now be developed, and the relation between the surface tension and the so-called surface energy will be obtained. There is one particular aspect to which special attention should be paid when dealing with the thermodynamics of a transition layer. The transition from the liquid to the gas phase occurs when a transition layer of atomic dimension is traversed. Thus no portion in the layer can be assumed to be so homogeneous that the thermodynamics of homogeneous phases is applicable. Here the procedure of Guggenheim[12] will be followed closely, because it leads to a very careful derivation of a formula which will be used frequently in this paper. Following Guggenheim, the transition region contained between two planes AB and A′B′ will be considered, the plane AB being in the uniform region of the gas phase and the plane A′B′ being in the uniform region of the liquid phase.

Now, let the volume V^σ and the area A be changed without changing the mass of the portion between AB and A′B′. The work done for a change dV^σ of the volume and a change dA of the area is

$$-p\, dV^\sigma + \gamma\, dA$$

If the substance consists of only one component, the most general variation of the internal energy U^σ of the surface layer is given by

$$dU^\sigma = T\, dS^\sigma - p\, dV^\sigma + \gamma\, dA + \mu\, dN^\sigma \qquad \text{(II.2)}$$

where μ and N^σ are the chemical potential and the number of molecules, respectively. S^σ is the entropy of the portion under consideration.

The Helmholtz free energy of the transition layer is given by

$$G^\sigma = U^\sigma - TS^\sigma + pV^\sigma - \gamma A \qquad \text{(II.3)}$$

The differential of G^σ, dG^σ, will have the following form, if Eq. II.2 is substituted for dU^σ in Eq. II.3

$$dG^\sigma = -S^\sigma dT + V^\sigma dp - A\, d\gamma + \mu\, dN^\sigma \qquad \text{(II.4)}$$

Since

$$G^\sigma = N^\sigma \mu \qquad \text{(II.5)}$$

Equation II.4 leads to the relation:

$$S^\sigma dT - V^\sigma dp + A\, d\gamma + N^\sigma d\mu = 0 \qquad \text{(II.6)}$$

which is the Gibbs-Duhem relation for the surface layer. If each term of Eq. II.6 is divided by the area A of the transition layer, Eq. II.6 can be written

$$-d\gamma = S_u^\sigma dT - \tau\, dp + N_u^\sigma d\mu \qquad \text{(II.7)}$$

where S_u^σ and N_u^σ are the entropy and the number of molecules per unit area, given by $S_u^\sigma = S^\sigma/A$ and by $N_u^\sigma = N^\sigma/A$, and τ is the thickness of the layer, given by $\tau = V^\sigma/A$. The differential of the chemical potential, $d\mu$, in the last term of the right-hand side of Eq. II.7 can be expressed in terms of the quantities for the bulk phases:

$$d\mu = -s^l dT + v^l dp = -s^g dT + v^g dp \qquad \text{(II.8)}$$

In these formulas s^l, v^l, s^g and v^g refer to a molecule. Elimination of $d\mu$ and dp from Eqs. II.7 and II.8 leads to

$$-\frac{d\gamma}{dT} = (S_u^\sigma - n^\sigma s^l) - (\tau - n^\sigma v^l)\frac{s^g - s^l}{v^g - v^l} \tag{II.9}$$

Since

$$\begin{aligned}\mu &= u^l - T s^l + p v^l = u^g - T s^g + p v^g \\ &= 1/n^\sigma (u^\sigma - T s^\sigma + p\tau - \gamma)\end{aligned} \tag{II.10}$$

Equation II.9 gives

$$\gamma - T\frac{d\gamma}{dT} = (u^\sigma - n^\sigma u^l) - \frac{\tau - n^\sigma v^l}{v^g - v^l}(u^g - u^l) \tag{II.11}$$

The factor $\tau - n^\sigma v^l$ in the second term seems, at first sight, to depend on the choice of the planes AB and A′B′. However, it can easily be shown that this factor does not depend on the locations of the planes, so far as these are in the homogeneous regions of respective phases. At temperatures far below the critical point of the substance, the second term on the right-hand side of Eq. II.11 can be neglected in comparison with the first term. In such cases Eq. II.11 reduces to the form

$$\gamma - T\frac{d\gamma}{dT} = u^\sigma - n^\sigma u^l = U \tag{II.12}$$

The quantity U is the increase of energy for an increase of unit area of the surface and is called the surface energy. If the surface tension and its dependence on temperature are known, the surface energy can be obtained from Eq. II.12, though it must be born in mind that the formula is obtained from Eq. II.11 by neglecting the second term in comparison with the first one.

III. CALCULATION OF THE SURFACE ENERGY

Kassel and Muskat[19] were the first to attempt to calculate the surface energy after the quantum-mechanical theory of intermolecular potential was completed in 1930. They assumed the distribution function of liquid in two alternative ways. First, they assumed that the radial distribution function $g(R)$ is given by

(a) $g(R) = 0$ for $R < R_0$, $g(R) = 1$ for $R \geqq R_0$,

and secondly, by

(b) $g(R) = \exp[-\phi(R)/kT]$.

The agreement between the theory and the observed values was comparatively poor especially when assumption (b) was made for the molecular distribution function.

A formula which connects the surface energy with the distribution function and the intermolecular potential was derived by Fowler.[11] He assumed that there is a mathematical surface of density discontinuity where the density changes discontinuously from the value of the liquid in bulk to the value of the vapor, which can be taken to be zero at lower temperatures. This assumption will be criticized later in this paper. If, following the assumption, the molecular distribution of the liquid is uniform up to the surface of discontinuity as in the interior of the liquid, the surface energy is given by

$$U = -\frac{\pi}{2}[\varrho^{(1)}]^2 \int_0^\infty R^3 \phi(R) g(R)\, dR \qquad \text{(III.1)}$$

This formula can be used to calculate the surface energy of a liquid when both the intermolecular potential and the distribution function are known. Thus, the distribution function of liquid argon obtained by Eisenstein and Gingrich[10] and the known intermolecular potential give $U_{\text{calc}} = 27$ erg/cm^2, while the observed value, that is, the value obtained from the observed values of surface tension by Eq. II.12, is $U_{\text{obs}} = 35$ erg/cm^2. For mercury the distribution functions obtained by Boyd and Wakeham[5] and the interatomic potential obtained by Hildebrand, Wakeham, and Boyd[16] can be used. The calculated value is $U_{\text{calc}} = 490$ erg/cm^2, which can be compared with the observed value $U_{\text{obs}} = 500$ erg/cm^2.

Use of Eq. III.1 to calculate the surface energy requires the knowledge of the intermolecular potential $\phi(R)$ and the radial distribution function, but there are only a few substances for which these data are available. One way to avoid this difficulty is to make some general assumptions about the distribution function and to derive a formula which contains only the parameters of the intermolecular potential.

Now, it has often been emphasized that there is a remarkable similarity between the structures of solid and liquid states. Many investigations of the atomic or molecular arrangement in liquids by the method of x-ray diffraction have shown that there exists, even in the liquid state, short distance regularity in molecular distribution similar to that of the solid state, while long distance regularity does not exist. Some of the properties of liquids are intimately related to the long distance order while some are related mainly to the short distance order. The surface energy of liquids belongs to the latter class, so the assumption that the structure of a liquid is similar to that of a solid will not lead to serious error in deriving a formula which may be used to calculate the surface energy from the knowledge of intermolecular potentials.

Surface energy is defined as the increase in energy per unit area of the surface in an isothermal change. According to the classical theory, the mean value of the kinetic energy of a molecule is the same whether it is in the interior or on the surface of the liquid. Therefore we have only to calculate the increase in the total potential energy ot the system which results from an increase of the area of the surface.

The structure of the liquid near the surface is obviously different from that of the liquid in bulk. Thus the position of the outermost layer of molecules will not be at the same distance from its neighbors as it would occur in an infinite lattice. This circumstance was discussed in detail by Corner.[7] But, for the present, this difference may be neglected, and it will be assumed that the molecular arrangement is uniform up to the surface of the liquid.[13,15]

Now, the potential energy of the liquid may be divided into two parts: the potential energy when the molecules are at the cell centers; and the mean potential energy for the molecular motion around the cell centers. If the motion of a molecule is simple harmonic, the average potential energy of a molecule corresponding to the motion in any direction is given by $(1/2)kT$ irrespective of the frequencies; therefore it has the same value whether the molecule is in the interior or on the surface of the liquid, where the molecules are considered to oscillate with different frequencies from those of the interior molecules. Any difference in the frequencies of vibration of molecules will give rise to surface entropy, so that the difference in the frequencies cannot be neglected in calculating the surface free energy, that is, the surface tension. However, when the surface energy is calculated by classical theory, the mean potential energy due to deviations of molecules from cell centers may be taken to have the same value whether the molecules are in the interior or on the surface of a liquid, so long as the motion of each molecule can be assumed to be simple harmonic. The force acting on a molecule when it deviates from the cell centers is in reality more complicated than in the case of a harmonic oscillator, and the mean potential energy resulting from the molecular motion when the molecule is on the surface is certainly different from that when it is in the interior of the liquid; but it may be said that a large part of the mean potential energy will be canceled by taking differences. The part which remains will be small compared with that which arises from the lattice energy.

With these simplifying assumptions, the classical expression of surface energy is obtained in the form of the increase in potential energy per unit surface area when an infinite face-centered cubic lattice is divided into two semi-infinite halves. The intermolecular potential will be assumed to have the form of the Lennard-Jones 6—12 function

$$\phi(R) = 4\varepsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right] \qquad \text{(III.2)}$$

The calculation includes summation of the terms $(\sigma/R)^{12}$ and $(\sigma/R)^{6}$ over the lattice sites. The calculation of $\Sigma\ (\sigma/R)^{12}$ presents no difficulty, since the successive terms diminish rapidly, and calculations of the contributions from molecules within the fourth or fifth neighboring shells are sufficient for the purpose. For the calculation of $\Sigma\ (\sigma/R)^{6}$ some sort of extrapolation is necessary, since there is a substantial contribution from more remote molecules. We replace the neighboring molecules which are more than a certain arbitrary distance νa(a is the distance between nearest molecules; $\nu = 4$ or 5) by a continuous uniform distribution of density $\sqrt{2}/a^3$ and approximate to the sum $\Sigma\,(\sigma/R)^6$ over these outer neighbors by the integral of $(\sigma/R)^6$ over the continuous distribution. The result depends to some extent upon the crystal plane which is to be exposed. The dependence of the surface energy on the exposed face is shown below.

Exposed face: (100)-plane,

$$U = \frac{8}{a^2}\,\varepsilon\left[1.4\left(\frac{\sigma}{a}\right)^6 - \left(\frac{\sigma}{a}\right)^{12}\right] \tag{III.3}$$

Exposed face: (110)-plane,

$$U = \frac{8.8}{a^2}\,\varepsilon\left[1.35\left(\frac{\sigma}{a}\right)^6 - \left(\frac{\sigma}{a}\right)^{12}\right] \tag{III.4}$$

Exposed face: (111)-plane,

$$U = \frac{7.2}{a^2}\,\varepsilon\left[1.35\left(\frac{\sigma}{a}\right)^6 - \left(\frac{\sigma}{a}\right)^{12}\right] \tag{III.5}$$

These three formulas have similar forms, and the last one gives the smallest value for the surface energy. Another formula similar to the foregoing equations can be derived from Fowler's formula, Eq. III.1, by introducing a simplifying assumption concerning the molecular distribution. In Eq. III.1 $\varrho^{(1)}g(R)\cdot 4\pi R^2 dR$ is the average number of molecules which are in the distance between R and $R+dR$ from any specified molecule. If this number is denoted by $n(R)dR$, the surface energy can be given by

$$U = -\tfrac{1}{8}\varrho^{(1)}\int_0^\infty R\,n(R)\,\phi(R)\,dR$$

This formula may be rewritten

$$U = -\tfrac{1}{8}\varrho^{(1)}\sum n_i R_i \phi(R_i) \tag{III.6}$$

where n_i is the number of molecules at the distance r_i from a specified molecule. Assumption of face-centered cubic structure leads to

$$U = \frac{8}{a^2}\,\varepsilon\left[1.5\left(\frac{\sigma}{a}\right)^6 - 1.08\left(\frac{\sigma}{a}\right)^{12}\right] \tag{III.7}$$

Since Eqs. III.3, III.4, III.5, and III.7 are all derived by approximate treatments, it would not be very significant to decide which one is preferable to others. Hereafter Eq. III.5 will be used, since it gives the smallest value for the surface energy, so that it might be said that the appearance of the (111)-plane is most probable.

Equation III.5 can be written in a reduced form. If the reduced values

$$U^* = U\sigma^*/\varepsilon \quad \text{and} \quad V^* = V/N\sigma^3$$

are used, Eq. III.5 becomes

$$U^* = \frac{1.43}{V^{*2/3}}\left(\frac{2.70}{V^{*2}} - \frac{1}{V^{*4}}\right) \tag{III.8}$$

It is seen from this formula that U^* can be expressed as a function of V^* and that the reduced values of the surface energy are the same for all substances if the intermolecular potential is given by the expression of the form of Eq. III.2.

Values of surface energies calculated by Eq. III.5 and by Eq. III.7 are shown in Table I, together with the parameters of intermolecular potentials. The agreement between the theoretical and the observed values are fairly good especially for Eq. III.7. It will be noted that quantum-mechanical corrections have not been taken into consideration thus far. This effect will be considered later.

TABLE I. Parameters of Intermolecular Potentials and Comparison between Calculated and Observed Values of Surface Energies.

Substance	$\varepsilon \times 10^{15}$ (ergs)	σ (A)	U_{calc} (ergs/cm^2) Eq. III.5	Eq. III.7	U_{obs} (ergs/cm^2)
He	1.40	2.56	0.6	0.7	0.6
H_2	4.25	2.92	4.4	5.5	5.4
D_2	4.25	2.92	6.4	8.0	8.2
Ne	4.89	2.74	9.1	11.4	15
N_2	13.25	3.72	22.4	28.1	26
A	16.5	3.41	26.4	32.9	35

IV. RELATION BETWEEN THE SURFACE ENERGY AND THE HEAT OF VAPORIZATION

Since heat of vaporization arises from intermolecular forces, it can be predicted that there is a close relation between the surface energy and the heat of vaporization. A relation was derived by Stephan[28] who assumed that the work necessary to bring a molecule from the interior of the liquid to the surface is half the work necessary to take the molecule outside of the liquid.

Thus if q and v are the heat of vaporization and the volume per molecule, respectively, the following relation holds:

$$\lambda \equiv q/Uv^{2/3} = 2 \tag{IV.1}$$

according to Stephan's assumption. The constant λ is called Stephan's constant. Since Eq. IV.1 was derived by Stephan on a very crude assumption, a more precise derivation will now be given leading to some modification of the formula.[13] If the molecules are at rest at their equilibrium positions and there are n_i molecules at the distance r_i from any molecule, the work necessary to vaporize the liquid is

$$(N/2) \sum n_i \phi(r_i)$$

Now, if the molecules are assumed to execute harmonic oscillations, the mean potential energy of the motion is $\frac{3}{2}RT$ per mole, while the mean kinetic energy is $\frac{3}{2}RT$ per mole irrespective of whether the molecules are in the liquid or in the vapor. The difference of energies of the vapor and liquid phases is, therefore,

$$Q_i = -(N/2) \sum n_i \phi(r_i) - \tfrac{3}{2}RT$$

and, since the work $pV = RT$ is done when one mole of the liquid evaporates, the heat of vaporization per molecule is given by

$$Q = -(N/2) \sum n_i \phi(r_i) - \tfrac{1}{2}RT \tag{IV.2}$$

The last term $\frac{1}{2}RT$ of Eq. IV.2 gives only the order of magnitude of the correction for the difference of the modes of motion in the liquid and in the gas phases, since the above considerations are very crude. However, the term is retained in order to make the theory even a little more accurate. If the mean positions of the molecules are assumed to form a lattice of a known type, the summation in Eq. IV.2 can be obtained.

Thus the molecules up to the fourth or the fifth neighbors around a specified molecule are assumed to form a face-centered cubic lattice and more distant ones are assumed to be distributed uniformly. Then Q is given by the following formula:

$$Q = (N/2)\,\varepsilon\left[57.8\left(\frac{\sigma}{a}\right)^{6} - 48.4\left(\frac{\sigma}{a}\right)^{12}\right] - \tfrac{1}{2}RT \qquad \text{(IV.3)}$$

If this result is compared with Eq. III.5 the following relation between the heat of vaporization and the surface energy is derived:

$$\frac{q+\frac{1}{2}kT}{Uv^{2/3}} = 2^{1/3}\,\frac{7.2-6.06\,(\sigma/a)^{6}}{3.0-2(\sigma/a)^{6}} \qquad \text{(IV.4)}$$

The factor $[7.2-6.06(\sigma/a)^{6}]/[3.0-2(\sigma/a)^{6}]$ is approximately constant for a comparatively wide range of σ/a and has the value 2.1, so that the value of Stephan's constant becomes

$$\lambda = \frac{q+\frac{1}{2}kT}{Uv^{2/3}} = 2.4 \qquad \text{(IV.5)}$$

The preceding results are compared with observed values in Table II. Equation IV.3 is seen to give heats of vaporization of several liquids in close agreement with the observed values, and the values of the ratio $(q+kT/2)/Uv^{2/3}$ are seen to be fairly constant for different substances and to be near the value given by Eq. IV.5.

TABLE II. Relation between Heat of Vaporization and Surface Energy.

Substance	Q_{calc}(cal/mol)	Q_{obs}(cal/mol)	$(q+\frac{1}{2}kT)/Uv^{2/3}$
He	24	24	2.56
H_2	226	200	2.26
D_2	290	300	2.42
Ne	405	415	2.25
N_2	1520	1330	2.67
A	1670	1500	2.45

V. STATISTICAL-MECHANICAL TREATMENT OF THE SURFACE TENSION

We now proceed to the problem of surface tension. Fowler[11] assumed, as explained in Section II, that there is a mathematical surface of density discontinuity, one side of which is occupied by the liquid and the other side by the vapor. Assuming that the density of the vapor can be neglected and calculating the work done when the liquid is brought into two semi-infinite halves by an isothermal procedure, he obtained the following expression for the surface tension:

$$\gamma = \frac{\pi}{8} \varrho^{(1)2} \int_0^\infty R^4 \frac{d\phi(R)}{dR} g(R) dR \qquad \text{(V.1)}$$

where $\varrho^{(1)}$ is the number density of the liquid phase.

The first attempt to express the surface tension in terms of the intermolecular potential and the distribution functions near the transition layers was made by Kirkwood and Buff.[20] They calculated the stress tensor in the region near the transition layer and obtained the expression for the principal stresses p_T and $p_\mathrm{N} (= p)$. According to their theory the normal stress p_N which is equal to the vapor pressure of the substance is given by

$$\begin{aligned} p_\mathrm{N} = p &= kT \varrho_\alpha{}^{(1)} - (1/6) \iiint R_{12} \frac{d\phi}{dR_{12}} \varrho_\alpha{}^{(2)} (R_{12}) dv_{12} \\ &= kT \varrho_\beta{}^{(1)} - (1/6) \iiint R_{12} \frac{d\phi}{dR_{12}} \varrho_\beta{}^{(2)} (R_{12}) dv_{12} \qquad \text{(V.2)} \end{aligned}$$

To calculate the tangential stress $p_\mathrm{T} = p'$, it is convenient to define a rectangular coordinate system (x, y, z) with the (x, y)-plane parallel to the transition layer and the z-axis normal to the surface and directed from liquid to vapor. The tangential stress is the sum of the momentum transport and the force transmitted across a strip of unit width, perpendicular to the transition layers and extending from $z = -l/2$ in the interior of the liquid to $z = l/2$ in the gas phase. Kirkwood and Buff expressed this stress Σ_x in terms of the intermolecular force and the pair distribution function. Thus they obtained

$$\Sigma_x = -\int_{-l/2}^{l/2} p_{\mathrm{T}}(z_1)dz_1,$$

$$p_{\mathrm{T}}(z_1) = p'(z_1) = kT\varrho^{(1)}(z_1) - \tfrac{1}{2}\int \frac{x_{12}^2}{R_{12}}\frac{d\phi}{dR_{12}}\,\varrho^{(2)}(z_1, \boldsymbol{R}_{12})dv_{12}, \qquad \text{(V.3)}$$

where a molecule numbered 1 is assumed to be at a point $\boldsymbol{R}_1$ in the negative side of the (y, z)-plane and a molecule numbered 2 is situated at a point in the positive side of the (y, z)-plane. Substitution of Eqs. V.2 and V.3 into Eq. II.1 yields the expression for the surface tension in the form

$$\gamma = \int \frac{1}{R_{12}}\frac{d\phi}{dR_{12}}\left[z_{12}[\Gamma_{\mathrm{S}}^{(2)}]_1 + \frac{x_{12}^2}{2}\,[\Gamma_{\mathrm{S}}^{(2)}]_0\right]dv_{12} \qquad \text{(V.4)}$$

where

$$[\Gamma_{\mathrm{S}}^{(2)}]_\nu = \int_{+\infty}^{\infty} z^\nu \varrho_{\mathrm{S}}^{(2)}(z_1, \boldsymbol{R}_{12})dz_1 \qquad \text{(V.5)}$$

and

$$\varrho_{\mathrm{S}}^{(2)}(z_1, \boldsymbol{R}_1) = \varrho^{(2)}(z_1, \boldsymbol{R}_{12}) - \varrho_{\alpha\beta}^{(1)} \qquad \text{(V.6)}$$

$$\varrho_{\alpha\beta}^{(2)} = [1-A(z)]\varrho_\alpha^{(2)} + A(z)\varrho_\beta^{(2)} \qquad \text{(V.7)}$$

where $A(z)$ is the unit step function, that is, $A(z) = 0$ for $z < 0$ and $A(z) = 1$ for $z \geqq 0$.

If the physical transition zone is allowed to shrink to a mathematical surface, so that

$$\left.\begin{array}{l} \varrho^{(1)}(z) = \varrho_\alpha^{(1)},\ z \leqq 0,\ \varrho^{(1)}(z) = 0,\ z > 0 \\ g^{(2)}(z_1, \boldsymbol{R}_{12}) = g_\alpha^{(2)}(R_{12}),\ z_1 \leqq 0,\ z_1 + z_{12} \leqq 0 \end{array}\right\} \qquad \text{(V.8)}$$

then Eq. V.4 leads to the following expression for the surface tension:

$$\gamma = [\pi\varrho_\alpha^{(1)2}/8]\int_0^\infty R^4\frac{d\phi}{dR}g_\alpha^{(2)}(R)dR \qquad \text{(V.9)}$$

Equation V.9 is identical with Fowler's expression for the surface tension at an interface between a liquid phase and a vapor phase of negligible density. Since in deriving the equation Fowler was forced to introduce the approximation of a mathematical surface of discontinuity almost at the beginning, he did not obtain the general equation as Kirkwood and Buff did.

Another way of deriving the expression for the surface tension will be shown, the argument being based on the method which was adopted by Born and Green[4] in deriving the equation of state of condensed phases. Buff[6] was the first to apply Born and Green's method to the theory of surface tension. Similar derivations were made also by MacLellan[23] and by Harasima.[14] Here the derivation by the last author will be closely followed.

Consider a system of N molecules enclosed in a cubic vessel of edge length a, and let the system consist of a liquid film which is stretched parallel to one of the walls (the $x-y$ plane), the other part (above and under the film) of the vessel being filled with the vapor of the liquid. The thickness of the film is taken to be of macroscopic order of magnitude, but small compared with a. The film is thick enough so that, at positions in the film not very near the interface, it has the same properties as a bulk liquid. The free energy F of the whole system is given by

$$\exp(-F/kT) = \frac{1}{N!}(2\pi mkT/h^2)^{3N/2}\int\int\ldots\int\exp(-\Phi/kT)\prod_{i=1}^{N} dr_i \qquad (V.10)$$

where Φ is the potential energy of the system which is assumed to be of the form

$$\Phi = \sum_{i>j}\phi_{ij}(R_{ij}) .$$

Now, one of the walls which is perpendicular to the x-axis will be shifted outward by a length $a\varepsilon$, and simultaneously another wall perpendicular to the z-axis will be shifted inward by a length $a\varepsilon$, these being conducted under isothermal conditions. The volume of the whole system as well as the area of the interface between the vapor and the walls of the vessel are not changed during the procedure so long as quantities of the order of magnitude ε^2 are neglected, and the area of each of the two interfaces between the liquid and the vapor is increased by the amount $a^2\varepsilon$.

To follow the method of Born and Green, the length a will be taken to be the unit of length before the walls are shifted, and $a(1+\varepsilon)$, a, $a(1-\varepsilon)$ will be taken to be the units of length along the x-, y-, and z-directions, respectively, after the walls are shifted. Thus reduced coordinates θ_{ix}, θ_{iy} and θ_{iz}, given by

$$x_i = a\theta_{ix},\ y_i = a\theta_{iy},\ z_i = a\theta_{iz}$$

are used before the walls are shifted, and those given by

$$x_i = a(1+\varepsilon)\theta_{ix},\ y_i = a\theta_{iy},\ z_i = a(1-\varepsilon)\theta_{iz}$$

are used after the walls are shifted.

Then the expression for the partition function, before the walls are shifted, is given by

$$\exp(-F/kT)$$
$$= a^{3N}(2\pi mkT/h^2)^{3N/2}/(N!)\int\int\ldots\int \exp(-\Phi/kT)\prod_{i=1}^{N} d\theta_{ix}d\theta_{iy}d\theta_{iz}$$

and that after the walls are shifted, by

$$\exp(-F/kT)$$
$$= a^{3N}(2\pi mkT/h^2)^{3N/2}/(N!)\int\int\ldots\int \exp(-\Phi'/kT)\prod_{i=1}^{N} d\theta_{ix}d\theta_{iy}d\theta_{iz}$$

in which the integrations over θ_{ix}, θ_{iy}, and θ_{iz} are from 0 to 1 in both cases. The values of the potential energies Φ and Φ' are, of course, different for the same values of the reduced coordinates θ_{ix}, θ_{iy}, and θ_{iz}, and since ε is taken to be small, Φ' can be expanded as follows:

$$\Phi' = \sum_{i>j}\phi_{ij}\left(R_{ij}+\varepsilon\frac{x_{ij}^2-z_{ij}^2}{R_{ij}}\right)$$
$$= \Phi+\varepsilon\sum_{i>j}\frac{x_{ij}^2-z_{ij}^2}{R_{ij}}\phi'(R_{ij})$$

From these equations the surface tension is obtained, after some calculations, as

$$\gamma = \frac{(F'-F)}{2a^2\varepsilon} = \tfrac{1}{2}\int\int\int\int\frac{d\phi_{12}}{dR_{12}}\frac{x_{12}^2-z_{12}^2}{R_{12}}\,\varrho^{(2)}(z_1, R_{12})\,dz_1dv_{12} \quad \text{(V.11)}$$

This is the final equation for the surface tension expressed in terms of the intermolecular potential and the pair distribution function. In the next section the relation between this expression and that given by Eq. II.1 will be discussed together with some comments on the meaning of stress across a strip whose width is of an atomic dimension.

Before going to the next section it will be shown that Eq. V.11 can be put in a slightly different form, if the superficial pair density introduced by Kirkwood and Buff[20] is used.

Let the density $\varrho_{\alpha\beta}{}^2$ be defined with respect to an arbitrary Gibbs dividing surface:

$$\varrho_{\alpha\beta}{}^{(2)} = [1-A(z)]\varrho_\alpha{}^{(2)}+A(z)\varrho_\beta{}^{(2)} \tag{V.12}$$

where $A(z) = 0$ for $z < 0$, $A(z) = 1$ for $z \geqq 0$, and $\varrho_\alpha{}^{(2)}$ and $\varrho_\beta{}^{(2)}$ are the pair distribution functions in the homogeneous liquid and vapor, respectively. Since $\varrho_{\alpha\beta}{}^{(2)}$ is spherically symmetric with respect to r_{12}, the integral

$$\tfrac{1}{2}\iiiint \frac{d\phi}{dR}\,\frac{x^2-z^2}{R}\,\varrho_{\alpha\beta}{}^{(2)}\,dz_1\,dv$$

vanishes. Subtraction of this expression from Eq. V.11 and use of the superficial pair density defined by Eq. V.6 lead to the following expression of surface tension:

$$\gamma = \tfrac{1}{2}\iiiint \frac{d\phi}{dR}\,\frac{x^2-z^2}{R}\,\varrho_s{}^{(2)}(z_1, \boldsymbol{R})\,dz_1\,dv \tag{V.13}$$

or

$$\gamma = \tfrac{1}{2}\iiint \frac{d\phi}{dR}\,\frac{x^2-z^2}{R}\,[\Gamma_s{}^{(2)}]_0\,dv \tag{V.14}$$

where

$$[\Gamma_s{}^{(2)}]_0 = \int_{-\infty}^{\infty}\varrho_s{}^{(2)}(z_1, \boldsymbol{R})\,dz_1.$$

VI. STRESSES IN THE TRANSITION LAYER

It is well known that Pascal's law holds in a fluid in which the stress across any elementary plane is perpendicular to the plane. In the transition layer, where the density changes from the value for bulk liquid to the value for gaseous state in traversing a layer of atomic dimension, Pascal's law does not hold, and the stress across a strip parallel to the boundary is different from that across a strip perpendicular to the boundary.

In discussing the stress in a transition layer of atomic dimension, some remarks are necessary concerning the definition of stress. Let LM be any plane of atomic dimension in a fluid. The stress across the plane consists of two parts, one arising from momentum transport and the other arising from intermolecular forces. The former is given by $\varrho^{(1)}kT$ in the classical case,* but there is some ambiguity as to the definition of the latter.[18, 23, 24] Consider two molecules P and Q on either side of the plane LM. One way of defining the stress from intermolecular forces is to assume the force between P and Q to contribute to the stress across LM if the line which connects the two molecules passes through LM. The other way is to consider first a cylindrical part perpendicular to LM, LM itself forming the base of the cylinder. Let the infinite plane which includes LM be denoted by XY. The force between the molecules in the cylinder and those in the semi-infinite part on the other side of the infinite plane XY is assumed to form the stress across LM. In the latter case, the force between the molecules P and Q, which are so situated that the line connecting them does not pass through LM, is counted as a part of the stress across LM. If LM is of macroscopic dimension or if the molecular distribution varies only in the direction perpendicular to LM, the two ways of defining the stress give the same result for the stress across LM. If LM is of microscopic dimension and the molecular distribution varies in a direction not perpendicular to LM, as when LM is taken perpendicular to the transition layer, the two definitions do not lead to the same result.

In the transition layer the density is uniform in the (x, y) plane which is parallel to the transition layer. Let a small plane of area dS be taken perpendicular to the plane (x, y). The pressure across such a plane will be called the tangential pressure. Let the positions of two molecules P and Q be given by the position vectors $\boldsymbol{r}_1(x_1, y_1, z_1)$ and $\boldsymbol{r}_2(x_2, y_2, z_2)$, and let $\boldsymbol{r}_2 - \boldsymbol{r}_1$ be denoted by $\boldsymbol{R}$. Then the force across LM in the sense of the first definition is given by

$$[\boldsymbol{F}]_{\mathrm{I}} = -\iint \frac{d\phi}{dR}\frac{\boldsymbol{R}}{R}\,\varrho^{(2)}(\boldsymbol{r}_1, \boldsymbol{R})\,d\boldsymbol{r}_1\,d\boldsymbol{r}_2 \qquad \text{(VI.1)}$$

---

* In the quantum-mechanical case it is given by $\varrho^{(1)}kT_1$, where T_1 is the kinetic temperature. It is defined by $\frac{3}{2}NkT_1 = \text{trace }(\boldsymbol{p}^{(1)2}\varrho_1/2m)$, where $\boldsymbol{p}^{(1)}$ is the momentum operator.

where the force is taken to be positive when it is in the sense of repulsion. Let the intersection of the line PQ and the plane LM be C(O, y, z), and let $\overline{\mathrm{PC}} = s$ and the angle between $\overrightarrow{\mathrm{PC}}$ and the x-axis be θ, the azimuth being denoted by φ. The change of variables given by

$$\left.\begin{aligned} &x_1 = -s\cos\theta, \quad y_1 = Y - s\sin\theta\cos\varphi, \\ &x_1 = (R-s)\cos\theta, \; y_1 = Y + (R-s)\sin\theta\cos\varphi, \\ &z_1 = Z - s\sin\theta\sin\varphi \\ &z_1 = Z + (R-s)\sin\theta\sin\varphi \end{aligned}\right\} \qquad \text{(VI.2)}$$

yields

$$[\boldsymbol{F}_\mathrm{T}]_\mathrm{I} = -\boldsymbol{t}(dS/2)\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\int_s^{\infty}\frac{d\phi}{dR}\frac{{s_x}^2}{s^4}\varrho^{(2)}(\boldsymbol{r}_1, \boldsymbol{R})R^2s^2\,dR\,ds\,d\theta\,d\varphi \qquad \text{(VI.3)}$$

where $\boldsymbol{t}$ is the unit vector in the x-direction. Putting

$$s_x = s\cos\theta \quad \text{and} \quad s = (z_1 - \zeta)/\sin\theta\sin\varphi \qquad \text{(VI.4)}$$

we have

$$[\boldsymbol{F}_\mathrm{T}]_\mathrm{I} = -\boldsymbol{t}(dS/2)\iiint\frac{d\phi}{dR}\frac{x^2}{Rz}dv\int_{z_1-z}^{z_1}\varrho^{(2)}(\zeta, \boldsymbol{R})\,d\zeta \qquad \text{(VI.5)}$$

Thus the total stress per unit area across a plane perpendicular to the surface at a point $z = z_1$ is given, according to the first definition, by

$$[p_\mathrm{T}(z_1)]_\mathrm{I} = kT\varrho^{(1)}(z_1) - \tfrac{1}{2}\iiint\frac{d\phi}{dR}\frac{x^2}{Rz}dv\int_{z_1-z}^{z_1}\varrho^{(2)}(\zeta, \boldsymbol{R})d\zeta \qquad \text{(VI.6)}$$

According to the second definition, the stress arising from intermolecular forces is the sum of forces between pairs of molecules: one (P) in the cylinder in the domain $x < 0$ with the base dS, and the other (Q) in the domain $x > 0$.

It is easy to show that the resultant force $\boldsymbol{F}_\mathrm{T}$ is given by

$$[\boldsymbol{F}_\mathrm{T}]_\mathrm{II} = -\boldsymbol{t}(dS/2)\iiint\frac{d\phi}{dR}\frac{x^2}{R^2}\varrho^{(2)}(z_1, \boldsymbol{R})dv \qquad \text{(VI.7)}$$

and the total stress per unit area is given according to the second definition, by

$$[p_{\mathrm{T}}(z_1)]_{\mathrm{II}} = kT\varrho^{(1)}(z_1) - \tfrac{1}{2}\iiint \frac{d\phi}{dR}\,\frac{x^2}{R}\,\varrho^{(2)}(z_1, \boldsymbol{R})\,dv \quad \text{(VI.8)}$$

It is seen that the expressions for the tangential stress, Eqs. VI.6 and VI.8 obtained by the two alternative ways of defining the stress, differ from each other. Though $[p_{\mathrm{T}}(z_1)]_{\mathrm{I}}$ and $[p_{\mathrm{T}}(z_1)]_{\mathrm{II}}$ are different, they lead to the same result when integrated over z_1. However, if $p_{\mathrm{T}}(z_1)$ is multiplied by a function of z_1 before integration, the result will differ according to which definition is adopted. The first definition might seem to be more reasonable than the second one. However, it is not without arbitrariness.

When dS is taken at the position $z = z_1$ and parallel to the surface layer, it can be shown similarly to the derivation of Eq. VI.3 that the stress arising from intermolecular forces is, according to the first definition, given by

$$[\boldsymbol{F}_{\mathrm{N}}]_{\mathrm{I}} = -\,\boldsymbol{n}\,dS\,\tfrac{1}{2}\iiiint \frac{d\phi}{dR}\,\frac{s_z^{\,2}}{s^4}\,\varrho^{(2)}(\zeta, R)R^2 s^2 \sin\theta\,ds\,d\theta\,d\varphi,$$

where $\boldsymbol{n}$ is the unit vector in the z-direction. Putting, as in the case of $[\boldsymbol{F}_{\mathrm{T}}]_{\mathrm{I}}$,

$$s_z = s\cos\theta \quad \text{and} \quad s = \frac{z_1 - \zeta}{\cos\theta}$$

$[\boldsymbol{F}_{\mathrm{N}}]_{\mathrm{I}}$ can be brought to a more compact form:

$$[\boldsymbol{F}_{\mathrm{N}}]_{\mathrm{I}} = -\,\boldsymbol{n}\,dS\tfrac{1}{2}\iiint dv\int_{z_1 - z_{12}}^{z_1} \frac{d\phi}{dR}\,\frac{z}{R}\,\varrho^{(2)}(\zeta, \boldsymbol{R})\,d\zeta$$

Thus the total stress per unit area is

$$[p_{\mathrm{N}}(z_1)]_{\mathrm{I}} = kT\varrho^{(1)}(z_1) - \tfrac{1}{2}\iiint dv\,\frac{d\phi}{dR}\,\frac{z}{R}\int_{z_1 - z_{12}}^{z_1} \varrho^{(2)}(\zeta, \boldsymbol{R})\,d\zeta \quad \text{(VI.9)}$$

This expression is just the same as that which can be obtained according to the second definition, so that

$$[p_{\mathrm{N}}(z_1)]_{\mathrm{I}} = [p_{\mathrm{N}}(z_1)]_{\mathrm{II}} = p_{\mathrm{N}}(z_1) \tag{VI.10}$$

Next it will be shown that $p_{\mathrm{N}}(z_1)$ as obtained in the preceding is independent of z_1. Differentiation of Eq. VI.9 with respect to z_1, leads to

$$\frac{dp_{\mathrm{N}}(z_1)}{dz_1} = kT\,\frac{d\varrho^{(1)}(z_1)}{dz_1} - \tfrac{1}{2}\iiint \frac{d\phi}{dR}\,\frac{z_1}{R}[\varrho^{(2)}(z_1, \boldsymbol{R}) - \varrho^{(2)}(z_1 - z, \boldsymbol{R})]dv$$

Since

$$\varrho^{(2)}(z_1 - z, \boldsymbol{R}) = \varrho^{(2)}(z_1, -\boldsymbol{R}),$$

the foregoing expression can be simplified

$$\frac{dp_{\mathrm{N}}(z_1)}{dz_1} = kT\,\frac{d\varrho^{(1)}(z_1)}{dz_1} - \iiint \frac{d\phi}{dz}\,\frac{z}{R}\,\varrho^{(2)}(z_1, \boldsymbol{R})dv$$

The right-hand side of this equation vanishes by the integral equation of Born and Green which states that

$$\frac{d\varrho^{(1)}(z_1)}{dz_1} = \frac{1}{kT}\iiint \frac{d\phi}{dR}\,\frac{z}{R}\,\varrho^{(2)}(z_1, \boldsymbol{R})dv \tag{VI.11}$$

Thus we have

$$p_{\mathrm{N}}(z_1) = \text{independent of } z_1 \tag{VI.12}$$

By taking z_1 in the interior of the liquid or the gas phase, it is thus clear that $p_{\mathrm{N}}(z_1)$ is equal to the pressure of either phase, which was denoted by p in Section II.

In Section V, it was shown that the surface tension γ can be expressed in the rather compact form of Eq. V.11. It will now be shown that Eq. V.11 can be put in the form of Eq. II.1.

Let $f(x)$ be any function of the variable x which diminishes sufficiently rapidly for large absolute values of x. Then for any parameter α the following equation holds:

$$\int_{-\infty}^{\infty} f(x)dx = (1/\alpha)\int_{-\infty}^{\infty} dx \int_{x-\alpha}^{x} f(\zeta)d\zeta \tag{VI.13}$$

If x is replaced by z and $f(\zeta)$ is taken to be the function

$$\varrho_{\mathrm{s}}^{(2)}(z_1, \boldsymbol{R}) = \varrho_{\mathrm{s}}^{(2)}(z_1, \boldsymbol{r}_1 + \boldsymbol{R})$$

Equation VI.13 becomes

$$\int_{-\infty}^{\infty} \varrho_s^{(2)}(z_1, \mathbf{R})\,dz_1 = (1/\alpha)\int_{-\infty}^{\infty} dz_1 \int_{z_1-\alpha}^{z_1} \varrho_s^{(2)}(\zeta, \mathbf{R})\,d\zeta \tag{VI.14}$$

This expression is useful in modifying Eq. V.14. The integral having z^2 in the integrand will be denoted by I.

$$I = \tfrac{1}{2}\iiint \frac{d\phi}{dR}\,\frac{z^2}{R}\,[\Gamma_s^{(2)}]_0\,dv \tag{VI.15}$$

where $[\Gamma_s^{(2)}]_0$ is given in Eq. V.14. If Eq. VI.14 is applied to Eq. VI.15, the integral I can be expressed as

$$I = \tfrac{1}{2}\iiint \frac{d\phi}{dR}\,\frac{z^2}{R}\,dv\left[\frac{1}{\alpha}\int_{-\infty}^{\infty} dz_1 \int_{z_1-\alpha}^{z_1} \varrho_s^{(2)}(\zeta, \mathbf{R})\,d\zeta\right]$$

The value of the last double integral does not depend on the value of α. Thus if α is replaced by z, the preceding equation becomes

$$I = \tfrac{1}{2}\iiiint \frac{d\phi}{dR}\,\frac{z}{R}\,dz_1\,dv \int_{z_1-z}^{z_1} \varrho_s^{(2)}(\zeta, \mathbf{R})\,d\zeta$$

and Eq. V.14 is put in the form

$$\gamma = \int_{-\infty}^{\infty}\Bigg[\tfrac{1}{2}\iiint dv\,\frac{d\phi}{dR}\,\frac{x^2}{R}\,\varrho_s^{(2)}(z_1, \mathbf{R}) - \tfrac{1}{2}\iiint dv \int_{z_1-z}^{z_1} \frac{d\phi}{dR}\,\frac{z}{R}\,\varrho_s^{(2)}(\zeta, \mathbf{R})\,d\zeta\Bigg]dz_1 \tag{VI.16}$$

Equation VI.16 remains valid if $\varrho_s^{(2)}(z_1, R)$ and $\varrho_s^{(2)}(\zeta, R)$ are replaced by $\varrho^{(2)}(z_1, R)$ and $\varrho^{(2)}(\zeta, R)$, respectively. Thus if two quantities $p_T(z_1)$ and $p_N(z_1)$ are defined by

$$p_T(z_1) = kT\,\varrho^{(1)}(z_1) - \tfrac{1}{2}\iiint \frac{d\phi}{dR}\,\frac{x^2}{R}\,\varrho^{(2)}(z_1, \mathbf{R})\,dv, \tag{VI.17}$$

and

$$p_N(z_1) = kT\,\varrho^{(1)}(z_1) - \tfrac{1}{2}\iiint dv\,\frac{d\phi}{dR}\,\frac{z}{R}\int_{z_1-z}^{z_1} \varrho^{(2)}(\zeta, \mathbf{R})\,d\zeta, \tag{VI.18}$$

Eq. VI.16 becomes

$$\gamma = \int_{-\infty}^{\infty} [p_N - p_T(z_1)]\,dz_1$$

which is equivalent to Eq. II.1.

Equations VI.17 and VI.18 are equivalent to Eqs. VI.8 and VI.9, respectively, and this completes the verification of the equivalence of the derivation of the formula from the stress consideration and from the statistical mechanical procedure.

VII. CRITIQUE OF THE ASSUMPTION OF A MATHEMATICAL PLANE OF DENSITY DISCONTINUITY

In any attempt to establish a theory of surface tension, it is very natural to assume, as a first approximation, that the transition from the liquid phase to the gas phase occurs discontinuously at a mathematical plane. As stated in Section V, Fowler introduced this assumption and obtained Eq. V.9 for the surface tension. The nature of this assumption will now be studied more closely by calculating the normal pressure p_N and the tangential pressure p_T.[14, 21] The assumption is stated as

$$\begin{aligned}&\varrho^{(1)}(z_1) = \varrho_\alpha^{(1)} \quad z \leqq 0, \quad \varrho^{(1)}(z_1) = 0 \qquad z_1 > 0\\ &\varrho^{(2)}(z_1, R)\\ &\qquad = \varrho_\alpha^{(1)2} g(R) \quad z_1 < 0,\ z_1 + z < 0, \quad \varrho^{(2)}(z_1, R) = 0 \quad z_1 > 0 \text{ or } z_1 + z > 0\end{aligned} \tag{VII.1}$$

where $g(R)$ is the radial distribution function of the homogeneous liquid phase.

The normal pressure can be calculated from Eq. VI.9, and is given by the expression

$$\begin{aligned}p_\mathrm{N} &= p_0 + \frac{2\pi}{3}\varrho_\alpha^{(1)2}\int_{-z_1}^{\infty} R^3\frac{d\phi}{dR}g(R)dR\\ &\quad - \frac{\pi}{3}\varrho_\alpha^{(1)2}z_1^3\int_{-z_1}^{\infty}\frac{d\phi}{dR}g(R)dR + \pi z_1\varrho_\alpha^{(1)2}\int_{-z_1}^{\infty}R^2\frac{d\phi}{dR}g(R)dR\end{aligned} \tag{VII.2}$$

where p_0 is the pressure in the interior of the liquid or gas phase.

The tangential pressure can be calculated either from Eq. VI.6 or from Eq. VI.8. Both equations give the same result in this particular case, yielding

$$\begin{aligned}[p_\mathrm{T}(z_1)]_\mathrm{I} &= [p_\mathrm{T}(z_1)]_\mathrm{II} = p_0 + \frac{\pi}{3}\varrho_\alpha^{(1)2}\int_{-z_1}^{\infty}R^3\frac{d\phi}{dR}g(R)dR\\ &\quad - \frac{\pi}{6}\varrho_\alpha^{(1)2}z_1^3\int_{-z_1}^{\infty}\frac{d\phi}{dR}g(R)dR + \frac{\pi}{2}z_1\varrho_\alpha^{(1)2}\int_{-z_1}^{\infty}R^2\frac{d\phi}{dR}g(R)dR\end{aligned} \tag{VII.3}$$

Equation VII.2 shows that the normal pressure p_N is far from being constant. Numerical calculations were made for liquid argon at 90° K, using the analytical approximation of the distribution function given by Kirkwood and Buff:[20]

$$g(R) = \left(\frac{a_1}{R}\right)^s \exp\left[\left(\frac{a_m}{a_1}\right)^t - \left(\frac{a_m}{R}\right)^t\right], \quad 0 \leqq R \leqq a_1 \qquad \text{(VII.4)}$$
$$= 1, \qquad a_1 < R$$

For the intermolecular potential, the Lennard-Jones form as modified by Rushbrooke,

$$\phi(R) = \frac{8.62 \times 10^{-8}}{R^{11.4}} - \frac{1.11 \times 10^{-10}}{R^6}$$

was used. Figure 2 shows that the numerical value of the normal pressure p_N is far from being constant, having the value 200 atm at the surface and attaining the maximum value 660 atm at $z_1 = -2.4$ A.

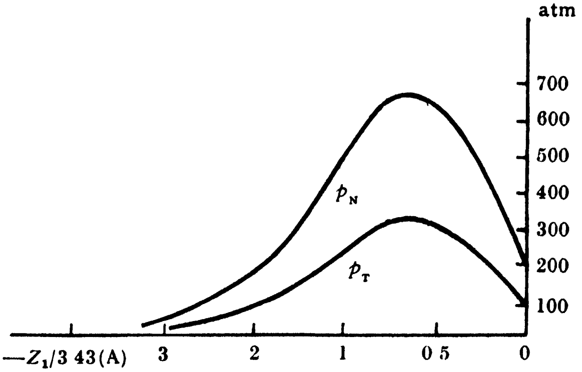


Fig 2 Normal and tangential pressures versus z_1 calculated by Eqs. VII.2 and VII.3.

VIII. APPROXIMATE THEORIES OF SURFACE TENSION

Rigorous expressions for surface tension in terms of the intermolecular potential and distribution functions were derived in Section V, but numerical calculations based on those expressions are not possible in their rigorous form, and they will still be very much involved even if some approximations, such as the superposition approximation for the pair distribution functions, are used. Because of this, there have been several theories based on an approximate model which have made numerical calculations of surface tension possible. It will be noted that, though the theories are very approximate, they nevertheless give a vivid picture of the nature of the liquid-vapor transition layer and emphasize the essential features of the region.

Since surface tension is the free energy of the layer, both the energy and the entropy of the layer must be considered, the latter furnishing us with a more difficult problem. The energy term arises, as discussed in Section IV, because molecules in the surface layer have fewer neighboring molecules than those in the interior of the liquid. The surface entropy can, if the free volume theory of liquid is adopted, be attributed to two origins. First, the free volume of a surface molecule is larger than that in the liquid, since the former is surrounded by fewer molecules than the latter, so that the force acting on the molecule is weaker in the former case than in the latter. Secondly, the entropy which arises from the number of ways of distributing the molecules over the sites will be larger for the surface layer, since more holes are expected at the surface layer than in the liquid. Though the above explanation of the origin of surface entropy is based on the free volume theory of liquid state, similar arguments will also be possible if the theory is based on more exact considerations.

According to the theory of Ono[25] the volume of the vessel containing a system composed of a liquid and its vapor is divided into a large number of cells. The size of the cells will be of the order of the volume which is assigned to one molecule of the liquid. Most of the cells in the lower part of the vessel will be occupied by molecules and most of the cells in the upper part of the vessel will be vacant, while at and near the transition layer the state of mixture of molecules and holes will be present with varying ratios. The ratios of molecules and holes at each molecular layer determine the entropy arising from the number of ways of distributing the molecules over the sites and, at the same time, determine the free volume of molecule at each layer of the transition region; and the presence of holes makes the potential energy of the surface layer larger. All these contribute to the surface free energy and hence to the surface tension. In this way Ono obtained numerical results of surface tension in good agreement with observed values.

Prigogine and Saraga[26] simplified the problem to a considerable extent, rendering the numerical calculations much more amenable. Resorting to the cell theory of liquids and using a well-type potential for the intermolecular forces, they showed how potential energy is increased and how the free volume is modified at the surface of a liquid. Assuming the existence of holes in the superficial layer, they were able to show how numerical values of surface tension, surface energies, surface entropies, and Stephan's ratio can be obtained, all of them being compared with observed values. They showed that the introduction of the existence of holes in the theory much improves the agreement with experiments. Table III shows the results of their calculations for liquid argon. The agreement is almost complete. The treatment of Prigogine and Saraga will be explained later when the quantum effect in the theory of surface tension is considered.

TABLE III. Superficial Thermodynamical Functions of Liquid Argon $T = 85°$ K (Prigogine and Saraga[26]).

	γ (ergs/cm^2)	U (ergs/cm^2)	S (ergs/cm^{2}deg)	Stephan's ratio
Calc.				
Without assuming holes	9	25.8	0.19	4
Assuming holes	13.0	37.3	0.27	3.1
Obs	13.2	35.3	0.26	2.4

Another approach to the theory of surface tension by an approximate procedure was proposed by Tolman[30] and improved by Hill.[17] The latter assumed that the contribution to surface tension which arises from entropy considerations is determined only by the local density and that the contributions from energy considerations can be obtained by integrating the potential energies from all the other molecules of the system. He used a simplified form of pair distribution function, that is

$$g(R) = 1,\ R \geqq \sigma \quad \text{and} \quad g(R) = 0,\ R < \sigma$$

where σ is the diameter of a molecule. This kind of assumption for the form of the distribution function, together with the assumption of the local nature of the entropy term in the expression of chemical potential, might make the theory somewhat inaccurate. Hill obtained, from the condition of equality of local chemical potential, an integral equation which he solved by a numerical procedure.

IX. QUANTUM-MECHANICAL TREATMENT

Before entering into the problem of quantum effects in the theory of surface tension or surface energy, some considerations based on the principle of corresponding states for these quantities will be presented. In order to consider the surface tension from the standpoint of corresponding states, it is not necessary to resort to expressions such as Eq. V.11. The principle of corresponding states for surface tension can be derived directly from Eq. V.10 for the free energy. If the area of the interface between the liquid and the vapor is A, the surface tension is given by

$$\gamma = -kT \frac{\partial}{\partial A} \ln \int\!\!\int \cdots \int \exp\left(-\Sigma \phi_{ij}/kT\right) \prod_{i=1}^{N} d\boldsymbol{r}_i \qquad \text{(IX.1)}$$

The form of the intermolecular potential is assumed to be of the form of the Lennard-Jones type, that is, as given by Eq. III.2. The reduced values

$$\left.\begin{aligned} &T^* = kT/\varepsilon,\ A^* = A/\sigma^2,\ R^* = R/\sigma,\ \boldsymbol{r}^* = \boldsymbol{r}/\sigma, \\ \text{and}\quad & \\ &\gamma^* = \gamma\sigma^2/\varepsilon \end{aligned}\right\} \qquad \text{(IX.2)}$$

will be used. Then the reduced surface tension will be given by

$$\gamma^* = -T^* \frac{\partial}{\partial A^*} \ln \int\!\!\int \cdots \int \exp\left[-\Sigma \frac{4}{T^*}\left\{\left(\frac{1}{R_{ij}^*}\right)^{12} - \left(\frac{1}{R_{ij}^*}\right)^{6}\right\}\right] d\boldsymbol{r}_1^* \ldots d\boldsymbol{r}_N^*$$

so that

$$\gamma^* = f(T^*) \tag{IX.3}$$

that is, treated by classical theory, the reduced surface tension can be written as a universal function of the reduced temperature so long as the form of the intermolecular potential is given by Eq. III.2.

Surface energy is given by Eq. II.12, so that in reduced variables, it can be written

$$U^* = \gamma^* - T^* \frac{\partial \gamma^*}{\partial T^*} \tag{IX.4}$$

where

$$U^* = U \frac{\sigma^2}{\varepsilon} \tag{IX.5}$$

De Boer and Lunbeck[9] showed that the reduced surface tension can be expressed as a function of the reduced temperature and the quantum mechanical parameter:

$$\Lambda^* = h/\sigma\sqrt{m\varepsilon} \tag{IX.6}$$

In what follows it will be shown that the surface energies also obey a similar law and further that parametrical dependence of U^* on Λ^* can be derived, at least qualitatively, if some approximate considerations are used. The values of U^* and those of Λ^* for several liquids are shown in Table IV. In Fig. 3 the values of U^* are plotted as a function of Λ^*. The values of U^* except for those

TABLE IV. Reduced Surface Energy and Quantum Mechanical Parameter.

Substance	U (ergs/cm^2)	Temp range (° K)	U^*	Λ^*
He^3	0.16	1.5-3.4	0.075	3.05
He^4	0.36	1.6-4.3	0.168	2.64
H_2	5.4	15.1-20.1	0.904	1.73
D_2	8.2	18.7-21.1	1.38	1.22
Ne	15	24.8-28.3	2.31	0.591
N_2	26	77.2-90.1	2.72	0.225
A	35	85.1-90.1	2.47	0.187

of He^3 and He^4 are not those at 0° K, but those in the liquid region shown in Table IV. Since He^3 and He^4 are liquid at 0° K, the values at 0° K can be extrapolated from the measurements by Allen and Misener[1] for He^4, and by Lovejoy[22] for He^3. Figure 3 shows these values. The solid curve gives the results of computations by a method which will be shown later. It can be seen from

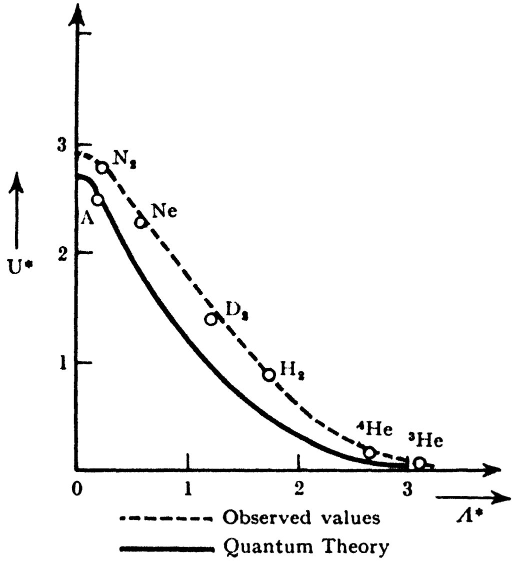


Fig. 3. U^* versus Λ^*.

the figure that quantum effects are most remarkable for helium and hydrogen and that considerable effects are observed even for such liquids as neon.

Toda[29] derived a quantum-mechanical formula corresponding to the classical one, that is, Eq. V.11 by using the theory of density matrices. The expression for surface tension in terms of the density matrix ϱ of a film-vapor system is given by

$$\gamma = (1/2l^2)\left[2\,\mathrm{Tr}\left\{-\frac{\hbar^2}{2m}\Sigma\left(\frac{\partial^2}{\partial z^2}-\frac{\partial^2}{\partial x^2}\right)\varrho\right\}\Big/\mathrm{Tr}\,\varrho\right.$$
$$\left.+\iint\frac{x_{12}{}^2-z_{12}{}^2}{2r_{12}}\frac{d\phi}{dr_{12}}\varrho_1{}^{(1)}\varrho_2{}^{(1)}g(\boldsymbol{r}_1,\boldsymbol{r}_2)d\boldsymbol{r}_1 d\boldsymbol{r}_2\right] \qquad \text{(IX.7)}$$

where l is the edge-length of the cubic container, and $\varrho_1^{(1)}$, $\varrho_2^{(2)}$ denote the number densities at $\boldsymbol{r} = \boldsymbol{r}_1$ and $\boldsymbol{r} = \boldsymbol{r}_2$. Since, however, this type of formula is not fitted to numerical calculations, an approximate theory which is based on quantum-mechanical cell theory will now be shown.[15]

The theory is closely related to the theory of the quantum effect upon volumes and energies of condensed phases. De Boer and Blaisse[8] showed that by use of quantum-mechanical cell theory a relation between the reduced volume V_0^* at 0° K and the reduced energy E_0^* at 0°K can be derived. These quantities are defined by

$$V_0^* = V_0/N\sigma^3, \; E_0^* = E_0/N\varepsilon \tag{IX.8}$$

Their derivation consisted in expanding the pressure in a power series of the parameter Λ^*, and was valid only for small values of Λ^*. The procedure which will now be adopted in this paper is not so refined as de Boer and Blaisse's theory, but it will not be required that Λ^* is small. The procedure is the same as that adopted by Prigogine and Philippot[27] in their theory of energies of liquid helium, and it will be applied to other liquids than liquid helium. These substances are, of course, solid at 0° K except for helium. However, it will be assumed that the same method can be applied to these substances in the following treatment, considering the comparative crudeness of our theory which does not discriminate between liquid and solid states.

In Prigogine and Philippot's theory which was applied to liquid helium, the structure of the liquid is considered to be of a lattice-like form, and the energy at 0° K is assumed to be the sum of the potential energy Φ, corresponding to the configuration in which all the molecules are at the lattice points of a face-centered cubic lattice, and the zero-point energy E_r for the motion of molecules. It is very easy to show that Φ is given by

$$\Phi = 24.26\, N\varepsilon \left[\left(\frac{\sigma}{a}\right)^{12} - 1.191\left(\frac{\sigma}{a}\right)^{6}\right] \tag{IX.9}$$

If the reduced values

$$\Phi^* = \Phi/N\varepsilon, \; V^* = V/N\sigma^3 \tag{IX.10}$$

are used, Eq. IX.9 reduces to

$$\Phi^* = 6.07 \left(\frac{1}{V^{*4}} - \frac{2.382}{V^{*2}} \right) \tag{IX.11}$$

Though the importance of the zero-point energy is stressed by many authors,[2, 31] it is very difficult to calculate it. If the calculations are based on the quantum-mechanical cell theory, the Schrödinger equation for a molecule which is under the potential field resulting from other molecules surrounding the central molecule must be solved. It is often assumed that each molecule is a hard sphere moving inside the cell in which it is locked when the density of the phase is high. Then the zero-point energy is given by

$$E_{\mathrm{r}} = \frac{Nh^2}{8m(a-\sigma)^2}. \tag{IX.12}$$

where a is the distance between two neighboring cell centers and σ is the diameter of a molecule. Besides the mode of motion in which each molecule moves in the cell, there is another mode in which the molecules roam from cell to cell. In Eq. IX.12 the latter mode is not taken into consideration. In their theory of liquid helium, Prigogine and Philippot used the equation

$$E_{\mathrm{r}} = \frac{3Nh^2}{8\delta m(a-\sigma)^2} \tag{IX.13}$$

in which the parameter δ was introduced to account for the above-mentioned mode of molecular motion together with the type of lattice which the centers of the cells are assumed to form. The same value of δ as that which Prigogine and Philippot used will also be adopted in this paper, that is $\delta = 4.5$.

Thus the form of the zero-point energy is obtained, giving the total energy in the reduced form

$$E^* = 6.07 \left(\frac{1}{V^{*4}} - \frac{2.38}{V^{*2}} \right) + \frac{1}{12} \frac{\Lambda^{*2}}{(2^{1/6} V^{*1/3} - 1)^2} \tag{IX.14}$$

The values of the volume V_0^* and the energy E_0^* for the equilibrium state are determined by the condition of minimum energy

$$(\partial E^*/\partial V^*)_{V_0^*} = 0 \tag{IX.15}$$

for each value of Λ^*. Agreement of these quantities with observed values is exceptionally good, showing that the Prigogine and Philippot treatment applied to substances not limited to liquid He^3 and He^4 gives quantum effects in good agreement with experimental values.[15]

The success in deriving the Λ^* dependence of V_0^* and E_0^* suggests the applicability of the same model to the calculation of surface energies. The volume in which a molecule moves in a cell, and accordingly the zero-point energy, is different according to whether the molecule is in the interior or on the surface of the liquid. In this respect Prigogine and Saraga's[26] theory of surface tension is helpful. The general features of their theory have been introduced in Section VIII without deriving any formula. Some details of their theory will now be given in so far as they are concerned with the problem of this section. They assumed that in the surface layer the motion of any molecule parallel to the surface of the liquid is the same as it is in the interior of the liquid, while in the direction perpendicular to the surface the motion of the molecules in the surface layer is such that the expression for free volume of one of these molecules is obtained by replacing the factor $a-\sigma$, for this direction in the case of a molecule in the interior of the liquid, by $a-\sigma/2$.

The same idea will be adopted to discuss the zero-point energy concerning the surface energy of a liquid. The decrease in zero-point energy of a molecule when it emerges from the interior to the surface of a liquid is thus

$$\frac{h^2}{8\delta m}\left[\frac{1}{(a-\sigma)^2}-\frac{1}{(a-\sigma/2)^2}\right]$$

If it is assumed that the surface is the (111)-plane of the lattice, the area per molecule is $(\sqrt{3}/2)a^3$ and the decrease in the zero-point energy per unit area is given by

$$\Delta E_r=\frac{h^2}{4\sqrt{3}\delta ma^2}\left[\frac{1}{(a-\sigma)^2}-\frac{1}{(a-\sigma/2)^2}\right]$$

which can be written in terms of the reduced values

$$\Delta E_r^* = \frac{\Lambda^{*2}}{4\sqrt{3}\cdot 2^{1/3}\delta\cdot V^{*2/3}}\left[\frac{1}{(2^{1/6}V^{*1/3}-1)^2}-\frac{1}{(2^{1/6}V^{*1/3}-1/2)^2}\right] \quad \text{(IX.16)}$$

The surface energy of the condensed phase at 0° K is obtained if Eq. IX.16 is subtracted from the expression Eq. III.8, of the surface energy without zero-point energy correction. The final formula is

$$\begin{aligned} U_0^* = {} & \frac{1.43}{V_0^{*2/3}}\left(\frac{2.70}{V_0^{*2}}-\frac{1}{V_0^{*4}}\right) \\ & -\frac{\Lambda^{*2}}{39.3V_0^{*2/3}}\left[\frac{1}{(2^{1/6}V_0^{*1/3}-1)^2}-\frac{1}{(2^{1/6}V_0^{*1/3}-1/2)^2}\right] \end{aligned} \quad \text{(IX.17)}$$

Since the values of V_0^* as a function of Λ^* are given by Eq. IX.15 which expresses the equilibrium condition at 0° K the surface energy U_0^* can be obtained as a function of Λ^*, that is, as

$$U_0^* = U_0^*(\Lambda^*) \quad \text{(IX.18)}$$

The solid curve in Fig. 3 shows the calculated relation between U_0^* and Λ^*. Since the experimental values are those obtained from experimental data of surface tension in the liquid region, the comparison between the theory and experiments is qualitative rather than quantitative. However, as seen from the figure, it may be said that quantum effects concerning surface energy have been deduced from free volume theory at least in a qualitative way, considering that satisfactory numerical agreement is not to be expected by such a crude simplified theory as given in this paper.

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RECENT DEVELOPMENTS IN MOLECULAR ORBITAL THEORY

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CONTENTS

I. INTRODUCTION

The molecular orbital theory is one of the two approximate theories which have been used to investigate the electronic structures of atoms and molecules. This theory, like its counterpart, the valence bond theory, was advanced very soon after the advent of wave mechanics twenty-five years ago, but it is only in recent years that the molecular orbital theory has come into general use for describing not only the ground states, but also the excited states of polyatomic molecules.[76]

Three recent developments in the molecular orbital theory of electronic structure are particularly worthy of note. These are: first, the successful analysis and quantitative interpretation of the spectra of unsaturated hydrocarbons and their simple derivatives;[57] secondly, the development of a sound descriptive theory of the structures of electron-deficient compounds; and thirdly, the elucidation of the principles underlying the structures and stabilities of inorganic metal complexes. These three topics are largely independent and each could occupy in itself a review of this length. However, the recent advances in the theory of inorganic metal complexes have been admirably covered in a recent review by

Moffitt and Ballhausen,[41] and the application of the molecular orbital theory to electron-deficient compounds, particularly the hydrides of boron, by Eberhardt, Crawford, and Lipscomb has been fully described by these authors in their original papers.[14] The present review will, therefore, be devoted entirely to those developments in the molecular orbital theory which have been associated with its application to the electronic spectra of unsaturated hydrocarbons. These developments form in themselves a relatively coherent story, the main lines of which are now clear, and it seems a suitable moment at which to put the history of the subject into perspective. Before doing this, however, it will be convenient to outline the general premises of the molecular orbital theory.

II. THE METHOD OF MOLECULAR ORBITALS

The fundamental premise of molecular orbital theory is that the electrons in a molecule may be assigned, not more than two at a time, to orbitals (i.e., three-dimensional wave functions) which extend over any number of atoms in the molecule. These molecular orbitals (MO) must be orthogonal and normalized, and orthogonality is obtained by demanding that each orbital be an eigenfunction of some one-electron Hamiltonian operator whose precise form may or may not be specified though it must be Hermitean. Two electrons in the same molecular orbital must, of course, have their spins opposed. If there are one or more orbitals containing one electron then there is a certain freedom in the total spin, and its z-component, associated with the unpaired electron or electrons. The majority of molecules, however, have all their electrons paired, and in such a case it is usually a reasonable approximation to assign the $2m$ electrons to m molecular orbitals each of which is doubly occupied.

The molecular orbital theory may be developed to various degrees of sophistication, and two elaborations of the foregoing premises are particularly worthy of discussion. The first is the so-called Hückel theory,[21] in which the one-electron Hamiltonian is not specified precisely but is assumed to be of the form $T+V$, where V is a potential which is the same for all the electrons under consideration. In the development of this theory several further approximations are introduced. The first is that each molecular orbital can be adequately represented as a linear combination of atomic orbitals (LCAO) centered on the various atoms. This assumption is expressed by the equation

$$\psi = \sum_r c_r \phi_r \quad \text{or} \quad \psi_j = \sum_r c_{jr} \phi_r \tag{1}$$

The coefficients c_r in this expansion may then be obtained from the variational principle, which leads to the set of simultaneous equations

$$(H_{rr} - E)c_r + \sum_s{}' (H_{rs} - S_{rs} E)c_s = 0 \tag{2}$$

where

$$\begin{aligned} H_{rs} &\equiv \int \phi_r H \phi_r \, dv \equiv \alpha_r \\ H_{rs} &\equiv \int \phi_r H \phi_s \, dv \\ S_{rs} &\equiv \int \phi_r \phi_s \, dv \end{aligned} \tag{3}$$

and E is an energy eigenvalue associated with ψ. The next assumption commonly made is that, if ϕ_r and ϕ_s are adjacent, $H_{rs} - S_{rs}E$ may be approximated by a quantity β_{rs} which is independent of their environment, and that otherwise $H_{rs} - S_{rs}E = 0$. This assumption is only accurate if S_{rs} is small, and so it is customary to make the stronger assumption $S_{rs} = \delta_{rs}$. The conditions of orthonormality then take the form

$$\sum_r c_{jr} c_{kr} = \delta_{jk} \tag{4}$$

which are automatically satisfied by molecular orbitals ψ_j, ψ_k corresponding to different eigenvalues $E_j \neq E_k$. Finally it is usually assumed in dealing with unsaturated molecules in their ground states that the total energy of the electrons is additive in the individual electron energies, that is

$$E = \sum_j \nu_j E_j \tag{5}$$

where ν_j is the number of electrons in the orbital ψ_j. The electron population of ϕ_r and the order of the bond between ϕ_r and ϕ_s are defined by the equations

$$q_r \equiv p_{rr} = \sum_j \nu_j c_j^2, \qquad p_{rs} = \sum_j \nu_j c_{jr} c_{js} \tag{6}$$

and these quantities are found to be of use in the interpretation of various molecular properties, particularly those relating to the ground state.[7–10]

III. THE SELF-CONSISTENT FIELD MO THEORY

Before describing these applications, however, it is best to pass on immediately and describe the self-consistent field (SCF) molecular orbital theory. The reason for this is that the Hückel theory, neglecting as it does any detailed consideration of electron repulsion, becomes inadequate to deal with molecules in their excited states. When one is discussing the ground state, electron repulsion may be allowed for by regarding α_r and β_{rs} as empirical parameters to be put into a semiempirical theory; but it is electron repulsion which mixes together excited configurations and separates singlet and triplet levels arising from the same excited configuration. Furthermore, no specification is given for calculating α_r and β_{rs} in the Hückel theory, if only because the one-electron Hamiltonian is undefined. In the self-consistent orbital theory, therefore, one retains the assumption that the electrons occupy molecular orbitals in pairs, but one attempts to determine the forms of these orbitals from the variational principle using the complete Schrödinger Hamiltonian for all the electrons. An example will make this clear. If one is discussing the ground state of a molecule in which all the electrons are paired, one assigns these electrons a wave function of the form

$$
\begin{aligned}
{}^1\chi_0 &\equiv |\psi_1 \bar{\psi}_1 \cdots \psi_j \bar{\psi}_j \cdots \psi_m \bar{\psi}_m| \\
&\equiv \{(2n)!\}^{-1/2} \begin{vmatrix} \psi_1(1), & \bar{\psi}_1(1), & \ldots, \psi_m(1), & \bar{\psi}_m(1) \\ \psi_1(2), & \bar{\psi}_1(2), & \ldots, \psi_m(2), & \bar{\psi}_m(2) \\ & \vdots & & \\ \psi_1(2m), & \bar{\psi}_1(2m), & \ldots, \psi_m(2m) & \bar{\psi}_m(2m) \end{vmatrix}
\end{aligned}
\tag{7}
$$

In this determinant $\psi_j(\mu)$ indicates that electron μ has been assigned to orbital ψ_j with spin $\frac{1}{2}$ and $\bar{\psi}_j(\mu)$ represents the assignment of electron μ to orbital ψ_j with spin $-\frac{1}{2}$. In accordance with the Pauli exclusion principle, this wave function is antisymmetric under a permutation of any two electrons. The principle of the self-consistent method is then to minimize the integral

$$\int {}^1\chi_0 \mathscr{H} \, {}^1\chi_0 \, d\tau, \tag{8}$$

where

$$\mathscr{H} = \sum_{\mu} H^c(\mu) + \sum_{\mu<\nu}\sum \frac{e^2}{r_{\mu\nu}}$$

and

$$H^c(\mu) = T_\mu + V^c(\mu) \tag{9}$$

subject to the ψ_j being orthonormal,* and this leads, as originally shown by Fock,[15] to the following set of simultaneous integro-differential equations:

$$\begin{aligned} F(\mu)\psi_j(\mu) \equiv H^c(\mu)\psi_j(\mu) + \sum_{i=1}^{m}\Bigg\{ 2\int \psi_i{}^*(\nu)\frac{e^2}{r_{\mu\nu}}\psi_i(\nu)d(\nu)\cdot\psi_j(\mu) \\ - \int \psi_i{}^*(\nu)\frac{e^2}{r_{\mu\nu}}\psi_j(\nu)d(\nu)\cdot\psi_i(\mu)\Bigg\} = E_j\psi_j(\mu) \end{aligned} \tag{10}$$

These equations reduce the problem to that of determining the eigenfunctions and eigenvalues of a three-dimensional linear Hermitean operator F which itself involves the eigenfunctions which are to be determined. In principle, therefore, the equations can be solved by an iterative procedure in which one postulates an initial set of eigenfunctions, calculates a new set from Fock's equations, and repeats this process until convergence is obtained. This, however, is an extremely arduous task, even for atoms, and for molecules it is absolutely necessary to impose further restrictions on the molecular orbitals ψ_j before it becomes even remotely practicable to determine the form of these orbitals. The most important of these further restrictions is the assumption embodied

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* T_μ is the kinetic energy of electron μ and $V^c(\mu)$ its potential energy in the field of the "core," i.e., the nuclei and any remaining electrons whose distribution may be regarded as fixed.[38]

in Eq. 1. The first person to have developed the mathematical consequences of this assumption in the self-consistent theory seems to have been Roothaan.[67] He established that the LCAO assumption converts Fock's equations into a set of nonlinear simultaneous algebraic equations which take the form

$$\sum_s F_{rs} c_{js} = \sum_s S_{rs} c_{js} E_j \tag{11}$$

In this equation F_{rs} is defined by its matrix element between ϕ_r and ϕ_s, namely

$$F_{rs} \equiv H_{rs}{}^c + \sum_t \sum_u p_{tu} \left(G_{rt,su} - \tfrac{1}{2} G_{rt,us} \right) \tag{12}$$

where

$$\begin{aligned} H_{rs}{}^c &\equiv \int \phi_r{}^*(\mu) H^c(\mu) \phi_s(\mu) d(\mu), \\ p_{tu} &\equiv 2 \sum_{i=1}^{m} c_{it} c_{iu}, \end{aligned} \tag{13}$$

and

$$\begin{aligned} G_{rt,su} &\equiv \int \int \phi_r{}^*(\mu) \phi_t{}^*(\nu) \frac{e^2}{r_{\mu\nu}} \phi_s(\mu) \phi_u(\nu) d(\mu) d(\nu) \\ &\equiv (rt|G|su) \equiv (rs|tu) \end{aligned} \tag{14}$$

S_{rs} is the overlap integral $\int \phi_r{}^*(\mu) \phi_s(\mu) d(\mu)$.

The solution of Roothaan's equations, therefore, demands a knowledge of the following types of integral. First, overlap integrals between atomic orbitals, which are relatively easily calculated. Secondly, the matrix elements of H^c between pairs of atomic orbitals. These correspond to the Coulomb and the resonance integrals in the Hückel theory. Thirdly various types of electron repulsion integral typified by

$$G_{rt,su},\ G_{rr,ss},\ G_{rs,rs},\ \text{etc.}$$

It is the evaluations of these last integrals which presents the greatest problem in *a priori* calculations. These electron repulsion integrals may be classified according to the number of different atomic orbitals which appear in them. The simplest repulsion integral is the one-center integral $G_{rr,rr}$. The next simplest are the Coulomb and exchange integrals $G_{rs,rs}$ and $G_{rr,ss}$, respectively, and standard methods are available for calculating these.[70] More difficult to compute are integrals of the type $G_{rr,rs}$, and as yet no analytical methods are available for calculating integrals involving three or four atomic orbitals, such as

$$G_{rr,st},\ G_{rs,rt},\ G_{rs,tu}$$

For these reasons Roothaan's formalism in its precise form has been applied only to diatomic molecules, and the prospects of extending it without further simplification to polyatomic molecules seem remote.

Having outlined the way in which the method of molecular orbitals, either in the simple form or in the more sophisticated form developed by Roothaan, may be applied in principle to the ground states of closed shell molecules, we may now turn to the more recent developments which have borne fruit in relation to experimental measurements.

IV. AROMATIC HYDROCARBON SPECTRA

The possibility of a systematic interpretation of aromatic hydrocarbon spectra first presented itself with the publication of Clar's extensive and careful measurements summarized and discussed in his book *Aromatische Kohlenwasserstoffe.*[5] Clar pointed out that there are certain family resemblances between the electronic spectra of condensed aromatic hydrocarbons; in particular he distinguished four types of electronic band appearing in most of these spectra and defined them by the labels p, α, β and β'. At a later date, but independently, Klevens and Platt[22] made further systematic measurements on these spectra, and rediscovered the regularities recognized by Clar. Platt[58] proposed a daring interpretation of these regularities based upon the idea that in a "cata-condensed" hydrocarbon — one in which all the carbon atoms lie on the perimeter of the molecule — every π-electron moves in a molecular orbital with a characteristic angular momentum as though the electron were moving freely in a circular potential field. Platt recognized that in fact the motion of an electron around the perimeter of a cata-condensed hydrocarbon cannot be "free" in the same sense as the motion of an unimpeded electron, but suggested that nevertheless it might be possible to classify the excited states of these molecules by assigning to each state a quantum number representing the total angular momentum of the electrons. If one examines the possible wave functions for an electron confined to a circle, one finds that the orbital of lowest energy is nondegenerate and has zero angular momentum, whereas the upper orbitals are all doubly degenerate, with angular momentum $\pm l$* where l is a positive integer. A closed shell will, therefore, be obtained if the total number of π-electrons is $4l' + 2$, where l' is the quantum number of the uppermost electrons, and it is an interesting fact that the stable cata-condensed hydrocarbons have 6, 10, 14, . . electrons contributed, of course, by the same number of carbon atoms. Four transitions are clearly possible in which an electron of angular momentum $\pm l'$ is excited to an orbital of angular momentum $\pm(l'+l)$. For two of these transitions the change in l is ± 1 and for the other two, l changes by $\pm(2l'+1)$. In the absence of perturbations, therefore, the first two transitions would be degenerate and allowed and the other two would also be degenerate but forbidden. However, owing to the periodic potential experienced by the electron as it moves round the perimeter the upper states of the first two transitions interact with one another, giving two upper states labeled by Platt as ^1B_a and ^1B_b, and distinguished by the direction of their transition moments from the ground state. (In naphthalene, for example, the former has a transition moment across the molecule and the latter along it.) A similar situation occurs with the upper states of the transitions for which l changes by $2l'+1$. These also split giving two components which Platt calls ^1L_a and ^1L_b. However, transitions to both these states are forbidden by the angular momentum selection rule, and Platt uses this fact to account for the relative weakness of the transitions which Clar classified as α and p. The outstanding attributes of Platt's theory were its obvious novelty and simplicity, but the success of his theory presented a challenge to the theoreticians to justify the drastic approximations upon which it was based.

Logically, though not historically, the next step was taken by Moffitt.[39] Moffitt pointed out that Platt's perimeter model could be reformulated within the framework of the Hückel theory if it

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* in units of $h/2\pi$.

were assumed that a cata-condensed hydrocarbon has molecular orbitals appropriate to a regular polygon with $4l'+2$ vertices. Moffitt made the additional observation that one could explain the difference in intensity and vibrational structure between the ^1L_a and ^1L_b bands by investigating how the two transitions would be mixed with the ^1B_a and ^1B_b transitions under the influence of vibrational and other perturbations. He showed, for example, that a distortion of the C—C bonds would mix ^1L_a with the ^1B states but that ^1L_b was unaffected by such a perturbation. Furthermore, he showed that a perturbation which affected individual atoms rather than chosen pairs of atoms would produce a marked effect on the intensity of the ^1L_b transition but not on the ^1L_a. An important example of the former type of perturbation is the introduction of a crosslink such as the central link in the naphthalene molecule; Moffitt's theory, therefore, provided a rough method of allowing for the presence in a cata-condensed hydrocarbon of interior bonds, which were completely ignored in Platt's perimeter theory. Moffitt[40] also succeeded in interpreting in a semiquantitative manner the trends in absorption frequency in the four principal bands as one progresses along the series of polyacenes, *viz.*, benzene, naphthalene, anthracene, etc.

The success of Platt's theory and the extension of it by Moffitt led to a bizarre theoretical situation in which the high-powered methods of wave mechanics seemed to be less effective in their application to an important field of experiment than much simpler and cruder conceptions based upon intuition rather than rigorous mathematical foundations. This situation, however distressing as it may have appeared at the time to the highbrows, gave good cause for hope that a satisfactory and yet simple theory could not be far off, and that the mathematical bugbears of the self-consistent orbital theory might well prove to be unimportant when it came to applying this theory to practical problems. Indeed, subsequent developments fulfilled such hopes more rapidly and more completely than could have been believed at the time by even the most optimistic workers in the field.

In order to appreciate the essential elements in the present highly successful theory of aromatic hydrocarbon spectra, it is necessary to trace back to their origin a number of lines of thought which have been incorporated into this theory. Two crucial questions were outstanding; first, what is the importance of atomic orbital overlap in determining the energies of molecular states, and, secondly, to what extent is it necessary[59] to invoke configurational interaction[11] in order to describe the wave functions of excited states and the energies of these states?

We will discuss first the question of atomic orbital overlap. If one adopts the simple Hückel theory without overlap and identifies the energy of an electronic transition with the difference in energy between an occupied and an unoccupied molecular orbital, one finds that it is necessary to adopt different values for the C—C resonance integral according as one is interpreting the resonance energies of molecules in their ground states or their excitation energies to higher states. An early paper by Coulson[6] on the electronic spectra of polyacenes showed that the quantitative theory of the ground state and the excited states of these molecules could be made consistent if one took into account the overlap integral S between neighboring carbon atoms; this has the effect of crowding together in the energy scale the bonding molecular orbitals and spreading out the antibonding orbitals, which is what is required to bring the Hückel theory into agreement with experiment. Coulson's paper, however, was concerned with the excited singlet states only, and it is known that the excited triplet states of these molecules lie at substantially lower energies than the corresponding singlets. This difference arises, as has been known for many years, from electron repulsion, and it was clear that electron repulsion must be taken into account at some point in any complete theory. It was, therefore, by no means clear that atomic orbital overlap was even the most important factor responsible for the quantitative failure of the Hückel theory as applied to excited states. Mention should be made at this point, of the still earlier pioneer work of Goeppert-Mayer and Sklar.[17] These authors as far back as 1938 examined theoretically the electronic spectrum of benzene using a Hamiltonian which included explicitly the repulsion between the π-electrons. They showed that the energies of the first three excited states of this molecule

(B_{2u}, B_{1u}, and E_{1u}) were separated by electron repulsion both from one another and from the corresponding triplets, and that these energy differences could be interpreted in terms of reasonable values for the Coulomb repulsion integrals between atomic orbitals. They did not find it possible to evaluate all the many-center integrals required, and errors crept into their numerical calculations, but subsequent work[11, 12, 56, 68] has left little doubt that the 1800 A band of benzene has an E_{1u} upper state and that the upper states of the 2600 A and 2100 A bands are B_{2u} and B_{1u}, respectively. There was, therefore, even at that time clear evidence that electron repulsion must be included in any final theory, though aromatic molecules with less symmetry than benzene clearly presented a much more difficult problem.

An attempt to examine the significance of electron repulsion as an effect independent of atomic orbital overlap was made by Pople[61] in 1953. Pople examined the ground states of aromatic hydrocarbons by the self-consistent MO theory and introduced the approximation which has since become known as the "zero differential overlap approximation." This approximation applies to the overlap integrals S_{rs} and the repulsion integrals $G_{rs,\,tu}$. Its meaning can be most clearly understood by noting that, *if* the product of every pair of two atomic orbitals is everyhere zero, then every overlap integral will vanish and all electron repulsion integrals except those of the form $G_{rs,\,rs}$, which may be more simply denoted as γ_{rs}. Pople, therefore, assumed the relationships

$$S_{rs} = \delta_{rs}, \quad G_{rs,\,tu} = \delta_{rt}\delta_{su}\gamma_{rs} \tag{16}$$

but in order to avoid trivial conclusions he allowed the resonance integral $H_{rs}{}^{c}$ between adjacent atomic orbitals to have a finite value. With these assumptions Roothaan's equations can be greatly simplified and may be written in the form

$$\sum_{s} F_{rs} c_{js} = E_j c_{jr}$$

where

$$\begin{aligned} F_{rr} &= H_{rr}{}^{c} + \tfrac{1}{2} q_r \gamma_{rr} + \sum_{s}{}' q_s \gamma_{rs}, \\ F_{rs} &= H_{rs}{}^{c} - \tfrac{1}{2} p_{rs} \gamma_{rs} \end{aligned} \tag{17}$$

and q_r, p_{rs} are defined by Eq. 6.

The advantage of these equations is that they have the same form as the equations of the Hückel theory, though of course the matrix elements F_{rr} and F_{rs} have a different interpretation. The diagonal element F_{rr} comprises the kinetic energy of an electron in ϕ_r and its potential energy in the field of the core and of all the other electrons under consideration. Now, under many circumstances an electron in ϕ_r will be more or less equally attracted and repelled by the atomic cores and outer electrons of other atoms; this situation will obtain, for example, in alternant hydrocarbons which according to the Hückel theory have a uniform distribution of their π-electrons over the carbon atoms. In such a case F_{rr} will depend only on the nature of atom r, not its environment. The off-diagonal elements F_{rs} take the place of the resonance integrals in the Hückel theory. In the Hückel theory, the resonance integral β_{rs} is zero unless r and s are bonded; however, this is not necessarily true of the element F_{rs} owing to the presence of the term $-\frac{1}{2}p_{rs}\gamma_{rs}$. In alternant hydrocarbons, however, the Hückel bond orders p_{rs} vanish between pairs of atoms in the "same set,"* so that the elements F_{rs}, like the resonance integrals, vanish unless r and s are in different sets. The upshot of all this, as Pople showed, is that his equations, Eqs. 17, when applied to alternant hydrocarbons yield solutions which have all the "pairing" properties of the Hückel molecular orbitals. Pople thus succeeded in showing that the Hückel scheme can be very easily adapted to include electron repulsion, at least under the assumption of zero differential overlap.

As will be seen from this account, Pople's simplification of Roothaan's self-consistent theory was aimed at clarifying the description of the ground state, particularly of alternant hydrocarbons.[65] It was not concerned, in the first instance, with the characteristic problems which arise when one is discussing excited electronic states. However, Pople and Hush[63] developed from it a theory of the ionization potentials and electron affinities of aromatic hydrocarbons, based on a consideration of the Hartree-Fock eigenvalues E_j. According to Koopmann's theorem, the ionization potential of a closed shell should approximate to the

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* i. e., atoms separarted by an even number of bonds.

Hartree-Fock eigenvalue of the highest occupied molecular orbital; the electron affinity should approximate to the eigenvalue of the lowest unoccupied molecular orbital. According to Pople's theory, the mean of these two quantities should be the same for all alternant aromatic hydrocarbons and equal to the work function of graphite; Pople and Hush showed that this relationship is verified by experiment. Brickstock and Pople[1] extended the theory to radicals and ions.

At the same time as Pople was developing his adaptation of Roothaan's theory, other related lines of thought were being pursued on both sides of the Atlantic. A particularly troublesome question at that time was: how far is it possible to describe the excited states of molecules by single determinant wave functions, or small numbers of such determinants? In other words, how far is it necessary to invoke interaction between excited configurations in order to account quantitatively for the energies and intensities of electronic transitions?

At this juncture it may be as well to stress a point which is sometimes overlooked in discussions of electronic structure. It is usually taken for granted that the best wave functions available for practical purposes are those obtained by a thoroughgoing application of the variational principle to a previously chosen set of arbitrary functions. It should, however, be stressed that the variational principle only provides an *upper bound* for the energy of a state of given symmetry. The variational principle may be positively misleading if one is interested in properties of the wave function other than its total energy. Moffitt in 1951[38] published an important paper in which he discussed this question from a fundamental point of view, which has since become known as the "atoms in molecules" approach. He pointed out that no orbital theory could be expected to yield better results for molecules than for atoms, but that the simple orbital theory fails to account for even the order of atomic energy levels in as simple an atom as carbon. Moffitt, therefore, suggested that the correct use of orbital theories is in calculating *differences*, that is, to say, the difference between some property of a molecule and the same property of the atoms of which it is composed. Orbital theories are not accurate enough to predict atomic properties, and no attempt should be made to use them for this purpose. Moffitt drew attention to one quantity in particular which enters into molecular calculations, but is essentially an atomic parameter. This is the repulsion energy between two electrons in the same atomic orbital and is sometimes called the "(11|11) integral." Upon integrals of this type depend the energies of various types of molecular transition: in particular the singlet-triplet separation of the V_1 configuration of ethylene is directly proportional to it. Unfortunately, as Moffitt pointed out, the calculated value of this integral, for a carbon $2p$ Slater orbital, is 17 ev, whereas the atomic spectrum of carbon indicates the much lower value of 11 ev. This demonstrates, in Moffitt's view, the relative uselessness of orbital theories for fully nonempirical calculations. Indeed, he recommended that one should recognize the necessity of making full use of atomic data in molecular calculations and employing such data in conjunction with semiempirical rather than nonempirical theories. Calculations on the O_2 molecule confirmed this suggestion.[37]

Moffitt's paper was not directly concerned with the molecular orbital theory as such, but the problem to which he drew attention, namely the best method of evaluating electron repulsion integrals, must be answered adequately before one can assess the extent of configurational interaction in this theory. Moffitt and Scanlan[42, 43] showed that in the quantitative problems arising in C_2H_4, C_6H_6, and other systems, configurational interaction is considerably reduced if one adopts empirical values for the one-center integral rather than the much higher nonempirical values.

The reviewer has taken space to discuss Moffitt's paper not because it was intended as a direct contribution to molecular orbital theory, but because it provides the best justification at present available for a set of approximations which have now become associated with the names of Pariser and Parr.

In a series of papers published in 1953, Pariser, Fumi, and Parr[16, 51, 54, 55] put forward a set of simplifying assumptions which together constituted a semiempirical theory for the interpretation of aromatic hydrocarbon spectra.

In order to make clear the nature of their approximations, it will be as well to state one or two well-known principles which are essential to any theory of electronic structure. Any approximate calculation of the wave functions and energies of excited states must proceed in three stages. The first stage is to limit consideration to a relatively small number of functions in terms of which it is proposed to expand the electronic wave functions required. The second stage is to evaluate the matrix elements of the Hamiltonian, and of unity, between these functions. The third stage, which is quite perfunctory, is then to solve the variational problem for the energies and eigenfunctions. The approximations of Pariser and Parr are concerned with stages one and two. They proposed that the wave function of the ground state or of a singlet excited state should be expressed in the form

$$\bar{\psi} = a_0\,{}^1\chi_0 + \sum_{j(\leq m)}\sum_{k(>m)} a_j^k\,{}^1\chi_j^k$$

where

$${}^1\chi_0 = |\psi_1\bar{\psi}_1 \cdots \psi_j\bar{\psi}_j \cdots \psi_m\bar{\psi}_m|$$

and

$${}^1\chi_j^k = \{|\psi_1\bar{\psi}_1 \cdots \psi_j\bar{\psi}_k \cdots \psi_m\bar{\psi}_m| - |\psi_1\bar{\psi}_1 \cdots \psi_k\bar{\psi}_j \cdots \psi_m\bar{\psi}_m|\}/\sqrt{2}$$

In these expressions $\psi_1, \psi_2, \ldots$ are molecular orbitals of the usual LCAO type. Pariser and Parr used for their calculations molecular orbitals obtained by solving the Hückel equations which are not, in general, consistent with Roothaan's equations. Two points should be noted at this stage. First of all it is assumed that doubly excited configurations such as ${}^1\chi_{ij}^{kl}$ are unimportant in the wave function of the ground state or a singly excited state. This is admittedly a questionable assumption, but to exclude multiply excited configurations simplifies the theory very considerably. Secondly, as already remarked, the Pariser and Parr theory makes no use of self-consistent orbitals. If orbitals ψ_j were self-consistent, there would in fact be no interaction between ${}^1\chi_0$ and ${}^1\chi_j^k$; the ground state would be simply ${}^1\chi_0$, and this term would be excluded from the excited states. It would be perfectly possible in principle to incorporate the subsequent assumptions of Pariser and Parr into a self-consistent theory, but these authors prefer to work with the

Hückel orbitals and to allow for the lowering of the ground state by interaction with singly excited configurations.

The second part of Pariser and Parr's theory is concerned with the matrix elements between the terms ${}^1\chi_0$, ${}^1\chi_i^k$. These depend ultimately upon the matrix elements of unity, of the core Hamiltonian, and of the electron repulsion in the system of atomic orbitals. Pariser and Parr, like Pople, introduced the zero differential overlap approximation which abolishes overlap between different atomic orbitals and includes all electron repulsion integrals except those of the type

$$G_{rs,rs} \equiv \gamma_{rs}$$

Such a drastic approximation necessarily changes the status of the theory from "nonempirical" to "semiempirical," and Pariser and Parr realized that in these circumstances there was no point in adopting "nonempirical" values for any integrals appearing in their theory.

The decision to replace nonempirical by empirical values for the integrals must have required heart-searching, but has amply justified the grounds on which it was taken. Like Moffitt, Pariser and Parr realized the fundamental role played by the (11|11) integral and the prime necessity of evaluating it correctly. Like Moffitt, they disregarded the theoretical value of 16.93 ev obtained from Slater orbitals and used Mulliken's values for the ionization potential and electron affinity of a carbon atom in the valence state (sp^2, p) to obtain an empirical value of 10.53 ev instead. The remaining electron repulsion integrals were assigned values tending to e^2/R for large distances, and the matrix elements of H^c were assigned values in keeping with experimental data on ethylene and benzene. Pariser and Parr admitted a certain degree of arbitrariness in the choice of their numerical values, but emphasized the possibility of correlating in a quantitative manner a good deal more experimental data than theoretical parameters. Subsequent work, on other aromatic molecules, has justified this scheme.

The essential points of Pariser and Parr's treatment are, therefore, (1) the decision to work in terms of Hückel molecular orbitals and to restrict consideration to unexcited and singly excited configurations; (2) to adopt empirical rather than theoretical values for the various integrals which are required in the quantitative calculations. Their theory does not make any reference to the method of the self-consistent field.

The next development in the theory of aromatic hydrocarbon spectra was a paper by Dewar and Longuet-Higgins.[13] These authors were concerned particularly with the spectra of alternant hydrocarbons in which, at least according to the Hückel theory, the molecular orbital energies are grouped symmetrically around the zero of binding energy. They drew attention to the fact that electron repulsion might mix together particularly strongly a pair of excited configurations whose energies on the Hückel theory were equal. If the molecular orbitals are, in order of increasing energy,

$$\psi_1, \psi_2, \ldots, \psi_m, \psi_{m+1}, \ldots, \psi_{2m}$$

then the orbitals ψ_j and ψ_{2m+1-j} will have equal and opposite binding energies. Hence the configurations ${}^1\chi_m{}^{m+2}$ and ${}^1\chi_{m-1}{}^{m+1}$ would on the Hückel theory be degenerate and between these configurations there would be strong interaction. Dewar and Longuet-Higgins pointed out that this interaction was required by symmetry in the case of benzene and in cyclic polyenes of formula $(CH)_{4p+2}$ and that in these molecules the resulting upper states would be precisely those postulated by Moffitt in his LCAO perimeter theory. However, the pairing properties of the Hückel orbitals are maintained even in hydrocarbons such as pyrene, in which some atoms lie within the perimeter. Dewar and Longuet-Higgins showed that mixing between the configurations ${}^1\chi_m{}^{m+2}$ and ${}^1\chi_{m-1}{}^{m+1}$ leads to two excited states and that transitions to these two states from the ground state have very different intensities. In the polyacenes the band at longer wavelengths is the weaker and can be identified with the α band of Clar. The band at shorter wavelengths on the other hand, is strong and is Clar's β band. The weakness of the α band arises from a quasi-fortuitous cancellation of transition moments to the two components of the upper state. Like the theory of Pariser and Parr, the theory of Dewar and Longuet-Higgins rested on the assumptions of zero differential overlap and limited configurational interaction in the Hückel system of molecular orbitals. And like Moffitt,[39] Dewar and Longuet-Higgins attached particular importance to interaction between degenerate configurations. These authors, however, recognized that although their postulated wave functions might be reasonable representations of excited states, their theory as it stood represented a somewhat unsatisfactory mixture of naïveté and sophistication in that electron repulsion was, as it were, added as an afterthought to a theory which was not designed to include it explicitly.

This deficiency was, however, made good almost at once by Pople.[62] He pointed out that if the ground state were represented by a single determinant, constructed from self-consistent molecular orbitals of the type which he discussed in his 1953 paper, then the singly excited configurations ${}^1\chi_j{}^k$ have energies given by the standard formula

$$\langle {}^1\chi_j{}^k|\mathscr{H}|{}^1\chi_j{}^k\rangle-\langle {}^1\chi_0|\mathscr{H}|{}^1\chi_0\rangle = E_k-E_j+2J_{jk}-K_{jk}$$

where J_{jk} and K_{jk} are the Coulomb and exchange integrals between ψ_j and ψ_k. Pople had already established that in his simplified self-consistent theory the orbital eigenvalues E_i of an alternant hydrocarbon are paired as in the Hückel theory and he showed that the other terms in the excitation energy would be the same for the configurations ${}^1\chi_i{}^{j'}$ and ${}^1\chi_j{}^{i'}$ provided that $i+i' = j+j' = 2m+1$. Thus the degeneracy of the configurations ${}^1\chi_m{}^{m+2}$ and ${}^1\chi_{m-1}{}^{m+1}$ is maintained in the simple self-consistent theory, and does not depend on the neglect of electron repulsion, as might have been expected. Furthermore the transition moments from the ground state to these two configurations are equal if the atomic orbitals do not overlap, as had been pointed out by Dewar and Longuet-Higgins for the Hückel orbitals. It follows that in the self-consistent scheme there is a first-order splitting of ${}^1\chi_i{}^{j'}$ and ${}^1\chi_j{}^{i'}$ into their sum and their difference, to the former of which a transition from the ground state is in general allowed, but to the latter forbidden. In a paper published soon afterwards by Lefèbvre and Moser[25] it was suggested that the degeneracy between ${}^1\chi_i{}^{j'}$ and ${}^1\chi_j{}^{i'}$ will arise in the absence of zero differential overlap provided only that (1) the molecular orbitals have the usual pairing properties and (2) that the sum of the penetration integrals at every atom is the same.

The suggestion, on which there was general agreement, that interactions between pairs of configurations ${}^1\chi_i^{j'}$ and ${}^1\chi_j^{j'}$ are particularly important in the spectra of alternant hydrocarbons left unsettled the question how much interaction need be considered between nondegenerate configurations. This question could only be answered by quantitative calculations on a series of molecules and such a set of calculations was carried out by Pariser.[53] Pariser investigated the excited states of the polyacenes using the adjusted parameters suggested by Pariser and Parr, and calculated the wave functions and energies of the first few electronic states of the polyacenes assuming these wave functions to be expressible in terms of unexcited and singly excited configurations only. In this way he succeeded in obtaining excellent agreement with experimental energies and intensities both for singlet and for triplet states[32, 71] and made predictions as to the locations of hitherto unobserved states. He showed that the assumption of zero differential overlap leads to a clearcut distinction between what he described as "plus" and "minus" states. The wave functions of the minus states are linear combinations of wave functions of the type ${}^1\chi_i^{j'}-{}^1\chi_j^{i'}$ or ${}^3\chi_i^{j'}-{}^3\chi_j^{i'}$, and the wave functions of the plus states are linear combinations of functions of the type

$${}^1\chi_k^{k'} \text{ and } {}^1\chi_i^{j'}+{}^1\chi_j^{i'}, \quad \text{or} \quad {}^3\chi_k^{k'} \quad \text{and} \quad {}^3\chi_i^{j'}+{}^3\chi_j^{i'}$$

The ground state is to be regarded as a minus state. The only transitions which have appreciable moments are those between plus and minus states. Pariser showed incidentally that, in naphthalene at least, the interaction between "degenerate" configurations is of predominant importance, and that further interaction makes only a relatively small difference to the scheme of electronic energy levels. Pariser also found, as had been discovered by Pople, that there should be certain degeneracies between upper singlet and triplet states which might lead to anomalously rapid transitions between such states. Pariser's assignments of the naphthalene and anthracene spectra, both in absorption and emission, agree entirely with the most reliable experimental work on polarization of the emitted or absorbed light. Very recently Pariser[52] has carried out a similar program of calculation on the azulene molecule which is, of course, nonalternant. He has found that the spectra of this molecule can also be described in terms of the same theoretical approximations, invoking only singly excited configurations expressed in terms of Hückel orbitals. Butadiene has been discussed in similar terms by Pullman and Berthod,[66] and a series of cyclic polyenes and radicals by Longuet-Higgins and McEwen.[30]

It may be said, therefore, that the electronic spectra of aromatic hydrocarbons are now well understood. The essential features of the present theory are

(1) that, if suitable molecular orbitals are adopted in the determinant representing the wave function of the ground state, then the excited states may be adequately represented in terms of singly excited configurations alone, provided that,

(2) if these molecular orbitals are not self-consistent, then singly excited configurations contribute to the ground state and the unexcited configuration contributes to the excited states, and provided also that,

(3) atomic orbital overlap is neglected and the integrals determining the matrix elements of the Hamiltonian are evaluated semiempirically rather than by nonempirical calculation.

Some qualification of these conditions is necessary, in that it is not yet clear how much latitude is allowable in the choice of "suitable" molecular orbitals. Moffitt's theory, following Platt, is based on the hypothesis that perimeter orbitals are adequate; the calculations of Pariser show that the Hückel orbitals give good results; the theory of Pople, which derives from that of Roothaan, is based on self-consistent orbitals and is in some ways a more satisfying scheme, though it has not yet been applied as fully as Pariser and Parr's scheme to any molecule in which the self-consistent orbitals differ from the Hückel orbitals. It seems clear from the work of Moser and Lefèbvre[44] that an accurate account of the naphthalene spectrum can only be obtained if one takes into account more extensive mixing of singly excited configurations than was invoked by Dewar and Longuet-Higgins. It is not yet clear, however, how far the assumption of zero differential overlap is essential to the general correctness of the present theory. Attempts to rationalize this approximation and the related approximation of neglecting all except Coulomb repulsion integrals between atomic orbitals have been made by various authors. Hall[18, 19] has suggested that one can justify these approximations by interpreting the functions ϕ_r not as atomic orbitals localized on individual atoms but as suitable combinations of these localized orbitals. His specification for obtaining these orthonormal functions involves the use of a "standard excited state" in which one electron is assigned to each LCAO molecular orbital of the unsaturated molecule, the electron spins all being in the same direction. The details of this method are outlined in Hall's papers; it is, however, essential to realize that in his method the standard excited state is an entirely hypothetical state and that Hall's ultimate conclusions do not depend for their validity on its actual existence. A related endeavor is that of McWeeny[34] who, following Löwdin,[31] has discussed the use of "orthogonalized atomic orbitals" and found in them a good justification for the apparently drastic assumptions introduced by Pariser and Parr and by Pople.

V. OPEN SHELL MOLECULES

A related problem, which up to the time of writing has received less thorough study, is how to represent the electronic states of unsaturated molecules in which the ground state is not a singlet. The most obvious molecules of this type are the hydrocarbon radicals such as allyl and benzyl. One of the first attempts at a systematic theory of these radicals was that of Pople and Nesbet[64] who pointed out that it is possible to obtain an improvement in the calculated energy of a single determinant wave function for the ground state if one allows the electrons of spin $\frac{1}{2}$ to occupy orbitals which are spatially different from the orbitals containing the electrons of spin $-\frac{1}{2}$. Pople and Nesbet derived from the variational principle sets of equations for the orbitals associated with the two values of the spin. However, these equations are more difficult to solve than the equations of Roothaan, and there is an important disadvantage in the scheme which they originally proposed. This disadvantage is that their wave function for a radical is in general not an eigenfunction of S^2, where S is the total spin. Consequently a wave function of this type is not suitable for a theory of electronic spectra in which the classification into singlet, triplet, etc. states is of fundamental significance. For this reason Longuet-Higgins and Pople[28] developed an alternative theory of the states of hydrocarbon radicals in which they retained the idea of doubly occupied molecular orbitals for the paired electrons and sought a wave function of the type

$$^2\chi_0 \equiv |\psi_1 \bar{\psi}_1 \cdots \psi_{m-1} \bar{\psi}_{m-1} \psi_m|$$

for the ground state. Making a further plausible approximation they arrived at a series of equations for the occupied orbitals and proved that in an alternant radical these orbitals and the corresponding upper orbitals satisfy the pairing properties characteristic of alternant radicals in the Hückel scheme. On this basis they were able to show that the singly excited configurations ${}^2\chi_m{}^{k'}$ and ${}^2\chi_k{}^m$ are degenerate if $k+k' = 2m$, and give rise to a pair of states of which one has a zero transition moment from the ground state. Their results appeared to be consistent with the rather meagre experimental data on the electronic spectra of such radicals. Brion, Lefèbvre, and Moser[2] subsequently showed that the additional approximation introduced by Longuet-Higgins and Pople is not essential to the pairing property of the molecular orbitals of an alternant radical; and the method which these authors have outlined for calculating self-consistent orbitals in such systems promises to be very useful in this and other cases in view of its rapid convergence. McWeeny has proposed a closely related method of solving the self-consistent equations,[35] based on the method of steepest descents, though he has so far applied it only to closed shell situations.[36]

VI. MORE COMPLEX MOLECULES

The establishment of a satisfactory theory of the electronic spectra of aromatic hydrocarbons has paved the way for a useful theory of unsaturated molecules of other kinds. The problem of relating the electronic spectrum of a substance to its molecular structure includes the question how the electronic states of a composite molecule are related to those of its constituent parts. For example, how is the spectrum of biphenyl or of aniline related to that of benzene? To express the problem in this form is immediately to see the lines along which a solution may be sought. If one considers the composite molecule $R—S$, one may attempt to express the wave function for an electronic state in terms of the wave functions for the residues R and S taken separately. If the interaction between R and S is weak one may make use of the already existing theory of molecular interactions. Three types of interaction are particularly important, namely (a) the inductive or field effect of one fragment on the other, which can be discussed along the same lines as the Stark effect; (b) London type interactions between the two residues, of which an important special case is resonance interaction when R and S are identical; and (c) interactions involving the transfer of electrons from R to S or *vice versa*. These different effects have been recognized independently: Sklar[69] discussed the effect of simple substituents on benzene in terms of inductive interactions and derived some useful rules for intensities and spectral shifts in polysubstituted benzenes;[75] Simpson[72–74] showed that a satisfactory account of polyene and cyanine spectra could be given if the double bonds were supposed to enter into resonance interaction, and Mulliken's highly successful theory of molecular complex spectra[45–47] is based on the hypothesis that the colors of molecular complexes arise from transitions involving an essentially nonpolar ground state and a polar excited state (or *vice versa*). Many other authors have contributed to the development of these ideas:[75] Platt introduced in his paper on the cata-condensed hydrocarbons[58] the concept of "polarization diagrams," in order to interpret the relative intensities of the ^1L and ^1B transitions. These are essentially maps of the matrix element of the electric density between the ground state and an excited state, and Longuet-Higgins[26] has stressed the importance of the transition density between excited states in determining the effects of perturbations on a spectrum. Longuet-Higgins and

Murrell[27, 29] have shown in two papers how the above three effects may be systematically described by molecular orbital theory: the basic idea underlying their treatment is that the wave functions of a composite molecule may be expressed with reasonable accuracy in terms of singly excited configurations expressed in terms of molecular orbitals localized on the constituent parts. Nagakura[50] has shown that in nitro compounds one of the strong absorption bands is associated with the transfer of an electron to a vacant orbital of the nitro group, and Murrell and Longuet-Higgins[49] have suggested that the 2350 A band in aniline involves the transfer of an electron from the NH_2 group to the ring. Both of these might therefore be described as intramolecular charge transfer bands. Making use of these ideas, Murrell[48] has shown how the effect of steric hindrance on the intensity on a band often provides a criterion as to whether the band is due to intramolecular charge transfer or not.

VII. FREE-ELECTRON MO THEORY

Space does not unfortunately permit more than a mention of the free-electron molecular orbital theory and its application to the spectra of unsaturated hydrocarbons and heteromolecules. The very recent calculations of Ham and Ruedenberg[20] on unsaturated hydrocarbons cover a more extensive range than the LCAO calculations of Pariser, with which they agree very well. It seems fair, however, to say that in spite of brilliant exploratory work in this field the free-electron theory in its present form still lacks foundations as secure as those which have now been provided for the LCAO theory. A particular difficulty in the free-electron molecular orbital theory is the proper inclusion of electron repulsion; various ways have been devised of introducing it into the theory but the validity of these expedients still rests on goodwill rather than on rigor. Nevertheless the free-electron theory, in the hands of Platt[60] and Kuhn,[23, 24] has already pointed the way to a sound theory of the spectra of linear and branched systems, and there seems little doubt that the next few years will witness advances in the theory of dye spectra[3, 4] as important as those which have already occurred in the theory of simpler molecules.

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INTERMOLECULAR FORCES AND EQUATION OF STATE OF GASES

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CONTENTS

I. ADDITIVE AND NONADDITIVE VAN DER WAALS INTERACTIONS

The intermolecular potential in gases is usually assumed to be additive. It has been pointed out, however, that the effect of potential nonadditivity on the equation of state of gases does not seem to be negligible (Kihara[9]). The simplest system for which the nonadditivity of the intermolecular potential plays a role is the system composed of three spherically symmetric atoms, which will be treated in Section I. The aim of Sections I. A and I. B is to investigate quantum-mechanically the van der Waals interaction between three distant atoms. By use of the results, a model of nonadditive potential is introduced in Section I. C, which model will be applied, in Part II, to the equation of state of gases.

A. Van der Waals Interactions by Perturbation Theory

As a preparation let us first summarize London's[15] theory of the van der Waals interaction between two neutral atoms. Let $\mathbf{r}_1$ and $\mathbf{r}_2$ be the positions of the two atoms, and let $\mathbf{r}_2-\mathbf{r}_1 = r_{12}\mathbf{e}_{12}$, r_{12} being the distance between them. The distance is assumed to be so large that the dipole-dipole interaction predominates as the origin of intermolecular forces.

Under this assumption the total Hamiltonian of the two-body system can be divided into two parts,

$$H = H^0+J \tag{I.1}$$

Here H^0 is the unperturbed Hamiltonian for the system of two independent atoms; $J \equiv J(12)$ is the interaction which will be treated as a small perturbation and is given by

$$J(12) = \mathbf{p}(1)\cdot T(12)\cdot \mathbf{p}(2) \tag{I.2}$$

where

$$T(12) = (\mathbf{1}-3\mathbf{e}_{12}\mathbf{e}_{12})/r_{12}^3 \tag{I.3}$$

$\mathbf{p}(i)$ being the electric dipole of the ith atom. Let us denote by E_n the eigenvalues of H^0, E_0 being unperturbed energy of the ground state, and denote by $\langle n|J|m\rangle$ the nm matrix element of J in the representation in which H^0 is diagonal: $\langle n|H^0|m\rangle = E_n\delta_{nm}$. Then the energy W of the ground state is given, up to second-order perturbation, by

$$W = E_0+W_2(r_{12}) \tag{I.4}$$

$$W_2(r_{12}) = \sum_{n\neq 0} \frac{\langle 0|J|n\rangle\langle n|J|0\rangle}{E_0-E_n} \tag{I.5}$$

since $\langle 0|J|0\rangle = 0$ for spherically symmetric atoms in the ground state. From this expression $W_2(r_{12})$ is negative (attractive) and inversely proportional to the sixth power of the distance r_{12}.

The unperturbed Hamiltonian H^0 is a sum of two parts,

$$H^0 = H(1)+H(2)$$

$H(i)$ being the Hamiltonian for the ith atom. Let $\varepsilon_\varrho(1)$ and $\varepsilon_\sigma(2)$ be eigenvalues of $H(1)$ and $H(2)$, respectively, $\varepsilon_0(i)$ being the unperturbed energy of the ground state of the ith atom, so that

$$E_n = \varepsilon_\varrho(1)+\varepsilon_\sigma(2)$$

for $n \equiv (\varrho, \sigma)$, in particular

$$E_0 = \varepsilon_0(1)+\varepsilon_0(2)$$

Let, furthermore,

$$\delta_\varrho(1) = \varepsilon_\varrho(1)-\varepsilon_0(1), \quad \delta_\sigma(2) = \varepsilon_\sigma(2)-\varepsilon_0(2)$$

so that

$$E_n-E_0 = \delta_\varrho(1)+\delta_\sigma(2)$$

Then we have

$$W_2(r_{12}) = -\sum_{\varrho,\sigma\neq 0}\sum \frac{\langle 00|J|\varrho\sigma\rangle\,\langle\varrho\sigma|J|00\rangle}{\delta_\varrho(1)+\delta_\sigma(2)}$$

$$= -\sum_{\varrho,\sigma\neq 0}\sum \frac{\langle 0|\mathbf{p}(1)|\varrho\rangle\cdot T(12)\cdot\langle 0|\mathbf{p}(2)|\sigma\rangle\langle\sigma|\mathbf{p}(2)|0\rangle\cdot T(21)\cdot\langle\varrho|\mathbf{p}(1)|0\rangle}{\delta_\varrho(1)+\delta_\sigma(2)}$$

Here the summation is to be taken over $\varrho \neq 0$ and $\sigma \neq 0$ since $\langle 0|\mathbf{p}|0\rangle = 0$.

The last expression can be transformed into

$$W_2(r_{12}) = -\sum_{\varrho,\sigma\neq 0}\sum \frac{|\langle 0|p_x(1)|\varrho\rangle|^2|\langle 0|p_x(2)|\sigma\rangle|^2}{\delta_\varrho(1)+\delta_\sigma(2)}\ \text{trace}\ T(12)\cdot T(21)$$

p_x indicating the x-component of $\mathbf{p}$. Because, for any tensor T, $\langle 0|\mathbf{p}(1)|\varrho\rangle \cdot T \cdot \langle\varrho|\mathbf{p}(1)|0\rangle$ can be rewritten as $\langle\varrho|\mathbf{p}(1)|0\rangle \langle 0|\mathbf{p}(1)|\varrho\rangle : T$; and $\sum'\langle 0|\mathbf{p}(i)|\varrho\rangle\langle\varrho|\mathbf{p}(i)|0\rangle$ summed over an orthonormal set which spans an irreducible representation space of the rotation group, is rotation invariant, i.e., unit tensor times $\sum' \langle 0|p_x(i)|\varrho\rangle\langle\varrho|p_x(i)|0\rangle$. The trace can be evaluated as follows:

$$\begin{aligned} &\text{trace}\ T(12)\cdot T(21) \\ &= r_{12}^{-6}\ \text{trace}\ (\mathbf{1}-3\mathbf{e}_{12}\mathbf{e}_{12})\cdot(\mathbf{1}-3\mathbf{e}_{21}\mathbf{e}_{21}) \\ &= r_{12}^{-6}\ \text{trace}\ (\mathbf{1}+3\mathbf{e}_{12}\mathbf{e}_{12}) = 6r_{12}^{-6} \end{aligned}$$

Thus we finally obtain

$$W_2(r_{12}) = -\mu_{12}r_{12}^{-6} \tag{I.6}$$

$$\mu_{12} = 6\sum_{\varrho,\sigma\neq 0}\sum\frac{|\langle 0|p_x(1)|\varrho\rangle|^2|\langle 0|p_x(2)|\sigma\rangle|^2}{\delta_\varrho(1)+\delta_\sigma(2)} \tag{I.7}$$

Now let us consider a system composed of three spherically symmetric atoms located at $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_3$, for which

$$\mathbf{r}_j-\mathbf{r}_i = r_{ij}\mathbf{e}_{ij}, \quad |\mathbf{e}_{ij}| = 1$$

The Hamiltonian is of the form of Eq. I.1 with

$$H^0 = H(1)+H(2)+H(3),$$
$$J = J(12)+J(23)+J(31)$$

The energy W of the ground state is given, up to third-order perturbation, by

$$W = E_0+W_2(r_{12}, r_{23}, r_{31})+W_3(r_{12}, r_{23}, r_{31}) \tag{I.8}$$

$$W_2 = \sum_{n\neq 0}\frac{\langle 0|J|n\rangle\langle n|J|0\rangle}{E_0-E_n} \tag{I.9}$$

$$W_3 = \sum_{n,m\neq 0}\sum\frac{\langle 0|J|n\rangle\langle n|J|m\rangle\langle m|J|0\rangle}{(E_0-E_n)(E_0-E_m)} \tag{I.10}$$

where the identity $\langle 0|J|0\rangle = 0$ has been used.

The second-order perturbation W_2 is a sum of three two-body interactions,

$$W_2(r_{12}, r_{23}, r_{31}) = -\mu_{12}r_{12}^{-6}-\mu_{23}r_{23}^{-6}-\mu_{31}r_{31}^{-6} \tag{I.11}$$

This part of the intermolecular potential is therefore additive. (The additivity holds not only for the dipole interaction but for all interactions so far as the energy derivable by the second-order perturbation is concerned, see Margenau.[16])

The nonadditive part of the intermolecular potential comes first from the third-order perturbation W_3. (The third-order perturbation for a system of two atoms vanishes.) Since the matrix elements $\langle n|J|n'\rangle \equiv \langle\varrho\sigma\tau|J|\varrho'\sigma'\tau'\rangle$ vanish for $\varrho\neq\varrho'$, $\sigma\neq\sigma'$, $\tau\neq\tau'$, the interaction W_3 is a sum of six terms of the type

$$\sum_{\varrho,\sigma,\tau\neq 0}\sum\sum\frac{\langle 000|J|\varrho\sigma 0\rangle\langle\varrho\sigma 0|J|\varrho 0\tau\rangle\langle\varrho 0\tau|J|000\rangle}{[\delta_\varrho(1)+\delta_\sigma(2)]\,[\delta_\varrho(1)+\delta_\tau(3)]}$$

which term reduces to

$$\sum_{\varrho,\sigma,\tau\neq 0}\sum\sum \frac{|\langle 0|p_x(1)|\varrho\rangle|^2 |\langle 0|p_x(2)|\sigma\rangle|^2 |\langle 0|p_x(3)|\tau\rangle|^2}{[\delta_\varrho(1)+\delta_\sigma(2)]\,[\delta_\varrho(1)+\delta_\tau(3)]}$$
$$\text{trace } T(12)\cdot T(23)\cdot T(31).$$

The trace can be evaluated as follows:

$$\begin{aligned}
&\text{trace } T(12)\cdot T(23)\cdot T(31)\\
&\quad = (r_{12}r_{23}r_{31})^{-3}\,\text{trace}\,[(\mathbf{1}-3\mathbf{e}_{12}\mathbf{e}_{12})\cdot(\mathbf{1}-3\mathbf{e}_{23}\mathbf{e}_{23})\cdot(\mathbf{1}-3\mathbf{e}_{31}\mathbf{e}_{31})]\\
&\quad = 3(r_{12}r_{23}r_{31})^{-3}[-2+3\{(\mathbf{e}_{31}\cdot\mathbf{e}_{12})^2+(\mathbf{e}_{12}\cdot\mathbf{e}_{23})^2+(\mathbf{e}_{23}\cdot\mathbf{e}_{31})^2\}\\
&\qquad\qquad -9(\mathbf{e}_{12}\cdot\mathbf{e}_{23})(\mathbf{e}_{23}\cdot\mathbf{e}_{31})(\mathbf{e}_{31}\cdot\mathbf{e}_{12})]\\
&\quad = 3(r_{12}r_{23}r_{31})^{-3}(3\cos\theta_1\cos\theta_2\cos\theta_3+1)
\end{aligned}$$

Here θ_1, θ_2, θ_3 are inner angles of the triangle formed by the three atoms, for example,

$$\cos\theta_1 = -\mathbf{e}_{31}\cdot\mathbf{e}_{12} = (r_{31}{}^2+r_{12}{}^2-r_{23}{}^2)/2r_{31}r_{12},$$

and use has been made of the relation

$$\cos^2\theta_1+\cos^2\theta_2+\cos^2\theta_3 = 1-2\cos\theta_1\cos\theta_2\cos\theta_3$$

Thus we obtain finally

$$W_3(r_{12}, r_{23}, r_{31}) = \nu(r_{12}r_{23}r_{31})^{-3}(3\cos\theta_1\cos\theta_2\cos\theta_3+1) \qquad (\text{I.12})$$

with

$$\begin{aligned}
\nu = 6\sum_{\varrho,\sigma,\tau\neq 0}\sum\sum &\{[\delta_\varrho(1)+\delta_\sigma(2)]^{-1}[\delta_\varrho(1)+\delta_\tau(3)]^{-1}\\
&+[\delta_\varrho(1)+\delta_\sigma(2)^{-1}[\delta_\sigma(2)+\delta_\tau(3)]^{-1}\\
&+[\delta_\varrho(1)+\delta_\tau(3)]^{-1}[\delta_\sigma(2)+\delta_\tau(3)]^{-1}\}\\
&\cdot|\langle 0|p_x(1)|\varrho\rangle|^2\,|\langle 0|p_x(2)|\sigma\rangle|^2\,|\langle 0|p_x(3)|\tau\rangle|^2
\end{aligned}$$

or

$$\begin{aligned}
\nu = 12\sum_{\varrho,\sigma,\tau\neq 0}\sum\sum &[\delta_\varrho(1)+\delta_\sigma(2)]^{-1}[\delta_\sigma(2)+\delta_\tau(3)]^{-1}[\delta_\tau(3)+\delta_\varrho(1)]^{-1}\\
&\cdot[\delta_\varrho(1)+\delta_\sigma(2)+\delta_\tau(3)] \qquad\qquad (\text{I.13})\\
&\cdot|\langle 0|p_x(1)|\varrho\rangle|^2\,|\langle 0|p_x(2)|\sigma\rangle|^2\,|\langle 0|p_x(3)|\tau\rangle|^2
\end{aligned}$$

The nonadditive correction was first investigated by Muto[20] and by Axilrod and Teller,[1] each for a simplified atomic model. It is to be emphasized that in the present treatment no particular assumption (other than the spherical symmetry) has been made.

The nonadditive correction is positive (repulsive) in case all θ_i's are smaller than 117° and negative (attractive) in case one of the θ_i's is larger than 126°.

In the particular case of a system of three harmonic oscillators with angular frequencies ω_i, the matrix elements $\langle 0|p_x(i)|\varrho\rangle$ vanish, except the element $\langle 0|p_x(i)|1\rangle$ for which $\delta_1(i) = \hbar\omega_i$, $2\pi\hbar$ being Planck's constant $(i = 1, 2, 3)$. Hence

$$\mu_{12} = \frac{2}{3}\,\frac{\langle 0|p(1)^2|0\rangle\,\langle 0|p(2)^2|0\rangle}{\hbar(\omega_1+\omega_2)},$$

$$\nu = \frac{4}{9}\,\frac{\omega_1+\omega_2+\omega_3}{\hbar^2(\omega_1+\omega_2)(\omega_2+\omega_3)(\omega_3+\omega_1)}\langle 0|p(1)^2|0\rangle\,\langle 0|p(2)^2|0\rangle\,\langle 0|p(3)^2|0\rangle$$

where use has been made of the relationship $\langle 0|p^2|0\rangle = 3\langle 0|p_x{}^2|0\rangle$.

For a harmonic oscillator with mass m, charge e, and angular frequency ω, $\langle 0|p^2|0\rangle$ is given by $3\hbar e^2/2m\omega$ which is $3\hbar\omega/2$ times the polarizability $\alpha = e^2/m\omega^2$. We can therefore eliminate ω from the above expressions by use of the relation

$$\tfrac{3}{2}\hbar\omega = \frac{\langle 0|p^2|0\rangle}{\alpha}.$$

obtaining

$$\mu_{12} = \frac{\pi_1\pi_2}{\pi_1+\pi_2}\,\alpha_1\alpha_2 \tag{I.14}$$

$$\nu = \frac{(\pi_1+\pi_2+\pi_3)\pi_1\pi_2\pi_3}{(\pi_1+\pi_2)(\pi_2+\pi_3)(\pi_3+\pi_1)}\,\alpha_1\alpha_2\alpha_3 \tag{I.15}$$

in which

$$\pi_i = \langle 0|p(i)^2|0\rangle/\alpha_i$$

In case three molecules of a system are identical, the energy W of the ground state is of the form

$$W = E_0 - \mu(r_{12}{}^{-6}+r_{23}{}^{-6}+r_{31}{}^{-6}) + \nu(r_{12}r_{23}r_{31})^{-3}(3\cos\theta_1\cos\theta_2\cos\theta_3+1) \tag{I.16}$$

For a system of three identical harmonic oscillators, we have

$$\mu = \tfrac{1}{2}\alpha\langle 0|p^2|0\rangle \tag{I.17}$$

$$\nu = \tfrac{3}{8}\alpha^2\langle 0|p^2|0\rangle \tag{I.18}$$

from which we obtain a very simple relation

$$\boxed{4\nu = 3\alpha\mu} \tag{I.19}$$

Equations I.14, I.15, I.17, I.18, and I.19 contain no model constant of the harmonic oscillator. In fact these relations hold for any spherically symmetric atom with the accuracy of the variation method. Details will be given in the next section.

B. Van der Waals Interactions by Variation Method

For the purpose of evaluating the energy W of the ground state, the variation method is effective. A system of identical atoms will be treated by this method in detail; that of unlike atoms will be noted briefly at the end of the section. A theorem will be first shown.

For a system of three identical harmonic oscillators the ground-state energy W given by Eq. I.8 agrees, up to the term proportional to the cube of the interaction J, with the result of variation calculation by use of the simplest trial function

$$\psi = (1+AJ)\psi_0 \tag{I.20}$$

Here ψ_0 is the unperturbed eigenfunction of the ground state, and A is the variation parameter assumed to be real.

In general, an upper limit for the ground-state energy obtainable with this trial function is given by the minimum of the expectation value of the Hamiltonian H^0+J for the function ψ:

$$\langle 0|(1+AJ)(H^0+J)(1+AJ)|0\rangle/\langle 0|(1+AJ)^2|0\rangle$$

This expression becomes, since $\langle 0|J|0\rangle = 0$, $\langle 0|H^0J|0\rangle = \langle 0|JH^0|0\rangle = 0$, and $\langle 0|H^0|0\rangle = E_0$,

$$[E_0+2A\langle 0|J^2|0\rangle+A^2\langle 0|JH^0J|0\rangle+A^2\langle 0|J^3|0\rangle]/[1+A^2\langle 0|J^2|0\rangle]$$

which is equal, up to the term proportional to J^3, to

$$E_0+2A\langle 0|J^2|0\rangle+A^2[\langle 0|JH^0J|0\rangle+\langle 0|J^3|0\rangle-E_0\langle 0|J^2|0\rangle]$$

This takes a minimum with respect to variation of A when

$$A=\langle 0|J^2|0\rangle/[E_0\langle 0|J^2|0\rangle-\langle 0|JH^0J|0\rangle-\langle 0|J^3|0\rangle]$$

the minimum being

$$E_0+\frac{\langle 0|J^2|0\rangle^2}{E_0\langle 0|J^2|0\rangle-\langle 0|JH^0J|0\rangle-\langle 0|J^3|0\rangle}$$

The last value is equal, up to the term of J^3, to

$$E_0+\frac{\langle 0|J^2|0\rangle^2}{E_0\langle 0|J^2|0\rangle-\langle 0|JH^0J|0\rangle}+\frac{\langle 0|J^2|0\rangle^2\langle 0|J^3|0\rangle}{[E_0\langle 0|J^2|0\rangle-\langle 0|JH^0J|0\rangle]^2} \qquad \text{(I.21)}$$

It is easy to see that Eq. I.21 coincides with Eq. I.8 for a system of three identical harmonic oscillators. Thus for this particular system the lowest upper limit for the ground-state energy obtainable with Eq. I.20 is exact up to the term corresponding to the third-order perturbation. It is therefore reasonable to adopt the trial function, Eq. I.20, also for real systems composed of identical molecules.

It will be shown in the following, by use of the trial function and Eq. I.21, that Eqs. I.19 and I.17:

$$4\nu=3\alpha\mu, \quad 2\mu=\alpha\langle 0|p^2|0\rangle \qquad \text{(I.22)}$$

hold for spherically symmetric atoms with the accuracy of variation method.

We must first calculate

$$\langle 0|JH^0J|0\rangle=\langle 0|J(12)H^0J(12)|0\rangle+\langle 0|J(23)H^0J(23)|0\rangle+\langle 0|J(31)H^0J(31)|0\rangle$$

in which, for example,

$$\langle 0|J(12)H^0J(12)|0\rangle$$
$$=\langle 0|J(12)H(1)J(12)|0\rangle+\langle 0|J(12)H(2)J(12)|0\rangle+\langle 0|J(12)H(3)J(12)|0\rangle$$

The right-hand side of

$$\langle 0|J(12)H(1)J(12)|0\rangle=\langle 0|\mathbf{p}(2)\cdot T(12)\cdot\mathbf{p}(1)H(1)\mathbf{p}(1)\cdot T(12)\cdot\mathbf{p}(2)|0\rangle$$

can be transformed, by virtue of the spherical symmetry of the operator $H(1)$, into

$$\varkappa\varepsilon_0\langle 0|\mathbf{p}(2)\cdot T(12)\cdot\mathbf{p}(1)\mathbf{p}(1)\cdot T(12)\cdot\mathbf{p}(2)|0\rangle$$

Here ε_0 is the unperturbed energy of the ground state of an atom, $3\varepsilon_0 = E_0$; the coefficient $\varkappa$ is a dimensionless constant of the atom. We thus obtain

$$\langle 0|J(12))H(1)J(12)|0\rangle = \varkappa\varepsilon_0\langle 0|J(12)^2|0\rangle$$

furthermore

$$\langle 0|J(12)H^0J(12)|0\rangle = (2\varkappa+1)\varepsilon_0\langle 0|J(12)^2|0\rangle$$

and finally

$$\langle 0|JH^0J|0\rangle = (2\varkappa+1)\varepsilon_0\langle 0|J^2|0\rangle \tag{I.23}$$

Substituting Eq. I.23 into Eq. I.21 we have

$$3\varepsilon_0 + \frac{\langle 0|J^2|0\rangle}{2(1-\varkappa)\varepsilon_0} + \frac{\langle 0|J^3|0\rangle}{[2(1-\varkappa)\varepsilon_0]^2} \tag{I.24}$$

The matrix elements $\langle 0|J^2|0\rangle$ and $\langle 0|J^3|0\rangle$ can be calculated in the same way as in the preceding section, the results being

$$\langle 0|J^2|0\rangle = \tfrac{2}{3}\langle 0|p^2|0\rangle^2({r_{12}}^{-6}+{r_{23}}^{-6}+{r_{31}}^{-6}),$$
$$\langle 0|J^3|0\rangle = \tfrac{2}{3}\langle 0|p^2|0\rangle^3(r_{12}r_{23}r_{31})^{-3}(3\cos\theta_1\cos\theta_2\cos\theta_3+1)$$

($p \equiv |\mathbf{p}|$). Substituting these values into Eq. I.24, we obtain Eq. I.16 with the coefficients

$$\mu = -\frac{1}{3}\frac{\langle 0|p^2|0\rangle^2}{(1-\varkappa)\varepsilon_0}, \qquad \nu = \frac{1}{6}\frac{\langle 0|p^2|0\rangle^3}{[(1-\varkappa)\varepsilon_0]^2} \tag{I.25}$$

In order to obtain Eq. I.22, therefore, we need only to prove that the polarizability α of an atom is given by

$$\alpha = -\frac{2}{3}\frac{\langle 0|p^2|0\rangle}{(1-\varkappa)\varepsilon_0} \tag{I.26}$$

The Hamiltonian of an atom in an electric field $\mathbf{F}$ is given by $H(1)+\mathbf{F}\cdot\mathbf{p}$. By use of a trial function similar to Eq. I.20, the energy gained by the interaction with the field is given by

$$\frac{\langle 0|\mathbf{F}\cdot\mathbf{pp}\cdot\mathbf{F}|0\rangle^2}{\varepsilon_0\langle 0|\mathbf{F}\cdot\mathbf{pp}\cdot\mathbf{F}|0\rangle-\langle 0|\mathbf{F}\cdot\mathbf{p}H(1)\mathbf{p}\cdot\mathbf{F}|0\rangle}$$

This expression is calculated, since

$$\langle 0|\mathbf{F}\cdot\mathbf{p}H(1)\mathbf{p}\cdot\mathbf{F}|0\rangle = \varkappa\varepsilon_0\langle 0|\mathbf{F}\cdot\mathbf{pp}\cdot\mathbf{F}|0\rangle$$

and

$$\langle 0|\mathbf{F}\cdot\mathbf{pp}\cdot\mathbf{F}|0\rangle = \tfrac{1}{3}F^2\langle 0|p^2|0\rangle, \qquad (F\equiv|\mathbf{F}|)$$

to be $\langle 0|p^2|0\rangle F^2/3(1-\varkappa)\varepsilon_0$ from which Eq. I.26 follows.

For rare-gas atoms $\langle 0|p^2|0\rangle$ can be evaluated from observed values of molar diamagnetic susceptibility χ_{mol} by use of the relation

$$\chi_{\text{mol}} = -\frac{L}{6m_ec^2}\langle 0|p^2|0\rangle \tag{I.27}$$

where m_e is the electron mass, c light velocity, $L = 6.0\times 10^{23}$. Observed values of α and χ_{mol} together with the derived values of $\langle 0|p^2|0\rangle$ and μ are given in Table I.

TABLE I. Polarizability α, Molar Diamagnetic Susceptibility χ_{mol}, and Derived Quantities.

	α	χ_{mol}	$\langle 0\|p^2\|0\rangle$	$\mu = \frac{1}{2}\alpha\langle 0\|p^2\|0\rangle$
He	0.201A^3	-1.9×10^{-6} cm^3	1.55×10^{-11} erg A^3	0.156×10^{-11} erg A^6
Ne	0.390	-7.2	5.9	1.15
A	1.62	-19.4	15.8	12.8
Kr	2.46	-28	23	28
Xe	3.99	-43	35	70

For a hydrogen atom we know that

$$\varepsilon_0 = -e^2/2a_0, \qquad \langle 0|p^2|0\rangle = 3e^2a_0^2, \qquad \varkappa = 0$$

where e is the electron charge and a_0 is the Bohr radius. Substituting these expressions into Eqs. I.25 and I.26, we obtain

$$\mu = 6e^2a_0^5, \qquad \nu = 18e^2a_0^8, \qquad \alpha = 4a_0^3$$

A higher approximation by use of the trial function

$$\psi = [1+AJ+B\{[p(1)+p(2)]J(12)+[p(2)+p(3)]J(23) + [p(3)+p(1)]J(31)\}]\psi, \quad (p(i) \equiv |\mathbf{p}(i)|)$$

gives

$$\mu = \frac{84}{13}e^2a_0^5, \quad \nu = \frac{3618}{169}e^2a_0^8, \quad \alpha = \frac{9}{2}a_0^3$$

From these values follow

$$\frac{4\nu}{3\alpha\mu} = \frac{268}{273} \quad \text{and} \quad \frac{2\mu}{\alpha\langle 0|p^2|0\rangle} = \frac{112}{117}$$

Hence the accuracy of Eqs. I.22 is sufficient at least for hydrogen atoms.

We have been considering a system of three identical atoms. With regard to a system of unlike atoms, we can similarly show that Eqs. 1.14 and 1.15 hold for spherically symmetric atoms with accuracy of the variation method by use of the trial function

$$\psi = [1+AJ(12)+BJ(23)+CJ(31)]\psi_0$$

with three variation parameters. The generalization of the relation $4\nu = 3\alpha\mu$ is

$$\nu = \frac{2R_1R_2R_3(R_1+R_2+R_3)}{(R_1+R_2)(R_2+R_3)(R_3+R_1)}$$

in which

$$\frac{1}{R_1} = \frac{1}{\mu_{12}\alpha_3} + \frac{1}{\mu_{31}\alpha^2} - \frac{1}{\mu_{23}\alpha_1}, \text{ etc.}$$

We have confined ourselves, to spherically symmetric atoms. It is interesting to note that polyatomic molecules with spherically symmetric polarizability (e.g. methane, CH_4 and carbon tetrafluoride, CF_4) can be treated in the same manner.

This section is chiefly based on Midzuno and Kihara.[19]

C. A Standard Model of the Intermolecular Potential

In the two preceding sections we treated potential energies between molecules at large separations. At small separations molecules are repelled from one another. Taking this fact into account let us approximate, as usual, the potential energy for a system of two spherical molecules by

$$U(r) \equiv \lambda r^{-12} - \mu r^{-6} \tag{I.28}$$

Here λ and μ are molecular constants which will be determined from the equation of state of gases.

Although the attractive part of the potential, $-\mu r^{-6}$, is taken from the van der Waals interaction previously discussed, we do not equate the constant μ with the corresponding value calculated quantum-mechanically. Nevertheless, we expect that the value of the model parameter μ and the quantum-mechanical value of μ are not far apart (compare Table IV).

The potential energy of a system of three identical molecules is of the form

$$U(r_{12}, r_{23}, r_{31}) \equiv U(r_{12}) + U(r_{23}) + U(r_{31}) + u(r_{12}, r_{23}, r_{31}) \tag{I.29}$$

in which $u(r_{12}, r_{23}, r_{31})$ indicates the effect of potential nonadditivity. Let us assume that its asymptotic formula at large separations is a good approximation to the potential u; i.e., we assume

$$u(r_{12}, r_{23}, r_{31}) = \nu(r_{12}r_{23}r_{31})^{-3}\,(3\cos\theta_1\cos\theta_2\cos\theta_3 + 1) \tag{I.30}$$

Here r_{ij} is the distance between the ith and jth molecules; θ_1, θ_2, θ_3 are inner angles of the triangle composed of the three molecules; and ν is given by the relationship

$$4\nu = 3\alpha\mu \tag{I.31}$$

α being the polarizability of a molecule. Our model will be used in the latter half of Part II.

II. SECOND AND THIRD CLUSTER INTEGRALS

In the first half of this part, the statistical thermodynamics of gases at moderate densities is reviewed and necessary formulas are derived. These formulas are combined, in the second half, with our model of the intermolecular potential to explain the compressibility data of gases.

A. Cluster Integrals and Equations of State

Let us consider a gas composed of N identical monatomic molecules of mass m in a vessel of volume V and at temperature T. Let E and S be the energy and the entropy of the system, respectively. Then, for the free energy of the system,

$$F \equiv E - TS \tag{II.1}$$

there is the differential relation

$$dF = -SdT - PdV + gdN \tag{II.2}$$

where P is the pressure and g the chemical potential. Let us further define the function I by

$$I \equiv F - gN \tag{II.3}$$

for which

$$dI = -SdT - PdV - Ndg$$

From the last relationship it follows that

$$P = -\left(\frac{\partial I}{\partial V}\right)_{T,g} \tag{II.4}$$

and

$$N = -\left(\frac{\partial I}{\partial g}\right)_{T,V} \tag{II.5}$$

which will be used shortly.

The free energy F and the function I can be calculated by means of the partition function $Z(T, V, N)$ according to

$$F = -kT \ln Z(T, V, N)$$

and

$$I = -kT \ln \sum_N Z(T, V, N) \exp (gN/kT) \tag{II.6}$$

where k is Boltzmann's constant.

The partition function for the present system is given, when quantum effects are negligible, by

$$Z^{(0)} = \frac{1}{N!}\left(\frac{mkT}{2\pi\hbar^2}\right)^{3N/2} \int_V \cdots \int_V \exp\left[-\frac{\Phi(\mathbf{r}_1, \ldots, \mathbf{r}_N)}{kT}\right] d\mathbf{r}_1 \ldots d\mathbf{r}_N \tag{II.7}$$

where $\Phi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ is the intermolecular potential energy of the N-molecule system, $\mathbf{r}_i$ being the position of ith molecule. The integral with respect to each $\mathbf{r}$ is to be taken over the volume V. The integrand $\exp(-\Phi/kT)$, which is called the Boltzmann factor, represents the probability of position in configuration space for a canonical ensemble normalized to unity when all the molecules are far away from each other.

When quantum effects must be taken into account, the Boltzmann factor must be replaced by its quantum generalization, the Slater sum, which will be denoted by $S(\mathbf{r}_1, \ldots, \mathbf{r}_N)$. Thus

$$Z = \frac{1}{N!}\left(\frac{mkT}{2\pi\hbar^2}\right)^{3N/2} \int_V \cdots \int_V S(\mathbf{r}_1, \ldots, \mathbf{r}_N)\, d\mathbf{r}_1 \ldots d\mathbf{r}_N \qquad \text{(II.8)}$$

An explicit expression for S will be given in the next section.

Ursell[27] has offered a powerful method of evaluating the partition function. Let us introduce a set of functions $B(\mathbf{r}_1, \ldots, \mathbf{r}_l)$ by the relations

$$\begin{aligned}
S(\mathbf{r}_1) &= B(\mathbf{r}_1) = 1, \\
S(\mathbf{r}_1, \mathbf{r}_2) &= B(\mathbf{r}_1, \mathbf{r}_2) + B(\mathbf{r}_1)B(\mathbf{r}_2), \\
S(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= B(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + B(\mathbf{r}_1, \mathbf{r}_2)B(\mathbf{r}_3) + B(\mathbf{r}_2, \mathbf{r}_3)B(\mathbf{r}_1) \\
&\quad + B(\mathbf{r}_3, \mathbf{r}_1)B(\mathbf{r}_2) + B(\mathbf{r}_1)B(\mathbf{r}_2)B(\mathbf{r}_3)
\end{aligned}$$

and so on. Then it can easily be shown that $B(\mathbf{r}_1, \ldots, \mathbf{r}_l)$ is different from zero only when $\mathbf{r}_1, \ldots, \mathbf{r}_l$ are near together (i.e., in the range of the intermolecular forces) or form a "cluster."

Mayer's[17] cluster integrals are defined by

$$b_l = \frac{1}{l!\,V}\int_V \cdots \int_V B(\mathbf{r}_1, \ldots, \mathbf{r}_l)\, d\mathbf{r}_1 \ldots d\mathbf{r}_l,$$

which are independent of the volume V so far as the number l is much smaller than N. In particular, $b_1 = 1$,

$$b_2 = \frac{1}{2V}\iint B(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_1 d\mathbf{r}_2 = \frac{1}{2V}\iint [S(\mathbf{r}_1, \mathbf{r}_2) - 1]\, d\mathbf{r}_1 d\mathbf{r}_2 \qquad \text{(II.9)}$$

$$\begin{aligned}
b_3 &= \frac{1}{3!V}\iiint B(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)\, d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \\
&= \frac{1}{6V}\iiint [S(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - S(\mathbf{r}_1, \mathbf{r}_2) - S(\mathbf{r}_2, \mathbf{r}_3) - S(\mathbf{r}_3, \mathbf{r}_1) + 2]\, d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3
\end{aligned} \qquad \text{(II.10)}$$

The "second cluster integral" b_2 is of the order of magnitude of the molecular volume, the "third cluster integral" b_3 the molecular volume squared, and so on.

In terms of these cluster integrals, the function I, Eq. II.6, is given by*

$$I = -kTV\sum_l b_l z^l \tag{II.11}$$

where

$$z \equiv \left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2} \exp\frac{g}{kT}$$

The free energy $F \equiv I+Ng$ is

$$F = I+NkT\ln\left[\left(\frac{2\pi\hbar^2}{mkT}\right)^{3/2} z\right] \tag{II.12}$$

and the energy $E = -T^2(\partial(F/T)/\partial T)_{V,N}$ is calculated to be

$$E = \tfrac{3}{2}NkT+VkT^2\sum_l \frac{db_l}{dT} z^l \tag{II.13}$$

Substituting Eq. II.11 into Eqs. II.4 and II.5, we have

$$P = kT\sum b_l z^l = kT(z+b_2z^2+b_3z^3+\dots) \tag{II.14}$$

and

$$N = V\sum lb_l r^l = V(z+2b_2z^2+3b_3z^3+\dots) \tag{II.15}$$

Eliminating z from these two relations, we finally obtain the equation of state in the form of a power series in the number-density $v^{-1} \equiv N/V$:

$$Pv = kT\left(1+\frac{-b_2}{v}+\frac{4b_2{}^2-2b_3}{v^2}+\dots\right) \tag{II.16}$$

or in the pressure P

$$Pv = kT\left[1-b_2\frac{P}{kT}+(3b_2{}^2-2b_3)\left(\frac{P}{kT}\right)^2+\dots\right] \tag{II.17}$$

Values of b_2 and b_3 derived from the compressibility data are given in Table II; they will be used in following sections.

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* See, for example, R. Becker, *Theorie der Wärme*, Springer, Berlin, 1955, p. 184.

TABLE II. Observed Cluster Integrals.

	T° K	b_2A^3	$b_3 \times 10^{-3}$ A^6	Reference
He	20.35	4.6	−0.52	Otto[23]
	65.15	−15.6	+0.14	
	90.15	−17.6	+0.37	
	123	−18.9	+0.45	
	173	−19.8	+0.52	
	223	−19.8	+0.53	
	273	−19.7	+0.67	Michels and Wouters[18]
	323	−19.2	+0.64	
	373	−18.8	+0.58	
	423	−18.4	+0.53	
Ne	65.2	34.8	+1.65	Holborn and Otto[7]
	90.6	13.6	−0.24	
	123	− 0.2	−0.30	
	173	−10.7	−0.05	
	223	−15.1	+0.14	
	273	−17.7	+0.28	
	373	−19.7		
	473	−21.7		
	573	−22.8		
	673	−22.8		
A	173	106.8		Holborn and Otto[7]
	223	62.7	+5.5	
	273	36.7	+0.4	
	323	18.3	−1.0	
	373	7.1	−1.4	
	423	− 1.9	−1.3	
	473	− 7.8	−1.2	
	573	−18.6		
Kr	273	104.5	+18.0	Beattie *et al.*[3]
	323	71.1	+ 7.0	
	373	47.9	+ 1.9	
	423	31.2	− 0.5	
	473	18.5	− 1.5	
	523	9.5	− 2.1	
	573	1.9	− 2.2	

When quantum effects are negligible, the second cluster integral, Eq. II.9 becomes

$$b_2^{(0)} = \frac{1}{2V}\iint\left[\exp\frac{-\Phi(\mathbf{r}_1, \mathbf{r}_2)}{kT} - 1\right] d\mathbf{r}_1 d\mathbf{r}_2$$

which can be reduced to a single integral with respect to $r = |\mathbf{r}_1 - \mathbf{r}_2|$:

$$b_2^{(0)} = 2\pi\int_0^\infty\left[\exp\frac{-U(r)}{kT} - 1\right] r^2 dr \qquad \text{(II.18)}$$

where $U(r)$ is the potential function between two molecules: $U(r) \equiv \Phi(\mathbf{r}_1, \mathbf{r}_2)$.

The classical expression for the third cluster integral, Eq. II.10, is

$$b_3^{(0)} = \frac{1}{6V}\iiint\left[\exp\frac{-\Phi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)}{kT} - \exp\frac{-\Phi(\mathbf{r}_1, \mathbf{r}_2)}{kT} - \exp\frac{-\Phi(\mathbf{r}_2, \mathbf{r}_3)}{kT} - \exp\frac{-\Phi(\mathbf{r}_3, \mathbf{r}_1)}{kT} + 2\right] d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3$$

This integral can be reduced to a triple integral

$$b_3^{(0)} = \frac{4\pi^2}{3}\iiint\left[\exp\frac{-U(r_{12}, r_{23}, r_{31})}{kT} - \exp\frac{-U(r_{12})}{kT} - \exp\frac{-U(r_{23})}{kT} - \exp\frac{-U(r_{31})}{kT} + 2\right] r_{12} r_{23} r_{31} dr_{12} dr_{23} dr_{31} \qquad \text{(II.19)}$$

in which

$$U(r_{12}, r_{23}, r_{31}) \equiv \Phi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \quad \text{for } r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$$

Here use has been made of the transformation

$$V^{-1} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 = 8\pi^2 r_{12} r_{23} r_{31} dr_{12} dr_{23} dr_{31}$$

of integration variables. The integral is to be taken over all values of r_{12}, r_{23}, r_{31}, which form three sides of a triangle.

B. Quantum Corrections to the Cluster Integrals

There are two types of quantum effects: the symmetry effect which results from the symmetry of the wave functions of a system with respect to interchange of molecular coordinates, and the diffraction effect which results from the wave nature of molecules. Except for helium at very low temperatures ($T \leqq 25°$ K) the symmetry effect is negligible; and only the diffraction effect will be considered in the following.

Let us start from the density matrix for a l-molecule system ($l = 2, 3, \ldots$),

$$\varrho(\mathbf{r}_1, \ldots, \mathbf{r}_l; \mathbf{r}'_1, \ldots, \mathbf{r}_l') = \sum_\nu \exp(-\beta E_\nu)\, \psi_\nu(\mathbf{r}_1, \ldots, \mathbf{r}_l)\, \bar{\psi}_\nu(\mathbf{r}'_1, \ldots, \mathbf{r}'_l) \tag{II.20}$$

in which, and in this section throughout, $\beta = 1/kT$. Here $\{\psi_\nu\}$ is a complete orthonormal set of energy eigenfunctions for the system, so that

$$\int \ldots \int \psi_\nu(\mathbf{r}_1, \ldots, \mathbf{r}_l)\, \bar{\psi}_{\nu'}(\mathbf{r}_1, \ldots, \mathbf{r}_l)\, d\mathbf{r}_1 \ldots d\mathbf{r}_l = \delta_{\nu\nu'} \tag{II.21}$$

for all ν and ν'; E_ν are energy eigenvalues corresponding to ψ_ν. In the limit of infinite temperatures, the density matrix becomes

$$\begin{aligned}\lim_{\beta\to 0} \varrho(\mathbf{r}_1, \ldots, \mathbf{r}_l; \mathbf{r}'_1, \ldots, \mathbf{r}'_l) &= \sum_\nu \psi_\nu(\mathbf{r}_1, \ldots, \mathbf{r}_l)\, \bar{\psi}_\nu(\mathbf{r}'_1, \ldots, \mathbf{r}'_l) \\ &= \delta(\mathbf{r}_1 - \mathbf{r}'_1) \ldots \delta(\mathbf{r}_l - \mathbf{r}'_l),\end{aligned} \tag{II.22}$$

in which $\delta(\mathbf{r}-\mathbf{r}')$ is the Dirac δ-function.

The density matrix satisfies the Bloch differential equation

$$\frac{\partial}{\partial\beta}\varrho(\mathbf{r}_1, \ldots, \mathbf{r}_l; \mathbf{r}'_1, \ldots, \mathbf{r}'_l) = -H\varrho(\mathbf{r}_1, \ldots, \mathbf{r}_l; \mathbf{r}'_1, \ldots, \mathbf{r}'_l) \tag{II.23}$$

with Hamiltonian

$$H = -\frac{\hbar^2}{2m}\sum_i \Delta_i + \Phi(\mathbf{r}_1, \ldots, \mathbf{r}_l) \tag{II.24}$$

($\Delta_i \equiv \nabla_i \cdot \nabla_i$, $\nabla_i \equiv \partial/\partial\mathbf{r}_i$) operating on the first argument $\mathbf{r}_1, \ldots, \mathbf{r}_l$ for which $H\psi_\nu = E_\nu\psi_\nu$. In the particular case where the potential energy vanishes, the solution of the Bloch equation with the "initial condition," Eq. II.22, is

$$\varrho(\mathbf{r}_1, \ldots, \mathbf{r}_l; \mathbf{r}'_1, \ldots, \mathbf{r}'_l) = \left(\frac{m}{2\pi\hbar^2\beta}\right)^{3l/2} \exp\left[-\frac{m}{2\hbar^2\beta}\sum_i (\mathbf{r}_i - \mathbf{r}'_i)^2\right]$$

We can therefore assume the general solution to be of the form

$$\varrho(\mathbf{r}_1, \ldots, \mathbf{r}_l; \mathbf{r}'_1, \ldots, \mathbf{r}'_l) = \left(\frac{m}{2\pi\hbar^2\beta}\right)^{3l/2} \exp\Bigl[-\frac{m}{2\hbar^2\beta}\sum_l (\mathbf{r}_i - \mathbf{r}'_i)^2 + \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_l; \mathbf{r}'_1, \ldots, \mathbf{r}'_l) \tag{II.25}$$

with

$$\Psi \to 0 \text{ for } \beta\Phi \to 0 \tag{II.26}$$

The diagonal element of the density matrix multiplied by $(2\pi\hbar^2\beta/m)^{3l/2}$ then becomes

$$(2\pi\hbar^2\beta/m)^{3l/2}\varrho(\mathbf{r}_1, \ldots, \mathbf{r}_l; \mathbf{r}_1, \ldots, \mathbf{r}_l) = \exp\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_l; \mathbf{r}_1, \ldots, \mathbf{r}_l) \tag{II.27}$$

Both sides of Eq. II.27 are quantum mechanical generalizations $S(\mathbf{r}_1, \ldots, \mathbf{r}_l)$ of the Boltzmann factor, since they indicate the probability of position in configuration space normalized to unity when Φ vanishes. They are called Slater sums.

Let us in the following denote $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_l; \mathbf{r}'_1, \ldots, \mathbf{r}'_l)$ simply by Ψ. Substituting Eq. II.25 into the Bloch equation, Eq. II.23, we have

$$\Phi + \frac{\partial\Psi}{\partial\beta} + \frac{1}{\beta}\sum_i (\mathbf{r}_i - \mathbf{r}'_i)\cdot\boldsymbol{\nabla}_i\Psi = \frac{\hbar^2}{2m}\sum_i [(\boldsymbol{\nabla}_i\Psi)^2 + \Delta_i\Psi] \tag{II.28}$$

Assuming that Ψ can be expanded into a power series in $\hbar^2/2m$,

$$\Psi = \Psi_0 + (\hbar^2/2m)\Psi_1 + (\hbar^2/2m)^2\Psi_2 + \ldots \tag{II.29}$$

we obtain from Eq. II.28, as regards the coefficients of $(\hbar^2/2m)^0$, $(\hbar^2/2m)^1$, $(\hbar^2/2m)^2, \ldots,$

$$\Phi + \frac{\partial\Psi_0}{\partial\beta} + \frac{1}{\beta}\sum_i (\mathbf{r}_i - \mathbf{r}'_i)\cdot\boldsymbol{\nabla}_i\Psi_0 = 0 \tag{II.30}$$

$$\frac{\partial\Psi_1}{\partial\beta} + \frac{1}{\beta}\sum_i (\mathbf{r}_i - \mathbf{r}'_i)\cdot\boldsymbol{\nabla}_i\Psi_1 = \sum_i (\boldsymbol{\nabla}_i\Psi_0)^2 + \sum_i \Delta_i\Psi_0 \tag{II.31}$$

$$\frac{\partial\Psi_2}{\partial\beta} + \frac{1}{\beta}\sum_i (\mathbf{r}_i - \mathbf{r}'_i)\cdot\boldsymbol{\nabla}_i\Psi_2 = 2\sum_i \boldsymbol{\nabla}_i\Psi_0\cdot\boldsymbol{\nabla}_i\Psi_1 + \sum_i \Delta_i\Psi_1, \tag{II.32}$$

and so on.

Taking Eq. II.26 into account, we have from Eq. II.30

$$\Psi_0(\mathbf{r}_1, \ldots, \mathbf{r}_l; \mathbf{r}_1, \ldots, \mathbf{r}_l) = -\beta\Phi(\mathbf{r}_1, \ldots, \mathbf{r}_l) \qquad \text{(II.33)}$$

Multiplying Eq. II.30 by ∇_i and Δ_i, we get

$$\nabla_i\Phi + \frac{\partial}{\partial\beta}\nabla_i\Psi_0 + \frac{1}{\beta}\nabla_i\Psi_0 + \frac{1}{\beta}\sum_i (\mathbf{r}_j - \mathbf{r}'_j)\cdot\nabla_j\nabla_i\Psi_0 = 0,$$

$$\Delta_i\Phi + \frac{\partial}{\partial\beta}\Delta_i\Psi_0 + \frac{2}{\beta}\Delta_i\Psi_0 + \frac{1}{\beta}\sum_j (\mathbf{r}_j - \mathbf{r}'_j)\cdot\nabla_j\Delta_i\Psi_0 = 0$$

from which, taking the limit $\mathbf{r}' \to \mathbf{r}$, we have

$$(\nabla_i\Psi_0)_{\mathbf{r}'\to\mathbf{r}} = -\tfrac{1}{2}\beta\nabla_i\Phi, \qquad (\Delta_i\Psi_0)_{\mathbf{r}'\to\mathbf{r}} = -\tfrac{1}{3}\beta\Delta_i\Phi$$

Inserting these into Eq. II.31, we obtain

$$\Psi_1(\mathbf{r}_1, \ldots, \mathbf{r}_l; \mathbf{r}_1, \ldots, \mathbf{r}_l) = \sum_i \left[\frac{\beta^3}{12}(\nabla_i\Phi)^2 - \frac{\beta^2}{6}\Delta_i\Phi\right] \qquad \text{(II.34)}$$

Similarly,

$$\begin{aligned}\Psi_2(\mathbf{r}_1, \ldots, \mathbf{r}_l; \mathbf{r}_1, \ldots, \mathbf{r}_l) &\\ = \sum_i\sum_i \Big[&-\frac{\beta^5}{60}\nabla_i\nabla_j\Phi : \nabla_i\Phi\nabla_j\Phi + \frac{\beta^4}{90}\nabla_i\nabla_j\Phi : \nabla_i\nabla_j\Phi \\ &+ \frac{\beta^4}{30}\nabla_i\Phi\cdot\nabla_i\Delta_j\Phi - \frac{\beta^3}{60}\Delta_i\Delta_j\Phi\Big]\end{aligned}$$

and so on. (The two-dot symbol means the scalar product of two tensors.)

Replacing $S(\mathbf{r}_1, \ldots, \mathbf{r}_l)$ by $\exp \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_l; \mathbf{r}_1, \ldots, \mathbf{r}_l)$ in the integrand of the cluster integral, we finally obtain quantum-mechanical expressions in the form

$$b_l = b_l^{(0)} + (\hbar^2\beta/4m)\, b_l^{(1)} + (\hbar^2\beta/4m)^2 b_l^{(2)} + \ldots \qquad \text{(II.35)}$$

for $l = 2, 3, \ldots$, $\beta = 1/kT$. Here $b_l^{(0)}$ is the classical expression for the lth cluster integral, $b_2^{(0)}$ and $b_3^{(0)}$ being given explicitly in the preceding section.

The final result for the second cluster integral is the following:

$$b_2^{(1)} = -\frac{2\pi}{3}\beta^2 \int_0^\infty U'^2 \exp(-\beta U) r^2 dr,$$

$$b_2^{(2)} = \frac{8\pi}{3}\beta^2 \int_0^\infty \left(\frac{U''^2}{10} + \frac{U'^2}{5r^2} + \frac{\beta U'^3}{9r} - \frac{\beta^2 U'^4}{72}\right) \exp(-\beta U)\, r^2 dr,$$

$$b_2^{(3)} = -64\pi\beta^2 \int_0^\infty \left(\frac{U'''^2}{840} + \frac{U''^2}{140r^2} + \frac{\beta U''^3}{756} + \frac{\beta U' U''^2}{180r} + \frac{\beta U'^3}{945r^3} \right.$$
$$\left. - \frac{\beta^2 U'^2 U''^2}{720} - \frac{\beta^2 U'^4}{6480r^2} - \frac{\beta^3 U'^5}{2160r} + \frac{\beta^4 U'^6}{25920}\right) \exp(-\beta U)\, r^2 dr$$

U being the intermolecular potential $U \equiv U(r) \equiv \Phi(\mathbf{r}_1, \mathbf{r}_2)$, the primes indicating derivatives.

The first quantum correction to the third cluster integral is

$$b_3^{(1)} = -\frac{4\pi^2}{9}\beta^2 \iiint (A_{12} + A_{23} + A_{31})\, r_{12} r_{23} r_{31}\, dr_{12}\, dr_{23}\, dr_{31}$$

where

$$A_{12} = \left[\left(\frac{\partial U(r_{12}, r_{23}, r_{31})}{\partial r_{12}}\right)^2 + \cos\theta_3 \frac{\partial U(r_{12}, r_{23}, r_{31})}{\partial r_{13}} \frac{\partial U(r_{12}, r_{23}, r_{31})}{\partial r_{23}}\right]$$
$$\cdot \exp[-\beta U(r_{12}, r_{23}, r_{31})] - [U'(r_{12})]^2 \exp[-\beta U(r_{12})]$$

with similar expressions for A_{23} and A_{31}, θ_i being the same as in Section I.1. The integral is to be taken over all values of r_{12}, r_{23}, r_{31}, which form three sides of a triangle.

The quantum correction to the second cluster integral in the form of series expansion in $(\hbar^2/4mkT)$ was first given by Wigner[28] and then by Uhlenbeck and Gropper.[26] Kirkwood[11] supplemented their method by furnishing a more convenient means of obtaining the expansion, which was used by Uhlenbeck and Beth[25] and by Gropper[6] in their recalculations of the quantum correction up to the term proportional to $(\hbar^2/4mkT)^2$. The term proportional to $(\hbar^2/4mkT)^3$ together with the correction to the third cluster integral was calculated by Kihara, Midzuno, and Shizume[10] (see also Kihara[9]) by use of Husimi's[8] elegant method.

C. Cluster Integrals for the Standard Potential

Both second and third cluster integrals can be calculated in neat forms for the standard intermolecular potential which was introduced in Section I.3.

By use of the potential, Eq. I.28, Lennard-Jones[13] evaluated the classical second cluster integral, Eq. II.18 in the form of a power series. Integrating by parts, he first obtained

$$b_2^{(0)} = \frac{2\pi}{3}\int_0^\infty \frac{1}{kT}\frac{dU(r)}{dr}\exp\left[-\frac{U(r)}{kT}\right]r^2dr$$

Expanding exp (μ/r^6kT) of exp $[-U(r)/kT]$ into a power series and integrating term by term, he obtained

$$b_2^{(0)} = \frac{\pi}{6}\left(\frac{\lambda}{kT}\right)^{\frac{1}{4}}\sum_{t=0}^{\infty}\Gamma\left(\frac{2t-1}{4}\right)\frac{y^t}{t!}$$

where Γ is the gamma-function and

$$y = (\mu/kT)(kT/\lambda)^{\frac{1}{2}}$$

Integrals $b_2^{(1)}$, $b_2^{(2)}$, and $b_2^{(3)}$, which are necessary for the quantum correction, can similarly be evaluated (de Boer and Michels;[4] Kihara, Midzuno, and Shizume[10]), the result being

$$b_2^{(1)} = -\frac{\pi}{18}\left(\frac{\lambda}{kT}\right)^{1/12}\sum_{t=0}^{\infty}(36t-11)\Gamma\left(\frac{6t-1}{12}\right)\frac{y^t}{t!},$$

$$b_2^{(2)} = \frac{\pi}{180}\left(\frac{\lambda}{kT}\right)^{-1/12}\sum_{t=0}^{\infty}(3024t^2+4728t+767)\,\Gamma\left(\frac{6t+1}{12}\right)\frac{y^t}{t!},$$

$$b_2^{(3)} = -\frac{\pi}{420}\left(\frac{\lambda}{kT}\right)^{-\frac{1}{4}}\sum_{t=0}^{\infty}(53568t^3+303216t^2 + 491076t+180615)\,\Gamma\left(\frac{2t+1}{4}\right)\frac{y^t}{t!},$$

By use of these, the second cluster integral is given by Eq. II.35 with $l = 2$.

As regards the classical third cluster integral, $b_3^{(0)}$ given by Eq. II.19, let us expand it into a series in ν, the measure of the potential nonadditivity,

$$b_3^{(0)} = (b_3^{(0)})_{\nu=0} + \nu\left(\frac{\partial b_3^{(0)}}{\partial \nu}\right)_{\nu=0} + \cdots$$

in which

$$(b_3^{(0)})_{\nu=0} = \frac{4\pi^2}{3}\iiint [f(r_{12},r_{23},r_{31}) - f(r_{12}) - f(r_{23}) - f(r_{31})]\, r_{12}r_{23}r_{31}\,dr_{12}\,dr_{23}\,dr_{31}$$

$$f(r) = \exp\,[-U(r)/kT] - 1,$$

$$f(r_{12}, r_{23}, r_{31}) = \exp\left[-\frac{U(r_{12})+U(r_{23})+U(r_{31})}{kT}\right] - 1$$

and

$$\left(\frac{\partial b_3^{(0)}}{\partial \nu}\right)_{\nu=0} = -\frac{4\pi^2}{3}\frac{1}{kT}\iiint \exp\left[-\frac{U(r_{12})+U(r_{23})+U(r_{31})}{kT}\right] \cdot \frac{3\cos\theta_1\cos\theta_2\cos\theta_3+1}{(r_{12}r_{23}r_{31})^3}\,dr_{12}\,dr_{23}\,dr_{31}$$

Higher terms in the series expansion are much smaller and can be neglected.

Using $R \equiv r_{12}$, $\xi \equiv r_{13}/R$, and $\eta \equiv r_{23}/R$ as integration variables, we transform $(b_3^{(0)})_{\nu=0}$ into

$$4\pi^2\int_0^1\int_{1-\xi}^1\left[\int_0^\infty \{f(R, \xi R, \eta R) - f(R) - f(\xi R) - f(\eta R)\}\, R^5 dR\right]\xi\eta\, d\eta\, d\xi$$

For the purpose of integration with respect to R, let us use tentatively

$$U(r) = \lambda r^{-12} - \mu r^{-m}$$

with $m > 6$ and later take the limit $m \to 6$. For $m > 6$ the integration can be performed term by term in the same way as in the foregoing, the result being

$$\int_0^\infty \{f(R, \xi R, \eta R) - f(R) - f(\xi R) - f(\eta R)\} R^5 dR = \left(\frac{\lambda}{kT}\right)^{\frac{1}{2}}\sum_{t=0}^{\infty} C_t y^t$$

in which

$$C_t = \frac{1}{12}\frac{1}{t!}\Gamma\left(\frac{tm-6}{12}\right)[\langle m\rangle^t \langle 12\rangle^{(6-mt)/12} - \langle 6\rangle]$$

Here the bracket notation has been used in the sense

$$\langle a\rangle \equiv 1 + \xi^{-a} + \eta^{-a}$$

Taking the limit $m \to 6$, we obtain

$$C_t=\frac{1}{12}\frac{1}{t!}\Gamma\left(\frac{t-1}{2}\right)[\langle 6\rangle^t\langle 12\rangle^{(1-t)/2}-\langle 6\rangle] \qquad \text{for } t\neq 1,$$

$$C_1=\frac{1}{12}[\xi^{-6}\ln\xi^{-12}+\eta^{-6}\ln\eta^{-12}-\langle 6\rangle\ln\langle 12\rangle]$$

Thus we have finally

$$(b_3^{(0)})_{\nu=0}=\left(\frac{\lambda}{kT}\right)^{\frac{1}{2}}\sum_{t=0}^{\infty}G_t y^t \tag{II.36}$$

where

$$G_t=4\pi^2\int_0^1\int_{1-\xi}^1 C_t\xi\eta\,d\eta\,d\xi$$

The values of G_t obtained by numerical integration are given in Table III.

TABLE III. Expansion Coefficients for the Third Cluster Integral.

t	G_t	H_t	I_t
0	11.278	2.350	+211.8
1	−17.733	1.080	− 80.22
2	+ 3.498	0.557	− 40.42
3	1.492	0.268	− 33.80
4	0.571	0.1203	− 20.55
5	0.201	0.0505	− 9.85
6	0.0662	0.0201	− 4.75
7	0.0206	0.0076	− 1.652
8	0.0062	0.0027	− 0.586
9	0.00178		− 0.197
10	0.00049		− 0.063
11	0.00014		

The nonadditive correction can be treated similarly; the result is

$$\left(\frac{\partial b_3^{(0)}}{\partial\nu}\right)_{\nu=0}=-\frac{1}{kT}\left(\frac{kT}{\lambda}\right)^{\frac{1}{2}}\sum_{t=0}^{\infty}H_t y^t \tag{II.37}$$

in which

$$H_t=\frac{\pi^2}{3}\frac{1}{t!}\Gamma\left(\frac{2t+1}{4}\right)\int_0^1\int_{1-\xi}^1\langle 6\rangle^t\langle 12\rangle^{-(2t+1)/4}\frac{3\cos\theta_1\cos\theta_2\cos\theta_3+1}{\xi^2\eta^2}d\eta\,d\xi.$$

The values of H_t calculated by Koba, Kaneko, and Kihara[12] are also given in Table III.

As regards the quantum correction $b_3^{(1)}$, we obtain

$$(b_3^{(1)})_{\nu=0} = \left(\frac{\lambda}{kT}\right)^{1/3} \sum_{t=0}^{\infty} I_t y^t \tag{II.38}$$

in which

$$\begin{aligned} I_t = & -\frac{4\pi^2}{9}\frac{1}{t!}\Gamma\left(\frac{3t-2}{6}\right) \\ & \cdot \int_0^1 \int_{1-\xi}^1 \{(3t+4)(3t-2)\left[\langle 12,\, 12\rangle \langle 12\rangle^{(2-3t)/6-2} \langle 6\rangle^t - \langle 6\rangle\right] \\ & -6t(3t-2)\left[\langle 12,\, 6\rangle \langle 12\rangle^{(2-3t)/6-1}\langle 6\rangle^{t-1} - \langle 6\rangle\right] \\ & +9t(t-1)\left[\langle 6,\, 6\rangle \langle 12\rangle^{(2-3t)/6}\langle 6\rangle^{t-2} - \langle 6\rangle\right]\}\, \xi\eta\, d\eta\, d\xi \end{aligned}$$

Here another bracket notation has been used in the sense

$$\begin{aligned} \langle a,\, b\rangle = & \langle a+b+2\rangle \\ & + \tfrac{1}{4}(\xi^{-a-2}+\xi^{-b-2})(1+\xi^2-\eta^2) \\ & + \tfrac{1}{4}(\eta^{-a-2}+\eta^{-b-2})(1+\eta^2-\xi^2) \\ & + \tfrac{1}{4}(\xi^{-a-2}\eta^{-b-2}+\eta^{-a-2}\xi^{-b-2})(\xi^2+\eta^2-1) \end{aligned}$$

The values of I_t are given in the same table.

The third cluster integral is approximated by a sum of three terms calculated in the preceding:

$$b_3 \approx (b_3^{(0)})_{\nu=0} + \nu\left(\frac{\partial b_3^{(0)}}{\partial \nu}\right)_{\nu=0} + \frac{\hbar^2}{4mkT}(b_3^{(1)})_{\nu=0} \tag{II.39}$$

D. Comparison with Experiment for Rare Gases

Comparing the calculated function for the second cluster integral with observed values given in Table II, we can determine two parameters λ and μ of the intermolecular potential, Eq. I.28. This potential can be rewritten in the form

$$U(r) = U_0\left[\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^{6}\right],$$

where U_0 is the depth to the potential minimum, and r_0 is the intermolecular distance corresponding to this minimum. The values of U_0, r_0, and μ for helium, neon, argon, and krypton are given in Table IV. The value of the model parameter u is, as we expected, not far from the corresponding μ-value in Table I, which value is a van der Waals interaction constant calculated quantum-mechanically.

TABLE IV. Model Constants Determined from the Second Cluster Integral.

	U_0/k	r_0	μ
He	10.8° K	2.88A	0.170×10^{-11} erg A^6
Ne	35.8	3.09	0.86
A	119	3.83	10.4
Kr	173	4.03	20.4

The calculated curves for the third cluster integral are compared in Figs. 1, 2, 3, and 4 with observed values given in Table II.

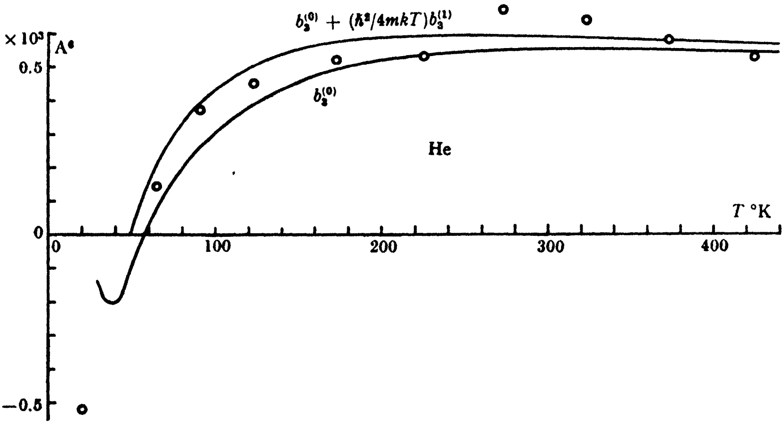

Fig. 1. Third cluster integral of helium, without quantum correction and with first-order quantum correction, compared with observed values.

The agreement is satisfactory although for helium further quantum corrections seem to be needed. In the same figures are also shown

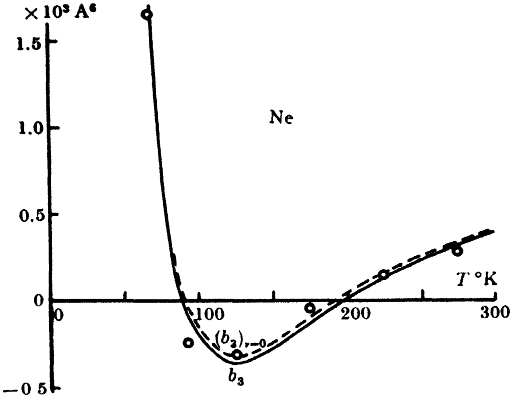

Fig. 2 Third cluster integral of neon for additive (broken line) and non-additive (full line) intermolecular potentials compared with observed values.

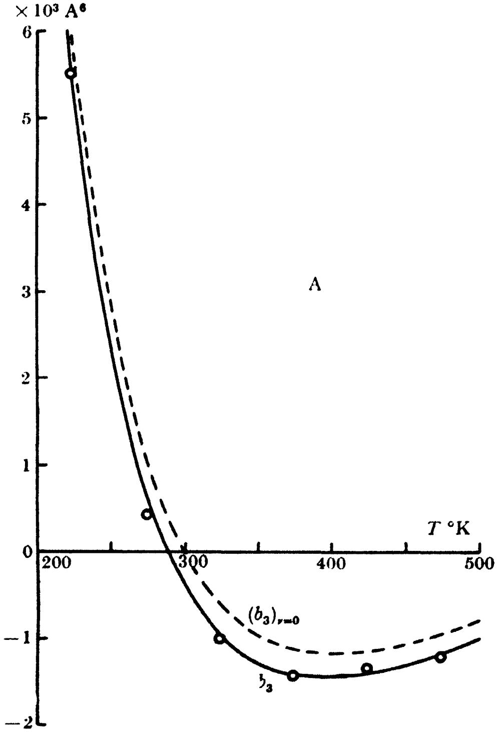

Fig. 3 Third cluster integral of argon

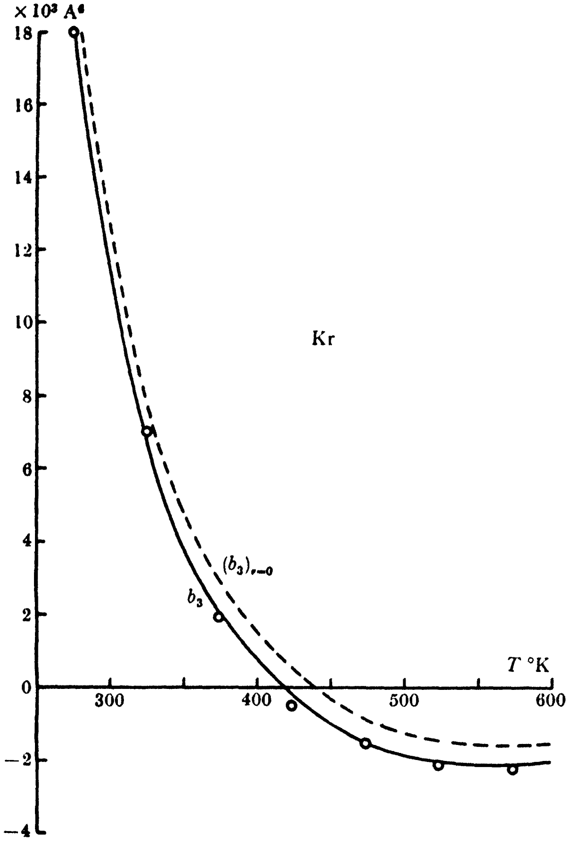

Fig. 4. Third cluster integral of krypton.

by broken curves the third cluster integrals calculated on the assumption of potential additivity.

Thus we have completed our analysis of the equation of state of rare gases (excepting xenon for which experimental data are not sufficient) by means of a nonadditive intermolecular potential.

III. DENSE GASES AND PHASE TRANSITIONS

Having treated gases of moderate densities, we discuss in this part dense gases composed of monatomic molecules. Theory of condensation at low temperatures is briefly reviewed first. Then, a phase transition at high temperatures and pressures, for which there has been little theoretical investigation, will be treated in detail.

A. Condensed Gases at Low Temperatures

The characteristic features of the cluster integrals b_l can be obtained by calculating them for the additive square-well potential

$$U(r) = \begin{cases} \infty & \text{for } r < r_0 \\ -U_0 & \text{for } r_0 < r < r_1 \\ 0 & \text{for } r_1 < r \end{cases} \qquad \text{(III.1)}$$

where U_0 is a positive constant and r_1/r_0 is a parameter indicating the width of the potential well. Figure 5 shows the "normalized"

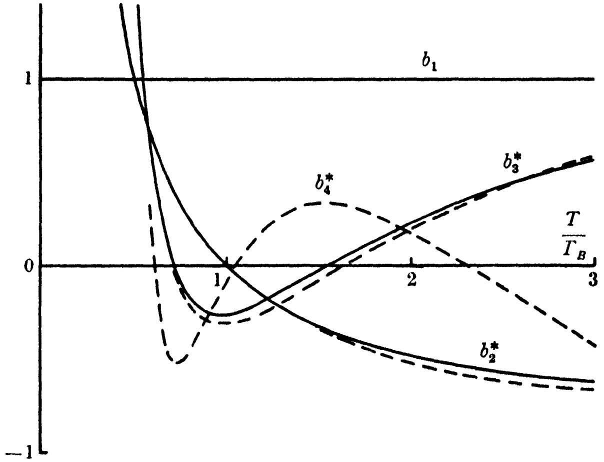

Fig. 5. Normalized cluster integrals for the square-well potential, Eq. III.1. Full lines are for $r_1/r_0 = 2$; broken lines are for $r_1/r_0 = \infty$.

classical cluster integrals

$$b_l^* \equiv b_l \Big/ \left[\left(T\frac{db_2}{dT}\right)_{T=T_B}\right]^{l-1}, \qquad l = 1, 2, \ldots$$

($b_1^* = b_1 = 1$) for $r_1/r_0 = 2$ and ∞. Here T_B is the Boyle temperature at which the second cluster integral vanishes. For $r_1/r_0 = \infty$ the normalized cluster integrals are given by

$$b_2{}^* = \frac{T_B}{T} - 1,$$

$$b_3{}^* = 2\left(\frac{T_B}{T} - 1\right)^2 - \frac{5}{16},$$

$$b_4{}^* = \frac{16}{3}\left(\frac{T_B}{T} - 1\right)^3 - \frac{15}{8}\left(\frac{T_B}{T} - 1\right) - 0.0956, \ldots$$

In a gas at temperatures sufficiently lower than its critical temperature, volume per molecule V/N is much larger than the molecular volume even in the saturated vapor; the cluster integrals are all positive and independent of the volume V.

A classical gas at low temperatures is probably like an ideal gas composed of clumps of molecules; a clump will again be called an l-cluster when the number of molecules in the clump is l. In other words clusters move freely in the container, intercluster force being neglected in comparison with the intracluster force. The partition function of an l-cluster is then given by

$$Z_l = Vb_l\left(\frac{mkT}{2\pi\hbar^2}\right)^{3l/2} \tag{III.2}$$

for a gas of monatomic molecules, because b_l is $(l!V)^{-1}$ times the Boltzmann factor $\exp\,[-\Phi(\mathbf{r}_1, \ldots, \mathbf{r}_l)/kT]$ integrated over the configuration for which l molecules form a cluster.

In fact, Eqs. II.14 and II.15 are in the form of the equation of state for an ideal gas,

$$PV = kT\sum N_l, \quad N = \sum lN^l \tag{III.3}$$

if

$$N_l \equiv Vb_lz_l \tag{III.4}$$

is interpreted as the number of l-clusters. Furthermore, the internal energy, Eq. II.13, of the gas can be transformed into

$$E = \sum N_l kT^2 \frac{\partial}{\partial T} \ln Z_l \tag{III.5}$$

and the free energy, Eq. II.12, can be rewritten as

$$F = -kT[\sum N_l \ln Z_l - \sum N_l(\ln N_l - 1)]$$

which is equivalent to

$$F = -kT \ln \frac{Z_1^{N_1} Z_2^{N_2} \ldots}{N_1! N_2! \ldots} \tag{III.6}$$

for large N_l's. Equations III.5 and III.6 indicate that Z_l plays the role of the partition function of an l-cluster. From Eqs. III.2 and III.4 follows

$$N_l/N_1^l = Z_l/Z_1^l$$

which shows that creation and annihilation of clusters are subject to the law of mass action.

For large l the free energy of a cluster, which is given by $-kT \ln Z_l$, will be sum of a term proportional to l and a term proportional to $l^{2/3}$, the latter corresponding to the surface free energy of a cluster. The cluster integrals with large l are therefore of the form

$$b_l = A \exp(-\tau l - \sigma l^{2/3}), \qquad \sigma > 0, \tag{III.7}$$

τ and σ being functions of the temperature. Here the factor A is a slowly varying function of l and the temperature, and it is proportional to the $(l-1)$th power of the molecular volume.

For $z \leqq \exp \tau$ all clusters are small; when the activity z increases and exceeds $\exp \tau$, even by a very slight amount, very large clusters appear. This phenomenon corresponds to condensation, $z = \exp \tau$ corresponding to the state of saturated vapor. Isothermal compressibility $-V^{-1}(\partial V/\partial P)_T$ takes a finite value at the condensation point as it should at low temperatures.

The theory of condensation briefly reviewed above is originally due to Mayer,[17] Frenkel,[5] and Band.[2] Lee and Yang[14] have satisfactorily treated the condensation problem for a lattice gas which is equivalent to an Ising model of ferromagnetism.

B. Condensed Gases at High Temperatures

Let us finally consider a gas at such high temperatures that the attractive part of the intermolecular potential is negligible. We assume the repulsive intermolecular potential to be

$$U(r) = \lambda r^{-3s}, \quad \lambda > 0,\ s > 1 \tag{III.7}$$

Then the cluster integrals are of the form

$$b_l = a_l \left(\frac{\lambda}{kT}\right)^{(l-1)/s} \tag{III.8}$$

so far as they are independent of the volume. Here a_l's are pure numbers: $a_1 = 1$, a_2 and a_3 being given in Table V.

TABLE V. Coefficients a_2 and a_3 in Eq. III.8.

$3s$	a_2	a_3
6	−3.71	24.78
9	−2.84	13.95
12	−2.57	11.28
15	−2.44	10.12
18	−2.36	9.49
∞	−2.09	7.40

For the potential, Eq. III.7, the equation of state can be expressed in such a form that PV/NkT is a one-variable function

$$\frac{PV}{NkT} = f(x) \quad \text{of} \quad x \equiv \left(\frac{\lambda}{kT}\right)^{1/s} \frac{N}{V} \tag{III.9}$$

since a dimensionless quantity composed of N/V, kT, and λ must be a function x. For small values of x, the function can be expanded in the form of Eq. II.16,

$$f(x) = 1 - a_2 x + (4a_2^2 - 2a_3)x^2 + \dots \tag{III.10}$$

At least the first few terms of this series are positive.

If, at such high temperatures, a phase transition between solid (crystalline) and fluid (amorphous) states is observed, then the melting curve is given by

$$\left(\frac{\lambda}{kT}\right)^{1/s} \frac{P}{kT} = \text{constant} \tag{III.11}$$

since a quantity composed of kT and λ with the dimension of pressure must be $kT(kT/\lambda)^{1/s}$ times a constant.

A phase transition is observed indeed even at temperatures several times higher than the critical temperature. Figure 6 shows an experimental result for helium by Simon, Ruhemann, and Edwards.[24] Observed values are well represented by a curve of the form of Eq. III.11 with $s = 2$, or $3s = 6$.

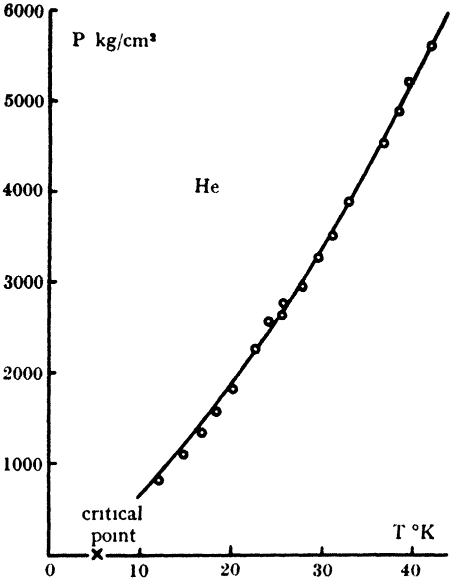

Fig. 6. Melting curve of helium at high pressures. The curve is for the potential, Eq. III.7, with $3s = 6$.

Clapeyron's relation

$$\frac{\delta S}{\delta V} \equiv \frac{S(\text{fluid}) - S(\text{solid})}{V(\text{fluid}) - V(\text{solid})} = \frac{dP}{dT}$$

becomes

$$T\delta S = (1+s^{-1})P\delta V \qquad \text{(III.12)}$$

Now, $P\delta V/NkT$ is a dimensionless quantity composed of P, kT, and λ, thus a function of $(\lambda/kT)^{1/s}P/kT$; hence it is a constant by virtue of Eq. III.11. Therefore, the latent heat of transition, $T\delta S$, is proportional to the melting temperature according to the present molecular model.

As regards energy increase at the melting, we have

$$\delta E = T\delta S - P\delta V = s^{-1}P\delta V$$

Thus $(E - s^{-1}PV)/NkT$ is continuous on the transition curve. Moreover it is constant:

$$(E - s^{-1}PV)/NkT = \tfrac{3}{2} - s^{-1} \qquad \text{(III.13)}$$

This equation can be derived from Eq. III.9 and the thermodynamical relation

$$\left(\frac{\partial E}{\partial V}\right)_{T,N} = T^2\left(\frac{\partial(P/T)}{\partial T}\right)_{V,N}$$

Equation III.13 can also be derived from a statistical point of view. The partition function Z of a system composed of N molecules in the volume $V \equiv Nv$ is of the form

$$Z = v^N\left(\frac{mkT}{2\pi\hbar^2}\right)^{3N/2} Z_0$$

Here Z_0 is a function of $v^s kT/\lambda$ and N; or, more precisely, $N^{-1}\ln Z_0$ is, for large N, a function of $v^s kT/\lambda$ only. Using the relations

$$F = -kT\ln Z,$$

$$E = -T^2\left(\frac{\partial}{\partial T}\frac{F}{T}\right)_{v,N} \quad \text{and} \quad P = -\frac{1}{N}\left(\frac{\partial F}{\partial v}\right)_{T,N}$$

we have

$$E = \tfrac{3}{2}NkT + kT^2\frac{\partial}{\partial T}\ln Z_0$$

and

$$P = \frac{kT}{v} + \frac{kT}{N}\left(\frac{\partial}{\partial v}\ln Z_0\right)_{T,N}$$

$$= \frac{kT}{v} + \frac{kT}{N}\frac{s}{v}T\left(\frac{\partial}{\partial T}\ln Z_0\right)_{v,N}$$

From these two expressions we obtain Eq. III.13 and moreover

$$\frac{E}{NkT} - \frac{3}{2} = \frac{1}{s}\left(\frac{Pv}{kT} - 1\right) = T\frac{\partial}{\partial T}\frac{\ln Z_0}{N} \qquad \text{(III.14)}$$

The intermolecular potential, Eq. III.7, is not a necessary condition for Eq. III.13. The necessary and sufficient condition is that $N^{-1}\ln Z_0$ is a function of kTv^s/λ only. In other words, the condition is that the ratio of the potential energy (> 0) in one configuration with the specific volume v_1 to the potential energy in another *similar* configuration with the specific volume v_2 always equals $(v_2/v_1)^s$. Under this weaker condition, where the additivity of the intermolecular potential is not assumed, most relations in the present section hold. Namely, if a phase transition between crystalline and amorphous states occurs, then the $(1+s^{-1})$th power of the transition temperature is proportional to the pressure and the latent heat is proportional to the transition temperature. In the next section we treat an Ising-Lattice model with the aforementioned similarity condition.

C. A Lattice Model of Hot Dense Gases

Our two-dimensional lattice model of gases at high temperatures and pressures is the following.

The N molecules occupy a half of the lattice sites of a square lattice of "volume" V with $2N$ sites. The specific volume $v \equiv V/N$ is, therefore, twice the cell volume. The number of pairs of nearest-neighboring sites is $4N$.

Following the notation used by Lee and Yang,[14] we use ↓ for an occupied site and ↑ for a vacant site; and we denote by [↓↓], [↑↑], and [↓↑] the number of pairs of nearest-neighboring occupied sites, the number of pairs of nearest-neighboring vacant sites, and the number of pairs between nearest-neighboring occupied and vacant sites, respectively. There are two identities:

$$2[\downarrow\downarrow]+[\downarrow\uparrow] = 4N \qquad \text{(III.15)}$$

$$2[\uparrow\uparrow]+[\downarrow\uparrow] = 4N \qquad \text{(III.16)}$$

The potential energy U_G of the lattice gas in a configuration is assumed to be linear in [↓↓] and proportional to v^{-s}:

$$U_G = N\lambda_0 v^{-s}+4[\downarrow\downarrow]\lambda v^{-s} \qquad \text{(III.17)}$$

in which λ_0 and λ are positive constants. Here $N\lambda_0 v^{-s}$ indicates the potential energy of the gas in the perfectly ordered state shown in

Fig. 8a; $(N\lambda_0+8N\lambda)v^{-s}$ indicates the energy in such a state that one-half domain of the lattice is completely occupied and the other half domain is completely vacant. In each configuration, the occupied sites alone make a square lattice, a cell of the former being twice as large as a cell of the latter. It is therefore natural to impose a condition between λ_0 and λ according to

$$N\lambda_0(v/2)^{-s} = (N\lambda_0+8N\lambda)v^{-s}$$

namely

$$(2^s-1)\lambda_0 = 8\lambda \tag{III.18}$$

By use of Eqs. III.15 and III.16, Eq. III.17 can be transformed into a symmetric form

$$U_G = N\lambda_0 v^{-s} + (4N-[\downarrow\uparrow]+[\downarrow\downarrow]+[\uparrow\uparrow])\lambda v^{-s} \tag{III.19}$$

The partition function Z_0 is

$$Z_0 = \exp\left(-\frac{N\lambda_0}{kTv^s}\right)\sum_{[\downarrow]=N}\exp\left[-\frac{(4N-[\downarrow\uparrow]+[\downarrow\downarrow]+[\uparrow\uparrow])\lambda}{kTv^s}\right]$$

Here $[\downarrow]$ indicates the number of occupied sites, and the summation is to be taken over all configurations with the condition that the number of occupied sites is N. This condition, however, can be removed. Because this particular sum is the maximum of all the sums with the condition $[\downarrow]=N'$ for $N'=0, 1, \ldots, 2N$; and hence

$$\sum_{[\downarrow]=N} < \sum_{N'=0}^{2N}\sum_{[\downarrow]=N'} < (2N+1)\sum_{[\downarrow]=N}$$

namely,

$$\frac{1}{N}\ln\sum_{[\downarrow]=N} < \frac{1}{N}\ln\sum_{N'}\sum_{[\downarrow]=N'} < \frac{1}{N}\ln\sum_{[\downarrow]=N} + \frac{1}{N}\ln(2N+1)$$

in which $N^{-1}\ln(2N+1)$ is negligible.

The partition function thus becomes

$$Z_0 \exp\left(-\frac{N\lambda_0}{kTv^s}\right)\sum\exp\left(-\frac{(4N-[\downarrow\uparrow]+[\downarrow\downarrow]+[\uparrow\uparrow])\lambda}{kTv^s}\right) \tag{III.20}$$

The summation here is to be taken over all configurations of occupied and vacant sites without any restriction.

The sum in Eq. III.20 is exactly the same as the partition function for the two-dimensional Ising model of antiferromagnetism in zero magnetic field, which function has been obtained by Onsager[22] (see also Newell and Montroll[21]). In terms of the parameter

$$L \equiv \lambda / kTv^{s}$$

and by use of the relation, Eq. III.18, between λ_0 and λ, the result for $N^{-1}T\partial \ln Z_0/\partial T$ is

$$T\frac{\partial}{\partial T}\frac{\ln Z_0}{N} = \frac{8}{2^{s}-1}L + 4L \qquad \text{(III.21)}$$
$$-2L \coth 2L[1+2\pi^{-1}(2\tanh^2 2L - 1)K_1(k_1)]$$

where

$$k_1 = 2\sinh 2L(\cosh 2L)^{-2}$$

and $K_1(k_1)$ is the complete elliptic integral of the first kind,

$$K_1(k_1) = \int_0^{\pi/2} (1 - k_1{}^2 \sin^2 \varphi)^{-\frac{1}{2}}\, d\varphi$$

The function

$$2\pi^{-1}(2\tanh^2 2L - 1)K_1(k_1)$$

is singular, although finite, at a critical point, where L is equal to L_c satisfying

$$\sinh 2L_c = 1, \; L_c = 0.4407 \qquad \text{(III.22)}$$

The equation of state of our gas is given by Eq. III.14

$$\frac{Pv}{kT} = 1 + sT\frac{\partial}{\partial T}\frac{\ln Z_0}{N} \qquad \text{(III.23)}$$

For the construction of a $P-v$ diagram, it is convenient to draw

$$\left(\frac{\lambda}{L_c kT}\right)^{1/s}\frac{P}{kT} \equiv \left(\frac{L}{L_c}\right)^{1/s}\frac{Pv}{kT}$$

as a function of

$$\left(\frac{L_c kT}{\lambda}\right)^{1/s} v \equiv \left(\frac{L_c}{L}\right)^{1/s}$$

The S-shaped curve in Fig. 7 shows the result for $s = 3$.

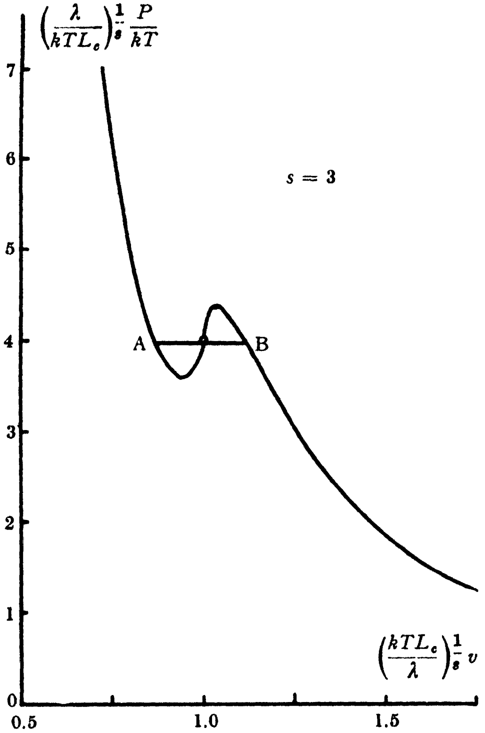

Fig. 7. The isotherm for a two-dimensional lattice model of hot dense gases.

The curve is vertical at $L = L_c$, where the derivative has a logarithmic singularity. A region of the curve including the singular point is thermodynamically unstable. One single homogeneous phase is therefore unstable in this region, and the system is divided into two phases (in a weak gravitational field) corresponding to the end points of the isobaric segment AB which forms, together with the original curve, two closed surfaces with the same area.

Thus we have seen that a first-order transition between ordered (crystalline) and disordered (amorphous) phases occurs in a system composed of molecules with a repulsive interaction only.

If the reader is unsatisfied with the assumption, Eq. III.17 because the first term on the right-hand side is not written in the form of a nearest-neighbor interaction, then he may choose a

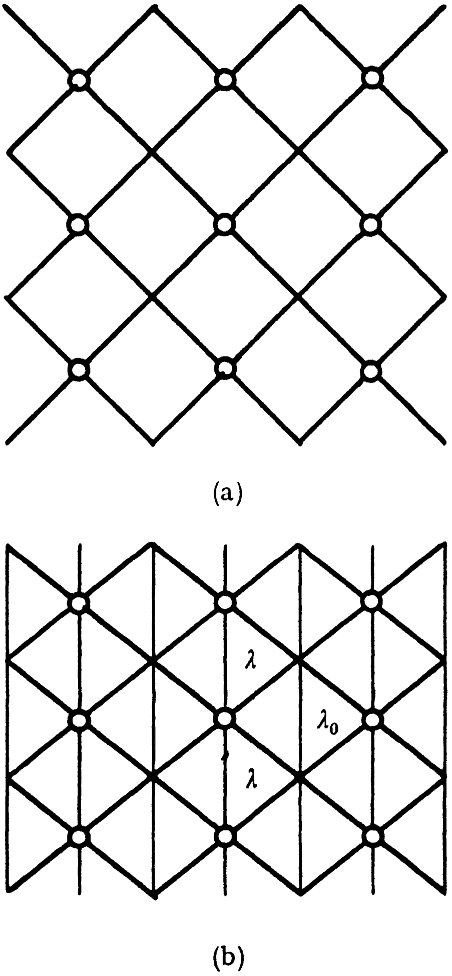

Fig. 8. (a) A perfectly ordered state in a square lattice. (b) A perfectly ordered state in a nonisotropic triangular lattice with constants of repulsion $\lambda > \lambda_0$.

nonisotropic triangular lattice with three kinds of nearest-neighbor repulsion, of which two are strong, one is weak, and all are proportional to v^{-s}. Its perfectly ordered state is shown in Fig. 8b. The mathematical procedure and the conclusion for this "pure" Ising lattice are similar to those of the modified Ising square lattice used in the foregoing.

IV. ACKNOWLEDGMENTS

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ON STATISTICAL MECHANICS AND ELECTROMAGNETIC PROPERTIES OF MATTER

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CONTENTS

I. GENERAL CONCEPTS

A. Statistical Mechanics and Electromagnetic Properties of Matter

It has been customary to treat a great many problems of what is usually called electron theory, and which deal with macroscopic properties of matter, without using statistical-mechanical methods. Amongst these problems we mention the derivation of Maxwell's equations in material bodies as first given by Lorentz[14] and also the theory of refraction of light (the so-called rigorous dispersion theory of Rosenfeld's monograph on electron theory.[8, 26] (In this type of theory, macroscopic observable quantities are obtained as averages of microscopic quantities over physically infinitesimal space and time regions and not as ensemble averages, usually considered in other fields of molecular physics.)

The statistical-mechanical methods are, however, currently used for a body of related problems, which concern the optical and electrical properties of matter. We mention, e.g., the theories of the dielectric constant by Yvon,[32] Kirkwood,[13] Brown,[1] de Boer *et al.*,[4] the theory of the index of refraction by Yvon,[32] and the theories of light scattering by Yvon[32] and by Fixman.[6] Partially these theories overlap with the first group of theories, although not quite the same points are emphasized and analyzed. Thus in the theory of refraction of light, as presented in Rosenfeld's monograph, one analyzes carefully the propagation of electromagnetic waves in material bodies and obtains also an approximate expression for the refractive index. Yvon's theory of the refractive index, on the other hand, yields a more exact expression for this constant, without any reference to the extinction theorem (i.e., the extinction of the incident field by part of the dipole field set up in the medium).

A third group of problems dealing with the properties of matter in an electromagnetic field, are usually only considered from a macroscopic point of view. These are, for example, problems dealing with the force exerted by an electromagnetic field on polarizable matter. The complications which are frequently encountered in such treatments are a consequence of the presence of long-range microscopic interactions (dipole-dipole forces) in the medium.

In the following sections it will be shown that a consistent application of statistical-mechanical methods may be of help in the discussion of the different types of problems mentioned in the foregoing, which are thus all considered from the same point of view.[15, 19, 20]

The rest of Section I contains a summary of the general concepts used throughout this article. Section II contains a statistical-mechanical derivation of Maxwell's equations in matter. Section III deals with the problem of the ponderomotive force in a dielectric. In Section IV we give the theory of refraction of light in a medium of isotropic molecules, having a polarizability which is a function of intermolecular distances. We also calculate in this section the polarizability as a function of intermolecular distances in a very simple case (helium gas). Finally, Section V is concerned with the theory of light scattering.

The general formalism which we use here is, however, not restricted to these topics but seems to offer a rather wide scope for the treatment of other problems concerned with the behavior of material bodies in an electromagnetic field.

B. Formalism

Let us consider a system of N atoms which we number by the index $k (k = 1, 2, \ldots, N)$. Each atom k consists of point particles (nucleus and electrons) with masses m_{ki} and with charges $e_{ki} (i = 1, 2, \ldots, n_k)$. The positions of the particles are denoted by the vectors $\mathbf{R}_{ki}$. The center of gravity of atom k has the position $\mathbf{R}_k$

$$\mathbf{R}_k = \sum_i m_{ki} \mathbf{R}_{ki}/m_k \tag{I.1}$$

where $m_k = \sum_i m_{ki}$ is the mass of the atom. The positions of the constituent particles with respect to the center of gravity of the atom are given by $\mathbf{r}_{ki}$

$$\mathbf{r}_{ki} = \mathbf{R}_{ki} - \mathbf{R}_k; \ \sum_i m_{ki} \mathbf{r}_{ki} = 0 \tag{I.2}$$

We shall use in the following the set of independent coordinates $\mathbf{R}_k$ and $\mathbf{r}_{ki}$, where $k = 1, 2, \ldots, N$ and $i = 1, 2, \ldots, n_k - 1$. The position of the (arbitrary) n_kth particle in every atom is determined by Eq. I.2. The momenta canonically conjugate to this set are $\mathbf{p}_k$ and $\mathbf{p}_{ki}$.*)

The probability distribution function in a phase space spanned by the preceding coordinates and momenta is

$$f = f(\mathbf{R}_k^N,\ \mathbf{r}_{ki}^{N(n_k-1)},\ \mathbf{p}_k^N,\ \mathbf{p}_{ki}^{N(n_k-1)},\ t) \tag{I.3}$$

Here $\mathbf{r}_{ki}^{N(n_k-1)}$, for instance, means that f depends on all coordinate vectors $\mathbf{r}_{ki}$, where i runs from 1 to n_k-1 and k from 1 to N. Integration of any quantity over the whole phase space will be denoted by

$$\langle\ldots\rangle = \int\ldots d\mathbf{R}_k^N\, d\mathbf{r}_{ki}^{N(n_k-1)}\, d\mathbf{p}_k^N\, d\mathbf{p}_{ki}^{N(n_k-1)} \tag{I.4}$$

The distribution function f is normalized in such a way that

$$\langle f\rangle = 1. \tag{I.5}$$

According to the principles of statistical mechanics the average of any dynamical quantity α

$$\alpha = \alpha(\mathbf{R}_k^N,\ \mathbf{r}_{ki}^{N(n_k-1)},\ \mathbf{p}_k^N,\ \mathbf{p}_{ki}^{N(n_k-1)};\ \mathbf{R},\ t) \tag{I.6}$$

which may depend not only on the state of the system but also explicitly on the coordinates in ordinary three-dimensional space and on the time, is then found from

$$\alpha_{\mathrm{Av}}(\mathbf{R}, t) = \langle\alpha f\rangle \tag{I.7}$$

If averages are to be taken of vectorial or tensorial quantities, Eq. I.7 should be applied to each of their components.

We also introduce a distribution function $h(\mathbf{R}^N)$ in the $3N$-dimensional coordinate space of the centers of gravity, defined by

---

* The formalism to be developed here is obviously not restricted to a system consisting of identical and (or) neutral atoms. Mixtures of atoms and (or) ions are therefore included in this treatment. For simplicity's sake, polyatomic molecules have not been considered specifically, but the formalism could evidently be generalized so as to include the latter. In the above notation, electrons with relative coordinates $\mathbf{r}_{ki}$ are supposed to be bound to a nucleus. If free electrons do occur they should be included by treating them formally on the same footing as the atoms.

$$h(\mathbf{R}^N) = \int f d\mathbf{p}_k{}^N d\mathbf{p}_{ki}{}^{N(n_k-1)} d\mathbf{r}_{ki}{}^{N(n_k-1)} \tag{I.8}$$

which will be needed for the developments of Sections IV and V.

C. Time Derivative of a Dynamical Quantity

In classical statistical mechanics, it follows from conservation of probability in phase space that

$$\frac{\partial f}{\partial t} = -\sum_k \nabla_{\mathbf{R}_k} \cdot f\dot{\mathbf{R}}_k - \sum_{k,i} \nabla_{\mathbf{r}_{ki}} \cdot f\dot{\mathbf{r}}_{ki} - \sum_k \nabla_{\mathbf{p}_k} \cdot f\dot{\mathbf{p}}_k - \sum_{k,i} \nabla_{\mathbf{p}_{ki}} \cdot f\dot{\mathbf{p}}_{ki} \tag{I.9}$$

where, for instance, the differential operator $\nabla_{\mathbf{R}_k}$ is the ordinary nabla operator, and $\dot{\mathbf{R}}_k$ the velocity in the $\mathbf{R}_k$-subspace.

We are now able to evaluate the time derivative of the average of a dynamical quantity α as follows

$$\frac{\partial \alpha_{\text{Av}}}{\partial t} = \frac{\partial}{\partial t}\langle \alpha f\rangle = \langle \frac{\partial \alpha}{\partial t} f\rangle + \langle \alpha \frac{\partial f}{\partial t}\rangle \tag{I.10}$$

where Eq. I.7 has been used.

Substituting Eq. I.9 into the second term of the last member of Eq. I.10 and applying Gauss' theorem we obtain, since f falls off rapidly as coordinates and momenta tend to infinity,

$$\frac{\partial \alpha_{\text{Av}}}{\partial t} = \langle \frac{d\alpha}{dt} f\rangle \tag{I.11}$$

where d/dt is the total time derivative in phase space, i.e.,

$$\frac{d\alpha}{dt} = \frac{\partial \alpha}{\partial t} + \sum_k \dot{\mathbf{R}}_k \cdot \nabla_{\mathbf{R}_k}\alpha + \sum_{k,i} \dot{\mathbf{r}}_{ki} \cdot \nabla_{\mathbf{r}_{ki}}\alpha + \sum_k \dot{\mathbf{p}}_k \cdot \nabla_{\mathbf{p}_k}\alpha + \sum_{k,i} \dot{\mathbf{p}}_{ki} \cdot \nabla_{\mathbf{p}_{ki}}\alpha \tag{I.12}$$

The simple result, Eq. I.11, has also been obtained by Irving and Kirkwood[9] by making use of Liouville's theorem. This, however, as the foregoing derivation shows, is not necessary at all, the law of conservation of probability being already sufficient.

A more detailed discussion of the assumption underlying Eq. I.9 when the system consists of particles interacting with the electromagnetic field, is given in Section II. For those applications of the theory presented here, in which only Coulomb interactions are taken into account (cf., for example, Section III) Eq. I.9 is of course the well-established expression for conservation of probability in the phase space of a conservative system, consisting of $\mathcal{N} = \sum_{k=1}^{N} n_k$ particles. For this last case, it has been shown by Irving and Zwanzig[10] that the theorem expressed by Eq. I.11 also holds in quantum-statistical mechanics if the function f is the Wigner distribution function and if the dynamical variable α is a polynomial of a degree not higher than the second in the momenta.

D. Definitions of Densities; Electric and Magnetic Moments

As has already been done in a similar case by Irving and Kirkwood,[9] we can express the probability, per unit volume, that the center of gravity of the kth atom (whatever its momentum and whatever the position of all other particles, including its own electrons) be at $\mathbf{R}$ at time t, in the following way

$$\langle \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \tag{I.13}$$

where $\delta(\mathbf{R}_k - \mathbf{R})$ represents Dirac's δ-function.

Now an atom may be said to lie within a certain volume whenever its center of gravity has its position inside that volume. Therefore we may define the average number of atoms per unit volume at position $\mathbf{R}$ at time t, which we will call the number density ϱ_n,

$$\varrho_n(\mathbf{R}, t) = \sum_k \langle \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \tag{I.14}$$

In the same way an atom will be said to contribute to the mass density $\varrho_m(\mathbf{R}, t)$ and the (true) charge density $\varrho_e(\mathbf{R}, t)$, respectively, when its center of gravity $\mathbf{R}_k$ is located at $\mathbf{R}$

$$\varrho_m(\mathbf{R}, t) = \langle \sum_{k,i} m_{ki} \delta(\mathbf{R}_k - \mathbf{R}) f \rangle = \langle \sum_k m_k \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \tag{I.15}$$

$$\varrho_e = \langle \sum_{k,i} e_{ki} \delta(\mathbf{R}_k - \mathbf{R}) f \rangle = \langle \sum_k e_k \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \tag{I.16}$$

where $e_k = \sum_i e_{ki}$ is the total charge of an atom.

Finally starting from the usual definitions of atomic electric dipole and quadrupole and magnetic dipole moments $\boldsymbol{\mu}_k^{el}$, q_k^{el}, and $\boldsymbol{\mu}_k^{m}$

$$\boldsymbol{\mu}_k^{el} = \sum_i e_{ki}\,\mathbf{r}_{ki} \tag{I.17}$$

$$\mathsf{q}_k^{el} = \tfrac{1}{2}\sum_i e_{ki}\,\mathbf{r}_{ki}\,\mathbf{r}_{ki} \tag{I.18*}$$

$$\boldsymbol{\mu}_k^{m} = \tfrac{1}{2}\,c^{-1}\sum_i e_{ki}\,\mathbf{r}_{ki}\wedge\dot{\mathbf{r}}_{ki} \tag{I.19}$$

(where the moments of the kth atom are defined with respect to the position $\mathbf{R}_k$ of its center of gravity as origin, and where c is the velocity of light) we obtain for the densities of these moments

$$\mathbf{P}(\mathbf{R}, t) = \langle\sum_{k,i} e_{ki}\,\mathbf{r}_{ki}\,\delta(\mathbf{R}_k-\mathbf{R})f\rangle \tag{I.20}$$

$$\mathsf{Q}(\mathbf{R}, t) = \langle\tfrac{1}{2}\sum_{k,i} e_{ki}\,\mathbf{r}_{ki}\,\mathbf{r}_{ki}\,\delta(\mathbf{R}_k-\mathbf{R})f\rangle \tag{I.21}$$

$$\mathbf{M}(\mathbf{R}, t) = \langle\tfrac{1}{2}c^{-1}\sum_{k,i} e_{ki}\,\mathbf{r}_{ki}\wedge\dot{\mathbf{r}}_{ki}\,\delta(\mathbf{R}_k-\mathbf{R})f\rangle \tag{I.22}$$

Densities of other atomic quantities (e.g. momentum) can be defined in a similar way.

E. Conservation Laws

The conservation laws for densities of atomic quantities are obtained by means of the theorem, Eq. I.11. The procedure will be outlined here for some of the densities given in Section I.D. A more complicated case is treated in Section III, where the balance equation for the average momentum in a dielectric fluid is set up.

The conservation of mass density is found from Eq. I.15 and the theorem, Eq. I.11:

$$\begin{aligned}\frac{\partial\varrho_m}{\partial t} &= \langle f\sum_k m_k\,\dot{\mathbf{R}}_k\cdot\nabla_{\mathbf{R}_k}\delta(\mathbf{R}_k-\mathbf{R})\rangle \\ &= -\nabla_{\mathbf{R}}\cdot\langle\sum_k m_k\,\dot{\mathbf{R}}_k\,\delta(\mathbf{R}_k-\mathbf{R})f\rangle = -\nabla_{\mathbf{R}}\cdot\varrho\,\mathbf{v}\end{aligned} \tag{I.23}$$

where

$$\mathbf{v} = \langle\sum_k m_k\,\dot{\mathbf{R}}_k\,\delta(\mathbf{R}_k-\mathbf{R})f\rangle/\langle\sum_k m_k\,\delta(\mathbf{R}_k-\mathbf{R})f\rangle \tag{I.24}$$

is the average (translational) velocity of the center of gravity of

---

* See Appendix I.

the atoms. With Eq. I.16 and the theorem, Eq. I.11, one obtains the law of conservation of charge,

$$\partial \varrho_e / \partial t = -\nabla_{\mathbf{R}} \cdot \mathbf{i} \tag{I.25}$$

where

$$\mathbf{i} = \langle \sum_k e_k \, \dot{\mathbf{R}}_k \, \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \tag{I.26}$$

is the average (true) current density.

The equation for the rate of change of the polarization **P** is obtained from Eqs. I.20 with I.11,

$$\frac{\partial \mathbf{P}}{\partial t} = -\nabla_{\mathbf{R}} \cdot \langle \sum_k \dot{\mathbf{R}}_k \boldsymbol{\mu}_k^{el} \delta(\mathbf{R}_k - \mathbf{R}) f \rangle + \langle \sum_k \dot{\boldsymbol{\mu}}_k^{el} \, \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \tag{I.27}$$

The first term on the right-hand side of this equation represents the change of polarization due to a transport of electric dipole moments, the second term the change in polarization due to a variation of the value of these moments. Equation I.27 may be rewritten

$$\frac{\partial \mathbf{P}}{\partial t} = -\nabla_{\mathbf{R}} \cdot \mathbf{v}\mathbf{P} - \nabla_{\mathbf{R}} \cdot \langle \sum_k (\dot{\mathbf{R}}_k) \boldsymbol{\mu}_k^{el} \delta(\mathbf{R}_k - \mathbf{R}) f \rangle + \langle \sum_k \dot{\boldsymbol{\mu}}_k^{el} \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \tag{I.28}$$

where

$$(\dot{\mathbf{R}}_k) = \dot{\mathbf{R}}_k - \mathbf{v} \tag{I.29}$$

and where the term **vP** represents the transport of polarization due to the average velocity **v**(cf. Eq. I.24). The second term on the right-hand side of Eq. I.28 can, for instance, account for a transport of electric moment caused by diffusion in a mixture of several atomic species.

In a similar way we obtain for the time derivative of **Q**

$$\frac{\partial \mathbf{Q}}{\partial t} = -\nabla_{\mathbf{R}} \cdot \mathbf{v}\mathbf{Q} - \nabla_{\mathbf{R}} \cdot \langle \sum_k (\dot{\mathbf{R}}_k) \mathsf{q}_k^{el} \delta(\mathbf{R}_k - \mathbf{R}) f \rangle + \langle \sum_k \dot{\mathsf{q}}_k^{el} \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \tag{I.30}$$

Finally, we give the following connection between the time derivative of the divergence of **Q** and the curl of the magnetization **M**

$$
\begin{aligned}
&\frac{\partial}{\partial t}\nabla_{\mathbf{R}}\cdot \mathbf{Q}-c\,\nabla_{\mathbf{R}}\wedge \mathbf{M}\\
&\quad = -\nabla_{\mathbf{R}}\cdot\nabla_{\mathbf{R}}\cdot \mathbf{v}\,\mathbf{Q}-\nabla_{\mathbf{R}}\cdot\{\nabla_{\mathbf{R}}\cdot\langle\sum_{k}(\dot{\mathbf{R}}_k)\,\mathbf{q}_k^{el}\,\delta(\mathbf{R}_k-\mathbf{R})f\rangle\} \qquad \text{(I.31)}\\
&\quad +\nabla_{\mathbf{R}}\cdot\langle\sum_{k,i} e_{ki}\,\mathbf{r}_{ki}\,\dot{\mathbf{r}}_{ki}\,\delta(\mathbf{R}_k-\mathbf{R})f\rangle \quad .
\end{aligned}
$$

This connection follows from the definitions of **Q** and **M** and Eq. I.30.

II. DERIVATION OF THE MAXWELL EQUATIONS FROM ELECTRON THEORY

A. Introduction

As is well known, Lorentz[14] was the first to give a derivation of Maxwell's equations in material bodies from the fundamental equations of his electron theory by averaging the microscopic field quantities over physically infinitesimal space and time regions. This procedure has with only slight modifications been taken over by various authors.[7, 27, 31] In his recent monograph on the theory of electrons, Rosenfeld[26] has given a very careful exposition of this derivation, which is based again upon the same kind of averaging procedure. However, even in this refined treatment the derivation is by no means straightforward from a mathematical point of view and requires rather too much verbal explanation. As a consequence, inconsistencies in the frequently implicit assumptions easily escape notice and we shall see that even Rosenfeld's work is not completely blameless in this respect. It should also be noted that the actual averaging process is only performed over space regions and the time averaging is not essential for obtaining the correct form of Maxwell's equations. Further, quantities like polarization and magnetization are defined here as space averages, whereas in an actual evaluation of these quantities from a molecular theory they are defined as ensemble averages (cf., for example, the theories of the dielectric constant by Yvon,[32] Kirkwood,[13] Brown,[1] de Boer *et al.*[4]), i.e., as in Section I.D.

It will be shown that a straightforward derivation of Maxwell's equations from electron theory can be given on the basis of ensemble averaging.[15] We will treat a very general case here, in particular it will be shown that there is no need to restrict ourselves, as is done usually, to a medium at rest or moving as a whole with uniform velocity with respect to the observer.

We first wish to investigate in more detail the application of the formalism of Section I to a system of particles interacting with the electromagnetic field.

The microscopic Lorentz field equations can be written in the following form (in rationalized gaussian units):

$$\nabla_{\mathbf{R}} \cdot \mathbf{b} = 0 \tag{II.1}$$

$$\dot{\mathbf{b}} = -c\, \nabla_{\mathbf{R}} \wedge \mathbf{e} \tag{II.2}$$

$$\nabla_{\mathbf{R}} \cdot \mathbf{e} = \sum_{k,i} e_{ki}\, \delta(\mathbf{R}_k + \mathbf{r}_{ki} - \mathbf{R}) \tag{II.3}$$

$$\dot{\mathbf{e}} = c\, \nabla_{\mathbf{R}} \wedge \mathbf{b} - \sum_{k,i} e_{ki} (\dot{\mathbf{R}}_k + \dot{\mathbf{r}}_{ki}) \delta(\mathbf{R}_k + \mathbf{r}_{ki} - \mathbf{R}) \tag{II.4}$$

where **e** and **b** are the microscopic electric and magnetic field strengths, respectively. The microscopic charge and current densities in Eqs. II.3 and II.4, which usually are treated as continuous functions of space and time, have been represented here consistently, with the help of Dirac's δ-function, as due to point charges and the motions thereof.

We also introduce the potentials **a** and φ, partially defined by

$$\mathbf{b} = \nabla_{\mathbf{R}} \wedge \mathbf{a} \tag{II.5}$$

$$\mathbf{e} = -c^{-1}\, \dot{\mathbf{a}} - \nabla_{\mathbf{R}}\, \varphi \tag{II.6}$$

and divide **e** into a solenoidal and an irrotational part

$$\mathbf{e} = \mathbf{e}^{s} + \mathbf{e}^{irr} \quad ; \quad \operatorname{div} \mathbf{e}^{s} = 0 \quad ; \quad \operatorname{curl} \mathbf{e}^{irr} = 0 \tag{II.7}$$

with

$$\mathbf{e}^{s} = -c^{-1}\, \dot{\mathbf{a}} \quad , \quad \mathbf{e}^{irr} = -\nabla_{\mathbf{R}}\, \varphi \tag{II.8}$$

It is now possible to write the equations of motion of fields and particles in the following form:

$$\dot{\mathbf{R}}^{\mathcal{N}} = \dot{\mathbf{R}}^{\mathcal{N}}(\mathbf{R}^{\mathcal{N}}, \mathbf{p}^{\mathcal{N}}; \mathbf{e}^{s}, \mathbf{a}) \tag{II.9}$$

$$\dot{\mathbf{p}}^{\mathcal{N}} = \dot{\mathbf{p}}^{\mathcal{N}}(\mathbf{R}^{\mathcal{N}}, \mathbf{p}^{\mathcal{N}}; \mathbf{e}^{s}, \mathbf{a}) \tag{II.10}$$

$$\dot{\mathbf{e}}^{s} = \dot{\mathbf{e}}^{s}\, (\mathbf{R}^{\mathcal{N}}, \mathbf{p}^{\mathcal{N}}; \mathbf{e}^{s}, \mathbf{a}) \tag{II.11}$$

$$\dot{\mathbf{a}} = \dot{\mathbf{a}}\, (\mathbf{R}^{\mathcal{N}}, \mathbf{p}^{\mathcal{N}}; \mathbf{e}^{s}, \mathbf{a}) \tag{II.12}$$

with the conditions

$$\operatorname{div} \mathbf{a} = 0 \quad ; \quad \operatorname{div} \mathbf{e}^{s} = 0 \tag{II.13}$$

and the supplementary condition

$$\operatorname{div} \mathbf{e}^{irr} = \sum_{k,\,i} e_{ki}\, \delta(\mathbf{R}_k + \mathbf{r}_{ki} - \mathbf{R}) \tag{II.14}$$

The vectors $\mathbf{R}^{\mathscr{N}}$ and $\mathbf{p}^{\mathscr{N}}$ denote here symbolically the position and momenta of all particles.

Equations II.9 and II.10 are the equations of motion of the particles. Equation II.11 is equivalent to the Maxwell equation, Eq. II.4, while Eq. II.12 is identical with the potential equation, Eq. II.6.

We note that the Maxwell equations, Eqs. II.1 and II.2 are simply a consequence of the potential equations, Eqs. II.5 and II.6, while the third Maxwell equation, Eq. II.3, is added as a supplementary condition (cf. Eq. II.14). We also note that if the conditions, Eqs. II.13 and II.14, are satisfied at some definite time, they are maintained at all times.

Equations II.9 to II.12 may in principle be partially solved, and Eqs. II.9 and II.10 may be rewritten in the form:

$$\dot{\mathbf{R}}^{\mathscr{N}} = \dot{\mathbf{R}}^{\mathscr{N}}(\mathbf{R}^{\mathscr{N}}, \mathbf{p}^{\mathscr{N}}; \mathbf{e}^{s}(0), \mathbf{a}(0); t) \tag{II.15}$$

$$\dot{\mathbf{p}}^{\mathscr{N}} = \dot{\mathbf{p}}^{\mathscr{N}}(\mathbf{R}^{\mathscr{N}}, \mathbf{p}^{\mathscr{N}}; \mathbf{e}^{s}(0), \mathbf{a}(0); t) \tag{II.16}$$

where $\dot{\mathbf{R}}$ and $\dot{\mathbf{p}}$ are now functions of $\mathbf{R}$, $\mathbf{p}$, and t and of some initial conditions for the fields $\mathbf{e}^{s}$ and $\mathbf{a}$ at the time $t = 0$ satisfying the conditions, Eq. II.13.

As a consequence of the form, Eqs. II.15 and II.16 of the particle equations of motion, it follows that *for some given initial conditions* $\mathbf{e}^{s}(0)$, $\mathbf{a}(0)$, *there passes only one trajectory at any time t through any point in the particle phase space.* This means that for an ensemble of systems with the same initial condition $\mathbf{e}^{s}(0)$ and $\mathbf{a}(0)$ the probability distribution function $f(\mathbf{R}^{\mathscr{N}}, \mathbf{p}^{\mathscr{N}}, t)$ in the particle phase space obeys a continuity equation, Eq. I.9, and that the theorem, Eq. I.11, holds for any dynamic variable $\alpha(\mathbf{R}^{\mathscr{N}}, \mathbf{p}^{\mathscr{N}})$.

We must, however, assume that the initial conditions $\mathbf{e}^{s}(0)$ and $\mathbf{a}(0)$ and the distribution function f can be chosen in such a way that the thermal behavior of the particle system is correctly described. (The choice of $\mathbf{e}^s(0)$, $\mathbf{a}(0)$ and of f, for $t = 0$, is *a priori* completely unrestricted).

The validity of this assumption (whose content is not equivalent to the content of the usual ergodic theorem) is, of course, difficult to assess, and represents, therefore, an additional postulate in the framework of our theory.

Obviously effects connected with the presence of random fields are not included in this description. However, such effects are also not contained in the macroscopic Maxwell equations, which we wish to derive in this section.

Finally we note that in the special ensemble of systems considered (i.e., with identical initial conditions $\mathbf{e}^s(0)$, $\mathbf{a}(0)$) the electric and magnetic field strengths $\mathbf{e}$ and $\mathbf{b}$ may be written

$$\mathbf{e} = \mathbf{e}(\mathbf{R}_k{}^N, \mathbf{r}_{ki}{}^{N(n_k-1)}, \mathbf{p}_k{}^N, \mathbf{p}_{ki}{}^{N(n_k-1)}; \mathbf{R}, t) \qquad \text{(II.17)}$$

$$\mathbf{b} = \mathbf{b}(\mathbf{R}_k{}^N, \mathbf{r}_{ki}{}^{N(n_k-1)}, \mathbf{p}_k{}^N, \mathbf{p}_{ki}{}^{N(n_k-1)}; \mathbf{R}, t) \qquad \text{(II.18)}$$

They may therefore be considered as dynamical quantities of the type, Eq. I.6, of the particles system, to which we may apply the theorem, Eq. I.11.

With respect to the time derivatives occurring in Eqs. II.2 and II.4, we notice that the field quantities $\mathbf{e}$ and $\mathbf{b}$ do not only depend explicitly on time, but that they also vary with time owing to the fact that the state of the system varies. Therefore $\dot{\mathbf{b}}$ and $\dot{\mathbf{e}}$ should be evaluated as total time derivatives in phase space (cf. Eq. I.12). After this discussion of the conditions under which the formalism of Section I applies to the system under consideration, we proceed to give a simple derivation of the macroscopic Maxwell equations in matter.

B. Derivation of the Maxwell Equations Corresponding to Eqs. II.1 to II.3

In this section we will apply the actual ensemble averaging process to the microscopic equations (II.1 to II.3) in succession. For Eqs. II.1 and II.2 this method yields simply, when Eqs. I.7 and I.11 are used, two of the Maxwell equations

$$\nabla_{\mathbf{R}} \cdot \mathbf{B} = 0 \qquad \text{(II.19)}$$

and

$$\frac{\partial \mathbf{B}}{\partial t} = -c\nabla_{\mathbf{R}} \wedge \mathbf{E} \tag{II.20}$$

where

$$\mathbf{B} = \langle \mathbf{b}f \rangle \tag{II.21}$$

and

$$\mathbf{E} = \langle \mathbf{e}f \rangle \tag{II.22}$$

are the macroscopic magnetic and electric field strengths.

For Eq. II.3 the derivation is somewhat more complicated. Taking the ensemble average of both members of (3) we obtain, using the definition, Eq. II.22,

$$\nabla_{\mathbf{R}} \cdot \mathbf{E} = \langle \sum_{k,i} e_{ki}\, \delta(\mathbf{R}_k + \mathbf{r}_{ki} - \mathbf{R}) f \rangle \tag{II.23}$$

Expanding the δ-function in powers of $\mathbf{r}_{ki}$, this expression may be written

$$\nabla_{\mathbf{R}} \cdot \mathbf{E} = \langle \sum_{k,i} e_{ki} (1 + \mathbf{r}_{ki} \cdot \nabla_{\mathbf{R}_k} + \tfrac{1}{2} \mathbf{r}_{ki} \mathbf{r}_{ki} \colon \nabla_{\mathbf{R}_k} \nabla_{\mathbf{R}_k} + \ldots) \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \tag{II.24}$$

The series, Eq. II.24, converges rapidly if the atomic distribution (i.e., the function f integrated over all coordinates except those belonging to an atom k) varies slowly with respect to its argument $\mathbf{R}_k$ over distances of the order of the atomic dimensions (mean values of $\mathbf{r}_{ki}$). All macroscopic quantities should therefore be slowly varying functions of space. Retaining in Eq. II.24 terms up to second order in $\mathbf{r}_{ki}$, this equation immediately reduces, as can be seen from the previously derived formulas, to

$$\nabla_{\mathbf{R}} \cdot \mathbf{E} = \varrho_e - \nabla_{\mathbf{R}} \cdot (\mathbf{P} - \nabla_{\mathbf{R}} \cdot \mathbf{Q}) \tag{II.25}$$

Introducing the electric displacement vector

$$\mathbf{D} = \mathbf{E} + \mathbf{P} - \nabla_{\mathbf{R}} \cdot \mathbf{Q} \tag{II.26}$$

we may write Eq. II.25 in the Maxwellian form

$$\nabla_{\mathbf{R}} \cdot \mathbf{D} = \varrho_e \tag{II.27}$$

As has been remarked already by Rosenfeld,[26] the definition, Eq. II.26, of **D** differs from the usual one by the inclusion of the quadrupole term which is ordinarily neglected. As Rosenfeld pointed out, however, it is consistent to retain the electric quadrupole term when in the fourth Maxwell equation, to be considered in the following section, the magnetization which is of the same order is taken into account.

C. Derivation of the Fourth Maxwell Equation

Let us now proceed with the last microscopic equation, Eq. II.4. Averaging both members, we obtain with Eqs. I.11, II.21, and II.22,

$$\begin{aligned}\frac{\partial \mathbf{E}}{\partial t} &= c\nabla_{\mathbf{R}} \wedge \mathbf{B} - \langle \sum_{k,i} e_{ki}(\dot{\mathbf{R}}_{ki} + \dot{\mathbf{r}}_{ki})\delta(\mathbf{R}_{ki}+\mathbf{r}_{ki}-\mathbf{R})f\rangle \\ &= c\nabla_{\mathbf{R}}\wedge\mathbf{B} - \langle \sum_{k,i} e_{ki}(\dot{\mathbf{R}}_{ki}+\dot{\mathbf{r}}_{ki})(1+\mathbf{r}_{ki}\cdot\nabla_{\mathbf{R}_k}+\tfrac{1}{2}\mathbf{r}_{ki}\mathbf{r}_{ki}:\nabla_{\mathbf{R}_k}\nabla_{\mathbf{R}_k}+\ldots)\delta(\mathbf{R}_k-\mathbf{R})\end{aligned} \tag{II.28}$$

where the δ-function has again been expanded in powers of $\mathbf{r}_{ki}$. Neglecting all terms higher than the second in $\mathbf{r}_{ki}$ and $\dot{\mathbf{r}}_{ki}$, and using the definitions and conservation laws of Sections I.D and E (cf. especially Eq. I.31), this equation then reduces (after some straightforward transformations) to

$$\begin{aligned}\frac{\partial \mathbf{E}}{\partial t} = {} & c\nabla_{\mathbf{R}} \wedge \mathbf{B} - \mathbf{i} - \frac{\partial(\mathbf{P}-\nabla_{\mathbf{R}}\cdot\mathsf{Q})}{\partial t} - c\nabla_{\mathbf{R}}\wedge\mathbf{M} \\ & - \nabla_{\mathbf{R}}\wedge(\mathbf{P}\wedge\mathbf{v}) - \nabla_{\mathbf{R}}\wedge\langle\sum_k \boldsymbol{\mu}_k^{el}\wedge(\dot{\mathbf{R}}_k)\delta(\mathbf{R}_k-\mathbf{R})f\rangle \\ & + \nabla_{\mathbf{R}}\cdot\{\nabla_{\mathbf{R}}\cdot(\mathbf{v}\mathsf{Q}-\mathsf{Q}\mathbf{v})\} \\ & + \nabla_{\mathbf{R}}\cdot\{\nabla_{\mathbf{R}}\cdot\langle\sum_k((\dot{\mathbf{R}}_k)\mathsf{q}_k^{el}-\mathsf{q}_k^{el}(\dot{\mathbf{R}}_k))\,\delta(\mathbf{R}_k-\mathbf{R})\,f\rangle\}\end{aligned} \tag{II.29}$$

With the help of the vector formula (see Appendix I)

$$\nabla_{\mathbf{R}}\cdot\{\nabla_{\mathbf{R}}\cdot(\mathbf{a}\mathsf{B}-\mathsf{B}\mathbf{a})\} = \nabla_{\mathbf{R}}\wedge(\nabla_{\mathbf{R}}\cdot\mathsf{B}\wedge\mathbf{a}), \tag{II.30}$$

where B is a symmetric tensor and $\mathbf{a}$ a vector, one finally obtains

$$\frac{\partial \mathbf{D}}{\partial t} = c\nabla_{\mathbf{R}}\wedge\mathbf{H} - \mathbf{i} \tag{II.31}$$

where $\mathbf{D}$ is the electric displacement vector defined by Eq. II.26, and we have introduced the magnetic displacement vector $\mathbf{H}$ (which is commonly called the magnetic field strength) defined by

$$\begin{aligned}\mathbf{H} = {} & \mathbf{B}-\mathbf{M}-c^{-1}(\mathbf{P}\wedge\mathbf{v}-\nabla_{\mathbf{R}}\cdot\mathsf{Q}\wedge\mathbf{v}) \\ & -c^{-1}\langle\sum_k\{\boldsymbol{\mu}_k^{el}\wedge(\dot{\mathbf{R}}_k)-\nabla_{\mathbf{R}}\cdot\mathsf{q}_k^{el}\wedge(\dot{\mathbf{R}}_k)\}\,\delta(\mathbf{R}_k-\mathbf{R})f\rangle\end{aligned} \tag{II.32}$$

It is very important to remark that again our definition of **H** Eq. II.32, differs from the customary one. Here, however, this is not due, as previously with respect to **D** (cf. Eq. II.26), to the inclusion of higher-order multipole moments, but to the fact that all possible motions of the particles are taken into consideration in a consistent way. In the usual space-time averaging treatment only two special cases are considered, i.e., systems at rest and systems moving with uniform velocity. It should be stressed, however, that in the first case, though the electric current is supposed to be due to moving particles (ions or electrons), the particles contributing to the electric or magnetic polarization are supposed to be at rest. This of course is inconsistent as the ions contributing to the true current density may well have dipole and higher moments. A similar objection can, *mutatis mutandis*, be made with regard to the case of uniformly moving bodies. It will be remembered (see the footnote on p. 312) that conduction electrons are to be treated formally as atoms. As a consequence, for certain values of the index k, e_k, and $\mathbf{R}_k$ simply refer to the charge and the position of a free electron. For these same values of k, therefore, no bound electrons with charges e_{ki} and positions $\mathbf{r}_{ki}$ exist. Thus the free electrons may well contribute to the mean electric charge and current densities, Eqs. I.16 and I.26 but not to the higher moment densities Eqs. I.20, I.21 and I.22.

In a few particular cases our general definition, Eq. II.32, reduces to a more familiar form.

(a) If in a certain medium the velocity $\mathbf{v} = 0$, and terms containing the "fluctuations" $(\dot{\mathbf{R}}_k)$ vanish, then

$$\mathbf{H} = \mathbf{B} - \mathbf{M} \tag{II.33}$$

We thus have specified clearly the condition under which the relation, Eq. II.33, between **H** and **B**, together with the definition Eq. I.22, of **M**, holds. This relation is usually (but not quite correctly) stated as being valid for any system at rest, including systems with ionic conduction (for such systems the "diffusion terms" containing $(\dot{\mathbf{R}}_k)$ do not, of course, vanish). However, on changing the definition of **M** in an appropriate manner, one could always justify the relation, Eq. II.33.

(b) Let us now suppose that only the terms containing $(\dot{\mathbf{R}}_k)$ vanish, while the common mean velocity $\mathbf{v}$ is constant with respect to time and space. Equation II.32 then reduces to

$$\mathbf{H} = \mathbf{B} - \mathbf{M} - c^{-1}(\mathbf{P} - \nabla_{\mathbf{R}} \cdot \mathbf{Q}) \wedge \mathbf{v} \tag{II.34}$$

This relation is usually derived[7,14] with the definitions, Eqs. I.20, I.21, and I.22 for the moment densities, for "systems moving with uniform velocity." Again we give a more exact qualification of such systems than the usual one. Here also it is true, that by changing the definition of **M**, Eq. II.34 could be made to hold in a more general case.

With the help of the familiar formula, Eq. II.34, where it is seen that as a consequence of motion the polarization contributes to the difference of **B** and **H** (i.e., gives rise to an effective magnetization), our general formula, Eq. II.32, can be easily understood. Indeed, Eq. II.32 simply expresses the fact that every electrically polarized particle (atom or ion) with a nonvanishing mean velocity gives its own contribution to the effective magnetization. We finally note that relation, Eq. II.26, between **D** and **E** was not affected by any motion of the particles. This is in agreement with earlier derivations of the Maxwell equations from electron theory. As is well known from a consistent relativistic treatment, first given by Dällenbach,[3,25] moving magnetic dipoles also contribute to the effective electric polarization, in agreement with the macroscopic Minkowski theory.[7,29]

D. General Remarks

After having accomplished formally the derivation of the Maxwell equations and having defined the macroscopic field quantities in terms of ensemble averages, it is perhaps useful to add a few remarks which may help to clarify the relation between the earlier Lorentz treatment and the present one.

In the first place we may repeat here the observation made by Irving and Kirkwood[9] in an analogous case, that the densities and average field quantities defined previously are point functions which already satisfy the macroscopic Maxwell equations. According to the principles of statistical mechanics, these ensemble averages correspond, speaking somewhat loosely, to time averages. In order to obtain the macroscopic observables, an additional space averaging process would be necessary. This second averaging process, however, does not modify anymore the form of the equations. On the other hand, in the Lorentz type of treatment, though various authors indicate that space as well as time averages must be taken in order to obtain the macroscopic quantities, only the first one is actually performed, the second one again not modifying the form of the equations. As Van Vleck[31] pointed out already, the smoothing out over infinitesimal space regions may be interpreted in a certain way as corresponding to a smoothing out in time. One could also say that space averaging corresponds to a peculiar kind of ensemble averaging, with a distribution function such that all configurations taken into account are related to each other by a rigid displacement of the system as a whole. From the foregoing it will be evident that the present method introducing an arbitrary distribution function in phase space, apart from allowing a mathematically more rigorous treatment, enables one to perform the averaging process in a more fundamental way.

Finally we note that the method applied here is based on classical statistical mechanics and on a classical model of the atom. Actually, however, the motion of electrons bound in the atoms should be treated on the basis of quantum mechanics. The same thing applies to the motion of conduction electrons in a metal, and at low temperatures even to the motion of the atoms themselves. Therefore it would certainly be gratifying if the present formalism could be extended to the case where the particles are treated quantum mechanically.

III. PONDEROMOTIVE FORCE IN A DIELECTRIC

A. Introduction

Whereas in the previous chapter we have given a statistical-mechanical derivation of the Maxwell equations, and therefore discussed the influence of matter on the equations governing the average electric and magnetic fields, we shall be concerned in this chapter with the influence of the fields on the equation of motion (hydrodynamic equation).

We shall not deal with this problem in full but restrict ourselves to a fluid system of electrically neutral identical atoms, and consider the case that all interactions, except the Coulomb interactions between the constituent particles of the system (the nuclei and electrons grouped into atoms) are neglected. The formalism of Section I then applies without further justification. Furthermore we have already stated that the theorem, Eq. I.11, with Eq. I.12 also holds in quantum-statistical mechanics for the conservative systems under consideration, if the distribution function f is the Wigner distribution function and if the dynamical variable α is a polynomial of degree not higher than the second in the momenta. In the following sections we therefore consider f to be the Wigner distribution function, thus correctly taking into account the quantum behavior of the atoms.

The discussion which we shall give is of interest in connection with the definitions of pressure and volume force in a system with long-range interactions (here the dipole-dipole forces between atoms). More specifically we shall be able to define the concepts of pressure and ponderomotive force in a dielectric in terms of averages over microscopic quantities.

The problem of determining the ponderomotive force in a dielectric is generally discussed from a macroscopic point of view. However, different expressions have been proposed for this force by various authors. We wish to mention here the two different expressions proposed by Kelvin and Helmholtz respectively. From thermodynamic arguments,[16] it can be established that no real contradiction exists between the Kelvin and Helmholtz expressions and that a different meaning must be given to the concept of pressure in each case. It will be seen that this ambiguity in the definitions of ponderomotive force and pressure may be understood on the basis of a statistical-mechanical derivation of these quantities and is in fact closely connected with the presence of long-range interactions between the atoms.[20] In the following section we come back to these points in more detail.

B. Balance of Translational Momentum of the Atoms

In this section the balance equation for translational momentum of the atoms will be set up. This equation will be necessary for the discussion of pressure and force in a system with long-range interactions. Taking the time derivative of $\varrho_m \mathbf{v}$ (cf. Eqs. I.15 and I.24), the density of translational momentum of the atoms, we find with Eq. I.11

$$\begin{aligned}\frac{\partial \varrho_m \mathbf{v}}{\partial t} &= -\nabla_{\mathbf{R}} \cdot \langle \sum_k m_k \dot{\mathbf{R}}_k \dot{\mathbf{R}}_k \delta(\mathbf{R}_k - \mathbf{R}) f \rangle + \langle \sum_k m_k \ddot{\mathbf{R}}_k \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \\ &= -\nabla_{\mathbf{R}} \cdot \varrho_m \mathbf{v}\mathbf{v} - \nabla_{\mathbf{R}} \cdot \langle \sum_k m_k (\dot{\mathbf{R}}_k)(\dot{\mathbf{R}}_k) \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \\ &\quad + \langle \sum_k m_k \ddot{\mathbf{R}}_k \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \\ &= -\nabla_{\mathbf{R}} \cdot (\varrho_m \mathbf{v}\mathbf{v} + \boldsymbol{\sigma}_K) + \sum_k \langle m_k \ddot{\mathbf{R}}_k \delta(\mathbf{R}_k - \mathbf{R}) f \rangle\end{aligned} \tag{III.1}$$

where

$$\boldsymbol{\sigma}_K = \langle \sum_k m_k (\dot{\mathbf{R}}_k)(\dot{\mathbf{R}}_k) \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \tag{III.2}$$

is the kinetic pressure tensor due to the translational motions of the atoms.

The last term on the right-hand side of Eq. III.1 represents the average force per unit volume acting on an atom due to external and interaction forces. As already stated we neglect all electromagnetic interactions, except the Coulomb interactions between the constituent particles, so that

$$m_k \ddot{\mathbf{R}}_k = \sum_i m_{ki} \ddot{\mathbf{R}}_{ki} = \sum_i e_{ki} \mathbf{E}^e(\mathbf{R}_{ki}) + \sum_i \nabla_{\mathbf{R}_{ki}} \sum_{l,j,l \neq k} V_{ki,lj} \tag{III.3}$$

where $\mathbf{E}^e(\mathbf{R}_{ki})$ is the external applied electric field, and

$$V_{ki,lj} = \frac{1}{4\pi} \frac{e_{ki} e_{lj}}{|\mathbf{R}_{ki} - \mathbf{R}_{lj}|} \tag{III.4}$$

is the Coulomb interaction energy between particles *ki* and *lj*.

We now develop the right-hand side of Eq. III.4 in a Taylor series around the center of gravity of the atoms. Retaining terms up to second order in $\mathbf{r}_{ki}$ and $\mathbf{r}_{lj}$ one obtains,* since the atoms

---

* In Eq. III.5 we have omitted for the sake of simplicity the second-order term $\frac{1}{2}\Sigma_i e_{ki} \mathbf{r}_{ki} \mathbf{r}_{ki} : \nabla_{\mathbf{R}_k} \nabla_{\mathbf{R}_k} \mathbf{E}^e$, arising from the interaction of the quadrupole moment $\frac{1}{2}\Sigma_i e_{ki} \mathbf{r}_{ki} \mathbf{r}_{ki}$ with the external electric field (see also the footnote on page 330).

are electrically neutral,

$$m_k \ddot{\mathbf{R}}_k = \{\nabla_{\mathbf{R}_k} \mathbf{E}^e(\mathbf{R}_k)\} \cdot \boldsymbol{\mu}_k - \sum_{l,\, l \neq k} (\nabla_{\mathbf{R}_k} \mathsf{T}_{kl}) : \boldsymbol{\mu}_k \boldsymbol{\mu}_l \tag{III.5}$$

where $\boldsymbol{\mu}_k$ is the electric dipole moment of atom k (cf. Eq. I.17; the superscript *el* has been omitted, since no magnetic moments occur in this section), and

$$\mathsf{T}_{kl} = (4\pi)^{-1} \nabla_{\mathbf{R}_k} \nabla_{\mathbf{R}_l} \frac{1}{|\mathbf{R}_k - \mathbf{R}_l|} \tag{III.6}$$

is the tensor characterizing dipole-dipole interaction.

With Eq. III.5 the last term on the right-hand side of Eq. III.1' becomes

$$\begin{aligned} \langle \sum_k m_k \ddot{\mathbf{R}}_k \delta(\mathbf{R}_k - \mathbf{R}) f \rangle &= \langle \sum_k \{\nabla_{\mathbf{R}_k} \mathbf{E}^e(\mathbf{R}_k)\} \cdot \boldsymbol{\mu}_k \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \\ &\quad - \langle \sum_{k,\, l,\, k \neq l} (\nabla_{\mathbf{R}_k} \mathsf{T}_{kl}) : \boldsymbol{\mu}_k \boldsymbol{\mu}_l \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \\ &= (\nabla_{\mathbf{R}} \mathbf{E}^e) \cdot \mathbf{P} - \langle \sum_{k,\, l,\, k \neq l} (\nabla_{\mathbf{R}_k} \mathsf{T}_{kl}) : \bar{\boldsymbol{\mu}}_k \bar{\boldsymbol{\mu}}_l \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \\ &\quad - \langle \sum_{k,\, l,\, l \neq k} (\nabla_{\mathbf{R}_k} \mathsf{T}_{kl}) : \{\boldsymbol{\mu}_k \boldsymbol{\mu}_l\} \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \end{aligned} \tag{III.7}$$

where $\mathbf{P}$, the polarization per unit volume, is given by Eq. I.20.

The mean moment $\bar{\boldsymbol{\mu}}_k$ is defined

$$\bar{\boldsymbol{\mu}}_k(\mathbf{R}_k) = \frac{\int \boldsymbol{\mu}_k f \prod_{k \neq l} d\mathbf{R}_l \prod_{l,j} d\mathbf{r}_{lj} \prod_l d\mathbf{p}_l \prod_{l,j} d\mathbf{p}_{lj}}{\int f \prod_{l \neq k} d\mathbf{R}_l \prod_{l,j} d\mathbf{r}_{lj} \prod_l d\mathbf{p}_l \prod_{l,j} d\mathbf{p}_{lj}}, \tag{III.8}$$

and the fluctuation term $\{\boldsymbol{\mu}_k \boldsymbol{\mu}_l\}$ as

$$\{\boldsymbol{\mu}_k \boldsymbol{\mu}_l\} = \boldsymbol{\mu}_k \boldsymbol{\mu}_l - \bar{\boldsymbol{\mu}}_k \bar{\boldsymbol{\mu}}_l \tag{III.9}$$

The second term of the last member of Eq. III.7 may be rewritten

$$\begin{aligned} \langle \sum_{k,\, l,\, k \neq l} (\nabla_{\mathbf{R}_k} \mathsf{T}_{kl}) : \bar{\boldsymbol{\mu}}_k \bar{\boldsymbol{\mu}}_l \delta(\mathbf{R}_k - \mathbf{R}) f \rangle \\ = [\nabla_{\mathbf{R}} \int^V \mathsf{T}(\mathbf{R}, \mathbf{R}') \cdot \mathbf{P}(\mathbf{R}')\, d\mathbf{R}'] \cdot \mathbf{P}(\mathbf{R}) \\ + \int^\infty \{\nabla_{\mathbf{R}} \mathsf{T}(\mathbf{R}, \mathbf{R}')\} : \mathbf{P}(\mathbf{R}) \mathbf{P}(\mathbf{R}') \{g(\mathbf{R}, \mathbf{R}') - 1\} d\mathbf{R}' \end{aligned} \tag{III.10}$$

where $\varrho_n(\mathbf{R})\varrho_n(\mathbf{R}')g(\mathbf{R}, \mathbf{R}')$ is the pair distribution function defined by

$$\varrho_n(\mathbf{R})\varrho_n(\mathbf{R}')g(\mathbf{R}, \mathbf{R}') = \langle \sum_{k, l, k\neq l} \delta(\mathbf{R}_k-\mathbf{R})\delta(\mathbf{R}_l-\mathbf{R}')f\rangle \tag{III.11}$$

and where use has been made of

$$\bar{\boldsymbol{\mu}}_k(\mathbf{R}) = \bar{\boldsymbol{\mu}}_l(\mathbf{R}) = \ldots = \mathbf{P}(\mathbf{R})/\varrho_n(\mathbf{R}) \tag{III.12}$$

since the atoms are identical.

The first term on the right-hand side of Eq. III.10 represents a contribution to the average force acting on an atom which is proportional to $(\mathbf{R}_k-\mathbf{R}_l)^{-4}$, i.e., derivable from a potential proportional to $(|\mathbf{R}_k-\mathbf{R}_l|)^{-3}$. This term can be interpreted as being the macroscopic long-range interaction in the medium.

The other term in Eq. III.10 contains contributions to the average force due only to the polarization of a region around the point **R** of dimensions of the order of the correlation length in the medium. For most fluid systems, this length will be sufficiently small so that this term may be considered as a short-range contribution to the force. This is also the case for the last term of Eq. III.7 which contains a contribution proportional to an inverse power of the interatomic distance higher than 4 due to the correlation between dipole moments of different atoms.* (In practice the power of the interatomic distance will be at least -7.)

Both of the short-range terms may be transformed into the divergence of a *local* pressure tensor (cf. Appendix II), so that

$$\begin{aligned}
&\langle \sum_{k, l, k\neq l} (\nabla_{\mathbf{R}_k}\mathsf{T}_{kl}) : \{\boldsymbol{\mu}_k\boldsymbol{\mu}_l\}\delta(\mathbf{R}_k-\mathbf{R})f\rangle \\
&\quad + \int^{\infty}\{\nabla_{\mathbf{R}}\mathsf{T}(\mathbf{R}, \mathbf{R}')\} : \mathbf{P}(\mathbf{R})\mathbf{P}(\mathbf{R}')\{g(\mathbf{R}, \mathbf{R}')-1\}d\mathbf{R}' \\
&\quad = \nabla_{\mathbf{R}}\cdot[\tfrac{1}{2}\langle \sum_{k, l, k\neq l} (\mathbf{R}_l-\mathbf{R}_k)(\nabla_{\mathbf{R}_k}\mathsf{T}_{kl}) : \{\boldsymbol{\mu}_k\boldsymbol{\mu}_l\}\delta(\mathbf{R}_k-\mathbf{R})f\rangle \\
&\quad + \tfrac{1}{2}\int^{\infty}(\mathbf{R}'-\mathbf{R})\{\nabla_{\mathbf{R}}\mathsf{T}(\mathbf{R}, \mathbf{R}')\} : \mathbf{P}(\mathbf{R})\mathbf{P}(\mathbf{R}')\{g(\mathbf{R}, \mathbf{R}')-1\}d\mathbf{R}'] \\
&\quad = \nabla_{\mathbf{R}}\cdot\boldsymbol{\sigma}_U
\end{aligned} \tag{III.13}$$

The tensor $\boldsymbol{\sigma}_U$ in the expression, Eq. III.13, can be interpreted as

---

* For very short distances $|\mathbf{R}_k - \mathbf{R}_l|$ there will, of course, be a stron repulsive interaction.

being a contribution to the pressure tensor due to short-range interatomic forces, such as dispersion force, exchange forces, etc., and also to density fluctuations.

C. Pressure and Ponderomotive Force in a Dielectric

Collecting the results of Eqs. III.7, III.10, and III.13, we may now rewrite Eq. III.1 as

$$\frac{\partial \varrho_m \mathbf{v}}{\partial t} = -\nabla_{\mathbf{R}} \cdot (\varrho_m \mathbf{v}\mathbf{v} + \boldsymbol{\sigma}) + \mathbf{F}^{(p)} \tag{III.14}$$

where

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_K + \boldsymbol{\sigma}_U \tag{III.15}$$

is a pressure tensor and

$$\mathbf{F}^{(p)} = [\nabla_{\mathbf{R}}\{\mathbf{E}^e(\mathbf{R}) - \int^V \mathsf{T}(\mathbf{R}, \mathbf{R}') \cdot \mathbf{P}(\mathbf{R}')d\mathbf{R}'\}] \cdot \mathbf{P}(\mathbf{R}) = (\nabla_{\mathbf{R}} \mathbf{E}) \cdot \mathbf{P} \tag{III.16}$$

is a force per unit volume.* In Eq. III.16, **E** is the average electric field strength at **R**, given, within the approximations of Section III.B, by

$$\begin{aligned} \mathbf{E}(\mathbf{R}) &= \mathbf{E}^e(\mathbf{R}) - \langle \sum_k \mathsf{T}(\mathbf{R}, \mathbf{R}_k) \cdot \boldsymbol{\mu}_k f \rangle \\ &= \mathbf{E}^e(\mathbf{R}) - \int^V \mathsf{T}(\mathbf{R}, \mathbf{R}') \cdot \mathbf{P}(\mathbf{R}')\, d\mathbf{R}' \end{aligned} \tag{III.17}$$

Before we identify $\boldsymbol{\sigma}$ with the total pressure tensor and $\mathbf{F}^{(p)}$ with the ponderomotive force, we wish to investigate the balance of total momentum of the charged particles.

Defining

$$\mathbf{g} = \langle \sum_{k,i} m_{ki} \dot{\mathbf{R}}_{ki}\, \delta(\mathbf{R}_{ki} - \mathbf{R}) f \rangle \tag{III.18}$$

as the total density of momentum, one can show that

$$\frac{\partial \mathbf{g}}{\partial t} = -\nabla_{\mathbf{R}} \cdot (\varrho_m \mathbf{v}\mathbf{v} + \boldsymbol{\sigma} + \boldsymbol{\sigma}') + \mathbf{F}^{(p)} \tag{III.19}$$

---

* The result of Eq. III.16 may also be written $(\mathbf{P} \cdot \nabla_{\mathbf{R}})\mathbf{E}$, since curl $\mathbf{E} = 0$. Inclusion of the term omitted in Eq. III.5 (see footnote p. 327) leads to the additional term $(\nabla_{\mathbf{R}} \nabla_{\mathbf{R}} \mathbf{E}^e) : \mathbf{Q}$, or in the approximation of Eq. III.5 $(\nabla_{\mathbf{R}} \nabla_{\mathbf{R}} \mathbf{E}) : \mathbf{Q}$, with $\mathbf{Q} = \langle \frac{1}{2} \Sigma_{k,i}\, e_{ki} \mathbf{r}_{ki} \mathbf{r}_{ki}\, \delta(\mathbf{R}_k - \mathbf{R}) f \rangle$ the density of quadrupole moment.

where the quantity

$$\boldsymbol{\sigma}' = \left\langle \left(\frac{d}{dt} \sum_i m_{ki} \mathbf{r}_{ki} \dot{\mathbf{r}}_{ki} \right) \delta(\mathbf{R}_k - \mathbf{R}) f \right\rangle \qquad \text{(III.20)}$$

Equation III.19 leads to an interpretation of $\boldsymbol{\sigma}+\boldsymbol{\sigma}'$ as the pressure tensor of the medium with $\boldsymbol{\sigma}'$ a contribution to the pressure tensor due to the internal degrees of freedom of the atoms.

Furthermore Eq. III.20 leads to an interpretation of $\mathbf{F}^{(p)}$ as the ponderomotive force per unit volume. The result Eq. III.16 for this ponderomotive force corresponds to the expression proposed by Kelvin by setting the ponderomotive force equal to the force exerted by the Maxwell field **E** on a point dipole of moment **P**.

We also wish to mention that the quantity $\boldsymbol{\sigma}'$ vanishes under certain frequently realized conditions, i.e., when the so-called adiabatic approximation holds for the internal motions of the atoms. In this case

$$\frac{\partial \mathbf{g}}{\partial t} = \frac{\partial \varrho_m \mathbf{v}}{\partial t} = -\nabla_{\mathbf{R}} \cdot (\varrho_m \mathbf{v}\mathbf{v} + \boldsymbol{\sigma}) + \mathbf{F}^{(p)} \qquad \text{(III.21)}$$

and the change in average total momentum is equal to the change in average translational momentum.

D. Alternative Form of Ponderomotive Force and Pressure at Equilibrium

In this section we wish to show that an alternative form for the ponderomotive force, proposed by Helmholtz, can also be justified by statistical-mechanical methods and that its relation to the ponderomotive force and pressure derived in the previous section is the same as found from purely thermodynamical arguments.[16] Helmholtz arrives at an expression for the ponderomotive force on the basis of macroscopic energy considerations for a dielectric subjected to reversible transformations. We are thus led to develop this part of the theory by considering a system in equilibrium. Since the system need not be uniform (due to the presence of a nonuniform external field), we shall divide it into a number of cells. Each cell contains a large number of atoms, but is sufficiently small to be considered macroscopically uniform. This means that all macroscopic quantities should be slowly varying functions of space coordinates.

We may represent the thermal behavior of a subsystem in a cell, which we assume to be of spherical shape, by a canonical ensemble. The distribution function will then be given by

$$f = e^{(F-H)/kT} \tag{III.22}$$

where $F(V, T)$ is the Helmholtz free energy, and H is the Hamiltonian of the subsystem. In the same approximation as introduced in Eq. III.5, the Hamiltonian reduces to

$$H = K + U = K + \frac{1}{8\pi} \sum_{k} \sum_{i,j,i\neq j} \frac{e_{ki}\, e_{kj}}{|\mathbf{r}_{ki} - \mathbf{r}_{kj}|} + \tfrac{1}{2} \sum_{k,l,k\neq l} \mathsf{T}_{kl} : \boldsymbol{\mu}_k \boldsymbol{\mu}_l - \sum_{k} \boldsymbol{\mu}_k \cdot \mathbf{E}^e \tag{III.23}$$

where K is the total kinetic energy and U the total potential energy. The second term in the last member of Eq. III.23 represents the Coulomb energy within each atom. The field $\mathbf{E}^e$ is the uniform external field for the spherical cell and therefore contains the field due to the average polarization of the remaining parts of the system. From Eqs. III.22 and III.23 the following relation can be obtained by the usual scale factor method:

$$\begin{aligned} -\,(\partial F/\partial V)_{T,\mathbf{E}^e} = {} & \frac{1}{3V} \{\langle \sum_{k} m_k \dot{R}_k^2 f\rangle - \langle \sum_{k} \mathbf{R}_\lambda \cdot (\nabla_{\mathbf{R}_k} U) f\rangle\} \\ & + \frac{1}{3V} \{\langle \sum_{k,i} m_{ki} \dot{r}_{ki}^2 f\rangle - \langle {\sum_{k,i}}' \mathbf{r}_{ki} \cdot (\nabla_{\mathbf{r}_{ki}} U) f\rangle\} \end{aligned} \tag{III.24}$$

where use has been made of the fact that the kinetic energy for each degree of freedom is equal to $\frac{1}{2}kT$. In the last term on the right-hand side of Eq. III.24 the prime indicates that the summation must be carried out only over independent coordinates $\mathbf{r}_{ki}$. Equation III.24 has been derived using the classical distribution function Eq. III.22. The same Eq. III.24 is obtained in quantum theory with the Wigner distribution function of a canonical ensemble. The last two terms in Eq. III.24 cancel if we assume that the quantity $\boldsymbol{\sigma}'$ (cf. Eq. III.20) vanishes, so that

$$
\begin{aligned}
-(\partial F/\partial V)_{T,\mathbf{E}^e} &= \frac{1}{3V}\langle\sum_k m_k \dot{R}_k{}^2 f\rangle - \frac{1}{3V}\langle\sum_k \mathbf{R}_k\cdot(\nabla_{\mathbf{R}_k}U)f\rangle \\
&= \frac{1}{3V}\langle\sum_k m_k \dot{R}_k{}^2 f\rangle - \frac{1}{6V}\langle\sum_{k,\,l,\,k\neq l}(\mathbf{R}_k-\mathbf{R}_l)\cdot(\nabla_{\mathbf{R}_k}\mathsf{T}_{kl}):\boldsymbol{\mu}_k\boldsymbol{\mu}_l f\rangle \\
&= \frac{1}{3V}\langle\sum_k m_k \dot{R}_k{}^2 f\rangle - \frac{1}{6V}\langle\sum_{k,\,l,\,k\neq l}(\mathbf{R}_k-\mathbf{R}_l)\cdot(\nabla_{\mathbf{R}_k}\mathsf{T}_{kl}):\{\boldsymbol{\mu}_k\boldsymbol{\mu}_l\}f\rangle \\
&\quad - \frac{1}{6V}\langle\sum_{k,\,l,\,k\neq l}(\mathbf{R}_k-\mathbf{R}_l)\cdot(\nabla_{\mathbf{R}_k}\mathsf{T}_{kl}):\overline{\boldsymbol{\mu}}_k\overline{\boldsymbol{\mu}}_l f\rangle \qquad \text{(III.25)} \\
&= \frac{1}{3V}\langle\sum_k m_k \dot{R}_k{}^2 f\rangle - \frac{1}{6V}\langle\sum_{k,\,l,\,k\neq l}(\mathbf{R}_k-\mathbf{R}_l)\cdot(\nabla_{\mathbf{R}_k}\mathsf{T}_{kl}):\{\boldsymbol{\mu}_k\boldsymbol{\mu}_l\}f\rangle \\
&\quad - \frac{1}{6V}\int^V\!\!\int^V(\mathbf{R}-\mathbf{R}')\cdot\{\nabla_{\mathbf{R}}\mathsf{T}(\mathbf{R},\mathbf{R}')\}:\mathbf{P}(\mathbf{R})\mathbf{P}(\mathbf{R}')\{g(\mathbf{R},\mathbf{R}')-1\}d\mathbf{R}\,d\mathbf{R}' \\
&\quad - \frac{1}{6V}\int^V\!\!\int^V(\mathbf{R}-\mathbf{R}')\cdot\{\nabla_{\mathbf{R}}\mathsf{T}(\mathbf{R},\mathbf{R}')\}:\mathbf{P}(\mathbf{R})\mathbf{P}(\mathbf{R}')d\mathbf{R}\,d\mathbf{R}'
\end{aligned}
$$

using Eqs. III.8, III.9, III.11, and III.23. Since the subsystem is uniform, the first three terms of the last member of Eq. III.23 may also be written

$$
\begin{aligned}
&\tfrac{1}{3}\langle\sum_k m_k \dot{R}_k{}^2\delta(\mathbf{R}_k-R)f\rangle \\
&\qquad -\tfrac{1}{6}\langle\sum_{k,\,l,\,k\neq l}(\mathbf{R}_k-\mathbf{R}_l)\cdot(\nabla_{\mathbf{R}_k}\mathsf{T}_{kl}):\{\boldsymbol{\mu}_k\boldsymbol{\mu}_l\}\delta(\mathbf{R}_k-\mathbf{R})f\rangle \qquad \text{(III.26)} \\
&\qquad -\tfrac{1}{6}\int^\infty(\mathbf{R}-\mathbf{R}')\cdot\{\nabla_{\mathbf{R}}\mathsf{T}(\mathbf{R},\mathbf{R}')\}:\mathbf{P}(\mathbf{R})\mathbf{P}(\mathbf{R}')\{g(\mathbf{R},\mathbf{R}')-1\}d\mathbf{R}'
\end{aligned}
$$

Comparing with Eqs. III.2 and III.13, it is seen that Eq. III.26 is $\frac{1}{3}$ of the trace of the pressure tensor $\boldsymbol{\sigma}$ (cf. Eq. III.15), i.e., the hydrostatic pressure of the medium

$$p = \tfrac{1}{3}\,\mathrm{Tr}\,\boldsymbol{\sigma} \qquad \text{(III.27)}$$

The mean velocity $\mathbf{v}$ which occurs in Eq. III.2 is zero here. Since T_{kl} is of the degree -3 in the components of $(\mathbf{R}_k-\mathbf{R}_l)$, the last term of Eq. III.25 reduces to

$$\frac{1}{2V}\int^V\!\!\int^V\mathsf{T}(\mathbf{R},\mathbf{R}'):\mathbf{P}(\mathbf{R})\mathbf{P}(\mathbf{R}')d\mathbf{R}\,d\mathbf{R}' = \tfrac{1}{2}\mathbf{P}\cdot\int^V\mathsf{T}(\mathbf{R},\mathbf{R}')\cdot\mathbf{P}\,d\mathbf{R}' \qquad \text{(III.28)}$$

because $\mathbf{P}$ and $-\int^V \mathsf{T}(\mathbf{R}, \mathbf{R}')d\mathbf{R}'$, the depolarization factor of the sphere, are uniform.

Finally one obtains for Eq. III.25

$$-(\partial F/\partial V)_{T,\mathbf{E}^e} = p + \tfrac{1}{2}\mathbf{P}\cdot\int^V \mathsf{T}(\mathbf{R}, \mathbf{R}')\cdot\mathbf{P}d\mathbf{R}' \qquad \text{(III.29)}$$

On the other hand, one may also obtain from Eqs. III.22 and III.23

$$(\partial F/\partial \mathbf{E}^e)_{V,T} = -\langle\sum_i \boldsymbol{\mu}_i f\rangle = -V\mathbf{P} \qquad \text{(III.30)}$$

The free energy F may be written as

$$F(V, T, \mathbf{E}^e) = F(V, T, 0) + \Delta F \qquad \text{(III.31)}$$

where ΔF is given by

$$\Delta F = \int(\partial F/\partial \mathbf{E}^e)\cdot d\mathbf{E}^e = -V\int P\cdot d\mathbf{E}^e = -\tfrac{1}{2}V\mathbf{E}^e\cdot\mathbf{P} \qquad \text{(III.32)}$$

Here Eq. III.30 has been used, and a linear relationship has been assumed between $\mathbf{P}$ and $\mathbf{E}^e$. Using Eqs. III.31 and III.32, Eq. III.29 may be transformed into

$$p = p^0 + \tfrac{1}{2}\mathbf{P}\cdot\mathbf{E} + \tfrac{1}{2}V(\partial\mathbf{P}/\partial V)_{T,\mathbf{E}^e}\cdot\mathbf{E}^e \qquad \text{(III.33)}$$

where

$$p^0 = -\{\partial F(T, V, 0)/\partial V\}_{T,\mathbf{E}^e} \qquad \text{(III.34)}$$

is the pressure the medium would have in the absence of an external field, but at the same volume and temperature. Use has also been made of the relation between the Maxwell field $\mathbf{E}$ and the external field (cf. Eq. III.17). It follows in a straightforward manner that

$$(\partial\mathbf{P}/\partial V)_{T,\mathbf{E}^e}\cdot\mathbf{E}^e = (\partial\mathbf{P}/\partial V)_{T,\mathbf{E}}\cdot\mathbf{E} \qquad \text{(III.35)}$$

so that one finally obtains

$$p = p^0 + \tfrac{1}{2}\mathbf{P}\cdot\mathbf{E} + \tfrac{1}{2}V(\partial\mathbf{P}/\partial V)_{T,\mathbf{E}}\cdot\mathbf{E} \qquad \text{(III.36)}$$

In statistical equilibrium the momentum equation (III.21) reads

$$\varrho_m d\mathbf{v}/dt = -\nabla_{\mathbf{R}}p + \mathbf{F}^{(p)} \quad ; \quad d/dt = \partial/\partial t + \mathbf{v}\cdot\text{grad} \qquad \text{(III.37)}$$

because the divergence of $\boldsymbol{\sigma}$ then reduces to the gradient of the scalar pressure p. If Eqs. III.16 and III.36 are introduced into

Eq. III.37 one obtains

$$\varrho_m d\mathbf{v}/dt = -\nabla_{\mathbf{R}} p^0 + \mathbf{F}^{(H)} \qquad \text{(III.38)}$$

with

$$\mathbf{F}^{(H)} = -\tfrac{1}{2}E^2\nabla_{\mathbf{R}}\varkappa - \tfrac{1}{2}\nabla_{\mathbf{R}}\{v(\partial\varkappa/\partial v)_T E^2\} \qquad \text{(III.39)}$$

where $\varkappa$ is the electric susceptibility ($\mathbf{P} = \varkappa\mathbf{E}$).

Equation III.39 is the Helmholtz expression for the ponderomotive force. We notice, however, from Eq. III.38 that if one defines the force in this way, the pressure must be defined to be p^0, i.e., the pressure of the medium in the absence of an external field. This corroborates the thermodynamic theory.

To conclude we may say that we have obtained in this section expressions for the pressure tensor and the ponderomotive force in terms of averages over microscopic quantities.

The statistical derivation shows that the Kelvin type of force has a wider range of validity than the Helmholtz expression since in the derivation of the latter it was necessary to assume statistical equilibrium.

Different expressions are possible, since one may change the definitions for both ponderomotive force and pressure in a consistent way (the sum of the negative divergence of the pressure tensor and the ponderomotive force must remain invariant under such transformations). However, in the different cases the physical meaning of the quantities remains clear through their expressions in terms of the microscopic quantities.

The ambiguity in the definitions of force and pressure is related to the presence of long-range interactions in the medium.

IV. REFRACTION OF LIGHT

A. Introduction

In the present section we shall discuss another aspect of the behavior of matter in an electromagnetic field. We shall analyze by means of statistical-mechanical methods the propagation of electromagnetic waves through a fluid. We shall assume that our system consists of optically isotropic, electrically neutral molecules and derive an explicit expression for the index of refraction of such a system.

In contrast to the present treatment there are two types of earlier theories of refraction of light. Yvon[32] has developed a statistical-mechanical theory of the refractive index. This theory is set up in such a way that an explicit expression is obtained for the index of refraction. It does not, however, contain an analysis of the optical phenomena (such as the extinction of the incident field) which are involved. These last aspects are considered very carefully in the other, electrodynamic, type of theory, which Hoek,[8] following work done by a number of authors,* has presented with great rigor. The disadvantage of this second method is that macroscopic quantities are not obtained by statistical-mechanical methods, but by averaging the microscopic quantities over physically infinitesimal volume elements. The result is that almost all the effect of density fluctuations is lost. Both of the theories mentioned assume furthermore the molecular polarizability to be a constant independent of intermolecular distances.

The statistical-mechanical theory[19] presented in Section IV.B follows closely the electrodynamic method outlined in Hoek's thesis[8] and Rosenfeld's monograph.[26] At the same time we shall take into account explicitly a variation of the polarizability due to molecular interaction.[11,17,18]

B. The Integral Equation for the Average Polarization

In Section I we have defined the average polarization per unit volume as

$$\mathbf{P}(\mathbf{R}) = \sum_i \langle \boldsymbol{\mu}_i \delta(\mathbf{R}_i - \mathbf{R}) f \rangle \qquad \text{(IV.1)}$$

With $\boldsymbol{\mu}_i$ the electric dipole moment of an atom (or molecule) i.

Using the coordinate distribution function $h(\mathbf{R}^N)$ (cf. Eq. I.8), we may rewrite Eq. IV.1 in the following form:

$$\mathbf{P}(\mathbf{R}) = \sum_i \langle \bar{\boldsymbol{\mu}}_i(\mathbf{R}^N) \delta(\mathbf{R}_i - \mathbf{R}) h \rangle \qquad \text{(IV.2)}$$

where the brackets now denote an integration over an N-dimensional coordinate space only, and where $\bar{\boldsymbol{\mu}}_i$ is the average value of

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* For a complete bibliography, see the thesis of H. Hoek (Ref. 8).

$\boldsymbol{\mu}_i$ for a specified configuration of the centers of gravity of the atoms.

We shall consider in the following a system of N identical optically isotropic molecules with uniform average number density ϱ (the index n for the number density has been omitted in this section). We assume that the following molecular equation holds for $\bar{\boldsymbol{\mu}}_i$ in the electric field $\mathbf{E}^0$ of an incident wave of circular frequency ω:

$$\bar{\boldsymbol{\mu}}_i = \boldsymbol{\alpha}_i \cdot [\mathbf{E}^0(\mathbf{R}_i) - \sum_j \mathsf{F}_{ij} \cdot \bar{\boldsymbol{\mu}}_j] \tag{IV.3}$$

where the polarizability tensor $\boldsymbol{\alpha}_i$ is a function of ω and of all intermolecular distances. (For a free molecule $\boldsymbol{\alpha}_i$ reduces to the scalar polarizability α_0.)

In Eq. IV.3 $-\mathsf{F}_{ij} \cdot \bar{\boldsymbol{\mu}}_j$ represents the field at the position of dipole i due to the oscillating dipole $\bar{\boldsymbol{\mu}}_j$. With the help of the Hertz vector $Y_{ij}\bar{\boldsymbol{\mu}}_j$, where Y_{ij} stands for

$$Y_{ij} = \mathrm{e}^{-ikR_{ij}}/4\pi R_{ij}; \quad k = \omega/c \tag{IV.4}$$

this field is given by

$$-\mathsf{F}_{ij} \cdot \bar{\boldsymbol{\mu}}_j = (\nabla_{\mathbf{R}_i} \nabla_{\mathbf{R}_i} + k^2 \mathsf{U}) \cdot Y_{ij} \bar{\boldsymbol{\mu}}_j \tag{IV.5}$$

where U is the unit tensor. For $k = 0$, F_{ij} reduces to the static tensor T_{ij} (cf. Eq. III.6). In Eq. IV.4, R_{ij} is the distance between the centers of molecules i and j.

We shall investigate in Section IV.C in more detail the conditions under which an equation of the form Eq. IV.3 holds for the average $\bar{\boldsymbol{\mu}}_k$ of $\boldsymbol{\mu}_k$. We shall in fact derive such an equation by computing this average, with certain restrictions imposed on the system.

We now introduce the average polarizability $\bar{\boldsymbol{\alpha}}_i = \bar{\boldsymbol{\alpha}}_j = \bar{\alpha}\,\mathsf{U}$, given by

$$\bar{\alpha}\mathsf{U} = \varrho^{-1} \sum_i \langle \boldsymbol{\alpha}_i\, \delta(\mathbf{R}_i - \mathbf{R}) h \rangle \tag{IV.6}$$

and the mean moment $\bar{\boldsymbol{\mu}}_i$* of dipole i defined by

$$\bar{\boldsymbol{\mu}}_i(\mathbf{R}_i) = \int \dots \int \bar{\boldsymbol{\mu}}_i h \prod_{j \neq i} d\mathbf{R}_j \Big/ \int \dots \int h \prod_{j \neq i} d\mathbf{R}_j \tag{IV.7}$$

where $\bar{\boldsymbol{\mu}}_i$ is still a function of the position $\mathbf{R}_i$ of dipole i. Since all dipoles are identical we also have, at an arbitrary position $\mathbf{R}$ in

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* See also Eqs. III.8 and III.12.

three-dimensional space

$$\tilde{\boldsymbol{\mu}}_i(\mathbf{R}) = \tilde{\boldsymbol{\mu}}_j(\mathbf{R}) = \tilde{\boldsymbol{\mu}}(\mathbf{R}) = \mathbf{P}(\mathbf{R})/\varrho \tag{IV.8}$$

On substituting Eq. IV.3 into Eq. IV.2 one obtains

$$\mathbf{P}(\mathbf{R}) = \sum_{i,j,i\neq j} \langle \boldsymbol{\alpha}_i \cdot [\mathbf{E}^0(\mathbf{R}_i) - \mathsf{F}_{ij} \cdot \tilde{\boldsymbol{\mu}}_j]\delta(\mathbf{R}_i - \mathbf{R})h\rangle \tag{IV.9}$$

With the help of Eqs. IV.6 and IV.7, Eq. IV.9 can also be written

$$\mathbf{P}(\mathbf{R}) = \varrho\bar{\alpha}[\mathbf{E}^0(\mathbf{R}) - \varrho^{-1}\int^V \sum_{i,j,i\neq j} \langle \mathsf{F}_{ij} \cdot \bar{\boldsymbol{\mu}}_j \delta(\mathbf{R}_i - \mathbf{R})\delta(\mathbf{R}_j - \mathbf{R}')f\rangle d\mathbf{R}'] + \mathbf{J}(\mathbf{R}) \tag{IV.10}$$

where the integration is performed over the volume V of the system, and $\mathbf{J}(\mathbf{R})$ is defined

$$\mathbf{J}(\mathbf{R}) = \int^V \sum_{i,j,i\neq j} \langle [\bar{\alpha}\mathsf{F}_{ij} \cdot \bar{\boldsymbol{\mu}}_j - \boldsymbol{\alpha}_i \cdot \mathsf{F}_{ij} \cdot \tilde{\boldsymbol{\mu}}_j]\delta(\mathbf{R}_i - \mathbf{R})\delta(\mathbf{R}_j - \mathbf{R}')h\rangle d\mathbf{R}' \tag{IV.11}$$

Equation IV.10 may be put into the alternative form

$$\mathbf{P}(\mathbf{R}) = \varrho\bar{\alpha}[\mathbf{E}^0(\mathbf{R}) - \int^V \mathsf{F}(\mathbf{R}, \mathbf{R}') \cdot \mathbf{P}(\mathbf{R}') \cdot g(\mathbf{R}, \mathbf{R}')d\mathbf{R}'] + \mathbf{J}(\mathbf{R}) \tag{IV.12}$$

where $g(\mathbf{R}, \mathbf{R}')$ is the correlation function, Eq. III.11, for pairs of molecules.

It can be shown (see Appendix III) that $\mathbf{J}(\mathbf{R})$ may be written as

$$\mathbf{J}(\mathbf{R}) = \varrho\bar{\alpha}\int^V \mathsf{K}(\mathbf{R}, \mathbf{R}') \cdot [\mathbf{E}^0(\mathbf{R}') - \int^V \mathsf{F}(\mathbf{R}', \mathbf{R}'') \cdot \mathbf{P}(\mathbf{R}'')g(\mathbf{R}', \mathbf{R}'')d\mathbf{R}'']d\mathbf{R}' \tag{IV.13}$$

where the kernel $\mathsf{K}(\mathbf{R}, \mathbf{R}')$ is a symmetric tensor such that

$$\int \mathsf{K}(\mathbf{R}, \mathbf{R}')d\mathbf{R}' = \mathsf{U}\,\Phi(\varrho, T, \omega) \tag{IV.14}$$

with Φ a function of density, temperature and frequency only for a system in thermal equilibrium.

We note that with the help of the well-known properties of the pair distribution function we have for one of the integrals occurring in Eqs. IV.12 and IV.13

$$\int^{V}\mathsf{F}(\mathbf{R},\mathbf{R}')\cdot\mathbf{P}(\mathbf{R}')g(\mathbf{R},\mathbf{R}')d\mathbf{R}' = \int_{v(\mathbf{R})}^{V}\mathsf{F}(\mathbf{R},\mathbf{R}')\cdot\mathbf{P}(\mathbf{R}')g(\mathbf{R},\mathbf{R}')d\mathbf{R}'$$
$$= \int_{v(\mathbf{R})}^{V}\mathsf{F}(\mathbf{R},\mathbf{R}')\cdot\mathbf{P}(\mathbf{R}')d\mathbf{R}' + \int_{v(\mathbf{R})}^{\infty}\mathsf{F}(\mathbf{R},\mathbf{R}')\cdot\mathbf{P}(\mathbf{R}')[g(\mathbf{R},\mathbf{R}')-1]d\mathbf{R}' \tag{IV.15}$$

Here we have first excluded from integration an (arbitrarily) small sphere centered at **R**. The second integration in the last member of Eq. IV.15 may be performed over the whole of space.

For later use we also introduce the notation $\mathbf{E}^{d}(\mathbf{R})$ for the field due to the average polarization

$$\mathbf{E}^{d}(\mathbf{R}) = -\int_{v(\mathbf{R})}^{V}\mathsf{F}(\mathbf{R},\mathbf{R}')\cdot\mathbf{P}(\mathbf{R}')d\mathbf{R}' \tag{IV.16}$$

Equation IV.12 combined with Eq. IV.13 is the fundamental integral equation connecting the average polarization to the electric field of the incident wave.

C. Generalization of the Lorentz-Lorenz Formula

We will now show that the integral Eq. IV.12 has a solution satisfying the wave equation

$$\Delta\mathbf{P}+k^{2}n^{2}\mathbf{P} = 0 \tag{IV.17}$$

with the accesory condition

$$\operatorname{div}\mathbf{P} = 0 \tag{IV.18}$$

The constant n in Eq.IV.17 will be shown to be identical with the refractive index of the medium.

In order to prove the aforementioned statement we will use Eqs. IV.17 and IV.18 as assumptions and show that n can then be chosen in such a way that Eq. IV.12 becomes an identity. This method has been used previously by several authors[26] starting from an integral equation analogous to Eq. IV.12 and obtained by averaging the molecular Eq. IV.3 over physically infinitesimal volume elements.

Let us choose for **P** a solution of Eqs. IV.17 and IV.18 representing a transverse plane wave propagated in an arbitrary direction. We then have

$$\mathbf{P}(\mathbf{R}') = \mathbf{P}(\mathbf{R})e^{-in\mathbf{k}\cdot(\mathbf{R}'-\mathbf{R})} \tag{IV.19}$$

where the vector $\mathbf{k}$ is the product of k and the unit vector in the direction of propagation.

Using Eq. IV.19, the integral Eq. IV.12 may be brought, after some straightforward transformations, into the form

$$\begin{aligned}\mathbf{P}(\mathbf{R}) = \frac{\varrho\bar{\alpha}}{1+\varrho\bar{\alpha}D(1+R)}\{&\mathbf{E}^0(\mathbf{R})+\mathbf{E}^d(\mathbf{R}) \\ &+\int^V \mathsf{K}(\mathbf{R},\mathbf{R}')\cdot[\mathbf{E}^0(\mathbf{R}')+\mathbf{E}^d(\mathbf{R}')]d\mathbf{R}'\}\end{aligned} \tag{IV.20}$$

with the definitions

$$D(\varrho,T,\omega) = \int_{v(\mathbf{R})}^{\infty} \mathbf{n}\cdot\mathsf{F}(\mathbf{R},\mathbf{R}')\cdot\mathbf{n}\, e^{-ink\cdot(\mathbf{R}'-\mathbf{R})}[g(\mathbf{R},\mathbf{R}')-1]d\mathbf{R}' \tag{IV.21}$$

$$R(\varrho,T,\omega) = \int^V \mathbf{n}\cdot\mathsf{K}(\mathbf{R},\mathbf{R}')\cdot\mathbf{n}\, e^{-in\mathbf{k}\cdot(\mathbf{R}'-\mathbf{R})}d\mathbf{R}' \tag{IV.22}$$

$\mathbf{n}$ denoting the unit vector in the direction of $\mathbf{P}(\mathbf{R})(\mathbf{k}\cdot\mathbf{n}=0)$.

On the other hand, it can be shown,[26] with the assumptions Eqs. IV.17 and IV.18 and providing $n^2 \neq 1$, that the field $\mathbf{E}^d(\mathbf{R})$ may be written as a sum of two terms, i.e.,

$$\begin{aligned}\mathbf{E}^d(\mathbf{R}) = &\frac{1}{3}\frac{n^2+2}{n^2-1}\mathbf{P}(\mathbf{R}) \\ &+\frac{1}{(n^2-1)k^2}\operatorname{curl}_{\mathbf{R}}\operatorname{curl}_{\mathbf{R}}\int^{\Sigma}[\mathbf{P}(\mathbf{R}')Y_n(\mathbf{R},\mathbf{R}')-Y(\mathbf{R},\mathbf{R}')\mathbf{P}_n(\mathbf{R}')]d\mathbf{R}'\end{aligned} \tag{IV.23}$$

The surface integral in Eq. IV.23 is performed over the boundary Σ of the system. The index n denotes the normal derivatives at the boundary in the outward directions. Each term on the right-hand side of Eq. IV.23 obeys a different wave equation. Indeed the first term is assumed to obey Eq. IV.17, whereas the second according to Eq.IV.4 must obey the wave equation *in vacuo.*

Combining now Eqs. IV.23 and IV.20, we obtain an equation containing two groups of terms each satisfying a different wave equation. Hence each group of terms must vanish separately. This yields two equations the first of which establishes the desired relation between the parameter n, the average polarizability, and the density and temperature of the medium

$$\frac{n^2-1}{n^2+2} = \frac{1}{3}\frac{\varrho\bar{\alpha}(1+R)}{1+\varrho\bar{\alpha}D(1+R)} \tag{IV.24}$$

The second equation expresses the extinction of the field $\mathbf{E}^0(\mathbf{R})$ by part of the dipole field and has the form

$$\begin{aligned}\mathbf{E}^0(\mathbf{R})+\frac{1}{(n^2-1)k^2}\,\mathrm{curl}_{\mathbf{R}}\,\mathrm{curl}_{\mathbf{R}}\int^{\Sigma}[\mathbf{P}(\mathbf{R}')Y_n(\mathbf{R},\mathbf{R}')&\\ -Y(\mathbf{R},\mathbf{R}')\mathbf{P}_n(\mathbf{R}')]d\mathbf{R}' = 0.&\end{aligned} \tag{IV.25}$$

We now proceed to show that the constant n may be identified with the complex refractive index of the medium. For this purpose we will evaluate the average electric field $\mathbf{E}(\mathbf{R})$ at an arbitrary point of the medium and show that this field obeys the same wave equation as the average polarization $\mathbf{P}$.

The average electric field $\mathbf{E}(\mathbf{R})$, in the approximation of this section (cf. Eq. IV.3) is given by

$$\mathbf{E}(\mathbf{R}) = \mathbf{E}^0(\mathbf{R})-\sum_j\langle \mathsf{F}(\mathbf{R},\mathbf{R}_j)\cdot\bar{\boldsymbol{\mu}}_j h\rangle \tag{IV.26}$$

where the summation over the index j includes the field of all dipoles. Equation IV.26 is easily transformed into

$$\begin{aligned}\mathbf{E}(\mathbf{R})&=\mathbf{E}^0(\mathbf{R})-\int^{V}\mathsf{F}(\mathbf{R},\mathbf{R}')\cdot\mathbf{P}(\mathbf{R}')d\mathbf{R}'\\ &=\mathbf{E}^0(\mathbf{R})-\int_{v(\mathbf{R})}^{V}\mathsf{F}(\mathbf{R},\mathbf{R}')\cdot\mathbf{P}(\mathbf{R}')d\mathbf{R}'-\int^{v(\mathbf{R})}\mathsf{F}(\mathbf{R},\mathbf{R}')\cdot\mathbf{P}(\mathbf{R}')d\mathbf{R}'\\ &=\mathbf{E}^0(\mathbf{R})+\mathbf{E}^d(\mathbf{R})-\int^{v(\mathbf{R})}\mathsf{F}(\mathbf{R},\mathbf{R}')\cdot\mathbf{P}(\mathbf{R}')d\mathbf{R}'\end{aligned} \tag{IV.27}$$

where the definition, Eq. IV.16, has been used.

Evaluating the last integral in Eq. IV.27 explicitly with the help of Eq. IV.5, we finally obtain in the limit of an infinitely small sphere around the point $\mathbf{R}$,

$$\mathbf{E}(\mathbf{R}) = \mathbf{E}^0(\mathbf{R})+\mathbf{E}^d(\mathbf{R})-\tfrac{1}{3}\mathbf{P}(\mathbf{R}) \tag{IV.28}$$

or with Eqs. IV.23 and IV.25

$$(n^2-1)\mathbf{E}(\mathbf{R}) = \mathbf{P}(\mathbf{R}) \tag{IV.29}$$

Thus $\mathbf{E}(\mathbf{R})$ is indeed propagated with the same velocity as $\mathbf{P}(\mathbf{R})$. This establishes the interpretation of n as the refractive index of the medium. We will discuss Eq. IV.24 which represents a generalization of the Lorentz-Lorenz formula in Section IV.E.

D. The Molecular Equation for the Dipole Moments

In the preceding section we have analyzed the propagation of light in a fluid, and obtained an expression for the refractive index, assuming that the averages $\bar{\boldsymbol{\mu}}_i$ obey a molecular equation (IV.3). We now wish to derive such an equation by actually computing the average $\bar{\boldsymbol{\mu}}_i$ of $\boldsymbol{\mu}_i$ for the case of isotropic nonpolar atoms with nondegenerate ground level. In doing this we shall also obtain an expression for the polarizability $\boldsymbol{\alpha}_i$ of atom i in terms of the polarizability α^0 of the free atom and of the intermolecular distances.

We note that in order to take the quantum behavior of the molecules into account, the function f in Eq. IV.1 should be the Wigner distribution function. Alternatively the average polarization, Eq. IV.1 may be computed with the quantum-mechanical density matrix. We shall assume that the so-called adiabatic approximation is valid in which the "internal" motion of the atoms is described by a wave function ψ satisfying a Schrödinger equation with a Hamiltonian which does not contain the kinetic energy of the center of gravity motions of the atoms. This wave function depends on the internal coordinates and also parametrically on coordinates $\mathbf{R}^N$. The adiabatic approximation holds when the atoms are in their ground state and the translational motion of the atoms is such that the internal modes are not excited through collisions. For the substances under consideration this is therefore a very good approximation over a wide temperature region. The average value of the dipole moment $\boldsymbol{\mu}_i$ for a given configuration of the centers of gravity does not depend in this approximation on the translational kinetic energy of the atoms and is therefore identical with $\bar{\boldsymbol{\mu}}_i$. We thus may write for $\bar{\boldsymbol{\mu}}_i$

$$\bar{\boldsymbol{\mu}}_i = \int \psi^* \boldsymbol{\mu}_i \psi \, d\tau \qquad \text{(IV.30)}$$

For simplicity we will first consider a system of two atoms (labeled 1 and 2) in a periodic external field $\mathbf{E}^0 \cos \omega t$. The frequency ω of the external field should be small compared to the frequency of the softest absorption line.

We impose the following restrictions on our calculation: (1) the molecules interact only through dipole forces; this implies that the mean intermolecular distance is not allowed to become smaller than a certain minimum value; (2) the external field may be considered uniform over the intermolecular distance, i.e., the wavelength is large with respect to that distance. The total Hamiltonian of the system is then given by

$$H = H_0 + \boldsymbol{\mu}_1 \cdot \mathbf{T} \cdot \boldsymbol{\mu}_2 - (\boldsymbol{\mu}_1 + \boldsymbol{\mu}_2) \cdot \mathbf{E}^0 \cos \omega t \qquad \text{(IV.31)}$$

where H^0 is the Hamiltonian of the system consisting of the two noninteracting molecules in the absence of the external field and $\mathbf{T}$ is the tensor characterizing the dipole interaction. The last two terms in Eq. IV.31 represent the perturbation Hamiltonian $\mathscr{H}'$.

The average value of the dipole moment will be calculated by means of Dirac's perturbation theory for nonstationary states, up to third order; the zero order refers to the free molecules in the absence of the field. Let the wave function of the system of the two interacting molecules in the external field be specified by ψ, an eigenfunction of the total Hamiltonian H. This wave function ψ may be expanded in a complete set of the energy eigenfunctions φ_n of the unperturbed system; the index n labels the various unperturbed eigenstates characterized by the energy E_n. We may then write

$$\psi = \sum_n b_n(t) \varphi_n \exp(E_n t/\hbar i) \qquad \text{(IV.32)}$$

If the molecules are sufficiently far apart, the zero-order wave function may be written in terms of the wave functions $u_{n_1}(1)$ and $u_{n_2}(2)$ of the free molecules,

$$\varphi_n = u_{n_1}(1) u_{n_2}(2) \qquad \text{(IV.33)}$$

The coefficients b_n of the expansion, Eq. IV.32, can be calculated in order of approximation (s), by integrating the well-known differential equation

$$\dot{b}_n^{(s)}(t) = (1/\hbar i) \sum_k \mathscr{H}'_{nk}\, b_k^{(s-1)} e^{i\omega_{nk} t} \qquad \text{(IV.34)}$$

with

$$\omega_{nk} = \hbar^{-1}(E_n - E_k) \ , \ \mathscr{H}'_{nk} = \int \varphi_n \mathscr{H}' \varphi_k \, d\tau \qquad \text{(IV.35)}$$

This differential equation will be used for both the time-dependent and time-independent part of the perturbation Hamiltonian.

The coefficients $b_n^{(0)}$ are given by

$$b_n^{(0)} = \delta_{0n} \tag{IV.36}$$

since we assume the free molecules to be in their ground state. Integration constants for coefficients $b_n^{(s)}$, $n \neq 0$, are put equal to zero; integration constants for coefficients $b_0^{(s)}$ are found by normalization.

If we substitute Eqs. IV.32 into Eq. IV.30, we obtain for the different orders of approximation (s) of $\bar{\mu}_1$

$$\bar{\mu}_1^{(s)} = \sum_{s'=0}^{s} \sum_{n,m} b_n^{*(s')} b_m^{(s-s')} (\mu_1)_{nm} e^{i\omega_{nm} t} \tag{IV.37}$$

$$(\mu_1)_{nm} = \int \varphi_n \mu_1 \varphi_m \, d\tau \tag{IV.38}$$

The average $\bar{\mu}_1$ will thus be expressed as a power series in $\mathbf{E}^0$ and T. However, only terms linear in $\mathbf{E}^0$ will be considered. The results for the first three orders of $\bar{\mu}_1$ are[11, 18]

$$\bar{\mu}_1^{(1)} = \alpha_0(\omega)\mathbf{E}^0 \cos \omega t \tag{IV.39}$$

where

$$\alpha_0(\omega)\mathsf{U} = \sum_{n_1 \neq 0} \frac{(\mu_1)_{0n_1}(\mu_1)_{n_1 0}}{\hbar\omega_{n_1 0}(1-\omega^2/\omega_{n_1 0}^2)} \tag{IV.40}$$

is the polarizability of a free molecule;

$$\bar{\mu}_1^{(2)} = -\alpha_0^2(\omega)\mathsf{T} \cdot \mathbf{E}^0 \cos \omega t \tag{IV.41}$$

$$\bar{\mu}_3^{(3)} = \alpha_0^3(\omega)[(C_1+1)\mathsf{T} \cdot \mathsf{T} + C_2\mathsf{T} : \mathsf{TU}] \cdot \mathbf{E}^0 \cos \omega t \tag{IV.42}$$

In Eq. IV.45 C_1 and C_2 are coefficients depending on the frequency ω and the energy spectrum of the free molecules. In general it is difficult to compute C_1 and C_2, but for special molecules and with some further simplifying approximations an evaluation of C_1 and C_2 can be obtained.[11, 18]

Collecting the results of Eqs. IV.39, IV.41, and IV.42, we have

$$\begin{aligned}\bar{\mu}_1^{(1)} = \alpha_0(\omega)[\mathsf{U} - \alpha_0(\omega)\mathsf{T} + \alpha_0^2(\omega)(C_1+1)\mathsf{T} \cdot \mathsf{T} \\ + \alpha_0^2(\omega)C_2\mathsf{T} : \mathsf{TU}] \cdot \mathbf{E}^0 \cos \omega t\end{aligned} \tag{IV.43}$$

Equation IV.43 may be written in the form

$$\tilde{\boldsymbol{\mu}}_1 = \boldsymbol{\alpha}_1 \cdot [\mathbf{E}^0 \cos \omega t - \mathsf{T} \cdot \tilde{\boldsymbol{\mu}}_2] \tag{IV.44}$$

where $\mathbf{E}^0 \cos \omega t - \mathsf{T} \cdot \tilde{\boldsymbol{\mu}}_2$ is representing the "internal field" acting on molecule 1, and $\boldsymbol{\alpha}_1$ is an effective polarizability tensor defined by this relation. Comparing Eqs. IV.43 and IV.44, it is seen that up to terms of order T^2

$$\boldsymbol{\alpha}_1(\omega) = \alpha_0(\omega)[\mathsf{U} + C_1(\omega)\alpha_0^2(\omega)\mathsf{T}\cdot\mathsf{T} + C_2(\omega)\alpha_0^2(\omega)\mathsf{T}:\mathsf{T}\mathsf{U} \ldots] \tag{IV.45}$$

For helium atoms the constants C_1 and C_2 have been evaluated.[11, 18] For small frequencies ω we may write

$$C_1(\omega) = C_1(0) + C'_1 \frac{\omega^2}{\omega_0^2} \tag{IV.46}$$

$$C_2(\omega) = C_2(0) + C'_2 \frac{\omega^2}{\omega_0^2} \tag{IV.47}$$

where ω_0 is an "average absorption frequency" of a helium atom. The values of the constants are

$$C_1(0) = 39/64, \qquad C_2(0) = 29/128$$
$$C'_1 = -329/256, \qquad C'_2 = -55/512$$

Neglecting retardation effects, Eq. IV.45 may easily be generalized to a system consisting of N molecules. The result for the effective polarizability $\boldsymbol{\alpha}_i$ of molecule i is

$$\boldsymbol{\alpha}_i(\omega) = \alpha_0(\omega)[\mathsf{U} + \alpha_0^2(\omega)\, C_1(\omega) \sum_{k \neq i} \mathsf{T}_{ik} \cdot \mathsf{T}_{ki} + \alpha_0^2(\omega)\, C_2(\omega) \sum_{k \neq i} \mathsf{T}_{ik} : \mathsf{T}_{ki}\, \mathsf{U}] \tag{IV.48}$$

where the summation is carried out over all pairs of molecules. Triplet interactions do not contribute in this order of approximation.

Equation IV.48 shows that for a uniform molecular distribution only the interactions with those molecules k which lie close to molecule i contribute to the deviation of $\boldsymbol{\alpha}_i(\omega)$ from $\alpha_0(\omega)\mathsf{U}$. This is consistent with the neglect of retardation effects for sufficiently small ω.

The influence of the molecular interaction increases the polarizability with respect to its value for the unperturbed molecule. Up to order T^2, there is an increase in the polarizability with decreasing intermolecular distance (increasing density). As the frequency of the applied field increases, $\Delta\boldsymbol{\alpha}(\omega)/\alpha_0^3(\omega) = (\boldsymbol{\alpha}(\omega)-\alpha_0(\omega)\mathsf{U})/\alpha_0^3(\omega)$ decreases, because of the negative sign of the coefficients C'_1 and C'_2. It is, however, important to note that the frequency effect introduced into Eq. IV.48 by $C'_1\omega^2/\omega_0^2$ and $C'_2\omega^2/\omega_0^2$ must remain small since we have supposed $\omega^2/\omega_0^2 < 1$.

The quantum-mechanical calculation of this section thus establishes the form of the molecular equation adopted in Sections IV.B and C, and furthermore yields an expression for the change in polarizability due to molecular interactions.

E. Variation of the Lorentz-Lorenz Function with Density

The relation between the refractive index and the polarizability established previously (cf. Eq. IV.24)

$$\varrho^{-1}\frac{n^2-1}{n^2+2} = \frac{\bar{\alpha}}{3}\,\frac{1+R}{1+\varrho\bar{\alpha}D(1+R)} \tag{IV.49}$$

shows that the Lorentz-Lorenz function $\varrho^{-1}(n^2-1)/(n^2+2)$ depends on density for two reasons: the average polarizability is a function of density, and statistical fluctuations occur both in the induced dipole moment and the polarizability of the molecules.

An alternative form for Eq. IV.49 is

$$\varrho^{-1}\frac{n^2-1}{n^2+2} = \tfrac{1}{3}\alpha_0(\omega)\,\frac{[1+(\Delta\bar{\alpha}(\omega)/\alpha_0(\omega))+G(\varrho,T,\omega)]}{1+\varrho\alpha_0(\omega)D[1+(\Delta\bar{\alpha}(\omega)/\alpha_0(\omega))+G(\varrho,\mathrm{T},\omega)]} \tag{IV.50}$$

where $G(\varrho,T,\omega) = \bar{\alpha}(\omega)R/\alpha_0(\omega)$ and $\Delta\bar{\alpha}(\omega) = \bar{\alpha}(\omega)-\alpha_0(\omega)$. Both $\Delta\bar{\alpha}/\alpha_0$ and $G(\varrho,T,\omega)$ can be expanded as power series in α_0, the polarizability of a free molecule (cf. Eq. IV.48 and Appendix III). Up to terms of order α_0^2 the function $G(\varrho,T,\omega)$ is given by

$$\begin{aligned} G_2(\varrho,T,\omega) &= \alpha_0^2(\omega)\varrho\int \mathbf{n}\cdot\mathsf{F}(\mathbf{R},\mathbf{R}'')\cdot\mathsf{F}(\mathbf{R}'',\mathbf{R})\cdot\mathbf{n}g(\mathbf{R},\mathbf{R}'')d\mathbf{R}'' \\ &\quad+\alpha_0^2(\omega)\varrho^2\int \mathbf{n}\cdot\mathsf{F}(\mathbf{R},\mathbf{R}'')\cdot\mathsf{F}(\mathbf{R}'',\mathbf{R}')\cdot\mathbf{n} \\ &\quad[g(\mathbf{R},\mathbf{R}'',\mathbf{R}')-g(\mathbf{R},\mathbf{R}'')g(\mathbf{R}'',\mathbf{R}')]e^{-in\mathbf{k}\cdot(\mathbf{R}'-\mathbf{R})}d\mathbf{R}'d\mathbf{R}'' \end{aligned} \tag{IV.51}$$

where $\varrho^3 g(\mathbf{R}, \mathbf{R}'', \mathbf{R}')$ is the distribution function for three particles. Up to this order $G(\varrho, T, \omega)$ is identical with the correction term found by Yvon taking a constant polarizability.

If the wavelength of the incident radiation is large compared to the correlation length between molecules (this is the case for visible light and gases at moderate density), it has been shown by Yvon that the integrals in Eq. IV.51 reduce in first approximation to the corresponding expressions of the static case (see Ref. 32, Eq. IV.34)

$$\begin{aligned} G_2(\varrho, T, \omega) &= S_2(\varrho, T, \omega) \\ &= \alpha_0^2(\omega)\varrho \int \mathbf{n} \cdot \mathsf{T}(\mathbf{R}, \mathbf{R}'') \cdot \mathsf{T}(\mathbf{R}'', \mathbf{R}) \cdot \mathbf{n} g(\mathbf{R}, \mathbf{R}'') d\mathbf{R}'' \\ &+ \alpha_0^2(\omega)\varrho^2 \int \mathbf{n} \cdot \mathsf{T}(\mathbf{R}, \mathbf{R}'') \cdot \mathsf{T}(\mathbf{R}'', \mathbf{R}') \cdot \mathbf{n} \qquad \text{(IV.52)} \\ &\qquad \{g(\mathbf{R}, \mathbf{R}'', \mathbf{R}') - g(\mathbf{R}, \mathbf{R}'') g(\mathbf{R}'', \mathbf{R}')\} d\mathbf{R}' d\mathbf{R}'' \end{aligned}$$

This is due to the fact that practically only a very small volume surrounding the point **R** contributes to the integrals and that inside this region all retardation effects can be neglected. In the same approximation the function $D(\varrho, T, \omega)$ given by Eq. IV.21 may be altogether neglected.

Hence in this order of approximation Eq. IV.50 may be written as

$$\varrho^{-1}(n^2-1)/(n^2+2) = \tfrac{1}{3}\alpha_0(\omega)[1+(\Delta\bar{\alpha}(\omega)/\alpha_0(\omega)) + S_2(\varrho, T, \omega)] \qquad \text{(IV.53)}$$

where now $\Delta\bar{\alpha}(\omega)$ must only be evaluated up to terms in $\alpha_0^3(\omega)$. The corresponding expression obtained by Yvon does, of course, not contain the term $\Delta\bar{\alpha}/\alpha_0$.

The function

$$R'(\omega) = \frac{3}{\varrho\alpha_0(\omega)} \frac{n^2-1}{n^2+2} - 1 = \frac{\Delta\bar{\alpha}(\omega)}{\alpha_0(\omega)} + S_2(\varrho, \mathrm{T}, \omega) \qquad \text{(IV.54)}$$

has been explicitly evaluated,[18] for helium gas, using the results of Section IV.D, at certain reduced temperatures $T^* = kT/\varepsilon$ (with ε the depth of the interaction potential at the position of minimum energy).

In order to give an idea of the magnitude of the various effects involved we give values of $R'(\omega)$ for the reduced temperatures $T^* = 1.33$ and $T^* = 2.49$ at two densities (50 and 100 amagat units) and for the values 0, 0.01, and 0.1 of the ratio ω^2/ω_0^2, neglecting quantum effects on the distribution functions (see Table I).

TABLE I. Values of $\Delta\bar{\alpha}(\omega)/\alpha_0(\omega)$, $S_2(\omega)$, and $R'(\omega)\times 10^4$, for Helium Atoms as a Function of Density, Frequency, and of the Reduced Temperature T^*.

d Amagat	$\dfrac{\Delta\bar{\alpha}(0)}{\alpha_0(0)}$	$R'(0)$	$\omega^2/\omega_0^2=0.1$			$\omega^2/\omega_0^2=0.01$		
			$\Delta\bar{\alpha}(\omega)/\alpha_0(\omega)$	$S_2(\omega)$	$R'(\omega)$	$\Delta\bar{\alpha}(\omega)/\alpha_0(\omega)$	$S_2(\omega)$	$R'(\omega)$
$T^* = 1.33$								
100	1.26	2.16	1.35	1.08	2.43	1.27	0.92	2.19
50	0.63	1.10	0.675	0.565	1.24	0.635	0.48	1.115
$T^* = 2.49$								
100	1.09	1.88	1.17	0.95	2.12	1.10	0.81	1.91
50	0.55	0.96	0.59	0.49	1.08	0.555	0.42	0.975

We only give values at 50 and 100 amagat units, since the theory is restricted to low densities and since $R'(\omega)$ is practically a linear function of ϱ in this region.

It is seen that the effect of the variation of the polarizability is of the same order of magnitude as the effect of statistical fluctuations in the dipole moments $\tilde{\mu}$ described by the functions S_2. For the highest frequencies which may be considered within the approximation introduced into the calculation, the correction to the Lorentz-Lorenz function is about 15 per cent larger than the corresponding correction for the static case, (i.e., to the Clausius-Mossotti function). A similar qualitative behavior may be expected for other noble gases under the same conditions.

Experimentally Uhlig, Kirkwood, and Keyes[30] observed an increase of the Clausius-Mossotti function for compressed CO_2 up to 200 atm. The experiments for the same gas by Michels and Michels[21] showed that at higher densities (corresponding to pressures of about 1000 atm.), the Clausius-Mossotti function decreases with increasing pressure. These experiments were later repeated with increased accuracy by Michels and Kleerekoper;[22] the result is that the Clausius-Mossotti function first increases with density, goes through a maximum at about 2000 atm. and then decreases. For monoatomic molecules only a few data are available. Michels, ten Seldam, and Overdijk[21] measured the change in the Clausius-Mossotti function with density for argon up to a density of about 5000 amagat, and Michels and Botzen[23] performed analogous experiments for the Lorentz-Lorenz expression $(n^2-1)V/(n^2+2)$. The same general results are obtained: the Clausius-Mossotti and Lorentz-Lorenz functions first increase slightly with increasing pressure and then decrease. Unfortunately the previous calculations are very difficult to perform for argon: no values have as yet been obtained in this case for the constants C_1 and C_2. On the other hand, de Boer, van der Maesen, and ten Seldam[4] have computed the function S_2 for argon. Assuming the polarizability to be constant, they obtained qualitatively a good agreement for the Clausius-Mossotti function with the experimental values. However, at low densities the experimental curve seems to increase twice as rapidly as their theory predicts. This is in agreement with the behavior predicted for helium if one takes the change in polarizability into account (cf. Table I).

V. MOLECULAR THEORY OF LIGHT SCATTERING

A. Introduction

A topic related to the subject of the previous chapter is the molecular theory of light scattering. Such a theory has been given by Zimm[33] and especially by Yvon.[32] More recently Fixman[6] has given a careful analysis of light scattering from the molecular point of view for a one-component system of isotropic scattering molecules. Fixman takes over, with some interesting modifications, Yvon's statistical-mechanical treatment and considers the connection of the molecular theory with the Einstein-Smoluchowski[5, 28] phenomenological theory of light scattering (at least up to the order of approximation to which it is reasonable to carry out the molecular theory).

In the following we shall follow in some respects Fixman's exposition of the subject, but introduce a more direct way* of expanding the microscopic electric field. In this last respect we follow closely our own presentation of the theory of refraction. The results obtained agree with those of Fixman.

B. The Microscopic Field

We consider again a uniform system of N optically isotropic nonpolar molecules, in an electric field $\mathbf{E}^0$ of an incident wave of circular frequency ω. As in Section IV, the average dipole moment $\tilde{\boldsymbol{\mu}}_i$ of molecule i for a given configuration of the center of gravity is assumed to be given by the molecular equation

$$\tilde{\boldsymbol{\mu}}_i = \boldsymbol{\alpha}_i \cdot [\mathbf{E}^0 - \sum_{k \neq i} \mathsf{F}_{ik} \cdot \tilde{\boldsymbol{\mu}}_k] \tag{V.1}$$

and the "microscopic" electric field $\tilde{\mathbf{e}}(\mathbf{R}_0)$, i.e., the field at an arbitrary point $\mathbf{R}_0$ averaged over the internal coordinates and momenta of the molecules, by (cf. IV.3)

$$\tilde{\mathbf{e}}(\mathbf{R}_0) = \mathbf{E}^0(\mathbf{R}_0) - \sum_i \mathsf{F}(\mathbf{R}_0, \mathbf{R}_i) \cdot \tilde{\boldsymbol{\mu}}_i \tag{V.2}$$

This field satisfies the partial differential equation

$$\left.\begin{aligned} k^2 \tilde{\mathbf{e}} - \operatorname{curl}_{\mathbf{R}} \operatorname{curl}_{\mathbf{R}} \tilde{\mathbf{e}} &= -k^2 \sum_i \tilde{\boldsymbol{\mu}}_i \delta(\mathbf{R}_i - \mathbf{R}) \\ \nabla_{\mathbf{R}} \cdot \tilde{\mathbf{e}} &= -\sum_i \tilde{\boldsymbol{\mu}}_i \cdot \nabla_{\mathbf{R}} \delta(\mathbf{R}_i - \mathbf{R}) \end{aligned}\right. \tag{V.3}$$

We wish to write the solution of Eq. V.3 in a form different from Eq. V.2 and more suitable for the present discussion. For this purpose we introduce the vector potential $\tilde{\mathbf{a}}$ and the scalar potential $\tilde{\varphi}$

$$\tilde{\mathbf{e}} = -\nabla \tilde{\varphi} - ik\tilde{\mathbf{a}} \tag{V.4}$$

and define a Hertz vector $\tilde{\boldsymbol{\pi}}$

$$in^2 k \tilde{\boldsymbol{\pi}} = \tilde{\mathbf{a}} \tag{V.5}$$

$$-\nabla \cdot \tilde{\boldsymbol{\pi}} = \tilde{\varphi} \tag{V.6}$$

where n^2 is for the moment an arqitrary constant.

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* The author is indebted to Mr. B. J. Postma for help with the presentation of the theory given in Section V.

Substituting Eqs. V.5 and V.6 into Eq. V.4, we obtain for $\tilde{\mathbf{e}}$

$$\tilde{\mathbf{e}} = \nabla\nabla\cdot\tilde{\boldsymbol{\pi}} + n^2k^2\tilde{\boldsymbol{\pi}} \tag{V.7}$$

From Eqs. V.7 and V.3 it then follows after a straightforward calculation that $\tilde{\boldsymbol{\pi}}$ satisfies the equation

$$\Delta\tilde{\boldsymbol{\pi}} + n^2k^2\tilde{\boldsymbol{\pi}} = -(1/n^2)\{\sum_i \tilde{\boldsymbol{\mu}}_i\delta(\mathbf{R}_i-\mathbf{R}) - (n^2-1)\tilde{\mathbf{e}}\} \tag{V.8}$$

where the right-hand side may be considered as a source function.

The solution of Eq. V.8 is

$$\tilde{\boldsymbol{\pi}}(\mathbf{R}_0) = \int^V \tilde{Y}(\mathbf{R}_0, \mathbf{R})\{\sum_i \tilde{\boldsymbol{\mu}}_i\delta(\mathbf{R}_i-\mathbf{R}) - (n^2-1)\tilde{\mathbf{e}}(\mathbf{R})\}d\mathbf{R} + \tilde{\boldsymbol{\pi}}^0(\mathbf{R}_0), \tag{V.9}$$

where

$$\tilde{Y}(\mathbf{R}_0, \mathbf{R}) = \frac{\exp\{-ink(|\mathbf{R}_0-\mathbf{R}|)\}}{4\pi n^2|\mathbf{R}_0-\mathbf{R}|} \tag{V.10}$$

and where $\tilde{\boldsymbol{\pi}}^0(\mathbf{R}_0)$ is the solution of the homogeneous equation corresponding to Eq. V.8.

From Eqs. V.7 and V.9 we then obtain for the solution $\tilde{\mathbf{e}}(\mathbf{R}_0)$ of Eq. V.3

$$\tilde{\mathbf{e}}(\mathbf{R}_0) = -\int^V \tilde{\mathsf{F}}(\mathbf{R}_0, \mathbf{R})\cdot\{\sum_i \tilde{\boldsymbol{\mu}}_i\delta(\mathbf{R}_i-\mathbf{R}) - (n^2-1)\tilde{\mathbf{e}}(\mathbf{R})\}d\mathbf{R} + \tilde{\mathbf{e}}^0(\mathbf{R}_0) \tag{V.11}$$

where

$$\tilde{\mathsf{F}}(\mathbf{R}_0, \mathbf{R}) = -(\nabla_{\mathbf{R}_0}\nabla_{\mathbf{R}_0} + k^2n^2\,\mathsf{U})\tilde{Y}(\mathbf{R}_0, \mathbf{R}) \tag{V.12}$$

and where the integral is over the volume V of the system.

The solution, Eq. V.11, is identical to the solution, Eq. V.2. We notice that Eq. V.11 explicitly reduces to Eq. V.2 if the arbitrary constant $n = 1$, since then $\tilde{\mathsf{F}}(\mathbf{R}_0, \mathbf{R}) = \mathsf{F}(\mathbf{R}_0, \mathbf{R})$ and since the solution of the homogeneous equation $\tilde{\mathbf{e}}^0$ is then simply the incident field $\mathbf{E}^0$ (cf. Eqs. V.7 and V.8).

On the other hand, if n is the index of refraction of the medium, the solution of the homogeneous equation is the average field **E**. Indeed if Eq. V.11 is averaged over all microscopic configurations, the first term vanishes, because of relation (Eq. IV.29) between the average polarization and the average field, so that the average field $\mathbf{E}(\mathbf{R}_0)$ must be equal to $\overset{\frown}{\mathbf{e}}{}^0(\mathbf{R}_0)$. From Eqs. V.7 and V.8 it follows furthermore, that, with n^2 the index of refraction, $\overset{\frown}{\mathbf{e}}{}^0$ satisfies the wave equation

$$\Delta \overset{\frown}{\mathbf{e}}{}^0 + n^2 k^2 \overset{\frown}{\mathbf{e}}{}^0 = 0 \tag{V.13}$$

i.e., the wave equation is also satisfied by the average field $\mathbf{E}$ (cf. Section IV.C).

For the discussion of the scattering of light, we wish to write $\overset{\frown}{\mathbf{e}}(\mathbf{R}_0)$ in the form of Eq. V.11 with n^2 the index of refraction. If $\mathbf{R}_0$ is any point in the medium not inside the refracted beam, then $\mathbf{E}(\mathbf{R}_0) = 0$, and we have simply

$$\overset{\frown}{\mathbf{e}}(\mathbf{R}_0) = -\int^V \tilde{\mathsf{F}}(\mathbf{R}_0, \mathbf{R}) \cdot \{\sum_i \overset{\frown}{\boldsymbol{\mu}}_i \delta(\mathbf{R}_i - \mathbf{R}) - (n^2-1)\overset{\frown}{\mathbf{e}}(\mathbf{R})\} d\mathbf{R} \tag{V.14}$$

According to Eq. V.2, for $\overset{\frown}{\mathbf{e}}(\mathbf{R}_0)$, the microscopic field, at a position where both $\mathbf{E}^0$ and $\mathbf{E}$ vanish, is due to the partial fields radiated by its dipoles *in vacuo.* Yvon[32] uses this form as a basis for the discussion of light scattering. According to Eq. V.14, however, this field can be considered as being due to scattering from local "fluctuations" of the refractive index, through a medium of refractive index n. This second form was adopted by Fixman,[6] whose presentation we follow in this respect. The advantage of Eq. V.14 is that, when averaged, its source function vanishes everywhere, whereas in Eq. V.2 the result $\mathbf{E}(\mathbf{R}_0) = 0$, (with $\mathbf{E}^0(\mathbf{R}_0) = 0$) corresponds to a destructive interference of the averaged fields emitted by the dipoles.

C. Expansion of the Microscopic Field as a Power Series in α_0

Equation V.14 may be rewritten in the form

$$\overset{\frown}{\mathbf{e}}(\mathbf{R}_0) = -\int^V \tilde{\mathsf{F}}(\mathbf{R}_0, \mathbf{R}) \cdot [\{\sum_i \overset{\frown}{\boldsymbol{\mu}}_i \delta(\mathbf{R}_i - \mathbf{R}) - \varrho \bar{\boldsymbol{\mu}}_i(\mathbf{R})\} \\ - (n^2-1)(\overset{\frown}{\mathbf{e}}(\mathbf{R}) - \mathbf{E}(\mathbf{R}))] d\mathbf{R} \tag{V.15}$$

where we have used again the relation $\mathbf{P} = \varrho \overset{\frown}{\boldsymbol{\mu}}_i = (n^2-1)\mathbf{E}$ between average polarization and average field.

According to Eqs. V.2 and IV.27 we may write

$$\begin{aligned}\overset{\frown}{\mathbf{e}}(\mathbf{R})-\mathbf{E}(\mathbf{R}) &= -\int^{V}\mathsf{F}(\mathbf{R},\mathbf{R}')\cdot\{\sum_{i}\overset{\frown}{\boldsymbol{\mu}}_{i}\delta(\mathbf{R}_{i}-\mathbf{R}')-\varrho\bar{\boldsymbol{\mu}}(\mathbf{R}')\}d\mathbf{R}' \\ &= -\int_{v(\mathbf{R})}^{V}\mathsf{F}(\mathbf{R},\mathbf{R}')\cdot\{\sum_{i}\overset{\frown}{\boldsymbol{\mu}}_{i}\delta(\mathbf{R}_{i}-\mathbf{R}')-\varrho\bar{\boldsymbol{\mu}}(\mathbf{R}')\}d\mathbf{R}' \\ &\quad -\tfrac{1}{3}\{\sum_{i}\overset{\frown}{\boldsymbol{\mu}}_{i}\delta(\mathbf{R}_{i}-\mathbf{R})-\varrho\bar{\boldsymbol{\mu}}(\mathbf{R})\} \end{aligned} \tag{V.16}$$

In the first term of the last member of Eq. V.16 an infinitely small sphere, $v(\mathbf{R})$, centered at $\mathbf{R}$, has been excluded from integration.

Introducing Eq. V.16 into Eq. V.15 one finally obtains

$$\begin{aligned}\overset{\frown}{\mathbf{e}}(\mathbf{R}_0) = -\frac{n^2+2}{3}\int^{V}\tilde{\mathsf{F}}(\mathbf{R}_0,\mathbf{R})\cdot[\sum_{i}\overset{\frown}{\boldsymbol{\mu}}_{i}\delta(\mathbf{R}_{i}-\mathbf{R})-\varrho\bar{\boldsymbol{\mu}}_{i}(\mathbf{R}) \\ +\varrho\alpha_0(1+\mathrm{R}')\int_{v(\mathbf{R})}^{V}\mathsf{F}(\mathbf{R},\mathbf{R}')\cdot\{\sum_{j}\overset{\frown}{\boldsymbol{\mu}}_{j}\delta(\mathbf{R}_{j}-\mathbf{R}')-\varrho\bar{\boldsymbol{\mu}}_{j}(\mathbf{R}')\}d\mathbf{R}']\,d\mathbf{R}\end{aligned} \tag{V.17}$$

where we have used the Lorentz-Lorenz relation in the form, Eq. IV.54 (R' is a power series in α_0 with a first nonvanishing term in α_0^2).

The field $\overset{\frown}{\mathbf{e}}(\mathbf{R}_0)$ may be expanded as a power series in $\alpha_0\mathsf{F}$. Up to terms in α_0^2 the function R' may be neglected as well as the variation of the polarizability with intermolecular distances. (Both R' and $\Delta\boldsymbol{\alpha}_i$ contribute to terms in α_0^3 and higher.)

The expansion of $\overset{\frown}{\mathbf{e}}(\mathbf{R}_0)$ is then found by substitution into Eq. V.19 of

$$\overset{\frown}{\boldsymbol{\mu}}_{i}(\mathbf{R}) = \bar{\boldsymbol{\mu}}(\mathbf{R})+\Delta\overset{\frown}{\boldsymbol{\mu}}_{i}(\mathbf{R}) \tag{V.18}$$

and

$$\begin{aligned}\Delta\overset{\frown}{\boldsymbol{\mu}}_{i} = \alpha_0\int^{V}\{\varrho^{-1}\sum_{k,l,k\neq l}\langle\mathsf{F}_{kl}\cdot\overset{\frown}{\boldsymbol{\mu}}_{l}\delta(\mathbf{R}_{k}-\mathbf{R})\,\delta(\mathbf{R}_{l}-\mathbf{R}')h\rangle \\ -\sum_{l\neq i}\mathsf{F}_{il}\cdot\overset{\frown}{\boldsymbol{\mu}}_{l}\delta(\mathbf{R}_{k}-\mathbf{R}')\}d\mathbf{R}'\end{aligned} \tag{V.19}$$

Equation V.19 follows from the definition Eq. V.1 of $\overset{\frown}{\boldsymbol{\mu}}_{i}$ if a variation in polarizability is neglected.

By iteration one finds for $\overset{\frown}{\mathbf{e}}(\mathbf{R}_0)$ up to terms in α_0^2

$$\begin{aligned}\overset{\frown}{\mathbf{e}}(\mathbf{R}_0) = -\frac{n^2+2}{3}\int^{V}\tilde{\mathsf{F}}(\mathbf{R}_0,\mathbf{R})\cdot[\bar{\boldsymbol{\mu}}(\mathbf{R})\delta(\mathbf{R}) \\ +\alpha_0\int_{v(\mathbf{R})}^{V}\mathsf{F}(\mathbf{R},\mathbf{R}')\cdot\bar{\boldsymbol{\mu}}(\mathbf{R}')\{\varrho g(\mathbf{R},\mathbf{R}')\delta(\mathbf{R}')-\delta(\mathbf{R},\mathbf{R}')+\varrho\delta(\mathbf{R}')\}d\mathbf{R}'\end{aligned}$$

$$+\alpha_0^2\int_{v(\mathbf{R})}^{V}\mathsf{F}(\mathbf{R},\mathbf{R}')\cdot\mathsf{F}(\mathbf{R}',\mathbf{R})\cdot\bar{\boldsymbol{\mu}}(\mathbf{R})\{\delta(\mathbf{R},\mathbf{R}')-\varrho g(\mathbf{R},\mathbf{R}')\delta(\mathbf{R})\}d\mathbf{R}'$$

$$+\alpha_0^2\int_{v(\mathbf{R})}^{V}\int_{v(\mathbf{R}')}^{V}\mathsf{F}(\mathbf{R},\mathbf{R}')\cdot\mathsf{F}(\mathbf{R},\mathbf{R}'')\cdot\bar{\boldsymbol{\mu}}(\mathbf{R}'')\,\{\delta(\mathbf{R},\mathbf{R}',\mathbf{R}'')$$

$$-\varrho^2 g(\mathbf{R},\mathbf{R}',\mathbf{R}'')\delta(\mathbf{R})+\varrho^2 g(\mathbf{R},\mathbf{R}')g(\mathbf{R}',\mathbf{R}'')\delta(\mathbf{R})-\varrho g(\mathbf{R}',\mathbf{R}'')\delta(\mathbf{R},\mathbf{R}')$$

$$+\varrho^2 g(\mathbf{R}',\mathbf{R}'')\delta(\mathbf{R}')-\varrho\delta(\mathbf{R}',\mathbf{R}'')\}\,d\mathbf{R}'d\mathbf{R}'']\,d\mathbf{R} \qquad \text{(V.20)}$$

with the definitions:

$$\delta(\mathbf{R})=\sum_i\delta(\mathbf{R}_i-\mathbf{R})-\langle\sum_i\delta(\mathbf{R}_i-\mathbf{R})h\rangle=\sum_i\delta(\mathbf{R}_i-\mathbf{R})-\varrho \qquad \text{(V.21)}$$

$$\begin{aligned}\delta(\mathbf{R},\mathbf{R}')&=\sum_{i,j,i\neq j}\delta(\mathbf{R}_i-\mathbf{R})\delta(\mathbf{R}_j-\mathbf{R}')-\sum_{i,j,i\neq j}\langle\delta(\mathbf{R}_i-\mathbf{R})\delta(\mathbf{R}_j-\mathbf{R}')h\rangle\\&=\sum_{i,j,i\neq j}\delta(\mathbf{R}_i-\mathbf{R})\delta(\mathbf{R}_j-\mathbf{R}')-\varrho^2 g(\mathbf{R},\mathbf{R}')\end{aligned} \qquad \text{(V.22)}$$

$$\begin{aligned}\delta(\mathbf{R},\mathbf{R}',\mathbf{R}'')=&\sum_{i,j,k,\,i\neq j,\,k\neq j,\,i\neq k}\delta(\mathbf{R}_i-\mathbf{R})\delta(\mathbf{R}_j-\mathbf{R}')\delta(\mathbf{R}_k-\mathbf{R}'')\\&-\langle\sum_{i,j,k,\,i\neq j,\,k\neq j,\,i\neq k}\delta(\mathbf{R}_i-\mathbf{R})\delta(\mathbf{R}_j-\mathbf{R}')\delta(\mathbf{R}_k-\mathbf{R}'')h\rangle \qquad \text{(V.23)}\\=&\sum_{i,j,k,\,i\neq j,\,k\neq j,\,i\neq k}\delta(\mathbf{R}_i-\mathbf{R})\delta(\mathbf{R}_j-\mathbf{R}')\delta(\mathbf{R}_k-\mathbf{R}'')-\varrho^3 g(\mathbf{R},\mathbf{R}',\mathbf{R}'')\end{aligned}$$

Infinitely small spheres $v(\mathbf{R})$ and $v(\mathbf{R}')$ have been excluded from the integrations in Eq. V.20. For a number of terms this is simply a consequence of the fact that such cavities were already excluded from integration in Eq. V.17. For all other terms this may be done because of the properties of the distribution functions and their fluctuations, Eqs. V.22 and V.23, at very small intermolecular distances.

Fixman[6] obtained a result identical with Eq. V.20, using however a different method of expanding Eq. V.17.

D. Intensity of Scattered Light

The scattered light will be measured after it passed through an analyzer specified by the unit direction **u**. We suppose that the scattered light is measured at some point inside the fluid, but far removed from the region illuminated by the Maxwell field **E**.

The intensity of scattered light $i(\mathbf{R}_0)$ is given by the statistical average

$$i(\mathbf{R}_0) = \langle \mathbf{u} \cdot \tilde{\mathbf{e}}(\mathbf{R}_0)\tilde{\mathbf{e}}^*(\mathbf{R}_0) \cdot \mathbf{u}h\rangle \tag{V.24}$$

where $\tilde{\mathbf{e}}^*(\mathbf{R}_0)$ is the complex conjugate of $\tilde{\mathbf{e}}(\mathbf{R}_0)$.

Introducing Eq. V.20 into Eq. V.24 one finds in first approximation (zero-order in α_0)

$$i(\mathbf{R}_0) = \left(\frac{n^2+2}{3}\right)^2 \int^V\!\!\int^V \mathbf{u} \cdot \tilde{\mathsf{F}}(\mathbf{R}_0, \mathbf{R}) \cdot \bar{\boldsymbol{\mu}}(\mathbf{R})\langle\delta(\mathbf{R})\delta(\mathbf{R}')h\rangle\bar{\boldsymbol{\mu}}^*(\mathbf{R}') \cdot \tilde{\mathsf{F}}^*(\mathbf{R}', \mathbf{R}_0) \cdot \mathbf{u}\,d\mathbf{R}\,d\mathbf{R}' \tag{V.25}$$

With $\bar{\boldsymbol{\mu}}(\mathbf{R}) = \varrho^{-1}(n^2-1)\mathbf{E}(\mathbf{R})$ and

$$\langle\delta(\mathbf{R})\delta(\mathbf{R}')h\rangle = \varrho\delta(\mathbf{R}-\mathbf{R}')+\varrho^2\{g(\mathbf{R}, \mathbf{R}')-1\} \tag{V.26}$$

Equation V.25 is very nearly equal to

$$i(\mathbf{R}_0) = \left(\frac{n^2+2}{3}\right)^2 (n^2-1)^2 \int^V \mathbf{u} \cdot \tilde{\mathsf{F}}(\mathbf{R}_0, \mathbf{R}) \cdot \mathbf{E}(\mathbf{R})\mathbf{E}^*(\mathbf{R}) \cdot \tilde{\mathsf{F}}^*(\mathbf{R}_0, \mathbf{R}) \cdot \mathbf{u}\varrho^{-1}\left\{1+\varrho\int^V (g(\mathbf{R}, \mathbf{R}')-1)d\mathbf{R}'\right\} d\mathbf{R} \tag{V.27}$$

since $g(\mathbf{R}, \mathbf{R}')$ reaches its asymptotic value 1 (neglecting terms of $O(1/N)$) over distances $|\mathbf{R}-\mathbf{R}'|$ small compared to the wavelength of the incident light.

If one is interested in the scattering from a macroscopic volume Ω whose dimensions are small compared to its distance to the point of observation, Eq. V.27 becomes

$$i(\mathbf{R}_0) = \frac{k^4\left(\dfrac{n^2+2}{3}\right)^2 (n^2-1)^2\varrho^{-1}\Omega}{16\pi D^2} |\mathbf{E}|^2\cos^2\gamma\left\{1+\varrho\int^\Omega (g(\mathbf{R}, \mathbf{R}')-1)\,d\mathbf{R}'\right\} \tag{V.28}$$

where we have used the following property of $\mathsf{F}(\mathbf{R}_0,\mathbf{R})$, $(\mathbf{u}\cdot(\mathbf{R}_0-\mathbf{R})=0)$:

$$\mathbf{u} \cdot \tilde{\mathsf{F}}(\mathbf{R}_0, \mathbf{R}) \cdot \mathbf{E}(\mathbf{R}) = \frac{k^2\, e^{-ink|\mathbf{R}_0-\mathbf{R}|}}{4\pi|\mathbf{R}_0-\mathbf{R}|}\mathbf{u} \cdot \mathbf{E}(\mathbf{R}) \text{ if } k|\mathbf{R}_0-\mathbf{R}| \gg 1 \tag{V.29}$$

and where

$$(\mathbf{u} \cdot \mathbf{E})/|\mathbf{E}| = \cos\gamma \tag{V.30}$$

In Eq. V.28, D is the mean distance from $\mathbf{R}_0$ to the volume Ω.

In a similar way the higher approximation for $i(\mathbf{R}_0)$ can be found. It turns out that terms in α_0 vanish.[6] For the calculation of terms in α_0^2 the reader is referred to the paper by Fixman.[6]

APPENDIX I

On Tensor Notation

The system of vector and tensor notation used in the present paper is the same as that explained in the appendix of Rosenfeld's book,[26] which in its turn is essentially that of Milne and Chapman.[2]

Thus, the exterior product of an ordered pair of vectors **a**, **b** is a tensor

$$\mathsf{T} = \mathbf{ab} \rightarrow T_{ik} = a_i b_k$$

The scalar product of two vectors **a**, **b** is written as

$$\mathbf{a} \cdot \mathbf{b} = \sum_i a_i b_i$$

while the vector product is denoted by

$$\mathbf{a} \wedge \mathbf{b} \rightarrow (\mathbf{a} \wedge \mathbf{b})_i = \sum_{k,l} \varepsilon_{ikl} a_k b_l$$

where ε_{ikl} represents the well-known isotropic tensor of the third order discussed among others by Jeffreys and Jeffreys,[12] for which the relation $\sum_l \varepsilon_{ikl} \varepsilon_{\mu\nu l} = \delta_{i\mu} \delta_{k\nu} - \delta_{i\nu} \delta_{k\mu}$ holds. The divergences of a vector and a tensor are written, respectively, as

$$\operatorname{div} \mathbf{a} = \nabla \cdot \mathbf{a} = \sum_i \frac{\partial a_i}{\partial x_i}$$

and

$$\operatorname{div} \mathsf{T} = \nabla \cdot \mathsf{T} \rightarrow (\operatorname{div} \mathsf{T})_k = \sum_i \frac{\partial \mathsf{T}_{ik}}{\partial x_i}$$

Further

$$\mathsf{S} : \mathsf{T} = \sum_{i,k} S_{ik} T_{ki}$$

$$\mathbf{a} \cdot \mathsf{T} \rightarrow (\mathbf{a} \cdot \mathsf{T})_k = \sum_i a_i T_{ik}$$

and so on.

Equation II.30 can be proved in the following way: The ith component of the right-hand member is

$$\begin{aligned}
&\sum_{k,l,m,\mu,\nu} \varepsilon_{ikl} \frac{\partial}{\partial x_k} \frac{\partial}{\partial x_m} \varepsilon_{l\nu\mu} B_{m\mu} a_\nu \\
&= \sum_{k,m,\mu,\nu} \Big(\sum_{l} \varepsilon_{ikl}\, \varepsilon_{\mu\nu l}\Big) \frac{\partial}{\partial x_k} \frac{\partial}{\partial x_m} B_{m\mu} a_\nu \\
&= \sum_{k,m,\mu,\nu} (\delta_{i\mu}\, \delta_{k\nu} - \delta_{i\nu}\, \delta_{k\mu}) \frac{\partial}{\partial x_k} \frac{\partial}{\partial x_m} B_{m\mu} a_\nu \\
&= \sum_{k,m} \frac{\partial}{\partial x_k} \frac{\partial}{\partial x_m} (a_k B_{mi} - B_{mk} a_i)
\end{aligned}$$

APPENDIX II

Derivation of Eq. III.13

Irving and Kirkwood[9] have shown that the expression

$$\Big\langle \sum_{k,l,k\neq l} (\nabla_{\mathbf{R}_k} \varphi_{kl}) \delta(\mathbf{R}_k - \mathbf{R}) f \Big\rangle$$

where φ_{kl} is a short-range interaction potential between two point atoms, reduces to

$$\nabla_{\mathbf{R}} \cdot \Big\langle \tfrac{1}{2} \sum_{k,l,k\neq l} (\mathbf{R}_l - \mathbf{R}_k)(\nabla_{\mathbf{R}_k} \varphi_{kl}) \delta(\mathbf{R}_k - \mathbf{R}) f \Big\rangle$$

when all macroscopic quantities are slowly varying functions of space coordinates. Taking $\nabla_{\mathbf{R}_k} \varphi_{kl} = (\nabla_{\mathbf{R}_k} \mathsf{T}_{kl}) : \{\boldsymbol{\mu}_k \boldsymbol{\mu}_l\}$, one obtains the equality of the first terms of both sides of Eq. III.13.

In a similar way we prove the equality of the other terms:

$$\begin{aligned}
&\int^{\infty} \{\nabla_{\mathbf{R}} \mathsf{T}(\mathbf{R}, \mathbf{R}')\} : \mathbf{P}(\mathbf{R})\mathbf{P}(\mathbf{R}')\{g(\mathbf{R}, \mathbf{R}') - 1\} d\mathbf{R}' \\
&= \int^{\infty}\!\!\int^{\infty} \{\nabla_{\mathbf{R}''} \mathsf{T}(\mathbf{R}'', \mathbf{R}')\} : \mathbf{P}(\mathbf{R}'')\mathbf{P}(\mathbf{R}')\{g(\mathbf{R}'', \mathbf{R}') - 1\} \\
&\qquad\qquad \delta(\mathbf{R}'' - \mathbf{R}) d\mathbf{R}' d\mathbf{R}'' \\
&= \int^{\infty}\!\!\int^{\infty} \tfrac{1}{2}\{\nabla_{\mathbf{R}''} \mathsf{T}(\mathbf{R}'', \mathbf{R}')\} : \mathbf{P}(\mathbf{R}'')\mathbf{P}(\mathbf{R}')\{g(\mathbf{R}'', \mathbf{R}') - 1\} \\
&\qquad\qquad \{\delta(\mathbf{R}'' - \mathbf{R}) - \delta(\mathbf{R}' - \mathbf{R})\} d\mathbf{R}' d\mathbf{R}'' \qquad \text{(A)}
\end{aligned}$$

where use has been made of the relations

$$\begin{aligned}
\nabla_{\mathbf{R}''} \mathsf{T}(\mathbf{R}'', \mathbf{R}') &= -\nabla_{\mathbf{R}'} \mathsf{T}(\mathbf{R}'', \mathbf{R}') \\
\mathsf{T}(\mathbf{R}'', \mathbf{R}') &= \mathsf{T}(\mathbf{R}', \mathbf{R}'') \\
g(\mathbf{R}'', \mathbf{R}') &= g(\mathbf{R}', \mathbf{R}'')
\end{aligned}$$

and of the fact, that the indices of $\mathbf{R}'$ and $\mathbf{R}''$ may be interchanged. Developing the second δ-function of the last member of Eq. A into a Taylor-series around $\mathbf{R}''$, one obtains as the first term of the series the last term of Eq. III.13. The higher-order terms may again be neglected if all macroscopic quantities are slowly varying functions of space coordinates.

APPENDIX III

We wish to show here that Eq. IV.11 may be put into the form of Eq. IV.13. For that purpose we introduce an auxiliary quantity $\tilde{\boldsymbol{\mu}}_k{}^\dagger$ defined by

$$\begin{aligned}\tilde{\boldsymbol{\mu}}_k{}^\dagger(\mathbf{R}') &= \boldsymbol{\alpha}_k \cdot [\mathbf{E}^0(\mathbf{R}') - \varrho^{-1} \sum_{j,l,l\neq j} \langle \mathsf{F}_{jl} \cdot \bar{\boldsymbol{\mu}}_l \delta(\mathbf{R}_j - \mathbf{R}') f \rangle] \\ &= \boldsymbol{\alpha}_k \cdot [\mathbf{E}^0(\mathbf{R}') - \int^V \mathsf{F}(\mathbf{R}', \mathbf{R}'') \cdot \mathbf{P}(\mathbf{R}'') g(\mathbf{R}', \mathbf{R}'')\, d\mathbf{R}''] \end{aligned} \tag{A}$$

The quantity $\tilde{\boldsymbol{\mu}}_k{}^\dagger$ therefore is the moment which would be induced in molecule k by an average internal field due to all other molecules, with a polarizability, however, still depending on the instantaneous configuration of the system.

With the help of Eq. A and Eq. IV.3, we may now write for $\tilde{\boldsymbol{\mu}}_k$

$$\tilde{\boldsymbol{\mu}}_k(\mathbf{R}') = \tilde{\boldsymbol{\mu}}_k{}^\dagger(\mathbf{R}') + \boldsymbol{\alpha}_k \cdot \varrho^{-1} \sum_{j,l,l\neq j} \langle \mathsf{F}_{jl} \cdot \bar{\boldsymbol{\mu}}_l \delta(\mathbf{R}_j - \mathbf{R}') f \rangle - \boldsymbol{\alpha}_k \cdot \sum_{l\neq k} \mathsf{F}_{kl} \cdot \tilde{\boldsymbol{\mu}}_l \tag{B}$$

Inserting this expression for $\tilde{\boldsymbol{\mu}}_k(\mathbf{R}')$ into Eq. IV.11 we obtain

$$\begin{aligned}\mathbf{J}(\mathbf{R}) = &\int^V \sum_{i,k,k\neq i} \langle \{ \bar{\boldsymbol{\alpha}} \cdot \mathsf{F}_{ik} \cdot \bar{\boldsymbol{\mu}}_k{}^\dagger - \boldsymbol{\alpha}_i \cdot \mathsf{F}_{ik} \cdot \tilde{\boldsymbol{\mu}}_k{}^\dagger \} \delta(\mathbf{R}_i - \mathbf{R}) \delta(\mathbf{R}_k - \mathbf{R}') f \rangle d\mathbf{R}' \\ &+ \varrho^{-1} \int^V \sum_{i,k,k\neq i} \langle \{ \bar{\boldsymbol{\alpha}} \cdot \mathsf{F}_{ik} \cdot \bar{\boldsymbol{\alpha}} - \boldsymbol{\alpha}_i \cdot \mathsf{F}_{ik} \cdot \boldsymbol{\alpha}_k \} \cdot \\ &\qquad \cdot \sum_{j,l,l\neq j} \langle \mathsf{F}_{jl} \cdot \tilde{\boldsymbol{\mu}}_l \delta(\mathbf{R}_j - \mathbf{R}') f \rangle \delta(\mathbf{R}_i - \mathbf{R}) \delta(\mathbf{R}_k - \mathbf{R}') f \rangle d\mathbf{R}' \\ &- \varrho^{-1} \int^V \sum_{i,k,k\neq i} \langle \bar{\boldsymbol{\alpha}} \cdot \mathsf{F}_{ik} \cdot \sum_{j,l,l\neq j} \langle \boldsymbol{\alpha}_j \cdot \mathsf{F}_{jl} \cdot \bar{\boldsymbol{\mu}}_l \delta(\mathbf{R}_j - \mathbf{R}') f \rangle \\ &\qquad \delta(\mathbf{R}_i - \mathbf{R}) \delta(\mathbf{R}_k - \mathbf{R}') f \rangle d\mathbf{R}' \\ &+ \int^V \sum_{i,k,l,k\neq i,l\neq k} \langle \boldsymbol{\alpha}_i \cdot \mathsf{F}_{ik} \cdot \boldsymbol{\alpha}_k \cdot \mathsf{F}_{kl} \cdot \tilde{\boldsymbol{\mu}}_l \delta(\mathbf{R}_i - \mathbf{R}) \delta(\mathbf{R}_k - \mathbf{R}') f \rangle d\mathbf{R}' \end{aligned} \tag{C}$$

This procedure may be repeated making use again of Eq. B. At any step of this successive approximation we may replace $\overline{\boldsymbol{\mu}}$ by $\overline{\boldsymbol{\mu}}^\dagger$ and neglect the fluctuation term of higher order thus making only a small error. The integrand in the expression for $\mathbf{J}(\mathbf{R})$ then becomes proportional to $\overline{\boldsymbol{\mu}}^\dagger$ and may be written, using Eq. A, as in Eq. IV.13.

Let us finally evaluate the kernel $\varrho\bar{\alpha}\mathsf{K}(\mathbf{R}, \mathbf{R}')$ in Eq. III.13 up to terms in $\alpha_0{}^3$ by substituting into Eq. C the expression, Eq. IV.48, for $\boldsymbol{\alpha}_i$. We then find

$$\begin{aligned}\varrho\bar{\alpha}\mathsf{K}(\mathbf{R}, \mathbf{R}') = {} & \alpha_0{}^3\varrho^3\int^V \mathsf{F}(\mathbf{R}, \mathbf{R}'')\cdot \\ & \cdot\,\mathsf{F}(\mathbf{R}'', \mathbf{R}')\{g(\mathbf{R}, \mathbf{R}'', \mathbf{R}') - g(\mathbf{R}, \mathbf{R}'')g(\mathbf{R}'', \mathbf{R}')\}\,d\mathbf{R}'' \\ & + \alpha_0{}^3\varrho^2\int^V \mathsf{F}(\mathbf{R}, \mathbf{R}'')\cdot\mathsf{F}(\mathbf{R}'', \mathbf{R})\,g(\mathbf{R}, \mathbf{R}'')\,\delta(\mathbf{R}-\mathbf{R}')\,d\mathbf{R}''\end{aligned} \tag{D}$$

where $\varrho^3 g(\mathbf{R}, \mathbf{R}', \mathbf{R}'')$ is the distribution function for three particles defined by

$$\varrho^3 g(\mathbf{R}, \mathbf{R}', \mathbf{R}'') = \sum_{i,k,l,k\neq i,l\neq k,l\neq i} \langle\delta(\mathbf{R}_i-\mathbf{R})\,\delta(\mathbf{R}_l-\mathbf{R}')\,\delta(\mathbf{R}_k-\mathbf{R}'')f\rangle \tag{E}$$

When Eq. D for $\mathsf{K}(\mathbf{R}, \mathbf{R}')$ is substituted into Eq. IV.22, we obtain Eq. IV.51 for the function $G_2(\varrho, T, \omega)$.

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THE APPLICATION OF THE THEORY OF STOCHASTIC PROCESSES TO CHEMICAL KINETICS *

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CONTENTS

I. INTRODUCTION

The standard theories of chemical kinetics are equilibrium theories in which a Maxwell-Boltzmann energy (or momentum or internal coordinate) distribution of reactants is postulated to persist during a reaction. In the collision theory, mainly due to Hinshelwood,[7] the number of energetic, reaction producing collisions is calculated under the assumption that the molecular velocity distribution always remains Maxwellian. In the absolute

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rate theory, developed particularly by Eyring,[4] the equilibrium assumption is stated (in its most refined form) in terms of a time invariant Boltzmann distribution of reactant molecules in the reactant valley far removed from the potential barrier. It has long been recognized that the equilibrium postulate is only an approximation of reality, since any process with a nonvanishing rate disturbs an initial equilibrium. Hence it is of interest to examine various models of chemical reactions to estimate the extent of departure from equilibrium and to develop techniques for analyzing reactions in which the departure is significant. "Microscopic" chemical kinetics or the adjustment of the energy distributions induced by reactions is the main theme of this paper.

This section is a review of previous treatments of this subject. Subsequent sections are an application of the theory of stochastic processes to chemical rate phenomena; the harmonic oscillator model of a diatomic molecule is used to obtain explicit results by the general formalism.

A. The Curtiss-Prigogine-Takayanagi Model

Curtiss,[3] Prigogine[15, 16] and collaborators, and Takayanagi[21] investigated the perturbation of an initial Maxwell velocity distribution by a chemical reaction. The perturbation of the energy distribution of internal degrees of freedom was neglected. A generalized Boltzmann equation was derived which incorporated effects such as (a) addition of energy to the system through the heat of reaction, and (b) the removal of highly energetic molecules from the system of colliding reactants by inelastic collisions (those which result in a chemical reaction). After postulating the probability of an inelastic collision to be small, the generalized Boltzmann equation was solved by the Chapman-Enskog method of using a perturbed distribution function f of the form

$$f = f_0(1+\Phi) \tag{I.1}$$

f_0 being the equilibrium Maxwellian velocity distribution, and Φ the perturbation induced by the chemical reaction.

Prigogine considered two relations between the probability (cross section) of inelastic collisions σ and the relative velocity modulus g; namely

$$\sigma = 1 - \exp(-\alpha g^2) \tag{I.2a}$$

and

$$\sigma = \begin{cases} 0 \text{ if } g < g_0 \\ 1 \text{ if } g \geqq g_0 \end{cases} \tag{I.2b}$$

where α and g_0 are related to the activation energy E_{act} of the reaction by

$$E_{\text{act}} = m/4\alpha = \tfrac{1}{4}mg_0^2 \tag{I.3}$$

where m is the mass of a molecule of the reacting species. Φ was found to depend only on E_{act}/kT in both of these cases. Quantitative results were very sensitive to the choice of σ. For $E_{\text{act}}/kT = 5$, Eq. I.2a produced a perturbation of the Maxwellian distribution which reduced the reaction rate to about 99 per cent of the equilibrium rate whereas Eq. I.2b resulted in a decrease to about 80 per cent. Curtiss, by employing Eq. I.2b found a reduction of the rate by about 20 per cent for $E_{\text{act}}/kT = 4$, and 10 per cent for $E_{\text{act}}/kT = 5$, in good agreement with Prigogine.

An important result of these studies is that the perturbation of the equilibrium distribution and the corresponding deviation from the equilibrium rate is quite small when $E_{\text{act}}/kT \geqq 5$ and that the use of the equilibrium theory of chemical reactions is justified under this condition. The other investigations described below are in essential agreement with this result.

The extension of the kinetic theory approach to include large values of σ (and hence large deviations from equilibrium) requires higher order perturbations for the solution of the Boltzmann equation. It is probably unprofitable to proceed in this difficult and laborious direction until one understands the detailed analytical dependence of the transition probability σ on the mechanism of molecular energy exchange and redistribution on collision. Currently available information on intermolecular forces is insufficient to establish this dependence.

B. The Model of Zwolinski and Eyring

Zwolinski and Eyring[24] schematically describe the reactants of a chemical reaction by one set of quantum energy states and the reaction product by another. These levels are not especially identified with translational states or those of internal degrees of freedom but are left quite general. Molecules in the reactant states are postulated to pass by collision with other molecules into the product states. Reactions which are first order in a species A were studied. In this case linear rate equations of the form (prime denoting omission of terms with $n = m$)

$$\frac{dx_n}{dt} = \sum_m{}' \{W_{nm}x_m - x_n W_{mn}\} \quad n = 0, 1, 2, \ldots \tag{I.4}$$

can be constructed to describe the rate of transition for species A between the various reactant and product levels. The W_{nm}'s are probabilities per unit time of transitions through collision from states m to states n. Note that the first subscript refers to the final state. The $x_n(t)$ is the fraction of molecules in state n at time t.

The rate constants W_{nm} in the Zwolinski-Eyring model are analogous to the inelastic collision cross section σ of the Prigogine-Curtiss model. They are calculable, in principle, from the quantum-mechanical theory of collisions, but, as pointed out above, our ignorance of intermolecular forces and interactions prevent us from deducing their analytical form or numerical values. In the absence of this information Zwolinski and Eyring assumed certain relations between the various rate constants and assigned plausible numerical values to enough of them so that all could be determined.

The solution of Eq. I.4 is given by

$$x_n(t) = \sum_j B_{nj} \exp t\lambda_j \tag{I.5}$$

where the λ'_j's are the characteristic roots of the matrix of the coefficients B_{nj} obtained by setting $x_n = B_n \exp \lambda t$. The B'_{nj}'s are components of the characteristic vectors of the matrix. Zwolinski and Eyring evaluated Eq. 1.5 numerically for a 4-level model to obtain the time dependent concentration $x_n(t)$. The rate of reaction, i.e., the rate of passage between the energy levels, was then obtained by computing the appropriate products $W_{nm}x_m$ and summing these products over the reactant and product levels.

Zwolinski and Eyring expressed the deviation of the actual rate from the equilibrium rate by forming the ratio Γ of the above calculated rate to the rate determined on the assumption that the concentration of the reacting species was given at all times by the equilibrium Maxwell-Boltzmann distribution. They found $\Gamma < 1$, the extent of the departure from equilibrium depending upon the numerical choice for the transition probabilities W_{nm}. The maximum deviation from the equilibrium rate found for a 4-level model was about 20 per cent.

Zwolinski and Eyring, and one of us[19] have suggested that an extension of this 4-level model to one of N levels with a systematic treatment of transitions between these levels would be instructive in the formulation of microscopic, nonequilibrium chemical kinetics. Such an extension is presented in Sections III to V of this paper. We have generalized the Zwolinski-Eyring discrete energy level model to N levels and have characterized the transitions of the molecules between levels as a one-dimensional random walk. This general formulation is developed in terms of the properties of stochastic matrices whose elements involve the transition probabilities. Chemical reactions, i.e., the removal of reactant species from the reaction system, are introduced into this level system via an absorbing barrier at level $N+1$. The rate of the chemical reaction is then given in terms of the mean first passage time $\bar{t}$, the average time required for a species to pass level N and reach the absorbing barrier for the first time.

C. The Model of Kramers

Kramers[11] proposed a Brownian motion model for a chemical reaction. In this model reactant molecules become activated through collisions with other molecules of the surrounding medium which acts as a constant temperature heat bath. After many collisional exchanges of energy, some of the reactant molecules acquire sufficient energy (the energy of activation) to cross over a potential barrier. This crossing constitutes the chemical reaction, and the rate of crossing is equal to the rate of the reaction. The interaction of the reactant molecules with the heat bath is analogous to the Brownian motion of a particle in a viscous medium under the action of a force whose potential is the potential energy surface along the reaction coordinate. The theory of reaction rates is then treated as a Brownian motion problem. The interaction (coupling) of the molecules with the heat bath is expressed through a viscosity coefficient η, such that a large value of η corresponds to a strong interaction between the molecules and the heat bath.

The rate of reaction is given by the diffusion current over the potential barrier, and the energy distribution of the reacting species along the reaction coordinate is given through the density distribution in momentum space. The calculation rests, as remarked by Kramers, on the construction and solution of the equation of diffusion obeyed by a density distribution of particles in phase space. A very clear presentation of the Kramers diffusion equation has been given by Chandrasekhar.[1, 2]

The coefficient of viscosity η plays the same role in the Kramers model as the cross section σ in the theory of Curtiss and Prigogine and the transition probabilities W_{nm} in the Zwolinski-Eyring treatment. Neither its value nor analytical form can be determined from our present knowledge of intermolecular forces. It is interesting to see how this factor enters into all the theories and models of "microscopic" nonequilibrium chemical kinetics. Its absence from equilibrium chemical kinetics is, of course, due to the fact that the properties of the equilibrium state are independent of the manner of its establishment.

Mathematical difficulties forced Kramers to restrict his discussion to the case in which the barrier height $Q = E_{\text{act}}$ is large compared to the mean thermal energy of the molecules kT and in which the diffusion over the barrier can be treated as a quasi-stationary process. Kramers showed that under these conditions the calculated reaction rate is very close to the equilibrium rate, as given by absolute rate theory, and that for $E/kT > 10$ the rate calculated from his model agrees with the equilibrium rate to within about 10 per cent over a rather wide range of η.

The results of Kramers and of Curtiss and Prigogine are in good agreement in showing that for $E_{\text{act}}/kT \geqq 10$ the departure of the actual rate from the equilibrium rate is quite small and can be neglected for all practical purposes. Our own results, which are developed in the following sections, are in excellent agreement with these findings. This does not answer, however, the question as to the deviation of the rate from the equilibrium rate when

$E_{\text{act}}/kT < 10$. Conceptual and mathematical difficulties prevent the application of the methods developed and described in Sections I.A to I.C to an analysis of this problem. The application of the theory of stochastic processes, however, permits the evaluation of reaction rates under these conditions and will be shown in Section VII to lead to results that may deviate considerably from the equilibrium rate when $E_{\text{act}}/kT \ll 10$.

II. DISCRETE ENERGY-LEVEL MODEL FOR UNIMOLECULAR REACTIONS

Our approach to the study of the departure from equilibrium in chemical reactions and of the "microscopic" theory of chemical kinetics is a discrete quantum-mechanical analog of the Kramers-Brownian-motion model. It is most specifically applicable to a study of the energy-level distribution function and of the rate of activation in unimolecular (dissociation)reactions. Our model is an extension of one which we used in a discussion of the relaxation of vibrational nonequilibrium distributions.[14, 18, 20]

We consider an ensemble of reactant molecules with quantized energy levels to be immersed in a large excess of (chemically) inert gas which acts as a *constant temperature* heat bath throughout the reaction. The requirement of a constant temperature T of the heat bath implies that the concentration of reactant molecules is very small compared to the concentration of the heat bath molecules. The reactant molecules are initially in a Maxwell-Boltzmann distribution appropriate to a temperature T_0 such that $T_0 < T$. By collision with the heat bath molecules the reactants are excited in a stepwise processs into their higher-energy levels until they reach "level" $(N+1)$ where they are removed irreversibly from the reaction system. The collisional transition probabilities per unit time W_{mn} which govern the rate of transfer of the reactant molecules between levels with energies E_n and E_m are functions of the quantum numbers n and m and can, in principle, be calculated in terms of the interaction of the reactant molecules with the heat bath.

The model described above corresponds to an unimolecular activation followed by dissociation

$$M + A \underset{k_{\text{deact}}}{\overset{k_{\text{act}}}{\rightleftarrows}} M + A^* \qquad \text{(II.1)}$$

$$A^* \xrightarrow[k_D]{} \text{dissociation product}$$

where M represents the heat bath molecules, A the reactant molecules, and A^* the reactants with energy greater than E_N. Since we have assumed that the concentration $[M] \gg [A]$, the activating and deactivating collisions suffered by the molecules A will take place predominantly with the heat bath molecules M, so that the activation process is of first order in $[A]$ and the differential equations governing the rate of activation will be linear in the concentration of the reacting species A.

The relevant stochastic process corresponding to our model of a chemical reaction is that of a one-dimensional random walk with an absorbing barrier. In this random walk, the probability per unit time W_{mn} that a "walker" will take a step from level n to m is a function of the distance from the origin, $n = 0$. The time dependent distribution of the reactant molecules among the energy levels $n = 0, 1, \ldots, N$ is then given by the fraction $x_n(t)$ of walkers $(\sum x_n(0) = 1)$ n levels from the origin at time t. The rate of activation, v_{act} is inversely proportional to the mean first passage time, which is the average time required (appropriately weighted for the initial distribution of walkers) for a walker to reach the absorbing level $(N+1)$ (i.e., to pass the level N) for the first time. The mean first passage time l also gives directly the time lag for activation for our ensemble of reactants.

Generally our transition probabilities W_{mn} are as difficult to obtain as the corresponding parameters used by Curtiss, Prigogine, Zwolinski and Eyring, and Kramers. However, if the reactant molecules can be treated as simple harmonic oscillators, and if *only weak interactions* exist between the oscillators and heat bath molecules, an explicit calculation of the collisional transition probabilities W_{mn} can be carried out. This was first done by Landau and Teller[6, 12] by using the following argument. The classical interaction energy of one of our oscillator molecules with a heat bath molecule depends on the displacement r of the atomic separation distance between the atoms of our diatomic molecule from its equilibrium value r_0. If the interaction with the heat bath is weak (and the adiabatic condition which requires the vibration period of the diatomic molecule to be short compared with collision times is satisfied), the interaction energy can be expanded as a power series in r and terms of order r^2 or higher can be neglected. The coefficients appropriate to a given collision depend on collision angles and relative velocities but these must be averaged over all possible collisions with each weighted according to a Maxwellian velocity distribution of heat bath molecules.

If the transition probability per collision, P_{10}, for the transition $0 \to 1$ can be determined, Landau and Teller show that the linear perturbation of the vibrations of the diatomic molecules by the heat bath induce other transitions with probabilities:

$$P_{mn} = [(m+1)\delta_{n-1,m} + m\delta_{n+1,m}]P_{10} = P_{nm} \tag{II.2}$$

per collision. Here

$$\delta_{nm} = \begin{cases} 1 & \text{if } m = n \\ 0 & \text{otherwise} \end{cases} \tag{II.3}$$

It is to be noted that these transition probabilities are exactly those associated with optical transitions of a harmonic oscillator in a radiation bath. Transitions are only possible between adjacent levels.

The transition probabilities per collision P_{mn} are related to the transition probabilities per unit time W_{mn} (for $n \to m$) by[18]

$$W_{n+1,n} = Z^* N^* e^{-\theta} P_{n,n+1} \tag{II.4}$$

$$W_{n,n+1} = Z^* N^* P_{n+1,n} \tag{II.5}$$

so that $W_{n,n+1}/W_{n+1,n} = \exp\theta$ as required by the principle of detailed balancing. The quantity Z^* is the collision number, i.e., the number of collisions per unit time suffered by the oscillator when the gas density is one molecule per unit volume, and N^* is the total concentration of heat bath molecules, and $\theta = h\nu/kT$.

We postulate the potential energy curve of a "dissociating harmonic oscillator" reactant as that shown in Fig. 1. It is a truncated harmonic oscillator potential with a finite number of equally spaced energy levels such that the level N is the last discrete level of the oscillator and the energy $E_{N+1} = h\nu(N+1)$ is the dissociation energy and the activation energy for the reaction. Here ν is the natural frequency of the oscillator.

In Sections III to VI we will discuss some of the general stochastic properties of an ensemble of molecules undergoing stepwise transitions in a discrete energy-level system with and without absorbing barriers. The development presented in these sections is quite general and pertains to any ensemble of reactant molecules in the quantized energy levels. We will derive general expressions for the time-dependent distribution of the molecules among these

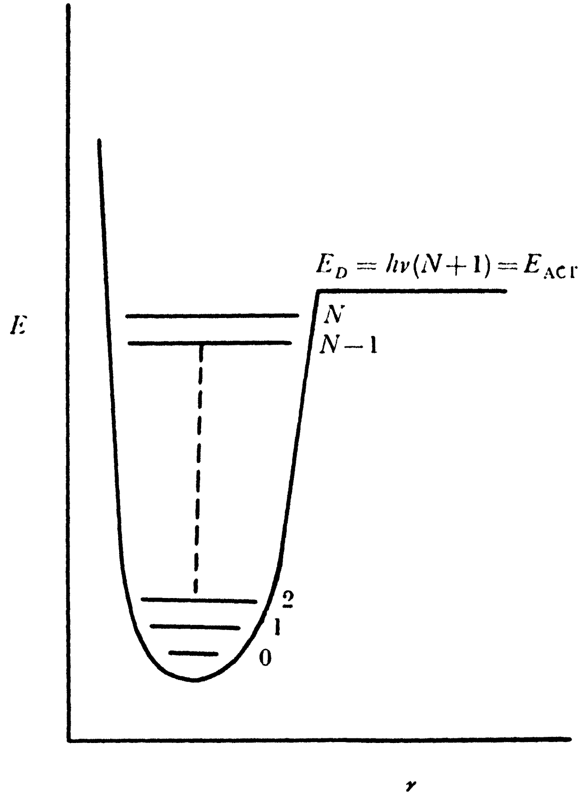

Fig. 1. Potential energy for a harmonic oscillator reactant with a dissociation "cut-off." The energy $E_D = h\nu(N+1)$ is the dissociation energy.

energy levels, for mean first passage times, and for the perturbation introduced into an initial equilibrium distribution by chemical reactions. In Section VII we will then apply some of these results to the study of a system of harmonic oscillator reactants with analytical forms for the transition probabilities given in the foregoing.

III. TRANSITIONS WITHOUT REACTION

Let us assume (a) that the energy levels of our molecules are $E_0, E_1, E_2, \ldots, E_N$; (b) that the fraction of molecules in the mth state at time t is $x_m(t)$; (c) that the transition probabilities per unit time W_{nm} from state m to n can be computed in terms of the interaction of the molecules with a heat bath (which is postulated to remain at temperature T) by application of quantum-mechanical time dependent perturbation theory (the W_{nm}'s being proportional to squares of absolute values of the matrix elements of the interaction energy); and (d) that the temporal variations of the level concentrations are described through the transport equation

$$\frac{dx_n}{dt} = \sum_{\substack{m=0,1,2,\ldots \\ m\neq n}} \{W_{nm}x_m - x_n W_{mn}\} = \sum_{m=0,1,\ldots} A_{nm}x_m \qquad \text{(III.1)}$$

The positive terms represent the increase in number of occupants of the nth level by transitions $m \to n$ while the negative sum corresponds to the loss associated with transitions $n \to m$. Critical discussions of the derivation and validity of transport equations such as Eq. III.1 have been made by van Hove[9] and Luttinger and Kohn.[10] We hope sometime to make an analogous analysis of the validity of these equations as they are applied to problems in chemical kinetics.

Various properties of the matrices $W = (W_{nm})$ and $A = (A_{nm})$ and of the vector $x = \{x_0(t), x_1(t), \ldots\}$ are immediately apparent in a system which suffers no loss of molecules (i.e., *when no reaction occurs*). The equilibrium distribution of x_n is

$$x_n(\infty) = Z^{-1} \exp(-\beta E_n), \; Z = \sum_n \exp(-\beta E_n) \qquad \text{(III.2)}$$

For detailed balance at equilibrium

$$W_{nm} \exp(-\beta E_m) = W_{mn} \exp(-\beta E_n) \qquad \text{(III.3)}$$

We note that

$$A_{nm} = W_{nm}(1-\delta_{nm})-\delta_{nm}\sum_{l} W_{ln}(1-\delta_{nl}) \tag{III.4}$$

so that for fixed m

$$\begin{aligned}\sum_n A_{nm} &= \sum_n W_{nm}(1-\delta_{nm})-\sum_l (1-\delta_{nl})\sum_n \delta_{nm} W_{ln}\\ &= \sum_n W_{nm}(1-\delta_{nm})-\sum_l W_{lm}(1-\delta_{lm})\end{aligned} \tag{III.5}$$

and

$$\sum_n A_{nm} = 0,\ m = 0,\ 1,\ \ldots \tag{III.6}$$

This is equivalent to the statement that particles are conserved during transitions.

If the property, Eq. III.6, is common to two matrices A and B, then it is also characteristic of their product $C = AB$, for

$$C_{nm} = \sum_l A_{nl} B_{lm} \tag{III.7a}$$

and

$$\sum_n C_{nm} = \sum_l B_{lm}\sum_n A_{nl} = 0 \tag{III.7b}$$

The matrix A can be symmetrized through the introduction of the new variables

$$y_n = x_n \exp\left(\tfrac{1}{2}\beta E_n\right) \tag{III.8}$$

for then Eq. III.1 becomes

$$\frac{dy_n}{dt} = \sum_{m=0,1,\ldots} A_{nm} e^{\frac{1}{2}\beta(E_n-E_m)} y_m = \sum_{m=0,1,\ldots} B_{nm} y_m \tag{III.9}$$

where

$$B_{nm} = A_{nm} \exp \tfrac{1}{2}(E_n-E_m)\beta \tag{III.10}$$

Since the off-diagonal elements of A_{nm} (see Eq. III.4) are W_{nm} the off-diagonal elements of B are, in view of detailed balance, Eq. III.3,

$$B_{nm} = W_{nm} \exp\{-\tfrac{1}{2}\beta(E_m-E_n)\} = B_{mn} \tag{III.11}$$

Solutions of the symmetrized transport equation exist in the form

$$y_n(t) = \sum_j c_j \psi_j(n) \exp \lambda_j t \tag{III.12}$$

where the $\psi_j(n)$'s and λ_j's (with $-\lambda_0 \leqq -\lambda_1 \leqq -\lambda_2 \leqq \ldots$) are, respectively, the normalized characteristic vectors and characteristic values of the matrix B, and the c_j's are related to the initial level distribution by

$$c_j = \sum_m y_m(0)\psi_j(m) = \sum_{m=0,1,\ldots} x_m(0)\psi_j(m) \exp \tfrac{1}{2}\beta E_m \qquad \text{(III.13)}$$

Also

$$x_n(t) = \exp\left(-\tfrac{1}{2}\beta E_n\right) \sum_j c_j \psi_j(n) \exp \lambda_j t \qquad \text{(III.14)}$$

The conservation conditions Eqs. III.6 and III.10 imply that

$$\sum_n B_{nm} \exp\left(-\tfrac{1}{2}\beta E_n\right) = 0; \qquad \text{(III.15)}$$

which means that

$$\psi_0(n) = \frac{\exp\left(-\tfrac{1}{2}\beta E_n\right)}{\{\sum_n \exp(-\beta E_n)\}^{1/2}} \qquad \text{(III.16)}$$

is a characteristic vector of B which has a characteristic value $\lambda_0 = 0$. Furthermore, since $\sum x_n(0) = 1$

$$c_0 = Z^{-1/2} \qquad \text{(III.17)}$$

Hence

$$x_n(t) = Z^{-1} \exp(-\beta E_n) + \sum_{j>0} c_j \psi_j(n) \exp(\lambda_j t) \qquad \text{(III.18)}$$

Since $x_n(t) \leqq 1$, all λ_j must be negative (we assume $\lambda_0 = 0$ is the only vanishing λ).

IV. REACTION AS AN ABSORBING BARRIER

The discussion of the last section can be generalized to include the possibility of a chemical reaction.[13] Consider the case in which the achievement of the $(N+1)$st level represents the completion of the reaction and in which the reaction occurs only by a molecule passing into the $(N+1)$st level. Any molecule which reaches this level is absorbed or "dies." The reaction rate is determined by the rate at which molecules in their "random walk" from level to level reach the $(N+1)$st level *for the first time*. In the language of the theory of stochastic processes the mean time for level $(N+1)$ to be reached is the ***mean first passage time*** for the Nth level (the time required to *pass N for the first time*).

We let $F(t)$ be the fraction of molecules which have not yet reached $(N+1)$ in the time interval $(0, t)$. Then

$$F(t) = \sum_{n=0}^{N} x_n(t) \tag{IV.1}$$

The fraction of molecules which dissociate in an infinitesimal time interval $(t, t+\delta t)$ is

$$-[F(t+\delta t)-F(t)] = -(dF/dt)\delta t \tag{IV.2}$$

If $P(t)$ is the distribution of first passage times for transitions past level N, the number of molecules which pass N in the interval $(t, t+\delta t)$ is $P(t)\delta t$. Since all passing molecules are immediately "absorbed" by the barrier at $(N+1)$

$$P(t) = -\frac{dF}{dt} = -\frac{d}{dt}\sum_{0}^{N} x_n(t) \tag{IV.3}$$

The mean first passage time is

$$\begin{aligned} \bar{t} &= \int_0^\infty tP(t)dt = -\int_0^\infty t\,\frac{d}{dt}\sum_0^N x_n(t)dt \\ &= \int_0^\infty \sum_0^N x_n(t)\,dt \end{aligned} \tag{IV.4}$$

We first consider in detail the case of molecules with simple selection rules which allow transitions between neighboring levels

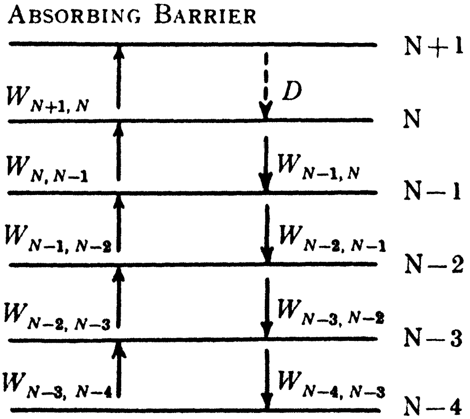

Fig. 2. Schematic diagram of nearest neighbor transitions.

only (see Fig. 2) and include the possibility that the "level" $(N+1)$ is only partially absorbing.

The transport equations, III.1, are now

$$dx_0/dt = -W_{10}x_0 + W_{01}x_1 \tag{IV.5a}$$

$$dx_j/dt = W_{j,j-1}x_{j-1} - (W_{j-1,j} + W_{j+1,j})x_j + W_{j,j+1}x_{j+1}, \quad j = 1, 2, \ldots, (N-1) \tag{IV.5b}$$

$$dx_N/dt = W_{N,N-1}x_{N-1} - (W_{N-1,N} + W_{N+1,N})x_N + D \tag{IV.5c}$$

where D represents the downflow rate from the state $(N+1)$. The characterization of D depends on the decomposition mechanism of molecules which leave the Nth state. We postulate the state $(N+1)$ to be a partially absorbing barrier with an absorption coefficient α such that of the normal rate of jump from level N to $N+1$, a fraction $\alpha W_{N+1,N}x_N$ is absorbed and "decomposes" while the remaining fraction $(1-\alpha)W_{N+1,N}x_N = \beta W_{N+1,N}x_N$ remains at the Nth level. To an observer at the Nth level this is equivalent to a flow rate $W_{N+1,N}x_N$ upward and $D = \beta W_{N+1,N}x_N$ downward, so that our required equation, IV.5c becomes

$$dx_N/dt = W_{N,N-1}x_{N-1} - (W_{N-1,N} + \alpha W_{N+1,N})x_N$$

where $\beta = 1-\alpha$ is the reflection coefficient of the state $(N+1)$. We shall usually be concerned with the perfect absorber $\alpha = 1$.

When $\alpha = 1$ the matrix A of Eq. IV.5 becomes

$$A = \begin{bmatrix} -W_{10} & W_{01} & 0 & 0 & 0\ldots & 0 & 0 \\ W_{10} & -(W_{01}+W_{21}) & W_{12} & 0 & 0\ldots & 0 & 0 \\ 0 & W_{21} & -(W_{12}+W_{32}) & W_{23} & 0\ldots & 0 & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & & \\ \cdot & \cdot & \cdot & \cdot & \cdot & & \\ \cdot & \cdot & \cdot & \cdot & \cdot & & \\ 0 & 0 & 0 & 0 & 0\ldots & -(W_{N-2,N-1}+W_{N,N-1}) & W_{N-1,N} \\ 0 & 0 & 0 & 0 & 0\ldots & W_{N,N-1} & -(W_{N-1,N}+W_{N+1,N}) \end{bmatrix} \tag{IV.6}$$

The conservation condition, Eq. III.6, is violated in the last column since

$$\sum_n A_{nN} = -W_{N+1,N} \neq 0 \tag{IV.7}$$

Hence the characteristic value $\lambda_0 = 0$ is perturbed to have a nonzero value. We can express A as

$$A = A_0 + \delta A \tag{IV.8}$$

where A_0 satisfies the conservation condition, and δA is a matrix whose elements are all zero except for $(\delta A)_{N,N} = -W_{N+1,N}$.

The distribution of first passage times $P(t)$, Eq. IV.3, can be expressed in terms of $x_n(t)$ by summing Eqs. IV.5a, IV.5b, and IV.5c:

$$P(t) = -(d/dt)\sum x_n(t) = W_{N+1,N}\, x_N(t) \tag{IV.9}$$

Then the mean first passage time is

$$l = \int_0^\infty t\,P(t)dt = W_{N+1,N}\int_0^\infty t x_N(t)dt \tag{IV.10}$$

These formulas are immediately generalizable to the case of transition to both nearest and next nearest neighbor levels (see Fig. 3). Here the conservation law is violated in the last two columns in such a way that if A_0 represents the part of A which satisfies the conservation conditions, Eq. III.6, then

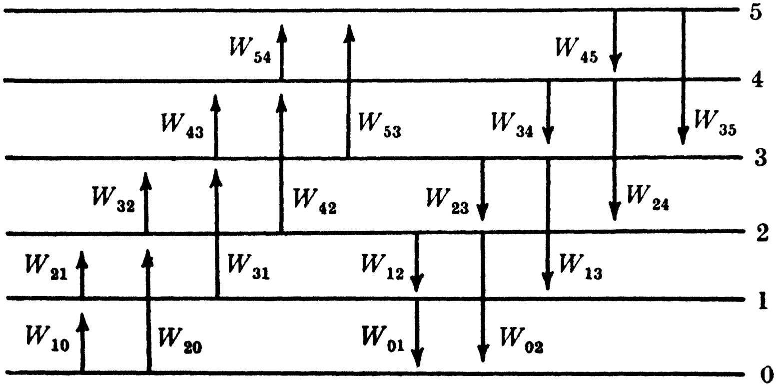

Fig. 3. Schematic diagram of nearest and next-nearest neighbor transitions.

$$\delta A = -\begin{bmatrix} 0 & 0 & \dots & 0 & 0 & 0 \\ 0 & 0 & \dots & 0 & 0 & 0 \\ \cdot & \cdot & \cdots & \cdot & \cdot & \cdot \\ 0 & 0 & \dots & 0 & 0 & 0 \\ 0 & 0 & \dots & 0 & W_{N+1,N-1} & 0 \\ 0 & 0 & \dots & 0 & 0 & W_{N+1,N} \end{bmatrix} \tag{IV.11}$$

Then

$$P(t) = \{W_{N+1,N}x_N(t)+W_{N+1,N-1}x_{N-1}(t)\} \tag{IV.12}$$

Under the more general conditions in which transitions can occur between levels n and $n\pm 1$, $n\pm 2, \dots, n\pm k$, the matrix δA has vanishing off-diagonal elements, and its diagonal elements are

$$[0, 0, \dots, 0, W_{N+1,N-k}, W_{N+1,N-k+1} \dots, W_{N+k,N}] \tag{IV.13}$$

Then

$$P(t) = \sum_{i=0}^{k} W_{N+1,N-i}\, x_{N-i}(t) \tag{IV.14}$$

V. GENERAL THEORY OF MEAN FIRST PASSAGE TIME

Let A be the transition probability matrix of the set of differential equations (analogous to Eq. IV.5) which describe the variation of level concentration with time in the presence of an absorbing barrier. Then the set of equations in matrix form is

$$dX(t)/dt = AX(t) \tag{V.1}$$

where $X(t)$ is a vector with components $x_0(t), x_1(t), \dots, x_N(t)$. The solution of this equation is

$$X(t) = e^{At}X(0) \tag{V.2}$$

$X(0)$ being the initial concentration vector. If all molecules are initially in the ground state

$$X(0) = \{1, 0, 0, \dots, 0\} \tag{V.3}$$

It is convenient to express the exponential matrix $\exp(At)$ as a linear combination of the characteristic matrices of A, the $f_j(A)$'s, which satisfy the relations[19]

$$Af_j(A) = \lambda_j f_j(A),\, j = 0, 1, 2, \dots, N \tag{V.4a}$$

$$f_k(A)f_j(A) = \delta_{kj}f_j(A) \tag{V.4b}$$

$$\sum_{j=0}^{N} f_j(A) = I \tag{V.4c}$$

where I is the identity matrix, and the λ_j's are the characteristic values of A. An explicit representation of $f_j(A)$ is

$$f_j(A) = \frac{(\lambda_0-A)(\lambda_1-A)\dots(\lambda_{j-1}-A)(\lambda_{j+1}-A)\dots(\lambda_N-A)}{(\lambda_0-\lambda_j)(\lambda_1-\lambda_j)\dots(\lambda_{j-1}-\lambda_j)(\lambda_{j+1}-\lambda_j)\dots(\lambda_N-\lambda_j)} \tag{V.5}$$

Since Eq. V.4a implies $G(A)f_j(A) = G(\lambda_j)f_j(A)$, when $G(\lambda)$ can be expressed as a power series in λ, we have

$$\begin{aligned} e^{At}I &= e^{At}\sum_{j=0}^{N} f_j(A) \\ &= \sum_{j=0}^{N} e^{At} f_j(A) = \sum_{j=0}^{N} e^{\lambda_j t} f_j(A) \end{aligned} \tag{V.5}$$

and

$$\begin{aligned} \int_0^\infty X(t)dt &= \sum_{j=0}^{N} \left\{ \int_0^\infty e^{\lambda_j t}\, dt \right\} f_j(A)X(0) \\ &= -\sum_{0}^{N} \lambda_j^{-1} f_j(A) X_0(0) = -\sum_{0}^{N} A^{-1} f_j(A) X(0) \\ &= -A^{-1}X(0). \end{aligned} \tag{V.6}$$

Let the characteristic equation whose roots are λ_j be

$$\lambda^{N+1} + a_1\lambda^N + \dots + a_N\lambda + a_{N+1} = 0 \tag{V.7a}$$

Then, since A satisfies its own characteristic equation:

$$A^N + a_1A^{N-1} + \dots + a_N I = -a_{N+1}A^{-1} \tag{V.7b}$$

Also, since the determinant of A is $(-1)^{N+1}a_{N+1}$

$$\int_0^\infty X(t)dt = \frac{(-1)^{N+1}}{\det A}\left\{ a_N I + a_{N-1}A + \dots + A^N \right\} X(0) \tag{V.8}$$

The a_j's are, of course, the invariants of the matrix A. For example $a_1 = -$ trace A and

$$\begin{aligned} a_N &= (-1)^N \sum_i \lambda_0\lambda_1 \dots \lambda_{i-1}\lambda_{i+1} \dots \lambda_N \\ &= (-1)^N \det A \sum_{i=0}^{N} \lambda_0^{-1} = (-1)^N \det A \text{ trace } A^{-1} \end{aligned} \tag{V.9}$$

Let $(i|A^m|j)$ represent the elements in the ith row and jth column of the matrix A^m. Then, from Eq. IV.4 which states that the mean first passage time from an initial jth state is

$$\begin{aligned}\bar{t} &= \int_0^\infty [x_0(t)+\ldots+x_N(t)]dt = -\sum_{i=0}^{N}(i|A^{-1}|j)\\ &= \frac{(-1)^{N+1}}{\det A}\sum_{l=0}^{N}a_l\sum_{i=0}^{N}(i|A^{N-l}|j)\end{aligned} \tag{V.10}$$

This formula simplifies considerably when all molecules are initially in the ground state and when det A is a continuant, as it is when only transitions between nearest neighbor states occur (for example in the case of the simple harmonic oscillator model). We recall that A as defined in Eq. IV.6 has the property

$$\sum_{i=0}^{N}(i|A|j) = 0 \text{ for } j = 0, 1, \ldots, N-1 \tag{V.11}$$

but not for $j = N$. Now

$$\begin{aligned}\sum_{i=0}(i|A^2|j) &= \sum_{i,k}^{N}(i|A|k)(k|A|j)\\ &= \sum_{k=0}^{N}(k|A|j)\sum_{i}(i|A|k)\\ &= -(N|A|j)W_{N+1,N}\\ &= 0 \text{ unless } j = N \text{ or } N-1\end{aligned} \tag{V.12}$$

By repeating this argument we find

$$\sum_{i=0}^{N}(i|A^3|j) = 0 \text{ unless } j = N,\ N-1, \text{ or } N-2, \text{ etc.} \tag{V.13a}$$

until

$$\sum_{i=0}^{N}(i|A^N|j) = 0 \text{ only for } j = 0. \tag{V.13b}$$

Since $\sum_i (i|I|j) = 1$ we finally obtain (after combining Eqs. V.10 and V.13)

$$\bar{t} = -\operatorname{trace} A^{-1} \tag{V.14}$$

If transitions are made from a given level to nearest and next nearest neighboring levels and if only the ground state is occupied initially, an argument similar to that used above implies that the terms $l = 0$ and $l = N$ contribute to $\bar{t}$.

An alternative formulation of the solution of Eq. V.1 is that given by Eq. III.4:

$$x_n(t) = e^{-\frac{1}{2}\beta E_n} \sum_{j=0}^{N} c_j \psi_j(n) e^{t\lambda_j} \tag{V.15}$$

where the ψ_j's and λ_j's are now the characteristic vectors and values of the symmetrized form of Eq. IV.6. The c_j's are given by Eq. III.13. The characteristic value $\lambda_j = 0$ is perturbed by the matrix δA which describes the absorbing barrier. We show in the next section that the equilibrium theory for our model of a chemical reaction can be obtained by applying perturbation theory to the determination of the corrected λ_0.

Equation IV.14 implies the mean first passage time to be

$$\begin{aligned} \bar{t} &= \int_0^\infty tP(t)dt \\ &= \sum_{j=0}^{N} \sum_{i=0}^{k} W_{N+1,N-i}\, e^{-\frac{1}{2}\beta E_{N-i}}\, c_j \psi_j(N-i) \lambda_j^{-2} \end{aligned} \tag{V.16}$$

VI. PERTURBATION THEORY AND EQUILIBRIUM THEORY OF CHEMICAL KINETICS

Let us suppose that $E_{N+1} \gg kT$. Then if level $(N+1)$ were not an absorbing barrier but merely the level of a typical highly excited state, the fraction of molecules with energy E_{N+1} would be very small at equilibrium. When level $(N+1)$ is an absorbing barrier we would expect rate processes associated with phenomenon such as propagation of shock waves through a diatomic gas to be governed by two time scales. First the initial Boltzmann distribution of the diatomic molecules would be transformed into the new Boltzmann distribution which corresponds to the final temperature of the gas after the passage of the shock wave. The characteristic time for this process is $\simeq -1/\lambda_1$. The molecules occasionally are excited to the $(N+1)$st level where a reaction occurs. The time associated with this process is determined by the variation of $-\lambda_0$ from 0 associated with the perturbation δA (Eq. IV.8) which arises from making level $(N+1)$ into an absorbing barrier.

The perturbed λ_0 is given by

$$\lambda_0 = \psi_0^{(0)} \cdot \delta A \cdot \psi_0^{(0)} \tag{VI.1}$$

where the squares of the elements of the unperturbed characteristic vector $\psi_0^{(0)}$, $[\psi_0^{(0)}(n)]^2$, form a Boltzmann distribution. Then in the case of nearest neighbor transitions only we find by combining Eqs. VI.1, IV.8, and III.16

$$\lambda_0 = -W_{N+1,N} Z^{-1} \exp(-\beta E_N) = -W_{N,N+1} Z^{-1} \exp(-\beta E_{N+1}) \quad \text{(VI.2)}$$

The time scale associated with the reaction processes is of the order of $-1/\lambda_0$, and the reaction rate is proportional to $-\lambda_0$.

The λ's other than λ_0 and the ψ's are changed but little (of $0(\exp -\beta E_{N+1})$) by the perturbation. Hence when $n \ll N$ the value of x_n at times $\gg -\lambda_1^{-1}$ is

$$x_n \simeq Z^{-1} \exp(-\beta E_n) \exp\{-tW_{N,N+1} Z^{-1} \exp(-\beta E_{N+1})\} \quad \text{(VI.3)}$$

so that

$$x_n/x_m \simeq \exp \beta(E_m - E_n) \text{ for } m, n \ll N \quad \text{(VI.4)}$$

and the Boltzmann ratio of level concentrations is preserved during the reaction. This is the usual hypothesis of the equilibrium theory of chemical kinetics.

The generalization of Eqs. IV.8 and IV.13 which is appropriate when transitions between more distant neighbors can occur is

$$\lambda_0 \simeq -Z^{-1}\{\sum_j W_{j,N+1}\} \exp(-\beta E_{N+1}) \quad \text{(VI.5)}$$

Unfortunately the mean first passage time is more difficult to deduce than λ_0 for, if we refer to Eq. V.16 (first in the case $k = 0$), we see that even when $|\lambda_0^{-1}| \gg |\lambda_1^{-1}|$

$$l \simeq W_{N+1,N}\, e^{-\frac{1}{2}\beta E_N}\, \psi_0(N) \lambda_0^{-2} Z^{-\frac{1}{2}} \quad \text{(VI.6)}$$

The unperturbed $\psi_0^{(0)}(N)$ is $Z^{-\frac{1}{2}} \exp(-\frac{1}{2}\beta E_N)$ which is already a small number. Hence it is quite possible for the perturbation in $\psi_0(N)$ to be of the same order of magnitude as the unperturbed $\psi_0^{(0)}(N)$ itself. All other $\psi_j^{(0)}(n)$'s would be necessary in order to ascertain whether or not this is the case. The rough order of magnitude of l can be obtained however from

$$\begin{aligned} l &\simeq W_{N,N+1} Z^{-1} \exp(-\beta E_{N+1}) \lambda_0^{-2} \\ &= Z W_{N,N+1}^{-1} \exp(\beta E_{N+1}) \end{aligned} \quad \text{(VI.7)}$$

The error obtained in using this formula for the harmonic oscillator molecule will be discussed in the next section.

VII. THE HARMONIC OSCILLATOR

The general theory developed in the previous sections can be applied immediately to the harmonic oscillator model of a diatomic molecule. The quantum-mechanical transition probabilities given in Section II yield the transport equation

$$dx_n(t)/dt = \varkappa\{ne^{-\theta}x_{n-1} - [n+(n+1)e^{-\theta}]x_n + (n+1)x_{n+1}\} \qquad \text{(VII.1a)}$$

where $\varkappa$ depends only on the coupling between molecules and heat bath and where $\theta = h\nu/kT$. These equations have been solved by the authors in the absence of an absorbing barrier.[14] In the presence of an absorbing barrier at level $(N+1)$ the top boundary condition is

$$dx_N/dt = \varkappa\{Ne^{-\theta}x_{N-1} - [N+\alpha(N+1)e^{-\theta}]x_N\} \qquad \text{(VII.1b)}$$

Here α is the absorption coefficient (which in the next few paragraphs we set equal to 1).

The symmetrical matrix B is obtained by letting

$$y_n = x_n \exp(\tfrac{1}{2}\theta n) \qquad \text{(VII.2)}$$

Then

$$dy_n/dt = \varkappa\{ne^{-\frac{1}{2}\theta}y_{n-1} - [n+(n+1)e^{-\theta}]y_n + (n+1)y_{n+1}e^{-\frac{1}{2}\theta}\};$$
$$n = 0, 1, \ldots, N-1 \qquad \text{(VII.3a)}$$

$$dy_N/dt = \varkappa\{Ne^{-\frac{1}{2}\theta}y_{N-1} - [N+\alpha(N+1)e^{-\theta}]y_N\} \qquad \text{(VII.3b)}$$

and B has the form (exhibited for $N = 3$)

$$B = \varkappa\begin{bmatrix} -e^{-\theta} & e^{-\frac{1}{2}\theta} & 0 & 0 \\ e^{-\frac{1}{2}\theta} & -(1+2e^{-\theta}) & 2e^{-\frac{1}{2}\theta} & 0 \\ 0 & 2e^{-\frac{1}{2}\theta} & -(2+3e^{-\theta}) & 3e^{-\frac{1}{2}\theta} \\ 0 & 0 & 3e^{-\frac{1}{2}\theta} & -(3+4\alpha e^{-\theta}) \end{bmatrix} \qquad \text{(VII.4)}$$

Det B, having nonvanishing elements only along the diagonal and first off-diagonal, is a continuant. Trace B^{-1} and hence the mean first passage time $\bar{t}$ from the ground state, past the Nth level is found in Eq. A1.15 of Appendix I to be

$$\begin{aligned} \varkappa l &= -\operatorname{trace} B^{-1} \\ &= \sum_{j=1}^{N+1} e^{j\theta} \left\{\frac{1}{j} + \frac{1}{j+1} + \ldots + \frac{1}{N+1}\right\} \qquad \text{(VII.5)} \\ &= e^{(N+1)\theta} \sum_{k=0}^{N} e^{k\theta} \left\{\frac{1}{N+1} + \frac{1}{N} + \ldots + \frac{1}{N+1-k}\right\}. \end{aligned}$$

This corresponds to a totally absorbing barrier ($\alpha = 1$) at level $(N+1)$.

It is shown in Eq. A1.17 that $N \to \infty$

$$\varkappa l = -\varkappa \operatorname{trace} B^{-1}$$

$$= \frac{e^{(N+1)\theta}}{(N+1)(e^{-\theta}-1)^2}\left\{1 + \frac{e^{-\theta}}{N(1-e^{-\theta})} + \frac{e^{-2\theta}}{2N(N-1)(1-e^{-\theta})^2} + 0(N^{-3})\right\} \qquad \text{(VII.6)}$$

The equilibrium theory first passage time is applicable in limit as $N \to \infty$. Hence corrections to it are to be expected when the second term in the product above is not negligible, i.e., when N is not much greater than $e^{-\theta}(1-e^{-\theta})^{-1}$. The mean first passage time and the rate of activation, $v_{\text{act}} \propto l^{-1}$, deviate from their equilibrium value by more than 10 per cent when

$$N(1-e^{-\theta}) < 10e^{-\theta} \qquad \text{(VII.7a)}$$

In the high-temperature limit this corresponds approximately to

$$Nh\nu/kT = E_{\text{act}}/kT < 10 \qquad \text{(VII.7b)}$$

which is in agreement with the results discussed in Section I.

The ratio of the equilibrium first passage time to that calculated on the basis of Eqs. VII.5 is plotted in Fig. 4 as a function of N for various values of θ. We shall see later that this ratio is exactly that of the reaction rate, based on Eq. VII.5, to the equilibrum rate.

The complete characteristic vector analysis of the harmonic oscillator model can be effected through the aid of Gottlieb polynomials.[5] Let us assume $x_n(t)$ to be a linear combination of products

$$l_n \exp\{\varkappa\mu t(e^{-\theta}-1)\} \qquad \text{(VII.8)}$$

Substitution of this quantity into Eqs. VII.1a and VII.1b shows that l_n satisfies the difference equation

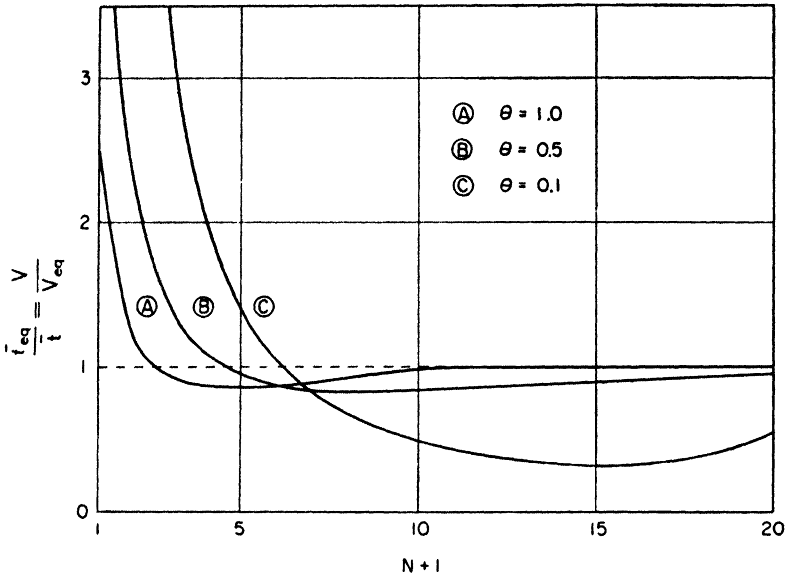

Fig. 4. The ratio of the equilibrium theory first passage time to exact first passage time as a function of number of levels for various values of $\theta = h\nu/kT$.

$$(e^{-\theta}-1)\mu l_n = ne^{-\theta} l_{n-1} - \{n+(n+1)e^{-\theta}\} l_n + (n+1) l_{n+1}, \quad n = 0, 1, \ldots, N \qquad \text{(VII.9a)}$$

where μ is a root of the end-condition equation

$$l_{N+1}(\mu) = (1-\alpha)e^{-\theta} l_N(\mu) \qquad \text{(VII.9b)}$$

The symmetrizing transformation

$$l_n = y_n e^{-\frac{1}{2}n\theta} \qquad \text{(VII.10)}$$

allows us to express the set, Eq. VII.9a in matrix form

$$By = \lambda y \qquad \text{(VII.11)}$$

where B is an $(N+1) \times (N+1)$ generalization of Eq. VII.4,

$$\lambda = \mu\varkappa(e^{-\theta}-1) \qquad \text{(VII.12)}$$

and

$$y = \{y_0, y_1, \ldots, y_N\}$$

In view of the symmetrical nature of the matrix B operating on the y vector we see that the characteristic vectors

$$y^{(k)} = \{y_0^{(k)}, y_1^{(k)}, \ldots, y_N^{(k)}\} \tag{VII.13}$$

which correspond to different characteristic values $\lambda_k = \mu_k(e^{-\theta}-1)$ must be orthogonal

$$y^{(k)} \cdot y^{(l)} = 0 \text{ if } k \neq l \tag{VII.14}$$

(the characteristic values being degenerate). Hence the solutions $l_n(\mu_j)$ which correspond to characteristic values $\mu_j(e^{-\theta}-1)$ satisfy the orthogonality condition

$$\sum_{n=0}^{N} e^{n\theta} l_n(\mu_j) l_n(\mu_k) = 0 \text{ if } j \neq k \tag{VII.15}$$

The Gottlieb polynomials $l_n(\mu)$ which are defined by

$$l_n(\mu) = e^{\theta\mu}\Delta^n\left\{\binom{\mu}{n} e^{-\theta\mu}\right\} \tag{VII.16}$$

or

$$l_n(\mu) = e^{-n\theta} \sum_{\nu=0}^{N} (1-e^{\theta})^{\nu} \binom{n}{\nu}\binom{\mu}{\nu} \tag{VII.17}$$

satisfy the recursion formula, Eq. VII.9a. Hence the end condition, Eq. VII. 1b, is satisfied by choosing μ to be a root of Eq. VII.9b.

The general solution of Eq. VII.1a is then

$$x_n(t) = \sum_{j=0}^{N} a_j l_n(\mu_j) \exp\{\mu_j(e^{-\theta}-1)t\varkappa\} \tag{VII.18}$$

where the coefficients a_j are given in terms of the initial distribution $x_n(0)$ through the aid of the orthogonality relation, Eq. VII.15

$$a_j = \sum_{n=0}^{N} x_n(0) l_n(\mu_j) e^{n\theta} \Big/ \sum_{n=0}^{N} l_n^2(\mu_j) e^{n\theta} \tag{VII.19}$$

Two special cases, the initial delta distribution and initial Boltzmann distribution are of interest. If

$$x_n(0) = \delta_{nm} \tag{VII.20}$$

$$\begin{aligned} a_j &= \sum_{n=0}^{N} \delta_{nm} l_n(\mu_j) e^{n\theta} \Big/ \sum_{n=0}^{N} l_n^2(\mu_j) e^{n\theta} \\ &= l_m(\mu_j) e^{m\theta} \Big/ \sum_{n=0}^{N} l_n^2(\mu_j) e^{n\theta} \end{aligned} \tag{VII.21}$$

Hence

$$x_n(t) = \sum_{j=0}^{N} \left\{ \frac{l_m(\mu_j)\, l_n(\mu_j)\, e^{m\theta}}{\sum_{s=0}^{N} l_s^2(\mu_j) e^{s\theta}} \right\} \exp\{\mu_j(e^{-\theta}-1)t\varkappa\} \tag{VII.22}$$

If $x_n(0)$ is a Boltzmann distribution with $\theta_0 \gg \theta$

$$x_n(0) = e^{-\theta_0}(1-e^{-\theta_0})$$

(we assume θ_0 to be sufficiently large so that $e^{-n\theta_0} \simeq 0$ when $n \geqq N$), then

$$\begin{aligned} a_j &\simeq \frac{[1-e^{-\theta_0}] \sum_{n=0}^{\infty} e^{-n(\theta_0-\theta)} l_n(\mu_j)}{\sum_{n=0}^{N} l_n^2(\mu_j) e^{n\theta}} \\ &= \left\{ \frac{1-e^{-(\theta_0-\theta)}}{1-e^{-\theta_0}} \right\}^{\mu_j} \Big/ \sum_{n=0}^{N} l_n^2(\mu_j) e^{n\theta} \end{aligned} \tag{VII.23}$$

and

$$x_n(t) = \sum_{j=0}^{N} \left\{ l_n(\mu_j) \left[\frac{1-e^{-(\theta_0-\theta)}}{1-e^{-\theta_0}} \right]^{\mu_j} \Big/ \sum_{m=0}^{N} l_m^2(\mu_j)\, e^{m\theta} \right\} e^{-\mu_j(1-e^{-\theta})t\varkappa} \tag{VII.24}$$

The distribution of mean first passage times $P(t)$ is obtained from Eq. IV.9:

$$\begin{aligned} P(t) &= -\frac{d}{dt} \sum x_n(t) = W_{N+1,N}\, x_N(t) \\ &= \alpha e^{-\theta}(N+1) x_N(t) \end{aligned}$$

so that

$$P(t) = \varkappa\alpha(N+1)e^{-\theta} \sum_{j=0}^{N} a_j l_N(\mu_j) \exp[-\mu_j(1-e^{-\theta})\varkappa t] \tag{VII.25}$$

In particular when all molecules are initially in the ground state

$$P(t) = \varkappa\alpha(N+1)e^{-\theta}\sum_{j=0}^{N} l_N(\mu_j)\exp(\lambda_j t)\{\sum_{n=0}^{N} l_n^2(\mu_j)e^{n\theta}\}^{-1} \qquad \text{(VII.26)}$$

The mean first passage time in this case is then

$$\begin{aligned} \bar{t} &= \int_0^\infty tP(t)dt \\ &= \varkappa\alpha(N+1)e^{-\theta}\sum_{j=0}^{N}\lambda_j^{-2} l_N(\mu_j)\{\sum_{n=0}^{N} l_n^2(\mu_j)e^{n\theta}\}^{-1} \end{aligned} \qquad \text{(VII.27)}$$

We can derive the equilibrium theory estimate of $\bar{t}$ by letting $N \to \infty$ and using some limit properties of $l_N(\mu)$ as $N \to \infty$. No chemical reaction takes place in this limit. It was shown by Gottlieb that as $N \to \infty$, the roots μ of $l_N(\mu) = 0$ approach $0, 1, 2, \ldots, N-1$. This means that the roots of Eq. VII.9b also approach nonnegative integers. Hence $\lambda_0 \to 0$ while $|\lambda_j|\varkappa > (1-e^{-\theta})$ for $j > 0$ so that the first term in Eq. VII.27 dominates all others and as $N \to \infty$

$$\bar{t} \sim \varkappa\,\alpha e^{-\theta}(N+1)\lambda_0^{-2} l_N(\mu_0)\Big/\sum_{n=0}^{N} l_n^2(\mu_0)e^{n\theta} \qquad \text{(VII.28)}$$

We have shown in Appendix II, Eqs. A2.9 and A2.10, that

$$\mu_0 \sim \frac{(N+1)\,\alpha(1-e^{-\theta})e^{-(N+1)\theta}}{[1-(1-\alpha)e^{-\theta}]} \qquad \text{(VII.29a)}$$

and

$$l_N(\mu_0) \sim e^{-N\theta}\left\{\frac{1-e^{\theta}}{1-(1-\alpha)e^{-\theta}}\right\} \qquad \text{(VII.29b)}$$

while (see Eq. A2.8)

$$l_n(\mu_0) \sim e^{-n\theta} + 0(e^{-N\theta}) \text{ for } n \ll N \qquad \text{(VII.29c)}$$

The denominator of Eq. VII.28 is, as $N \to \infty$

$$\sum_{n=0}^{N} l_n^2(\mu_0)e^{n\theta} \sim \sum_{n=0}^{N} l_n^2(0)e^{n\theta} = (1-e^{-\theta})^{-1} \qquad \text{(VII.29d)}$$

The first passage time given by Eq. VII.28 is that of equilibrium chemical kinetics since it corresponds to the expression for $x_n(t)$ (Eq. VII.18) which in the limit as $N \to \infty$ would be the Boltzmann distribution. Substitution of Eqs. VII.29a to VII.29d and VII.12 into Eq. VII.28 yields

$$\varkappa l \sim \frac{[1-(1-\alpha)e^{-\theta}]e^{(N+1)\theta}}{(N+1)\alpha(1-e^{-\theta})^2} \tag{VII.30}$$

which, when $\alpha = 1$ is exactly the same as the leading term in Eq. VII.6. The remainder of this article will concern this choice of α.

The relations $\beta E_{N+1} = (N+1)\theta = \beta E_{\text{act}}$, Eqs. II.2, II.5, the expression for the harmonic oscillator partition function $Z = (1-e^{-\theta})^{-1}$, and the definition of $\varkappa$:

$$\varkappa = Z^* P_{10} N^* \tag{VII.31}$$

(where Z^* and N^* are the collision numbers and heat bath molecule concentration defined in Section II) allow us to rewrite Eq. VII.30

$$l = Z^2(W_{N,N+1})^{-1} \exp(\beta E_{N+1}) = Z^2(W_{N+1,N})^{-1} \exp(\beta E_N) \tag{VII.32}$$

This differs by a factor Z from the estimate derived in Eq. VI.7 by the assumption that the characteristic value λ_0 of the transition probability matrix A can be determined by perturbation theory while the corresponding characteristic vector remains unchanged by the existence of an absorbing barrier. The significance of the error will be discussed presently.

The rate of activation v_{act} (in mole/cm³/sec) is inversely proportional to the mean first passage time l:

$$v_{\text{act}} = \varkappa(N+1)X(1-e^{-\theta})^2 e^{-(N+1)\theta} = X/l \tag{VII.33}$$

where X is the concentration of diatomic oscillator reactants in mole/cm³. The rate constant for activation, k_{act} is, according to its usual definition, and from Eqs. VII.31 and VII.33

$$k_{\text{act}} = v_{\text{act}}/XN^* = Z^* P_{10}(N+1)(1-e^{-\theta})^2 \exp(-\beta E_{\text{act}}) \tag{VII.34}$$

If we compare this equation with the Arrhenius equilibrium expression

$$k_{\text{act}} = A \exp(-\beta E_{\text{act}}) \tag{VII.35}$$

we find the frequency factor A of our model to be

$$A = Z^* P_{10}(N+1)(1-e^{-\theta})^2 \tag{VII.36}$$

Equations VII.33 and VII.36 correspond to the equilibrium values of l i.e., as $N \to \infty$. When $N\theta \ll 10$, v_{act} becomes (see Eq. VII.5)

$$v_{\text{act}} = \varkappa X \left[\sum_{j=1}^{N+1} e^{j\theta} \left(\frac{1}{j} + \frac{1}{j+1} + \ldots + \frac{1}{N+1} \right) \right]^{-1} \tag{VII.37}$$

Additional insight into stepwise activation processes is gained by expressing Eqs. VII.34 and VII.33 in the alternative form

$$\begin{aligned} v_{\text{act}} &= Z^{-2} X\, W_{N+1,N} \exp(-\beta E_N) \\ &= X_N^{(0)} (1-e^{-\theta}) W_{N+1,N} \end{aligned} \tag{VII.38}$$

where $X_N^{(0)} = XZ^{-1} \exp(-\beta E_N)$ is the equilibrium concentration of oscillators at the Nth level. This equation is to be interpreted as follows. If there were no reaction, the equilibrium concentration of oscillators in level N would be given by $X_N^{(0)}$. When there is a reaction, i.e., when the oscillators are removed irreversibly through passage upward from level N, the concentration X_N of oscillators in level N is less than the (closed system) Boltzmann equilibrium concentration $X_N^{(0)}$. In our model, this reduction in the concentration of oscillators in level N is given by the factor $(1-e^{-\theta})$ of Eq. VII.38. The product $(1-e^{-\theta})X_N^{(0)}$ thus represents the actual concentration of oscillators X_n in level N in a reacting system, and the product of this quantity with the transition probability per unit time $W_{N+1,N}$, gives the rate of activation to level $(N+1)$. Hirschfelder,[8] in discussing a simpler and more schematic model of stepwise activation in unimolecular reactions assumed the absorption coefficient α ($k_F/k_n = 1$ in Hirschfelder notation) to be 0.5 and obtained the equation

$$X_N = \left(\frac{1-e^{-\theta}}{2-e^{-\theta}} \right) X_N^{(0)} \tag{VII.39}$$

For $\theta = 1$ Hirschfelder thus finds $X_N/X_N^{(0)} = 0.387$ while we obtain $X_N/X_N^{(0)} = 0.632$ from Eq. VII.38. The difference in the numerical values is not important, being due to different models and different assumptions used by Hirschfelder and by us. The important point, as already expressed by Hirschfelder, is that in unimolecular reactions the concentration of molecules in the "activated state" is less than the value calculated for statistical equilibrium.

According to the "collision theory" of chemical kinetics, the rate constant for activation is given by the expression

$$k_{\mathrm{act}} = P_c Z^* \exp(-E_{\mathrm{act}}\beta) \qquad \text{(VII.40)}$$

where $Z^* \exp(-\beta E_{\mathrm{act}})$ is the number of collisions per unit time per unit gas density in which the relative kinetic energy of the collision partners along the line of centers at contact exceeds the energy E_{act} and where P_c is the probability per collision that such a collision will actually leave one of the collision partners with an energy $E \geqq E_{\mathrm{act}}$. A comparison of Eq. VII.40 with Eq. VII.35 yields

$$A = Z^* P_c \qquad \text{(VII.41)}$$

for the frequency factor of the rate of activation in the standard collision theory treatment.

As far as we are aware, no *a priori* calculations have even been carried out to evaluate P_c from the molecular properties of the collision partners. Its order of magnitude has only been found *a posteriori* for reaction systems. It is, therefore, impossible to make a direct numerical comparison between the frequency factors A found for the process of stepwise activation Eq. VII.36 and for the "all or nothing" kinetic theory activation Eq. VII.41. The following indirect comparison is, however, instructive. Measurements on the rate of activation of I_2 at about 300°K in various inert gases such as He, Ne, A, Kr, and N_2 have shown[22] that the frequency factor A is of the order of about 5×10^{16} cm^3/mole /sec. Since the collision number Z^* is only about 10^{14} cm^3/mole/sec at 300°K, even a value of $P_c = 1$, which corresponds to unit efficiency in direct collisional activation, could not raise the calculated A-value for the standard collision theory (Eq. VII.41) to the observed one. This is, of course, one of the old and vexing problems in chemical kinetics.[17]

We can also make an approximate calculation of the frequency factor A for the stepwise activation process (Eq. VII.36). The transition probability per collision is not known for I_2 in the various gases just listed. We can, however, estimate it to be about 10^{-4} on the basis of the results obtained by Herzfeld[6] for Cl_2 in Cl_2 and Br_2 in Br_2. At 300°K, $\theta \simeq 1$ and $N+1 \simeq 60$, based on

$\omega_e(I_2) \simeq 200\ \mathrm{cm}^{-1}$ and $D_e(I_2) \simeq 12{,}000\ \mathrm{cm}^{-1}$. Using these values and $Z^* = 10^{14}\ \mathrm{cm}^3/\mathrm{mole/sec}$, we obtain $A \simeq 2 \times 10^{11}\mathrm{cm}^3/\mathrm{mole/sec}$.

It appears from these calculations that the frequency factor calculated for a stepwise activation deviates even more from the experimental value than that calculated by the usual collision theory. Two points are to be noted however. If we had taken $P_{10} = 1$, as we did for P_c, we would have found $A \simeq 2 \times 10^{15}$ cm³/mole/sec which is closer to the experimental value of $A \simeq 10^{16}$ cm³/mole/sec. This comparison is, however, quite unrealistic since neither P_c nor P_{10} are unity; both quantities probably being several orders of magnitude smaller. The second, and significant point is that we have used, for mathematical convenience, a ***harmonic*** oscillator molecule in our model of a stepwise activation process. Owing to the selection rule $P_{n,m} = 0$ for $m \neq n \pm 1$ which limits transitions to adjacent levels only, we are considering the slowest possible process of stepwise activation. One would expect, intuitively, that the rate of stepwise activation would be more rapid for an *anharmonic* oscillator where transition can occur between any two energy levels and where in addition the level density increases with increasing energy.

In conclusion we summarize some of the principal points of this review:

(1) A formal treatment has been developed for the application of the theory of stochastic processes to reaction rate problems.

(2) On the basis of the model employed here, it has been shown that the rate of a chemical reaction will deviate from the equilibrium rate, as calculated from collision or absolute rate theory, when $E_{\mathrm{act}}/kT < 10$. The calculated deviation of about 20 per cent for $E_{\mathrm{act}}/kT = 5$ (see Fig. 4) is in good agreement with the results obtained previously by other authors. For $E_{\mathrm{act}}/kT \geqq 10$ the error in the rate as calculated by equilibrium theory is < 10 per cent.

(3) The rate of activation in a unimolecular dissociation reaction has been calculated for a stepwise process of activation involving transition only between adjacent energy levels (harmonic oscillator model with weak interactions). The experimental rate of activation is higher by several orders of magnitude than the rate obtained from these calculations. A process of stepwise activation involving

only weak collisional interaction is thus inadequate to account for the observed high rate of activation.

In conclusion the authors wish to thank Mr. George Weiss for several useful discussions concerning Section VII and Appendix II.

Note added in proof: In view of the failure of the harmonic oscillator model to account for the observed rate of activation in unimolecular dissociation reactions (the dissociation lag problem) these calculations have been repeated for a Morse anharmonic oscillator with transition between nearest and next-nearest neighbor levels [S. K. Kim, *J. Chem. Phys.* (to be published)]. The numerical evaluation of the analytical results obtained by Kim has not yet been carried out. From the results obtained by us and our co-workers [Bazley, Montroll, Rubin, and Shuler, *J. Chem. Phys.* (in press)] on the relaxation of vibrational nonequilibrium distributions of a system of Morse anharmonic oscillators it seems clear, however, that the anharmonic oscillator model *with weak interactions* (i.e., adiabatic perturbation type matrix elements) does not constitute much of an improvement on the harmonic oscillator model in giving the observed rates of activation. The answer to this problem would seem to lie in a recalculation of the collisional matrix elements for translational-vibrational energy exchange which takes account of the strong interactions in highly energetic collisions which can lead to direct dissociation.

APPENDIX I

Trace of the Inverse of the Matrix of a Continuant

Let us consider the matrix B of a continuant

$$B = \begin{vmatrix} a_1 & b_1 & 0 & 0 & \ldots & 0 & 0 \\ b_1 & a_2 & b_2 & 0 & \ldots & 0 & 0 \\ 0 & b_2 & a_3 & b_3 & \ldots & 0 & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot\;\cdot\;\cdot & \cdot & \cdot \\ & & & & & a_{n-1} & b_{n-1} \\ 0 & 0 & 0 & 0 & \ldots & b_{n-1} & a_n \end{vmatrix} \qquad \text{(A1.1)}$$

The mth diagonal element of B^{-1} is (since the elements of B^{-1} are the cofactors of the corresponding elements of A):

$$(m|B^{-1}|m) = D_{m+1}A_{m-1}/\det A \tag{A1.2}$$

where

$$A_m = \begin{vmatrix} a_1 & b_1 & 0 & 0 \dots 0 \\ b_1 & a_2 & b_2 & 0 \dots 0 \\ \cdot\ \cdot & \cdot\ \cdot & \cdot\ \cdot & \cdot\ \cdot\ \cdot\ \cdot\ \cdot \\ 0 & 0 & 0 & 0 \dots a_m \end{vmatrix} \tag{A1.3}$$

and

$$D_m = \begin{vmatrix} a_m & b_m & 0 & 0 & \dots 0 \\ b_m & a_{m+1} & b_{m+1} & 0 & \dots 0 \\ 0 & b_{m+1} & a_{m+2} & b_{m+2} & \dots 0 \\ \cdot\ \cdot & \cdot\ \cdot & \cdot\ \cdot & \cdot\ \cdot & \cdot\ \cdot\ \cdot\ \cdot \\ 0\ \cdot & \cdot\ \cdot & \cdot\ \cdot & \cdot\ \cdot & \dots a_m \end{vmatrix} \tag{A1.4}$$

By expanding A_m with respect to the mth row, we find

$$A_m = a_m A_{m-1} - b_{m-1}{}^2 A_{m-2} \tag{A1.5}$$

and by expanding D_m with respect to the first row we have

$$D_m = a_m D_{m+1} - b_m{}^2 D_{m+2} \tag{A1.6}$$

We define

$$A_0 = D_{n+1} = 1 \tag{A1.7}$$

and note that

$$A_n = D_1 = \det B \tag{A1.8}$$

Finally

$$\text{trace } B^{-1} = D_1{}^{-1} \sum_{m-1}^{n} D_{m+1} A_{m-1} \tag{A1.9}$$

The rest of this appendix is devoted to the calculation of trace B^{-1} when (Eq. VII.4)

$$b_m = me^{-\frac{1}{2}\theta} \quad \text{and} \quad a_m = -(m-1+me^{-\theta}) \tag{A1.10}$$

Then Eqs. A1.5 and A1.6 are, respectively,

$$A_m = -(m-1+me^{-\theta})A_{m-1} - (m-1)^2 e^{-\theta} A_{m-2} \tag{A1.11}$$

and

$$D_m = -(m-1+me^{-\theta})D_{m+1}-m^2\,e^{-\theta}\,D_{m+2} \qquad \text{(A1.12)}$$

We can now show by induction that

$$A_m = (-1)^m\, m!\, e^{-m\theta} \qquad \text{(A1.13)}$$

Clearly this is true of $m = 0$ and $m = 1$ since $A_0 = 1$ and $A_1 = -e^{-\theta}$. If it is true for A_{m-1} and A_{m-2}, it is true for A_m since direct substitution of Eq. A1.13 into the right-hand side of Eq. A1.11 yields

$$A_m=(-1)^m(m-1+me^{-\theta})(m-1)!\,e^{-(m-1)\theta}-(-1)^m(m-1)(m-1)!e^{-(m-1}$$
$$= (-1)^m m!\, e^{-m\theta}$$

as is required.

We can also show by induction that

$$D_{n-k} = (-1)^{k+1}n(n-1)\dots(n-k-1)$$
$$\cdot\left\{\frac{1}{n}+\frac{1}{n-1}\,e^{-\theta}+\frac{1}{n-2}\,e^{-2\theta}+\dots+\frac{1}{n-(k+1)}\,e^{-(k+1)\theta}\right\} \qquad \text{(A1.14)}$$
$$k = 0, 1, \dots, n$$

By definition $D_{n+1} = 1$. Equation A1.4 implies that $D_n = -(n-1+ne^{-\theta})$ which is the form given by Eq. A1.14. If Eq. A1.14 is valid for $D_{n-(k-1)}$ and $D_{n-(k-2)}$, then Eq. A1.12) implies

$$D_{n-k}=(-1)^{k+1}[(n-k-1)+(n-k)e^{-\theta}]n(n-1)\dots(n-k)\left\{\frac{1}{n}+\dots+\frac{1}{n-k}e^{-k}\right.$$
$$-(n-k)^2\,e^{-\theta}(-1)^{k+1}\,n(n-1)\dots(n-[k-1])\left\{\frac{1}{n}+\dots+\frac{e^{-(k-1)\theta}}{n-(k-1}\right.$$
$$= (-1)^{k+1}n(n-1)\dots(n-k-1)\left\{\frac{1}{n}+\dots+\frac{1}{n-k}\,e^{-k\theta}\right\}$$
$$+(-1)^{k+1}n(n-1)\dots(n-k)\,e^{-(k+1)\theta}$$

which is exactly Eq. A1.14 as is required to prove its validity by induction.

We now substitute Eqs. A1.14 and A1.13 into Eq. A1.9 to find

$$-\text{trace } B^{-1} = \sum_{k=0}^{n-1} e^{(k+1)\theta}\left\{\frac{1}{n}+\frac{e^{-\theta}}{n-1}+\dots+\frac{e^{-k\theta}}{n-k}\right\} \tag{A1.15}$$

$$= \sum_{j=1}^{n} e^{j\theta}\left\{\frac{1}{j}+\frac{1}{j+1}+\dots+\frac{1}{n}\right\} = e^{n\theta}\sum_{k=0}^{n-1} e^{-k\theta}\left\{\frac{1}{n}+\frac{1}{n-1}+\dots+\frac{1}{n-k}\right\}$$

The values of $-$ trace B^{-1} for the first few integers n are given in Table I.

TABLE I. Mean First Passage Time $\bar{t}$ as a Function of N.

N	$\bar{t}$
0	e^{θ}
1	$\frac{e^{2\theta}}{2}(1+3e^{-\theta})$
2	$\frac{e^{3\theta}}{6}(2+5e^{-\theta}+11e^{-2\theta})$
3	$\frac{e^{4\theta}}{12}(3+7e^{-\theta}+13e^{-2\theta}+25e^{-3\theta})$
4	$\frac{e^{5\theta}}{60}(12+27e^{-\theta}+47e^{-2\theta}+77e^{-3\theta}+137e^{-4\theta})$
5	$\frac{e^{6\theta}}{60}(10+22e^{-\theta}+37e^{-2\theta}+57e^{-3\theta}+87e^{-4\theta}+147e^{-5\theta})$

The asymptotic value of $-$ trace B^{-1} as $n \to \infty$ is easily obtained by noting that

$$\left\{\frac{1}{n}+\frac{1}{n-1}+\dots+\frac{1}{n-k}\right\} = \frac{1}{n}(k+1)+\frac{1}{n}\left\{\frac{1}{n-1}+\frac{2}{n-2}+\dots+\frac{k}{n-k}\right\}$$

$$=\frac{1}{n}(k+1)+\frac{1}{2}\frac{k(k+1)}{n(n-1)}+\frac{1}{n(n-1)}\left\{\frac{2.1}{n-2}+\frac{3.2}{n-3}+\dots+\frac{k(k-1)}{n-k}\right\}$$

$$=\frac{1}{n}(k+1)+\frac{1}{2}\frac{k(k+1)}{n(n-1)}+\frac{(k+1)k(k-1)}{3n(n-1)(n-2)}$$

$$+\frac{1}{n(n-1)(n-2)}\left\{\frac{3.2.1}{n-3}+\frac{4.3.2}{n-4}+\dots+\frac{k(k-1)(k-2)}{n-k}\right\}$$

Hence

$$-\text{trace } B^{-1} = e^{n\theta}\left\{\frac{1}{n}\sum_{k=0}^{n-1}(k+1)e^{-k\theta} + \frac{1}{2n(n-1)}\sum_{k=1}^{n-1} e^{-k\theta}k(k+1)\right.$$

$$\left. + \frac{1}{3n(n-1)(n-2)}\sum_{k=2}^{n-1} e^{-k\theta}(k+)k(k-1)+\dots\right\} \qquad \text{(A1.16)}$$

But

$$\sum_{k=0}^{n-1} (k+1)e^{-k\theta} = (1-e^{-\theta})^{-2} + 0(e^{-n\theta});$$

$$\sum_{k=2}^{n-1} (k+1)k(k-1)e^{-k\theta} = \frac{6e^{-2\theta}}{(1-e^{-\theta})^4} + 0(e^{-n\theta})$$

$$\sum_{k=1}^{n-1} (k+1)ke^{-k\theta} = 2e^{-\theta}(1-e^{-\theta})^{-3} + 0(e^{-n\theta})$$

Therefore

$$-\text{trace } B^{-1} = \frac{e^{n\theta}}{n(e^{-\theta}-1)^2}$$

$$\cdot\left\{1 + \frac{e^{-\theta}}{(1-e^{-\theta})(n-1)} + \frac{2e^{-2\theta}}{(1-e^{-\theta})^2(n-1)(n-2)} + 0(n^{-3})\right\} \qquad \text{(A1.17)}$$

APPENDIX II

On the Smallest Zero of $l_{N+1}(\mu) = (1-\alpha)\, e^{-\theta}\, l_N(\mu)$ as $N \to \infty$

As $N \to \infty$ the smallest zero of this equation approaches 0. Hence we must find the behavior of $l_N(\mu)$ as $\mu \to 0$ and $N \to \infty$.

By definition

$$l_n(\mu) = e^{-n\theta} + e^{-n\theta}\sum_{\nu=1}^{n} (1-e^{\theta})^{\nu}\binom{n}{\nu}\binom{\mu}{\nu} \qquad \text{(A2.1)}$$

As $\mu \to 0$

$$\binom{\mu}{\nu} = \frac{\mu(\mu-1)\dots(\mu-\nu+1)}{\nu!} \sim \frac{\mu}{\nu}(-1)^{\nu-1}$$

Hence

$$
\begin{aligned}
l_n(\mu) &\sim e^{-n\theta}-\mu e^{-n\theta}\sum_{\nu=1}^{n}\nu^{-1}(e^{\theta}-1)^{\nu}\binom{n}{\nu} \\
&= e^{-n\theta}-\mu e^{-n\theta}\sum_{\nu=1}^{n}\int_0^{e^{\theta}-1}\binom{n}{\nu}x^{\nu-1}\,dx \\
&= e^{-n\theta}-\mu e^{-n\theta}\int_0^{e^{\theta}-1}x^{-1}\left\{\sum_{\nu=0}^{n}x^{\nu}\binom{n}{\nu}-1\right\}dx \qquad \text{(A2.2a)} \\
&= e^{-n\theta}-\mu e^{-n\theta}\int_0^{e^{\theta}-1}x^{-1}\{(1+x)^{n}-1\}dx \\
&= e^{-n\theta}-\mu e^{-n\theta}I_n
\end{aligned}
$$

where

$$I_n=\int_1^{e^{\theta}}\frac{y^{n}-1}{y-1}\,dy \qquad \text{(A2.2b)}$$

Since

$$I_{n+1}-I_n=\int_1^{e^{\theta}}y^{n}dy=\frac{e^{(n+1)\theta}-1}{n+1}$$

and

$$I_0=0,\ I_1=e^{\theta}-1,$$

we have

$$
\begin{aligned}
e^{-(n+1)\theta}I_{n+1} &= \sum_{m=0}^{n}\left\{\frac{e^{(m+1)\theta}-1}{m+1}\right\}e^{-(n+1)\theta} \\
&= \sum_{m=0}^{n}\frac{e^{(m-n)\theta}}{m+1}+0(e^{-(n+1)\theta}\log n)
\end{aligned}
\qquad \text{(A2.3)}
$$

Since we are interested in asymptotic values of $e^{-n\theta}I_n$ as $n\to\infty$, we neglect the term of $0(e^{-(n+1)\theta}\log n)$ and find that

$$e^{-(n+1)\theta}I_{n+1}\sim\sum_{m=0}^{n}\frac{e^{(m-n)\theta}}{(m+1)}. \qquad \text{(A2.4)}$$

An immediate application of Abels' partial summation formula yields

$$\sum_{m=0}^{n}\frac{e^{m\theta}}{m+1}=\frac{1}{n+1}\left\{\frac{e^{(n+1)\theta}-1}{e^{\theta}-1}\right\}+\sum_{m=0}^{n}\frac{1}{(m+1)(m+2)}\left\{\frac{e^{(m+1)\theta}-1}{e^{\theta}-1}\right\} \qquad \text{(A2.5)}$$

But

$$\sum_{m=0}^{n}[(m+1)(m+2)]^{-1} < \sum_{m=0}^{\infty}(m+1)^{-2} = \pi^2/6$$

and

$$J_n = \sum_{m=0}^{n}\frac{e^{(m+1)\theta}}{(m+1)(m+2)} < \sum_{m=0}^{n}\frac{e^{(m+1)\theta}}{(m+1)^2} < \int_1^{n+1}\frac{e^{x\theta}}{x^2}\,dx$$

$$= \frac{1}{\theta}\,\frac{(e^{(n+1)\theta}-1)}{(n+1)^2} + \frac{2}{\theta}\int_1^{n+1}\frac{e^{x\theta}}{x^3}\,dx$$

also

$$\int_1^{n+1}\frac{e^{\theta x}}{x^3}\,dx < e^{(n+1)\theta}\int_1^{n+1}\frac{dx}{x^3} < \frac{e^{(n+1)\theta}}{2(n+1)^2}$$

Hence

$$0 < J_n < 2(n+1)^{-2}\exp{(n+1)\theta} \tag{A2.6}$$

so that as $n \to \infty$

$$e^{-(n+1)\theta}J_{n+1} \sim e^{\theta}/(n+1)(e^{\theta}-1) \tag{A2.7}$$

and as $\mu \to 0$

$$l_n(\mu) \sim e^{-n\theta} - \frac{\mu e^{\theta}}{n(e^{\theta}-1)} \tag{A2.8}$$

In this limit our characteristic equation

$$l_{N+1}(\mu) = (1-\alpha)e^{-\theta}l_N(\mu)$$

yields

$$\mu_0 \sim \frac{\alpha e^{-(N+1)\theta}(N+1)(1-e^{-\theta})}{[1-(1-\alpha)e^{-\theta}]} \tag{A2.9}$$

which approaches zero exponentially as $N \to \infty$. Substitution of Eq. A2.9 into Eq. (A2.8) yields

$$l_N(\mu) \sim e^{-N\theta}\left\{1 - \frac{\alpha e^{-\theta}}{[1-(1-\alpha)e^{-\theta}]}\right\} \tag{A2.10}$$

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