Fluid Mechanics Laboratory Publication No. 72-3

MONTE CARLO TRAJECTORY CALCULATIONS OF THE THREE-BODY RECOMBINATION AND DISSOCIATION OF DIATOMIC MOLECULES

Ven H. S<u>hui</u>

745073

by

February 1972

FLUID MECHANICS LABORATORY





DEPARTMENT OF MECHANICAL ENGINEERING MASSACHUSETTS INSTITUTE OF TECHNOLOGY



Security classification	
DOCUMEN	T CONTROL DATA - BAD
(Security classification of title, body of abstract and	indexing annotation must be entered when the overall report is classified)
1. ORIGINATING ACTIVITY (Corporate author)	24. REPORT SECURITY CLASSIFICATION
Massachusetts Institute of Technol	ogy Unclassified
Cambridge, Massachusetts	26 GROUP Fluid Mechanics Isherator
BEPORT TITLE	
Monte Carlo Trajectory Calculation	s of the Three-Body Recombination and
Dissociation of Diatomic Molecules	b of the infec body hecompany ton and
DESCRIPTIVE NOTES (Type of report and inclusive date	
	·
Ven H. Shui	•
February 1972	74. TOTAL NO. OF PAGES 75. NO. OF REFS
NOO11467_A_0204 0040	94. ORIGINATOR'S REPORT NUMBER(S)
NOUD I - 07-A-0204-0040	Fluid Mechanics Laboratory
ABRA On tour M 200	Publication No. 72-3
ARFA Order No. 322	
	90. OTHER REPORT NO(3) (Any other numbers that may be aseigne this report)
<i>d.</i>	
0. AVAILABILITY/LIMITATION NOTICES	
Distribution Unlimited	
Distribution online ted	
Also supported in part by the	A designed Designed Designed A designed
National Science Foundation	Advanced Research Projects Agency of th
Grant No. GP-32522X.	Department of Defense and monitored by
ABSTRACT	the Uffice of Naval Kesearch
The modified phase-space the	ary of reaction rates has been applied to the
ine modified phase-space the	ory of reaction rates has been applied to the
problem of the three-body recombined the descent	nation and dissociation of diatomic molecules.
The results illustrate the import	ant influence of the weak attractive minimum
and a shire while the first state of the sta	
in the third-body interaction pot	ential and the effect of barrier penetration
in the third-body interaction pot for recombination at low temperat	ential and the effect of barrier penetration ures. The system N_2 + Ar was used as a typica
in the third-body interaction pot- for recombination at low temperat illustrative example, and good ag	ential and the effect of barrier penetration ures. The system N_2 + Ar was used as a typica reement was obtained between the theoretical
in the third-body interaction pot for recombination at low temperat illustrative example, and good ag predictions and the experimental	ential and the effect of barrier penetration ures. The system $N_2 + Ar$ was used as a typica reement was obtained between the theoretical measurements of the reaction rate coefficients
in the third-body interaction pot for recombination at low temperat illustrative example, and good ag predictions and the experimental over the temperature range 200-12	ential and the effect of barrier penetration ures. The system N_2' + Ar was used as a typica reement was obtained between the theoretical measurements of the reaction rate coefficients 000 °K.
in the third-body interaction pot- for recombination at low temperat- illustrative example, and good ag predictions and the experimental over the temperature range 200-12	ential and the effect of barrier penetration ures. The system N_2 + Ar was used as a typica reement was obtained between the theoretical measurements of the reaction rate coefficients 000 °K.
in the third-body interaction pot- for recombination at low temperati illustrative example, and good ag predictions and the experimental is over the temperature range 200-12 The recrossing factor and the	ential and the effect of barrier penetration ures. The system N_2 + Ar was used as a typica reement was obtained between the theoretical measurements of the reaction rate coefficients 000 °K. e nonequilibrium factor were obtained from
in the third-body interaction pot- for recombination at low temperat- illustrative example, and good ag predictions and the experimental over the temperature range 200-12 The recrossing factor and the Monte Carlo trajectory calculation	ential and the effect of barrier penetration ures. The system N_2 + Ar was used as a typical reement was obtained between the theoretical measurements of the reaction rate coefficients 000 O K. e nonequilibrium factor were obtained from ns for states near the dissociation limit.
in the third-body interaction pot- for recombination at low temperat- illustrative example, and good ag predictions and the experimental over the temperature range 200-120 The recrossing factor and the Monte Carlo trajectory calculation The trajectories were sampled with	ential and the effect of barrier penetration ures. The system N_2 + Ar was used as a typical reement was obtained between the theoretical measurements of the reaction rate coefficients 000 °K. e nonequilibrium factor were obtained from ns for states near the dissociation limit. hin the reaction zone, with a weight propor-
in the third-body interaction pot- for recombination at low temperat- illustrative example, and good ag predictions and the experimental over the temperature range 200-120 The recrossing factor and the Monte Carlo trajectory calculation The trajectories were sampled with tional to the equilibrium reaction	ential and the effect of barrier penetration ures. The system N_2 + Ar was used as a typica reement was obtained between the theoretical measurements of the reaction rate coefficients 000 °K. e nonequilibrium factor were obtained from ns for states near the dissociation limit. hin the reaction zone, with a weight propor- n rate, and numerically integrated in both
in the third-body interaction pot- for recombination at low temperati- illustrative example, and good ag predictions and the experimental over the temperature range 200-12 The recrossing factor and the Monte Carlo trajectory calculation The trajectories were sampled with tional to the equilibrium reaction timewise directions to determine	ential and the effect of barrier penetration ures. The system N_2 + Ar was used as a typica reement was obtained between the theoretical measurements of the reaction rate coefficients 000 °K. e nonequilibrium factor were obtained from ns for states near the dissociation limit. hin the reaction zone, with a weight propor- n rate, and numerically integrated in both the complete histories of the collisions. A
in the third-body interaction pot- for recombination at low temperati- illustrative example, and good ag predictions and the experimental in over the temperature range 200-12 The recrossing factor and the Monte Carlo trajectory calculation The trajectories were sampled with tional to the equilibrium reaction timewise directions to determine simple, separable function for the	ential and the effect of barrier penetration ures. The system N_2 + Ar was used as a typica reement was obtained between the theoretical measurements of the reaction rate coefficients 000 °K. e nonequilibrium factor were obtained from ns for states near the dissociation limit. hin the reaction zone, with a weight propor- n rate, and numerically integrated in both the complete histories of the collisions. A e equilibrium transition rate $R(\varepsilon_1, \varepsilon_f)$ from
in the third-body interaction pot- for recombination at low temperati- illustrative example, and good ag predictions and the experimental over the temperature range 200-12 The recrossing factor and the Monte Carlo trajectory calculation The trajectories were sampled with tional to the equilibrium reaction timewise directions to determine simple, separable function for the initial energy states ε_1 to final	ential and the effect of barrier penetration ures. The system N_2 + Ar was used as a typica reement was obtained between the theoretical measurements of the reaction rate coefficients 000 °K. e nonequilibrium factor were obtained from ns for states near the dissociation limit. hin the reaction zone, with a weight propor- n rate, and numerically integrated in both the complete histories of the collisions. A e equilibrium transition rate $R(\varepsilon_1, \varepsilon_f)$ from energy states ε_f , which could be characterize
in the third-body interaction pot- for recombination at low temperat- illustrative example, and good ag predictions and the experimental over the temperature range 200-12. The recrossing factor and the Monte Carlo trajectory calculation The trajectories were sampled with tional to the equilibrium reaction timewise directions to determine simple, separable function for the initial energy states ε_1 to final by three parameters, was obtained	ential and the effect of barrier penetration ures. The system N_2 + Ar was used as a typica reement was obtained between the theoretical measurements of the reaction rate coefficients 000 °K. e nonequilibrium factor were obtained from ns for states near the dissociation limit. hin the reaction zone, with a weight propor- n rate, and numerically integrated in both the complete histories of the collisions. A e equilibrium transition rate $R(\varepsilon_1, \varepsilon_f)$ from energy states ε_f , which could be characterize to fit the numerical data and was used to sol
in the third-body interaction pot- for recombination at low temperat- illustrative example, and good ag predictions and the experimental over the temperature range 200-12 The recrossing factor and the Monte Carlo trajectory calculation The trajectories were sampled with tional to the equilibrium reaction timewise directions to determine simple, separable function for the initial energy states ε_1 to final by three parameters, was obtained the steady-state master equation.	ential and the effect of barrier penetration ures. The system N_2 + Ar was used as a typica reement was obtained between the theoretical measurements of the reaction rate coefficients 000 °K. e nonequilibrium factor were obtained from ns for states near the dissociation limit. hin the reaction zone, with a weight propor- n rate, and numerically integrated in both the complete histories of the collisions. A e equilibrium transition rate $R(\varepsilon_1, \varepsilon_f)$ from energy states ε_f , which could be characterize to fit the numerical data and was used to sol
in the third-body interaction pot- for recombination at low temperati- illustrative example, and good ag predictions and the experimental is over the temperature range 200-12. The recrossing factor and the Monte Carlo trajectory calculation The trajectories were sampled with tional to the equilibrium reaction timewise directions to determine simple, separable function for the initial energy states ε_1 to final by three parameters, was obtained the steady-state master equation.	ential and the effect of barrier penetration ures. The system N_2 + Ar was used as a typica reement was obtained between the theoretical measurements of the reaction rate coefficients 000 °K. e nonequilibrium factor were obtained from ns for states near the dissociation limit. hin the reaction zone, with a weight propor- n rate, and numerically integrated in both the complete histories of the collisions. A e equilibrium transition rate $R(\varepsilon_1, \varepsilon_f)$ from energy states ε_f , which could be characterize to fit the numerical data and was used to sol
in the third-body interaction pot- for recombination at low temperati- illustrative example, and good ag predictions and the experimental over the temperature range 200-12. The recrossing factor and the Monte Carlo trajectory calculation The trajectories were sampled with tional to the equilibrium reaction timewise directions to determine simple, separable function for the initial energy states ε_1 to final by three parameters, was obtained the steady-state master equation. Distributions of the trajector	ential and the effect of barrier penetration ures. The system N_2 + Ar was used as a typica reement was obtained between the theoretical measurements of the reaction rate coefficients 000 °K. e nonequilibrium factor were obtained from ns for states near the dissociation limit. hin the reaction zone, with a weight propor- n rate, and numerically integrated in both the complete histories of the collisions. A e equilibrium transition rate $R(\varepsilon_1, \varepsilon_f)$ from energy states ε_f , which could be characterize to fit the numerical data and was used to solve pries with respect to energies and impact eral typical trajectories are shown to diluct
in the third-body interaction pot- for recombination at low temperat- illustrative example, and good ag predictions and the experimental over the temperature range 200-12. The recrossing factor and the Monte Carlo trajectory calculation The trajectories were sampled with tional to the equilibrium reaction timewise directions to determine simple, separable function for the initial energy states ε_1 to final by three parameters, was obtained the steady-state master equation. Distributions of the trajector parameters are presented, and seven the important features of the column	ential and the effect of barrier penetration ures. The system N_2 + Ar was used as a typica reement was obtained between the theoretical measurements of the reaction rate coefficients 000 °K. e nonequilibrium factor were obtained from ns for states near the dissociation limit. hin the reaction zone, with a weight propor- n rate, and numerically integrated in both the complete histories of the collisions. A e equilibrium transition rate $R(\varepsilon_1, \varepsilon_f)$ from energy states ε_f , which could be characterize to fit the numerical data and was used to sol
in the third-body interaction pot- for recombination at low temperat- illustrative example, and good ag predictions and the experimental over the temperature range 200-12 The recrossing factor and the Monte Carlo trajectory calculation The trajectories were sampled with tional to the equilibrium reaction timewise directions to determine simple, separable function for the initial energy states ε_1 to final by three parameters, was obtained the steady-state master equation. Distributions of the trajector parameters are presented, and seven the important features of the col- tion rate from the "complex mechan	ential and the effect of barrier penetration ures. The system N_2 + Ar was used as a typica reement was obtained between the theoretical measurements of the reaction rate coefficients 000 °K. e nonequilibrium factor were obtained from ns for states near the dissociation limit. hin the reaction zone, with a weight propor- n rate, and numerically integrated in both the complete histories of the collisions. A e equilibrium transition rate $R(\varepsilon_1, \varepsilon_f)$ from energy states ε_f , which could be characterize to fit the numerical data and was used to sol ories with respect to energies and impact eral typical trajectories are shown to illustr lisions. The contribution to the overall reac nism" was also obtained.
in the third-body interaction pot- for recombination at low temperat- illustrative example, and good ag predictions and the experimental over the temperature range 200-12 The recrossing factor and the Monte Carlo trajectory calculation The trajectories were sampled with tional to the equilibrium reaction timewise directions to determine simple, separable function for the initial energy states ε_1 to final by three parameters, was obtained the steady-state master equation. Distributions of the trajector parameters are presented, and seven the important features of the col- tion rate from the "complex mechan D 100 1473	ential and the effect of barrier penetration ures. The system N_2 + Ar was used as a typical reement was obtained between the theoretical measurements of the reaction rate coefficients 000 °K. e nonequilibrium factor were obtained from ns for states near the dissociation limit. hin the reaction zone, with a weight propor- n rate, and numerically integrated in both the complete histories of the collisions. A e equilibrium transition rate $R(\varepsilon_1, \varepsilon_f)$ from energy states ε_f , which could be characterize to fit the numerical data and was used to sol ories with respect to energies and impact eral typical trajectories are shown to illustr lisions. The contribution to the overall reac nism" was also obtained.
in the third-body interaction pot- for recombination at low temperat- illustrative example, and good ag predictions and the experimental over the temperature range 200-12. The recrossing factor and the Monte Carlo trajectory calculation The trajectories were sampled with tional to the equilibrium reaction timewise directions to determine simple, separable function for the initial energy states ε_1 to final by three parameters, was obtained the steady-state master equation. Distributions of the trajecter parameters are presented, and seven the important features of the col- tion rate from the "complex mechan D 1 JAN 64 1473	ential and the effect of barrier penetration ures. The system N_2 + Ar was used as a typical reement was obtained between the theoretical measurements of the reaction rate coefficients 000 °K. e nonequilibrium factor were obtained from ns for states near the dissociation limit. hin the reaction zone, with a weight propor- n rate, and numerically integrated in both the complete histories of the collisions. A e equilibrium transition rate $R(\varepsilon_1, \varepsilon_f)$ from energy states ε_f , which could be characterize to fit the numerical data and was used to sol ories with respect to energies and impact eral typical trajectories are shown to illustre lisions. The contribution to the overall reaction is also obtained. Unclassified

Unclassified

the second s			
Security	Classifica	tion	

14.		LIN	KA	1.1N	КВ	LIN	КС
	KEY WORDS	ROLE	ΨT	ROLE	WT	ROLE	WT
1.	Chemical Kinetics						i.
2.	Diatomic Molecules						
3.	Dissociation						
4.	Monte Carlo Calculation						
5.	Nitrogen						
6.	Phase-Space Theory						
7.	Reaction Rates						
8.	Recombination						
9.	Trajectories						
	INSTRUCTIONS	t				L	

I. ORIGINATING ACTIVITY: Enter the name and address of the contractor, aubcontractor, grantee, Department of Defense activity or other organization (corporate author) issuing the report.

2a. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" ia included. Marking ia to be in accordance with appropriate security regulations.

2b. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forcea Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases abould be unclassified. If a meaningful title cannot be aelected without classification, show title classification in all capitals in parentheais immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progreas, aummary, annual, or final. Give the incluaive datea when a apecific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an abaolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.

7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedurea, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8a. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, &c, & 8d. PROJECT NUMBER: Enter the appropriate military department identification, auch as project number, subproject number, system numbers, taak number, etc.

9a. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers (either by the originator or by the sponsor), also enter this number(a).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those

impoaed by security classification, using standard statements auch as:

- (I) "Qualified requeaters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through .

. **

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

II. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory aponaoring (paying for) the reaearch and development. Include address.

13. ABSTRACT: Enter an abatract giving a brief and factual aummary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abatract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS). (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terma or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiera, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rulea, and weights is optional.

Unclassified

MONTE CARLO TRAJECTORY CALCULATIONS OF THE THREE-BODY RECOMBINATION

AND DISSOCIATION OF DIATOMIC MOLECULES

by

Ven H. Shui

Fluid Mechanics Laboratory

Department of Mechanical Engineering Massachusetts Institute of Technology



This research was supported in part by the Advanced Research Projects Agency of the Department of Defense and monitored by the Office of Naval Research under Contract No. N00014-67-A-0204-0040 and ARPA Order No. 322 and in part by the National Science Foundation Grant No. GP-32522X.

This document has been approved for public release and sale; its distribution is unlimited.

February 1972

MONTE CARLO TRAJECTORY CALCULATIONS OF THE THREE-BODY RECOMBINATION AND DISSOCIATION OF DIATOMIC MOLECULES

by

Ven H. Shui

ABSTRACT

The modified phase-space theory of reaction rates has been applied to the problem of the three-body recombination and dissociation of diatomic molecules. The results illustrate the important influence of the weak attractive minimum in the third-body interaction potential and the effect of barrier penetration for recombination at low temperatures. The system N₂ + Ar was used as a typical illustrative example, and good agreement was obtained between the theoretical predictions and the experimental measurements of the reaction rate coefficients over the temperature range 200-12000 ^oK.

The recrossing factor and the nonequilibrium factor were obtained from Monte Carlo trajectory calculations for states near the dissociation limit. The trajectories were sampled within the reaction zone, with a weight proportional to the equilibrium reaction rate, and numerically integrated in both timewise directions to determine the complete histories of the collisions. A simple, separable function for the equilibrium transition rate $R(\varepsilon_i, \varepsilon_f)$ from initial energy states ε_i to final energy states ε_f , which could be characterized by three parameters, was obtained to fit the numerical data and was used to solve the steadystate master equation.

Distributions of the trajectories with respect to energies and impact parameters are presented, and several typical trajectories are shown to illustrate the important features of the collisions. The contribution to the overall reaction rate from the "complex mechanism" was also obtained.

I. INTRODUCTION

The most general theoretical investigation of the problem of threebody recombination and dissociation is that carried out by Keck and his coworkers.¹⁻⁵ This theory is based on a phase space representation and is sufficiently general to include all previous classical theories as special cases. They applied the theory to the three-body recombination and dissociation of diatomic molecules with an inert third-body collisiou partner (including the $H + H + H_2$ recombination) and obtained good agreement between theory and experiment in general. In addition, their work illustrated the importance of such features as the weak attractive van der Waals forces betweer the recombining atoms and the inert thirdbody atoms for recombination at low temperatures, and the effects of electronically excited states and nonequilibrium internal distributions on the overall recombination and dissociation rates.

The steady-state reaction rate coefficient (to be compared with experimental measurements) is obtained as the triple product

-2-

$$k = k^{B}(N/N_{0})(k/k_{e})$$
 (1.1)

where k^{B} is the barrier rate.² The values of recrossing factors (N/N_{0}) and nonequilibrium factors (k/k_{e}) used in previous studies³⁻⁵ were deduced using the results of Monte Carlo trajectory calculations^{2,6} and master equation solutions⁷ in which the recombining atoms had similar masses. Also, the third body was considered to be purely repulsive. Results of Monte Carlo trajectory calculations of the dissociation of HCk in Ar have been presented recently⁸ which illustrated the special features of collisions involving highly asymmetric diatomic molecules and the importance of rotational motion in such collisions. Excellent agreement was obtained between the theoretical predictions and the shock-tube measurements of the dissociation rate coefficients of HCk over the temperature range 2500-5000 ^oK.

In this paper the results of Monte Carlo trajectory calculations are presented for systems which have a weak minimum in the three-body interaction potential, the system N₂ + Ar being used as an illustrative example. We shall not repeat details of the theory and calculations that were already presented in previous publications.¹⁻⁸ Instead, in Section II we shall summarize the interaction potentials used, and in Section III present the important features of the present calculations. The results and their comparison with experiment will be presented in Section IV, and Section V will contain our concluding discussions.

II. INTERACTION POTENTIALS

The interaction potential (V_0) of the three-body system (X-Y-M) was separated into two parts:

$$v_0 = v_{XY} + v_3$$
 (2.1)

where V_{XY} is the potential of the recombining atoms (X - Y), and V_3 is the potential due to the presence of the third body (M). The Morse potential function

$$V = D \exp[-\beta(r - r_e)] \{ \exp[-\beta(r - r_e)] - 2 \}$$
(2.2)

(2,3)

was used to represent V_{xy} . As was done before,^{2,3} the dumbbell model

$$V_3 \equiv V_{XM}$$
 for $r_{XM} < r_{YM}$

and

$$V_3 \equiv V_{YM}$$
 for $r_{XM} > r_{YM}$

was assumed for the potential V_3 , and V_{XM} and V_{YM} were represented by the Morse form, Equation (2.1).

The potential parameters for V_{XY} , V_{XM} , and V_{YM} required in the present calculations were determined in the same manner as in previous studies.³⁻⁵ Table I summarizes these parameters.

III. MONTE CARLO TRAJECTORY CALCULATIONS

The principles of the Monte Carlo technique used here have been explained previously,⁸ and a more general discussion may be found in the literature.⁹⁻¹¹ Details of the selection of initial conditions and of the itegration of equations of motion are contained in Reference 12. In general, total energy was conserved to within 0.01 kT, and the trajectories were followed in both time-wise directions from the initial point until the condition

$$|V_3| < 0.01 \text{ k7} \text{ and } r_3 > 0$$
 (3.1)

was satisfied $(r_3$ is the distance between the third body M and the center of mass of the molecule XY). However, for studies involving complexes, the alternative cutoff condition

-4-

$$|V_{XY}| < 0.01 \text{ kT}$$
 and $|V_{XM}| < 0.01 \text{ kT}$ and $r_1 > 0$

or

$$|V_{XY}| < 0.01 \text{ kT and } |V_{YM}| < 0.01 \text{ kT and } r_2 > 0$$

was also introduced. Here r_1 is the distance between the atom X and the center of mass of Y - M, and r_2 is the distance between the atom Y and the center of mass of X - M.

As was done in Reference 8, the recrossing correction factor (N/N_0) was obtained directly from the results of the trajectory calculations by counting. Also, the "one-way" equilibrium transition rate between energy states $\varepsilon = \varepsilon_i$ and $\varepsilon = \varepsilon_f$, per unit volume, per unit initial and final energies, was fitted by the empirical forms

$$R(\varepsilon_{i}, \varepsilon_{f}) = AG(\varepsilon_{f}) \exp(\alpha\varepsilon_{f} - \beta\varepsilon_{i})$$
(3.3a)

and

$$R(\Delta, \bar{\varepsilon}) = AG(\bar{\varepsilon}) \exp(-a\Delta - b\bar{\varepsilon})$$
 (3.3b)

where A, α , β , a, b are constants, G(') is a relatively slowly varying function, Δ is the absolute value of the energy transfer, $\overline{\epsilon}$ is the mean of the initial and final energies, and

$$\alpha = a - b/2$$
, and $\beta = a + b/2$. (3.4)

Various moments of the energy transfer with respect to $R(\varepsilon_i, \varepsilon_f)$ were used in the fitting procedure. In general, the m-th moment is defined as

$$Q_{m}(\varepsilon) \equiv \int_{-\infty}^{\varepsilon} \int_{\varepsilon}^{\infty} f(\varepsilon, \varepsilon_{i}, \varepsilon_{f}) R(\varepsilon_{i}, \varepsilon_{f}) (\varepsilon_{i} - \varepsilon_{f})^{m-1} S^{m} d\varepsilon_{i} d\varepsilon_{f}$$
(3.5)

where ε is the energy of the surface from which samples were taken (defined in Reference 8), f(ε , ε _i, ε _f) is a weighting-normalizing function, and

$$S^{m} = [(\bar{\varepsilon} - \varepsilon)/|\bar{\varepsilon} - \varepsilon|]^{m}$$
(3.6)

(3,2)

determines the sign of the odd moments. The corresponding "absolute" moments $|Q|_{m}(\varepsilon)$, are obtained by setting $S \equiv 1$, and the moments used in this paper $D_{m}(\varepsilon)$, correspond to

$$f(\varepsilon, \varepsilon_i, \varepsilon_f) = G(\varepsilon)/G(\varepsilon_f) \mathcal{R}_v(\varepsilon)$$
 (3.7)

where $\mathcal{R}_{v}(\varepsilon)$ is the variational rate for the surface $S(\varepsilon)$, defined in References 2 and 8.

Using Equations (3.5), (3.7), and relationships contained in Reference 8 and evaluating the integral by Monte Carlo methods, we obtain

$$D_{m}(\varepsilon) = \sum_{j=1}^{N_{0}} [G(\varepsilon)/G(\varepsilon_{f})] (x_{j}/n_{j})(\varepsilon_{1} - \varepsilon_{f})_{j}^{m-1} s^{m}/N_{0} \qquad (3.8)$$

where $x_j = 1$ if the trajectory is reactive, $x_j = 0$ otherwise, n_j is the number of crossings of that trajectory in the reactive direction, and N_0 is the total number of trajectories sampled on the surface $S(\varepsilon)$. This is the equation used in the actual calculation of the moments $D_m(\varepsilon)$ from data generated by trajectory calculations.¹³ Furthermore, following the procedures used in Reference 8, we obtain

$$A/\mathcal{R}_{u}(0) = C\alpha\beta \tag{3.9}$$

and

$$D_{m}(\varepsilon) = C\alpha\beta \exp(\varepsilon) \int_{-\infty}^{\varepsilon} \int_{\varepsilon}^{\infty} (\varepsilon_{1} - \varepsilon_{f})^{m-1} \exp(\alpha\varepsilon_{f} - \beta\varepsilon_{1}) S^{m} d\varepsilon_{1} d\varepsilon_{f}$$
(3.10)

which can be evaluated exactly to yield

$$|D|_{\mathbf{m}}(\varepsilon) = \begin{cases} (\mathbf{m} - 1)! \quad [(\beta^{\mathbf{m}} - \alpha^{\mathbf{m}})/b(\alpha\beta)^{\mathbf{m}-1}] \quad \mathbb{C} \exp[(1 - b)\varepsilon], \quad \mathbf{m} > 0; \\ (\alpha\beta/b)\ln(\beta/\alpha) \quad \mathbb{C} \exp[(1 - b)\varepsilon], \quad \mathbf{m} = 0; \end{cases}$$
(3.11)

since only the first absolute moment and the even moments are required in the present calculations. When a \gg b/2, a good approximation is

$$|\mathbf{D}|_{\mathbf{m}}(\varepsilon) \approx C \mathbf{m}! \mathbf{a}^{1-\mathbf{m}} \exp[(1-\mathbf{b})\varepsilon]$$
 (3.12)

The values of the parameters a, b, C were then derived from these moments, and the steady-state master equation was solved to yield the nonequilibrium correction factor k/k_{p} .

IV. RESULTS

4.1 The Equilibrium Transition Rate and Energy Transfer Moments

The low-order energy transfer moments calculated using Equation (3.8) are summarized in Table II. Figure 1 shows a plot of $[N(\varepsilon)/N_0(\varepsilon)]/[1 - exp(-kT/D)]$ versus ε for the system N_2 + Ar. Although the scatter in the data are considerable, the empirical form

$$N(\varepsilon)/N_{0}(\varepsilon) = C \exp[(1 - b)\varepsilon] [1 - \exp(-kT/D)]$$
(4.1)

where D is the well depth of the interaction potential between the third body and one of the recombining atoms does correlate the data with reasonable accuracy. Thus the parameters C and b were both determined from this figure.

The parameter C is the high-temperature limit of the barrier rate recrossing correction factor $N(0)/N_0(0)$. Recently Keck¹⁴ has suggested a new empirical expression

$$\frac{N(0)}{N_0(0)} = 1 - 0.7 \left[\frac{m_2}{m_1 + m_2} \left(\frac{m_3}{m_1 + m_3} \right)^{1/2} + \frac{m_1}{m_1 + m_2} \left(\frac{m_3}{m_2 + m_3} \right)^{1/2} \right]$$
(4.2)

which is able to correlate all the data obtained to date (including highly asymmetric diatomic molecules). The possible temperature dependence of the parameter b was also investigated, but the statistics were not good enough to give a definite answer, and the average value of b was used in the following calculations. The values of C and b are summarized in Table III.

A possible correlation of the parameter b and the atomic masses of the system is shown in Figure 2 where b is plotted versus $[m_3/(m_1 + m_2)]^{1/2}$. The straight line

$$b = \exp\{-0.25 \left[\frac{m_3}{(m_1 + m_2)}\right]^{1/2}\}$$
(4.3)

represents the data points quite well. However, results for the systems $H_2 + Ar$ or $H_2 + Xe$ are perhaps needed to verify this correlation since these systems have large values of the factor $[m_3/(m_1 + m_2)]^{1/2}$ (4.47 and 8.09, respectively). The data plotted in Figure 2 include the systems HCl + Ar, N_2 + Ar, Cl_2 + Ar, 0_2 + Xe, 0_2 + Ar, and I_2 + Ar.¹⁵

The parameter a was obtained by taking the average of the four values of $2|D|_1/D_2$ in Table II and using the relationship

$$2|D|_1/D_2 = \alpha\beta \tag{4.4}$$

which follows from Equation (3.11). The values of a for all the cases studied are summarized in Table III and plotted versus kT/D in Figure 3, where D is the well depth of the interaction potential for the recombining molecule. A weak temperature dependence of a is definitely observed in Figure 3, but the data are insufficient to determine any mass dependence. The line of best least-squares fit (solid straight line in the figure) shows scatters within the statistical errors. Consequently, for the data obtained to date, the parameter a can be reasonably well estimated from the formula

$$a = 3.47 (kT/D)^{0.232}$$
. (4.5)

The average energy transfers involved in reactive collisions of three-body recombination and dissociation processes are also of interest and can be evaluated directly from the moments summarized in Table II. The averaged absolute energy transfer per collision, $<\Delta>$, and the rootmean-square energy transfer per collision, $<\Delta^2>^{1/2}$, are plotted in Figure 4 versus kT/D where D is the well depth of the interaction potential of the molecule. The best least-squares-fit lines (solid lines in the figure) correlate the data reasonably well and can be represented by the following equations.

$$<\Delta > = 0.10 (kT/D)^{-0.30}$$

 $<\Delta^2 >^{1/2} = 0.22 (kT/D)^{-0.28}$ (4.6)

Tables IVa, IVb, and IVc show the distributions of the trajectories classified according to the nature of their end states (see Reference 8). The cases shown are

(a)
$$N_2 + Ar$$
 at 11500 ^oK (kT/D = 0.1), $\varepsilon = 0$;

- (b) $N_2 + Ar \text{ at } 100 \,^{\circ}\text{K} \, (\text{kT/D} = 0.0009), \ \varepsilon = 0$;
- (c) Same as (b), but with all trajectories that came from a bound N·Ar complex removed.

Although these distributions have similar general features as those obtained by Keck,⁶ one major difference is that the number of trajectories which cross the energy surface more than once in each direction increases as the temperature is lowered. This produced a temperature dependence of the recrossing factor N/N_0 although the total number of f + b trajectories did not vary significantly with temperature. This behavior illustrates the effects of the attractive minimum in the thirdbody interaction potential at low temperatures. It also explains the reason why Keck⁶ did not observe a similar temperature dependence for N/N_0 (he used purely repulsive third-body interaction potentials).

In order to complete the determination of the transition kernel, $R(\varepsilon_i, \varepsilon_f)$ and produce a map of its relative numerical distribution, the function $G(\varepsilon_f)$ in Equation (3.3) must first be found. The function

 $G(\varepsilon) = [1 - (-\varepsilon/\delta)^{1/2}]/[1 + (-\varepsilon/\delta)^{1/2}]$ (4.7)where $\delta = D/kT$, was used for $G(\varepsilon_f)$ in the present calculations since Keck² found that it was able to represent the numerical calculations of $\mathcal{R}_{v}(\varepsilon)/\mathcal{R}_{v}(0)$ with sufficient accuracy. The resulting numerical distributions of $R(\epsilon_i, \epsilon_f)/R_v(0)$ are shown in Figure 5 for N₂ + Ar at 11500 °K. The figures in the boxes represent the mean value of $R(\varepsilon_1, \varepsilon_f)/R_{y}(0)$ for the box. Because of the sampling technique employed, each value of ε used in the calculations yielded data in a quadrant that touches the diagonal $\varepsilon_1 = \varepsilon_f$, at a value of $\overline{\varepsilon} \equiv (\varepsilon_1 + \varepsilon_f)/2 = \varepsilon$. Data in overlapping quadrants agreed within the statistical errors and were averaged to obtain the results shown. The total number of trajectories sampled was approximately three hundred for each value of $\varepsilon(\varepsilon = 0, -1, -2, -3)$. The results shown were calculated for $\varepsilon_i > \varepsilon_f$ (recombination); however, since $R(\varepsilon_i, \varepsilon_f)$ is symmetrical in ε_i and ε_f , the values for $\varepsilon_i < \varepsilon_f$ may be obtained by reflection in the diagonal $\varepsilon_i = \varepsilon_f$. The maps show that $R(\varepsilon_i, \varepsilon_f)$ exhibits a sharp maximum ridge along $\varepsilon_1 = \varepsilon_f$, which corresponds to zero energy transfer; this dies off rapidly as $|\varepsilon_1 - \varepsilon_f|$ increases. Substitution of Equation (3.10) into Equation (3.3) yields

 $R(\varepsilon_{1}, \varepsilon_{f})/\mathcal{R}_{v}(0) = C\alpha\beta \quad G(\varepsilon_{f}) \exp(\alpha\varepsilon_{f} - \beta\varepsilon_{1}) \quad (4.8)$

Since the parameters α , β are simply related to the parameters a, b by Equation (3.4), Equation (4.8) could be used to generate the function

 $R(\varepsilon_i, \varepsilon_f)/R_v(0)$. The results are plotted in the upper left corner of Figure 5 as a contour map. It can be seen that the contour map reproduces all the important features of the corresponding actual distribution, and the agreement in general is very good.

Figure 6 shows a plot of $[\mathbb{R} (\Delta, \overline{\epsilon})/\mathcal{R}_{V}(0)]/[\mathcal{R}(\epsilon)/\mathcal{R}(0)]$ versus Δ . The factor $[\mathcal{R}(\epsilon)/\mathcal{R}(0)]$ was included for normalization purposes so that the data could be better represented by a single line. In the plot, the solid line passing through the bulk of the data points has a slope equal to the parameter a as determined above (see Table III). It can be seen that for $\Delta < 0.5$, the data points deviate considerably from this line; however, the region around $\Delta \approx 1$ has the most important contribution in the determination of the nonequilibrium correction factor, and the line fits the data very well in this region.

It can therefore be concluded that the functional form for $R(\varepsilon_i, \varepsilon_f)$ and the associated parameters determined above (Equation (3.3) and Table III) lead to a very good representation of the transition kernel. At the same time, it is still simple enough so that the steady-state master equation can be solved analytically without the usual reliance on a great deal of numerical computation.

The nonequilibrium correction factors were then calculated as was done in Reference 8.

4.2 Recombination and Dissociation Rate Coefficients

(1) The "Chaperon" Mechanism

One of the consequences of including an attractive well in the third-body interaction potential is that it provides a "chaperon" mechanism (or "complex" mechanism) in which long-lived X:N complexes

-11-

-12-

serve as an intermediate species in the reaction process, in addition to the usual "energy transfer" mechanism. Since the trajectory calculations provide complete histories of the collisions, those trajectories which contained a bound complex pair at the beginning $(t \rightarrow -\infty)$ of the collision could be identified by calculating the relative energies of the X-M and Y-M pairs. The results are shown in Figure 7 as a plot of N_C/N_{NC} versus kT/D_{XM} , where N_C/N_{NC} is the ratio of the effective number of reactive trajectories from the complex mechanism to that from the non-complex mechanism, and D_{XH} is the well depth of the third-body interaction potential (see Table I). The data plotted include results for the systems $N_2(X \ \frac{1}{2} \ \frac{1}{g}) + Ar$, $N_2(A \ \frac{3}{2} \ \frac{1}{u}) + Ar$, and $Cl_2(X \ \frac{1}{2} \ \frac{1}{g}) + Ar$ and can be represented very well by the line

$$N_{\rm C}/N_{\rm NC} = 0.74 \, (kT/D_{\rm XM})^{-3/2}$$
 (4.9)

The complete recombination process can now be represented by the following reactions:

$$X + M \xrightarrow{k_1} X \cdot M, \qquad (4.10a)$$

$$x + x \cdot M \xrightarrow{k_3} x_2 + M$$
, (4.10b)

$$x + x + M \xrightarrow{k_5} x_2 + M$$
 (4.10c)

The usual rate law is

$$d[x_2]/dt = -d[x]/2dt$$

= $k_3[x][x\cdot M] + k_5[x]^2 [M],$ (4.11)

and

$$N_{C}/N_{NC} = k_{3}[XM]/k_{5}[X][M]$$
 (4.12)

Since reactions (4.10a) in general proceed at much higher rates than reactions (4.10b) and (4.10c), local thermodynamic equilibrium may be assumed to exist between X, M, and X.M. Thus

$$[X][M]/[X \cdot M] = K_{\rho} = k_2/k_1$$
(4.13)

where K is the corresponding equilibrium constant.

It follows that

$$N_{C}/N_{NC} = k_{3}/(K_{e}k_{5})$$
 (4.14)

The classical phase integrals required for the determination of K $_{\rm e}$ were evaluated numerically for a Morse oscillator using the parameters listed in Table III. The results show that within the temperature range considered (0.5 < kT/D_{\rm XM} < 5) ,

$$K_e = C(kT/D_{XH})^{3/2}$$
 (4.15)

to a very good approximation, where C is a constant. Hence, from Equations (4.9) and (4.14), the ratio k_3/k_5 must be nearly independent of the temperature within the temperature range considered.

The problem of the "complex" mechanism and the "energy transfer" mechanism has been studied by a number of investigators, $^{16-22}$ and the equilibrium constant (Equation 4.13) has also been calculated in other studies. $^{23-26}$ For the purpose of comparing with all the available experimental measurements, however, the results are still very inconclusive.

The creation of the "complex" mechanism is, of course, by no means the only effect of the attractive minimum in the third-body interaction potential. Apart from the bound complexes (H - B < 0), which include both the truly bound (H < 0) and the quantum mechanically metastable (0 < H < B) complexes, one can define the quasidimers $(B < H < B_m)$ as was done by Kim and Ross.²⁶ "Energy transfer" can take place both during the repulsive and attractive phases of the collisions. In addition, the attractive minimum in the X + M interaction enhances reaction rates by increasing the density of representative points in the reaction region of the phase space (see Reference 5 for a discussion on this topic for the H + H + H₂ recombination). These contributions are all included in the classical phase-space theory of reaction rates developed by Keck and his coworkers.

The recent work of Clarke and Burns²⁷ shows some interesting features of the "complex" mechanism of the recombination of bromine. However, their comparisons and conclusions are meaningful only when the overall recombination rate is dominated by the complex mechanism. The work of Keck and his coworkers¹⁻⁵ and the present results clearly show that this condition is satisfied only when kT $\leq D_{\rm XM}$. At higher temperatures the energy transfer mechanism becomes more and more important, and the overall reaction cannot be represented by the complex mechanism alone.

(2) Barrier Penetration

Classically, the barrier surface provides an unambiguous dividing surface in phase space which separates the reactants (X + Y + M) from the products (XY + M) of the reactions under consideration. Ouantum mechanically, however, this surface has "holes" due to barrier penetration; i.e., some reactants can react and form products without passing through the barrier surface.

-14-

The effect of barrier penetration on reaction rates is twofold. First, it increases the barrier rate coefficient k_r^B by an amount equal to the effective recombination rate due to barrier penetration. Second, it may change the steady-state distribution of the population of energy states by supplying extra molecules to states near the barrier surface, resulting in a change of the nonequilibrium correction factor (k/k_{a}) . These effects must be evaluated by solving a new set of master equations which include barrier penetration as additional source terms. This completely destroys the simplicity shown in Section III and Reference 8 where the steady-state master equation was colved analytically for a separable kernel. Fortunately, for most practical potential energy barriers (in particular, the one used here), the transmission coefficient (probability of barrier penetration) at an energy & decays extremely rapidly as ε varies from 0 to - B/kT. Thus a new energy surface ($\varepsilon = \varepsilon_{\rm b}$) may be defined, such that the recombination rate due to barrier penetration at energy levels below $\varepsilon_{\rm b}$ is negligible compared with the recombination rate due to collisional deactivation through the energy surface $\varepsilon = \varepsilon_{\rm b}$. Using this surface as the new boundary (instead of $\varepsilon = 0$) and solving the steady-state master equation in a manner similar to that of Reference 8, the factor

$$[\mathcal{R}(\varepsilon_{b})/\mathcal{R}(0)][(k/k_{e})_{\varepsilon=\varepsilon_{b}}/(k/k_{e})_{\varepsilon=0}] \approx \exp(-b\varepsilon_{b}) \qquad (4.16)$$

btaired which must multiply the factor k/k_e in Equation (1.1) to

In order to determine ε_b , an effective recombination rate coefficient due to barrier penetration is defined as

include effects of barrier penetration.

was o

-15-

$$k_{p}(\varepsilon_{b}) \equiv \mathcal{R}_{p}(\varepsilon_{b}) [X]^{-2} [M]^{-1}$$
 (4.17)

where $\mathcal{P}_{p}(\varepsilon_{b})$ is the total barrier penetration rate for $\varepsilon < \varepsilon_{b}$ and is given by

$$\mathcal{R}_{p}(\varepsilon_{b}) [X]^{-2} = 2\sigma (8kT/\pi\mu)^{1/2} \int_{-B/kT}^{\varepsilon_{b}} T_{r}(\varepsilon) \exp(-\varepsilon) d\varepsilon . \quad (4.18)$$

Here σ is a collision cross-section, and $T_r(\varepsilon)$ is the transmission coefficient calculated using the semi-classical equation

$$T_{r}(\varepsilon) = \exp[-(2/h) \int_{x_{1}}^{x_{2}} \{2\mu[V(x)/kT - \varepsilon]\}^{1/2} dx]$$
(4.19)

where h is the Planck's constant, V(x) is the potential energy, and x_1 and x_2 are the two positions at which V/kT = ε . Equations (4.18) and (4.19) were then integrated numerically. The results for nitrogen are shown in Figure 8 where k_p is plotted versus ε_b , from which the new surface $\varepsilon = \varepsilon_b$ can be approximately located with the condition

$$k_{p}(\varepsilon_{b}) = k_{r}^{B}(N/N_{0}) . \qquad (4.20)$$

For example, for nitrogen at 100 °K, k_r^B (N/N₀) $\approx 10^{-32}$ cm⁶ molecule⁻² sec⁻¹ which gives $\varepsilon_b \approx -0.35$, and from Equation (4.16) the corresponding increase in rate due to barrier penetration is a factor of 1.3 approximately. It should be pointed out that because k_p varies rapidly with ε_b , the determination of ε_b is very insensitive to slight variations in σ , [M], and $k_r^B(N/N_0)$. Therefore, high accuracy is not required in estimating these quantities.

(3) Corrections Due to Deviations of the Morse Form from True Potentials

The Morse form (Equation (2.2) and Table I) used to represent the interaction potential V_{N_2} was found to deviate considerably, in the long-range asymptotic region, from the more accurate potential curves

given by Gilmore.²⁸ A plot of Gilmore's potentials versus the separation shows that the form $C_6 r^{-6}$ is a much better representation of the true potentials in this region $(r \ge 1.5 \text{ Å})$. The major effect of incorporating this modification is that it alters somewhat the position of the rotational maximum z_2 and thereby changes the barrier rate coefficient (Equation (2.9) of Reference 3) through the factor $z_2^2(z_2 - z_1)$. Denoting the new barrier rate coefficient by k_6^B , the ratio k_6^B/k_r^B is included in Table V. The corrections are fairly small, but they do introduce an additional weak negative temperature dependence.

(4) Contribtuion from the A ${}^{3}\Sigma_{u}^{+}$ State

The overall dissociation process for nitrogen may be described satisfactorily by the following set of reactions:

$$N_2(X \xrightarrow{1}\Sigma_g^+) + Ar \xrightarrow{k_1} N + N + Ar$$
 (4.21a)

$$N_2(X \xrightarrow{1} \Sigma_g^+) + N \xrightarrow{k_3} N_2(A \xrightarrow{3} \Sigma_u^+) + N$$
 (4.21b)

$$N_2(A \xrightarrow{3} \Sigma_u^+) + Ar \xrightarrow{k_5} N + N + Ar . \qquad (4.21c)$$

It has been pointed out previously (see Reference 3 and references quoted there) that the A ${}^{3}\Sigma_{u}^{+}$ state makes significant contributions to the overall reaction rates. In order to properly account for these contributions, the concentration [N₂(A ${}^{3}\Sigma_{u}^{+}$)] must be found. A steady-state analysis yields

$$[N_{2}(A^{3}\Sigma_{u}^{+})]_{s}/[N_{2}(A^{3}\Sigma_{u}^{+})]_{e} = \{1 + (k_{5}/k_{4})[Ar]/[N]\}^{-1}$$
(4.22)

where the subscript s denotes steady-state, and e denotes local equilibrium. Since the ratio k_5/k_4 was not known, the previous calculations^{3,4} simply assumed that the A ${}^{3}\Sigma_{u}^{+}$ state was in local thermal equilibrium with the ground state. Recently Flagan and Appleton²⁹ have obtained the expression

$$k_4 = 5.1 \times 10^{-3} T^{-2.23} cm^3 sec^{-1}$$
 (4.23)

for 6000° K \leq T $\leq 14000^{\circ}$ K, by matching the computed peak intensity of the nitrogen first-positive radiation with Wray's experimental measurements.³⁰ The result of the steady-state analysis, Equation (4.22), may therefore be used in calculating the rate coefficients. A plot of the ratio $[N_2(A \ ^3\Sigma_u^+)]_s/[N_2(A \ ^3\Sigma_u^+)]_e$ as a function of the temperature shows that the assumption of local thermodynamic equilibrium between the A-state and the ground state is valid for temperatures $\leq 4000^{\circ}$ K (which covers all recombination rate measurements), but the contribution from the A-state decreases rapidly at higher temperatures.

Taking into account effects of barrier penetration and corrections due to deviations of the Morse form from true interaction potentials for nitrogen, the results of the calculated recombination rate coefficients are summarized in Table V and plotted in Figure 9 as a function of the temperature. The theoretical points $\bigoplus [(k_r(X \ 1\Sigma_g^+) + k_r(A \ 3\Sigma_u^+)]$ and $\bigoplus [k_r(X \ 1\Sigma_g^+)]$ have been connected visually by full lines to help in comparing the results. The dashed line represents the theoretical predictions of $k_r(X \ 1\Sigma_g^+)$ without the corrections due to barrier penetration and deviations of V_{N_2} from the Morse form. It is seen from the figure that at low temperatures, the present theoretical predictions of the recombination rate coefficient, $[k_r(X \ 1\Sigma_g^+) + k_r(A \ 3\Sigma_u^+)]$, are in very good agreement with the experimental

-18-

measurements of Campbell and Thrush³¹ (Δ), and Clyne and Stedman³² (0); the more recent room temperature measurement of Brennen and Shane³³ (∇) is somewhat higher but also appears to be within the combined statistical errors. There still exists a discrepancy of about a factor of 6 between Clyne and Stedman's measurement at 90 °K and the theoretical prediction at 100 °K. However, since Clyne and Stedman used pure nitrogen in their experiment, the different efficiencies of \mathbb{N}_2 and Λr as third bodies may be responsible for this discrepancy. In this regard, experimental measurements at T ≈ 100 °K using Ar as the third body should be very useful.

For the purpose of effecting a comparison, the experimental dissociation rate measurements have been converted into equivalent recombination rate coefficients through the equilibrium constant. The results of Appleton, Steinberg, and Liquornick³⁴ (A) are in excellent agreement with the theoretical predictions. The results of Byron³⁵ (E) and Cary³⁶ (C) appear to be somewhat higher, but in view of the extent of experimental error and the uncertainties in the theory, the agreement is considered to be very good.

V. DISCUSSION

A number of trajectories for the collision of N_2 + Ar are shown in Figure 10 where two different coordinate systems have been used in order to show certain special features of the collisions more satisfactorily. One coordinate system has the argon atom stationary, with the two nitrogen atoms moving about and is particularly useful for illustrating the individual collisions between each nitrogen atom and the argon atom. The other coordinate system has the center of mass of the nitrogen molecule stationary with all three atoms in motion. This system offers a good visualization of the internal relative motion of the bound nitrogen molecule. A bound NAr complex is clearly illustrated in Figure 10(c).

It should be pointed out that for convenience of representation in two dimensions, the trajectories shown in Figure 10 have all three particles moving in the same plane. However, the calculations were, in general, three dimensional.

Typical reactive trajectories for N_2 + Ar collisions may be divided into the following types:

(i) Simple f + b Trajectories

The three atoms start as free particles and approach close enough for energy and momentum exchanges of appreciable amount to occur. One of the nitrogen atoms transfers sufficient energy to the argon atom. The latter moves away from the bound nitrogen molecule with increased kinetic energy, as in Figure 10(a).

(ii) Trajectories Involving Complexes

As shown in Figure 10(c), one nitrogen atom is initially hound to the argon atom by the weak attractive forces, forming an NAr complex. Another nitrogen atom approaches the complex, and its strong attractive valence forces acting on the first nitrogen atom pulls the latter away from the argon atom, resulting in a reactive trajectory. (111) Trajectories with Multiple Crossings of the Barrier Surface A high temperature trajectory of this type is shown in Figure 10(b) in which the argon atom exchanges energy and momentum with each of the two nitrogen atoms, resulting in the reactive transition ($b \rightarrow f \rightarrow b$).

At low temperatures, however, the attractive minimum in the NAr interaction potential becomes important, and a single nitrogen atom may exchange energy and momentum to and from the argon atom more than once during a collision, resulting in a trajectory with multiple crossings of the barrier surface.

Figures 11(a) and (b) show the time evolution of some of the trajectories examined above. The upper half of these figures plots the energy of the molecule [(H - B)/kT] versus the time ($v_e t$, where v_e is the ground state vibrational frequency of the molecule), and the lower half shows the quantities r_{XY} and r_3 as functions of time. It can be seen that the molecular vibrations are highly anharmonic, and the energy exchanges are typically of order kT or less (see also Figure 12).

For a collision to be reactive (consider recombination), the molecule must start in a free state and end in a bound state. The corresponding energy changes must be such that H - B < 0, where H is the Hamiltonian of the molecule, and B is the height of the rotational barrier. Figure 12 shows a distribution plot of ΔH and ΔB for the reactive trajectories of the case $N_2 + Ar$ at 11500 °K on the surface $\varepsilon = 0$. In Reference 8, it was shown that for HCL + Ar, recombination (the change from H - B > 0 to H - B < 0) is achieved by two equally

-21-

important mechanisms, i.e., reducing H and/or increasing B. For N_2 + Ar, on the other hand (see Figure 12), most recombinations are achieved by reducing H. This furnishes further evidence that rotational energy transfer in highly asymmetric molecules plays a relatively important part in chemical reactions.

The distributions of the energy of the recombined nitrogen molecules are shown in Figure 13 for several temperatures, where $F_{\chi\chi}$ is the total energy of the molecule, $B_{\chi\chi}$ is the height of the rotational barrier (see Reference 2), and $(E - E)_{\chi\chi}$ is a measure of the vibrational energy of the molecule. Figure 14 shows plots of the distribution of trajectories with respect to the impact parameter (h_M) and the kinetic energy (E_M^{\prime}/kT) , respectively, of the argon atom relative to the center of mass of the nitrogen molecule. The reactive trajectories are indicated by the shaded area in these figures.

For trajectories which involve bound N·Ar, complexes, we define the impact parameter (b_c) and the kinetic energy (E_c/kT) of the free nitrogen atom relative to the center of mass of the N·Ar complex. The distributions with respect to these two parameters are plotted in Figure 15 (for T = 100 °K). Again, the reactive (recombination) trajectories are indicated by the shaded area.

It is interesting to note the characteristics of the impact parameter distributions. The number of trajectories (N) approaches zero for $(b_M, b_C) \neq 0$. This is a geometrical effect. As (b_M, b_C) increases, N rises to a maximum and then dies off gradually when the interaction between the argon atom and the nitrogen molecule becomes weaker and weaker.

The results of the Monte Carlo trajectory calculations presented above indicate that the equilibrium transition rate for systems of diatomic molecules highly diluted in an inert gas heat bath can be represented satisfactorily by a simple, separable function which contains three characteristic parameters. It appears that these parameters can be correlated and predicted by the formulas obtained in this study although better statistics and additional data for other systems are probably needed for certain refinements in these formulas. Also, in order to understand more about the effects of the "complex" mechanism to the overall recombination rate coefficient at low temperatures, a detailed analysis of the corresponding master equations (with the appropriate transition rates) must be carried out. Finally, it is of great interest to wodify the present 'fonte Carlo tec'miques for use with three-body interaction potentials of a more general nature: in particular, for systems that involve strongly reacting third bodies. e.g., H + H + H.

VI. ACKNOWLERGMENT

The author is grateful to Professors J. C. Keck and J. P. Appleton for their guidance during the course of this work.

REFERENCES

- 1. J. C. Keck, J. Chem. Phys. 32, 1035 (1960).
- 2. J. C. Keck, Advances Chem. Phys. 13, 85 (1967).
- V. H. Shui, J. P. Appleton, and J. C. Keck, J. Chem. Phys. <u>53</u>, 2547 (1970).
- V. H. Shui, J. P. Appleton, and J. C. Keck, Symp. Combust. 13th, Salt Lake City, Utah, 19 (1971).

-23-

- 5. V. H. Shui and J. P. Appleton, J. Chem. Phys. 55, 3126 (1971).
- 6. J. C. Keck, Discussions Faraday Soc. <u>33</u>, 173 (1962).
- 7. J. C. Keck and G. F. Carrier, J. Chem. Phys. <u>43</u>, 2284 (1965).
- 8. V. H. Shui, J. P. Appleton, and J. C. Keck, accepted for publication in J. Chem. Phys.
- 9. J. M. Hammersley and D. C. Handscomb, <u>Monte Cerlo Methods</u>, John Wiley, New York, 1964.
- H. A. Meyer, ed., <u>Symposium on Monte Carlo Methods</u>, John Wiley, New York, 1956.
- 11. J. H. Halton, SIAM Rev. 12, 1 (1970).
- 12. V. H. Shui, Ph.D. Thesis, M.I.T., Feb. 1972.
- 13. The moments used in Reference 8, $K_m(\varepsilon)$, were defined by omitting the factor $G(\varepsilon)/G(\varepsilon_f)$ in Equation (3.7). The present definition is more general.
- 14. J. C. Keck, private communication.
- 15. Data for the systems $0_2 + X_e$, $0_2 + Ar$, and $I_2 + Ar$ are supplied by Professor J. C. Keck.
- 16. E. Rabinowitch, Trans. Faraday Soc. 33, 283 (1937).
- 17. D. L. Bunker and N. Davidson, J. Am. Chem. Soc. 80, 5090 (1958).
- 18. D. L. Bunker, J. Chem. Phys. <u>32</u>, 1001 (1960).
- 19. F. T. Smith, Discussions Faraday Soc. 33, 183 (1962).
- 20. G. Porter, Discussions Faraday Soc. 33, 198 (1962).
- 21. M. Eusuf and K. Laidler, Trans. Faraday Soc. 59, 2750 (1963).
- 22. S. K. Kim, J. Chem. Phys. 46, 123 (1967).
- T. J. Hill, J. Chem. Phys. <u>23</u>, 617 (1955). <u>Statistical Mechanics</u> (McGraw-Hill, New York, 1956), Chap. 5.

- 24. N. Bernardes and H. Primakoff, J. Chem. Phys. 30, 691 (1959).
 - D. E. Stogryn and J. O. Hirschfelder, J. Chem. Phys. <u>31</u>, 1531 (1959); ibid. 33, 942 (1960).
 - 26. S. K. Kim and J. Ross, J. Chem. Phys. <u>42</u>, 263 (1965).
 - 27. A. G. Clarke and G. Burns, J. Chem. Phys. 55, 4717 (1971).
 - 28. F. R. Gilmore, J. Ouant. Spectry. Radiative Transfer 5, 369 (1965).
 - R. C. Flagan and J. P. Appleton, accepted for publication in
 J. Chem. Phys.
 - 30. K. L. Wray, J. Chem. Phys. <u>44</u>, 623 (1966).
 - I. M. Campbell and B. A. Thrush, Proc. Roy. Soc. (London) <u>A296</u>,
 201 (1967).
 - 32. M. A. A. Clyne and D. H. Stedman, J. Phys. Chem. 71, 3071 (1967).
 - 33. W. Brennen and E. C. Shane, J. Phys. Chem. 75, 1552 (1971).
 - J. P. Appleton, M. Steinberg, and D. J. Liquornik, J. Chem. Phys.
 48, 599 (1968).
 - 35. S. Byron, J. Chem. Phys. <u>44</u>, 1378 (1966).
 - 36. B. Cary, Phys. Fluids 8, 26 (1965); 9, 1047 (1966); K. L. Wray and
 S. Byron, ibid. 9, 1046 (1966).

System	D(eV)	β(A ⁻¹)	r _e (A)
N ₂	9.90	2.66	1.10
$N_2(A {}^3\Sigma_u^+)$	3.68	2.70	1.29
NAr	0.017	1.49	3.18

Morse Potential Parameters

TABLE I



TABLE II

System*	T ^o k (kT/D)	ε	D 1	^D O	D ₂	D ₄		$\frac{2 \mathfrak{D} _1}{\mathfrak{D}_2}$	$(\frac{12D_2}{D_4})^{1/2}$
		0	.366	1.56	. 342	2.14	4,26	2.14	1.39
N. (X)	11500	-1	.373	.876	.391	2.30	2.34	1.91	1.43
2.07	(0.1)	-2	.344	.992	.381	2.74	2.83	1.81	1.30
		-3	•222	.744	.221	.824	3.35	2.01	1.30
		mea	in				3.21	1.97	1.48
		Ù	.501	1.52	.927	17.4	3.04	1.08	.80
$N_{a}(X)$	1000	-1	. 395	.600	.988	47.5	1.52	.80	.50
2	(.0087)	-2	.280	.479	.587	13.9	1.71	.955	.71
		-3	. 309	.456	.540	12.4	1.48	1.14	.72
		mea	n				1.94	.99	.68
		າ	.332	.481	. 817	47.1	1.45	.813	.46
$N_{a}(\mathbf{X})$	200	-1	.229	.234	.732 1	100.	1.02	.526	.29
2	(.0017)	-2	.191	.353	.471	14.6	1.85	.811	.62
		-3	.147	.144	.338	6.24	.98	.870	.81
		mea	n	*****			1.32	. 78	.54
		0	.183	.205	.454	L1.6	1.12	.807	.69
N_ (X)	100	-1	.128	.067	.503	40.2	.52.4	.509	.39
2	(.0009)	-2	.102	.053	.438	26.8	.520	.466	.44
		-3	.088	.067	.281 1	16.2	.762	.627	.46
		mean	n				.73	.60	.50

-27-

TABLE II

Summary of Energy Transfer Moments (Continued)

* System	T ^o k (kT/D)	3	2 ₁	D _O	D ₂			2 1 1 D2	$(\frac{12D}{D_{4}})^{1/2}$
	·····	0	.473	2.04	.784	17.5	4.31	1.21	.73
N ₂ (A)	1000	-1	. 381	.682	.658	9.40	1.79	1,16	.92
L	(.0234)	-2 3	.291 .233	.848 .606	.553 .387	10.4 3.21	2.91 2.60	1.05 1.20	.80 1,20
		mea	n n				2.90	1.16	.91
		0	.360	.782	.792	32.4	2.17	0.91	0.54
N, (A)	200	-1	.291	. 314	.886	96.3	1.08	0.66	0.33
2	(.0047)	-2	.201	.256	.548	19.9	1.27	0.73	0.57
		-3	.173	.162	.415	17.9	0.94	0.83	0.53
		mea	n			ب من من بنامي «د من من	1.36	0.78	0.49
		0	.217	.223	.694	38.8	1.03	.626	.464
N. (A)	100	-1	.158	.092	.504	18.7	.582	.628	.569
2	(.0023)	-2	.186	.244	.524	19.0	1.31	.748	.576
		-3	.164	. 099	.580	34.8	.604	.566	.448
		mea	n	1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 -		<u></u>	.882	.642	.514

* The third body is argon.

TABLE III

Summary of Characteristic Parameters

* System	T ^o k	kT/D	C	b	2 D ₁ /D ₂	a	1- (α/β) ²
	11500	.10	.42	.77	1.97	2.04	.54
N_ (X)	1000	.009	.44	.77	0.99	1.12	.76
2	200	.002	. 32	.77	0.78	0.94	.83
	100	.001	.25	.77	0.60	0.79	.88
	1000	.023	.48	.77	1.16	1.27	. 72
N ₂ (A)	200	.005	.36	.77	0.78	0.94	.83
-	100	.002	.24	.77	0.64	0.82	.87

for the Transition Kernel

* The third body is argon.

TABLE IV

Distribution of Trajectories with Respect to Class of Reaction and Number of Traverses of the Energy Surface ε .

(a) Ar + N₂ at 11500 °K (kT/D = 0.1), $\varepsilon = 0$.

Class	n	N 2		Total
(f n b)	103	12	3	118
(f n f)	68	9	1	78
(b n b)	87	3	0	90
(b n f)	10	3	1	14
Total	و بو بنه اس بنه اسراع الکار است.			300

Recrossing correction factor

 $N/N_{o} = (103 + 12/2 + 3/3) = 0.37$

(b) Ar + N₂ at 100 °K (kT/D = 0.0009), $\varepsilon = 0$.

(1			N ·			
	n <u>1</u>	2	3	4	2 5	Total
(f n b)	61	29	9	4	1	104
(f n f)	34	9	3	2	1	49
(b n b)	82	27	6	0	1	116
(b n b)	20	8	1	1	0	30
Total						299

Recrossing correction factor

 $N/N_{o} = (61 + 29/2 + 9/3 + 4/4 + 1/5)/299 = 0.27$

TABLE IV

Distribution of Trajectories with Respect to Class of Reaction and Number of Traverses of the Energy Surface E. (Continued)

(c) Ar + N₂ at 100 $^{\circ}$ K (kT/D = 0.0009), ε = 0, with non-complex trajectories only.

C1000			N			Wata 1
CIASS	n 1	2	3	4	2 5	TOTAT
(f n b)	30	15	1	1	0	47
(f n f)	19	3	2	0	0	24
(b n b)	79	24	4	0	1	108
(b n f)	19	8	1	1	0	29
Total						208

Recrossing correction factor

 $N/N_{o} = (30 + 15/2 + 1/3 + 1/4)/208 = 0.183$

:.

TABLE V	1
---------	---

tate	T ^o k	<u>kT</u> D	kr r	N	k ke	k ₆ k _r	$\frac{\mathcal{R}(\varepsilon_{b})(k/k_{e})\varepsilon_{b}}{\mathcal{R}(0)(k/k_{e})_{o}}$	k r
	11500	.1	9.92-34	.42	.22	.60	~ 1	6.14-3
1 _Σ +	1000	.009	3.04-33	.44	.60	.77	1.17	7.21-34
- 8	200	.002	9.91 ⁻³³	. 32	.74	1.07	1.26	3,15-3
	100	.001	2.82 ⁻³²	.25	.82	1.26	1.31	9.49-3
	1000	.023	6.72 ⁻³³	.48	.48	.67	1.17	1.20-3
³ Σ ⁺	200	.005	2.32-32	. 36	.69	.90	1.26	6.58-3
-	100	.002	6.69-32	.24	.77	1.06	1.31	1.70-32

Recombination Rate Coefficients for N_2 + Ar

FIGURES

- Plot of [N(ε)/N₀(ε)]/[1 exp(- kT/D)] versus ε for N₂ + Ar.
 T = 11500 °K; O, T = 1000 °K; O, T = 200 °K; O, T = 100 °K.
 Solid line is the best least-squares fit for all points. The slope of this line determines the parameter b.
- 2. Correlation of the parameter b with $[m_3/(m_1 + m_2)]^{1/2}$.
- 3. Correlation of the parameter a with kT/D, where D is the well depth of the interaction potential of the molecule. \blacktriangle , $N_2(X \stackrel{1}{\Sigma_g}^+) + Ar;$ \bigtriangleup , $N_2(A \stackrel{3}{\Sigma_u}^+) + Ar; \lor$, HCL + Ar; \bigtriangledown , $CL_2 + Ar; \odot$, $0_2 + Xe;$ O, $0_2 + Ar; \blacksquare$, $I_2 + Ar$. Solid line is the best least-squares fit for all points.
- 4. Plot of the averaged absolute energy transfer, < Δ >, and the rootmean-square energy transfer, < Δ^2 >^{1/2}, versus kT/D for reactive collisions. D is the well depth of the interaction potential of the molecule. Remainder of legend same as Figure 3.
- 5. Map of numerical distribution of the function $R(\varepsilon_i, \varepsilon_f)$ for $N_2 + Ar$ at 11500 ^OK. The contour map, calculated from Equation (4.8) using the fitted parameters, is plotted in the upper left corner to avoid overcrowding the figure. Comparison may be done by reflection through the diagonal $\varepsilon_i = \varepsilon_f$.
- 6. The function $[\mathbb{R}(\Delta, \overline{\varepsilon})/\mathbb{R}_{V}(0)]/[\mathbb{R}(\overline{\varepsilon})/\mathbb{R}(0)]$ is plotted versus Δ , the absolute value of energy transfer, for the case of N₂ + Ar at 11500 °K. •, $\overline{\varepsilon} = 0$; O, $\overline{\varepsilon} = -1$; •, $\varepsilon = -2$; Δ , $\overline{\varepsilon} = -3$. The factor $[\mathbb{R}(\overline{\varepsilon})/\mathbb{R}(0)]$ is included for normalization purposes so that the data can be better represented by a single line. The solid line which passes through the bulk of the data has a slope taken from Table III. See text, Section 4.1.

- ¹ c^{1/2} :::C, the ratio of the contribution from the "complex" mechanism to that from the noncomplex mechanism, is plotted versus kT/D₁₂₁? where D₁₂₁ is the well depth of the third-body interaction potential.
 •, N₂(x ¹Σ⁺_g) + Ar; O, N₂(A ³Σ⁺_u) + Ar; A, Ck₂ + Ar.
 Clot of the effective recombination rate coefficient due to barrier penetration versus energy, for N₂ at several temperatures.
 Comparison between theoretical predictions of the recombination rate coefficient and experimental measurements as a function of T.
 •, theoretical predictions of k_r(X ¹Σ⁺_g) + k_r(A ³Σ⁺_u); ●, theoretical predictions of k_r(X ¹Σ⁺_g); A, Campbell and Thrush³¹; O, Clyne and Stedman; ³² ∇, Brennen and Shane; ³³ (A), Appleton et al; ³⁴ (B), Byron; ³⁵ (C), Cary.³⁶ Solid and dashed lines, see text, Section 4.2.
- 10. Typical trajectories for N_2 + Ar collisions.
 - (a) Shows $f \neq b$ transition at 11500 °K.
 - (b) Shows $b \rightarrow f \rightarrow b$ transitions at 11500 °K. O, position when $b \rightarrow f$ transition occurred; \bullet , position when $f \rightarrow b$ transition occurred.
 - (c) Shows $f \neq b$ transition at 100 °K. In the upper part, the Ar atom is at the origin; whereas, in the lower part, the origin corresponds to the center of mass of N₂. The motion of the N·Ar bound complex is clearly illustrated.

The small dots on the trajectories indicate time intervals of $v_e t = 1$ in (a) and (b) and $v_e t = 10$ in (c) where v_e is the ground state vibrational frequency of the molecule.

- 11. Time evolution of typical trajectories. Upper half of the figure shows energy of the molecule [(H B)/kT] versus time $(v_e t)$. Lower half shows r_{12} and r_3 versus $v_e t$. r_e is the equilibrium separation, and v_e is the ground state vibrational frequency of the molecule.
 - (a) N₂ + Ar at 11500 $^{\circ}$ K,

(b) N₂ + Ar at 100 $^{\circ}$ K.

- 12. Distribution plot of reactive trajectories in the [Δ H, Δ B] plane for N₂ + Ar at 11500 ^OK.
- Energy distributions of nitrogen molecules formed by recombination in argon.
- 14. Distributions of trajectories (a) with respect to the impact parameter; (b) with respect to the kinetic energy of the third body (see text, Section V) for N₂ + Ar at several temperatures. Reactive trajectories are indicated by the shaded areas.
- 15. Distributions of trajectories with respect to the impact parameter and the relative kinetic energy defined for the complex mechanism (see text, Section V), for N·Ar + N at 100 ^OK. Reactive (recombination) trajectories are indicated by the shaded areas.

-35-



FIG. 1



FIG. 2













FIG. 6



FIG. 7

江福書



FIG. 8

•



FIG. 9





FIG. 11











FIG. 15