

FEBRUARY 1962 MMPP 167-3, 178-1
ORA 3710-2-P

Phoenix Library

**MICHIGAN MEMORIAL PHOENIX PROJECT
PHOENIX MEMORIAL LABORATORY
THE UNIVERSITY OF MICHIGAN**

UNIVERSITY
OF MICHIGAN

APR 16 1962

PHOENIX
LIBRARY

**ENERGETIC RECOIL ATOM REACTION MECHANISMS
PROGRESS REPORT NO. 2**

THIS WORK WAS SUPPORTED BY:

THE DEPARTMENT OF CHEMISTRY

THE MICHIGAN MEMORIAL PHOENIX PROJECT

THE UNITED STATES ATOMIC ENERGY COMMISSION
CONTRACT NO. AT(11-1)-912



ENERGETIC RECOIL ATOM REACTION MECHANISMS

Progress Report No. 2

Adon A. Gordus
Principal Investigator

February, 1962
Ann Arbor, Michigan

PREFACE

The following is a report of the work completed during the period, February 28, 1961 to February 15, 1962. These studies were supported by the U. S. Atomic Energy Commission, Division of Research, Contract No. AT(11-1)-912, the Department of Chemistry of The University of Michigan, and the Michigan Memorial-Phoenix Projects 167 and 178.

A progress report such as this can serve a very useful purpose. Because of the U. S. Atomic Energy Commission's depository library system and the excellent distribution facilities of the Technical Information Service at Oak Ridge, Tennessee, it is possible to make available through a progress report preliminary data and reports of research in progress or research which has recently been completed. Without such a distribution system one is tempted to submit preliminary reports to journals as "Letters to the Editor" or "Communications". Therefore, the progress report can assist in eliminating the amount of duplication of research reporting which exists in the scientific journals.

Many of the data, calculations, and conclusions stated in this report are an abridgement of information contained in manuscripts being prepared for publication in various journals. The reader is asked to consider these data and conclusions as tentative and not in final form.

Extensive discussions and sample calculations associated with the various mathematical models discussed herein will be found in the Ph.D. dissertation of Mrs. Chi-hua Hsiung. This dissertation will be available approximately May 1 and will be submitted to the Technical Information Service for distribution to the U. S. Atomic Energy Commission depository libraries.

TABLE OF CONTENTS

Preface-----	1
Table of Contents -----	ii
List of Tables -----	iii
List of Figures -----	iv
I. Introduction -----	1
II. Momentum Transfer to an Atom in a Molecule -----	2
III. Failure to Bond-Rupture Following Recoil Beta-Decay -----	7
IV. A Mathematical Model of Hot-Atom and Hot-Ion Reactions ---	8
V. A Mathematical Model for the Effects of Additives on Hot-Atom and Hot-Ion Reactions -----	24
VI. Specific Solutions for Five-Step Three-Dimensional Random Walks -----	31
VII. Effects of Additives on the Reactions of Alkanes with Br ⁸⁰ Activated by Isomeric Transition -----	32
VIII. Work in Progress -----	33
IX. Personnel and Publications -----	34
X. References -----	36

LIST OF TABLES

I.	Distribution of Imparted Energy, E_T -----	2
II.	Fraction of Internal Excitation Energy Deposited in the Bond Joining the Activated Atom to the Remainder of the Molecule -----	5
III.	Comparison of \bar{x} Values for a series of Molecules ---	6
IV.	Non-Rupture of a Bond Following Recoil Beta-Decay --	7
V.	Calculated Intercept Ratios -----	13
VI.	Yields of Hot-Atom Reactions -----	13
VII.	Calculated $I^{128} + CH_4$ Yields -----	26

LIST OF FIGURES

1.	Yield Ratio of HT/DT for T + H ₂ , D ₂ Reactions -----	11
2.	T + CH ₄ Moderation, T = 1.1 Å, T + CH ₄ Collisions -----	14
3.	T + CD ₄ Moderation, T = 1.1 Å, T + CD ₄ Collisions -----	15
4.	T + CH ₄ Moderation, T = 2.4 Å, T + CH ₄ Collisions -----	16
5.	T + CD ₄ Moderation, T = 2.4 Å, T + CD ₄ Collisions -----	17
6.	T + CH ₄ Moderation, T = 1.1 Å, T + H Collisions -----	18
7.	T + CD ₄ Moderation, T = 1.1 Å, T + D Collisions -----	19
8.	T + CH ₄ Moderation, T = 2.4 Å, T + H Collisions -----	20
9.	T + CD ₄ Moderation, T = 2.4 Å, T + D Collisions -----	21
10.	Helium Moderation of the T + CH ₄ Reaction -----	22
11.	Helium Moderation of the T + CD ₄ Reaction -----	23
12.	Calculated Moderation by Helium of the T + CH ₄ Reaction	25
13.	Calculated Moderation by Krypton of the Br + CH ₄ Reaction -----	27
14.	Calculated Moderation by Krypton of the I + CH ₄ Reaction -----	28
15.	Calculated Moderation by Xenon of the I + CH ₄ Reaction -	30

I. INTRODUCTION

The studies during this past year have been concerned principally with the development of various mathematical models of energetic recoil atom reaction mechanisms. In addition, about 500 reactor irradiations have been performed. Some of these data have been incorporated in articles which have or are about to appear in print. Other data are included in this report.

Work in progress, but not discussed in this report, includes: 1) construction of an automatic gas chromatograph with radioactivity detection, 2) effect of Co^{60} gamma radiation on mixtures of tagged halogen, methane, and inert-gas or molecular additive, 3) failure to bond-rupture of gaseous chlorocarbons, 4) effect of inert-gas and molecular additives on the gas phase reaction of CH_4 with Br^{80} activated by isomeric transition, 5) liquid phase (n,γ) failure to bond-rupture, 6) effects of additives on such reactions as $\text{I}^{128} + \text{CHF}_3$, 7) reactions of Cl^{38} activated by the $\text{Cl}^{37}(n,\gamma)\text{Cl}^{38}$ process.

II. MOMENTUM TRANSFER TO AN ATOM IN A MOLECULE

Presented on pages 3 and 4 are abstracts of two articles¹ accepted for publication in a February or March issue of the Journal of Chemical Physics. Since these articles will probably appear prior to the circulation of this report only a few additional comments will be provided.

When a net momentum impulse is transferred to an atom, of the total energy received by the atom, E_T , it is possible to calculate the external energy and the internal excitation energy received by the molecule. These equations are presented in Table I.

Table I. Distribution of Imparted Energy, E_T .

Species	External Energy	Internal Excitation Energy	
		Bond joining activated atom	Other bonds
Single Atom	E_T	0	0
Diatomic molecule	$\frac{m_N}{M} E_T$	$\frac{M-m_N}{M} E_T$	0
Polyatomic molecule	$\frac{m_N}{M} E_T$	$\xi \frac{M-m_N}{M} E_T$	$(1-\xi) \frac{M-m_N}{M} E_T$

In Table I, m_N is the atomic weight of the atom receiving the momentum impulse, M the molecular weight, and ξ a factor which can be calculated in terms of the complicated method discussed in reference 1. This ξ factor, which is the fraction of the internal excitation energy deposited in the bond joining the activated atom to the remainder of the molecule, is not discussed in this article, but can be calculated easily from the data presented in the article. Table II is a listing of these ξ factors for calculated values of E_T required for bond-dissociation.

Momentum Transfer to an Atom in a Molecule:
Internal Excitation and Bond Dissociation

Chi-hua Hsiung[†] and Adon A. Gordus

Department of Chemistry, The University
of Michigan, Ann Arbor, Michigan

ABSTRACT

An atom will dissociate from a compound if the atom receives a recoil momentum greater than some average value, Q° . Considering a polyatomic molecule as composed of point-mass atoms, there is derived an equation which relates Q° to the bond energy, bond angles and distances, and masses of the atoms in the molecule. The minimum net recoil energy required for bond rupture, the kinetic energy of the recoiling radicals, and the internal energy of the radical originally bonded to the activated atom are calculated for a series of simple alkyl halides.

Failure to Bond-Rupture and Nuclear Recoil
Following (n, γ) Activation*

Adon A. Gordus and Chi-hua Hsiung[†]

Department of Chemistry, The University
of Michigan, Ann Arbor, Michigan

ABSTRACT

Following the absorption of a thermal neutron by ^{127}I or ^{79}Br , the neutron-binding energy is frequently released in the form of a gamma-ray cascade. As a result of partial cancellation of gamma-ray momenta, a small fraction of the activated halogens will not receive sufficient recoil momentum to rupture from their parent compound. The gas-phase failures to bond-rupture following $^{127}\text{I}(\text{n},\gamma)$ ^{128}I and $^{79}\text{Br}(\text{n},\gamma)$ ^{80}Br activation experimentally were found to be: CH_3I - 1.09, CD_3I - 0.68, CF_3I - 0.12, CH_2I_2 - 0.068, $\text{C}_2\text{H}_5\text{I}$ - 0.082, $n\text{-C}_3\text{H}_7\text{I}$ - 0.66, $i\text{-C}_3\text{H}_7\text{I}$ - 0.30, CH_3Br - 0.25, CD_3Br - 0.20, CH_2Br_2 - 0.12, CF_3Br - 0.11, CF_2Br_2 - 0.093, CHClBr_2 - 0.087, CCl_3Br - 0.066, CHBr_3 - 0.05, CBr_4 - 0.03, $\text{C}_2\text{H}_5\text{Br}$ - 0.33, and $1,1\text{-C}_2\text{H}_4\text{Br}_2$ - 0.17 percent. These data are correlated with the calculated recoil energies required for bond rupture (preceding article). Using as a basis the distribution of net gamma-ray energies calculated by the random-walk method for the $^{35}\text{Cl}(\text{n},\gamma)^{36}\text{Cl}$ process, the kinetic-energy distributions of the dissociated ^{128}I or ^{80}Br are approximated. These data suggest that the extent of hot-atom reaction of ^{128}I or ^{80}Br with CH_4 should not depend upon the parent molecule from which the activated halogen dissociates.

Table II. Fraction of Internal Excitation Energy Deposited in the Bond Joining the Activated Atom to the Remainder of the Molecule.

Compound ^a	ξ	Compound ^a	ξ
Diatomic Molecules	1.000	CHClBr ₂	0.839
CH ₃ I	0.818	CHBr ₃	0.820
CD ₃ I	0.795	CBr ₄	0.936
CF ₃ I	0.719	C ₂ H ₅ Br	0.700
CH ₂ I ₂	0.700	1,1-C ₂ H ₄ Br ₂	0.813
C ₂ H ₅ I	0.599	CH ₃ Cl	0.840
i-C ₃ H ₇ I	0.665	CD ₃ Cl	0.819
n-C ₃ H ₇ I	0.623	CF ₃ Cl	0.872
CH ₃ Br	0.895	CHF ₂ Cl	0.803
CD ₃ Br	0.860	CH ₂ Cl ₂	0.757
CF ₃ Br	0.819	CF ₂ Cl ₂	0.862
CCl ₃ Br	0.874	CHCl ₃	0.814
CH ₂ Br ₂	0.775	CFCI ₃	0.864
CF ₂ Br ₂	0.858	CCl ₄	0.873
CCl ₂ Br ₂	0.868		

^aThe dissociating halogen is the last element listed in the formula.

These ξ factors indicate that an average of about 80% of internal excitation energy is deposited in the bond which joins the activated atom to the molecule. Thus, in general, bond rupture will occur in a polyatomic molecule when the total energy received by the atom is given by the equation:

$$E_{BN} = 0.80 \frac{M - m_N}{M} E_T \quad (1)$$

where E_{BN} is the bond-dissociation energy.

It is interesting to compare ξ values for a series of structurally similar compounds. Such data are given in Table III. Values of E_T° , the imparted energy required for bond-dissociation, are included in the table. It may appear

surprising that the $\bar{\nu}$ values should first decrease and then increase. This is due to a combination of effects: 1) When the radical attached to the activated atom is of low molecular weight it can be considered as a point mass. As the molecular weight of the radical increases (for constant E_T) it appears less like a point-mass radical and the energy absorbed as internal energy of the radical increases. Hence, $\bar{\nu}$ decreases. 2) For any compound, as E_T decreases, $\bar{\nu}$ increases. As the molecular weight of the radical becomes larger, a smaller amount of total recoil energy, E_T^0 , is required for bond-dissociation, since the factor $M-m_N/M$ increases. Thus, for a series of structurally similar molecules, $\bar{\nu}$ will increase as M increases.

Table III. Comparison of $\bar{\nu}$ Values for a Series of Molecules

Compound	$\bar{\nu}$	E_T^0 , ev.
CH ₃ Br	0.895	20.74
CD ₃ Br	0.860	18.54
CF ₃ Br	0.819	7.38
CCl ₃ Br	0.874	4.06
CBr ₄	0.936	2.98

It appears that, for a series of structurally similar compounds, the minimum $\bar{\nu}$ value is approached as the mass of the activated atom becomes approximately equal to the mass of the radical to which it is bonded.

III. FAILURE TO BOND-RUPTURE FOLLOWING RECOIL BETA DECAY

Carbon-14 or tritium beta particle emission will impart a recoil momentum to the N^{14} or He^3 product nucleus. Since the beta energy spectra are known for these two decay processes it is possible to calculate the percent of the decay events which result in an imparted energy less than some value, E_T . When the C^{14} or T is bound chemically, a certain fraction of the decay-product molecules should fail to bond-rupture. Experimental values of the extent of N^{14} or He^3 non-rupture have been determined by Wexler² and Snell and Pleasanton³ using a modified mass spectrometer. In addition, using chemical means, Wolfgang, Anderson, and Dodson⁴ have determined the N^{14} failure to bond-rupture in C^{14} -labeled C_2H_6 .

The expected failure to bond-rupture in the tritiated compounds can be calculated using the tritium beta-energy spectrum in conjunction with the mathematical model discussed in reference 1. A C-He⁺ bond energy of 0.05 ev was used in these calculations.

The method presented in reference 1 cannot be used directly to calculate the internal excitation and bond dissociation resulting from momentum transfer to an atom bonded to more than one atom. The C^{14} -containing compounds, CO_2 and C_2H_6 , therefore require a slight modification in the method.

Table IV contains both experimental and theoretical data of the failure to bond-rupture of various C^{14} and T compounds. Except for C_2H_6 , the agreement between experiment and theory is surprisingly good.

Table IV. Non-Rupture of a Bond Following Recoil Beta Decay

Atom Decaying	Molecule	Percent Non - Rupture Calculated	Experimental
T	CH ₃ T	< 1.0	0.06
T	C ₂ H ₅ T	< 1.0	0.2
T	CH ₂ TCH ₂ CH ₃	< 1.0	0.2
T	CH ₃ CHTCH ₃	< 1.0	0.2
C^{14}	CO ₂	78	81
C^{14}	C ₂ H ₆	84	56

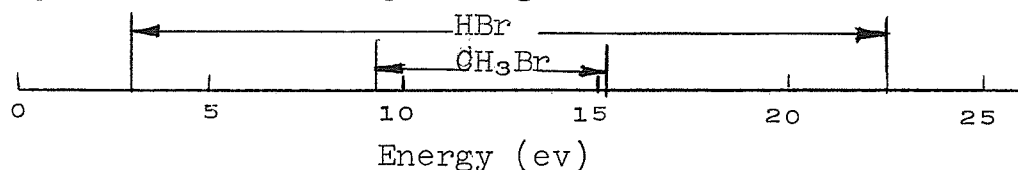
IV. A MATHEMATICAL MODEL OF THE HOT-ATOM AND HOT-ION REACTIONS

Many attempts have been made to explain hot-atom reactions mathematically. All models have been based, to a degree, on the neutron "cooling down" theory. Miller, Gryder, and Dodson⁵ have used the neutron model to describe certain hot-atom reactions in binary liquid systems. Capron and Oshima⁶, using a slightly similar method, obtained similar results for hot-atom reactions in single-component systems. Estrup and Wolfgang⁷, in a manner similar to that of Miller, et. al., developed an equation to describe such effects as inert-gas moderation of hot-atom reactions. The Estrup-Wolfgang model is limited in use to those systems for which experimental data are available since they provide no means for evaluating independently the two constants in their equation.

We have used Miller's method as a basis for development of a mathematical model of hot-atom reactions. Our method requires knowledge of only thermodynamic data and the transport properties of the substances in the reaction system.

Briefly, we have used the following method.

1. We have calculated, for each possible reaction process, the maximum and minimum energies of a hot-atom or hot-ion which will allow chemical stabilization.
2. Assuming that all hot-atoms or hot-ions initially possess energy greater than that which would lead to chemical stabilization, we next calculated the fraction of the hot-atoms which are reduced to energies which will permit chemical stabilization. Invariably, the stabilization energy ranges for two competing processes will overlap. For example, in the reaction of Br^{80} with CH_4 , two products, HBr^{80} and $\text{CH}_3\text{Br}^{80}$, are considered possible and, as indicated on the energy diagram below, the HBr range encloses the CH_3Br range.



3. The one main weakness with the model is the lack of information about the relative reaction probabilities in the energy ranges where two reaction products are possible. For the two products, HBr and CH₃Br, it was assumed that these reaction probabilities were equal. In most cases it is possible to assume a value of the relative reaction probabilities which is based partially on knowledge of the structural features of the molecule. In this approximation we were guided by the work of Urch and Wolfgang⁸. In the calculation of a yield ratio of two similar reactions, the reaction probability factor cancels out. Hence, the calculation of the CH₃T/CD₃T yield ratio will provide a more reliable indication of the validity of the model than would the calculation of the individual yields of CH₃T and CD₃T.
4. The above model can also be used to calculate the average reaction probability per energy increment. Estrup and Wolfgang⁷ define this term as I and determine its value from hot-atom data. We can calculate this value directly from thermodynamic and transport property data. The reaction probability factor discussed in Part 3 also appears in this calculation. When the ratio of I values for two compounds, such as CH₄ and CD₄ is calculated, this probability factor cancels out.
5. If an inert gas or any other reactive or non-reactive additive is present in the system, we can modify the equations to include the collisions of the hot-atom with the additive. This model, then, is similar to an extent to the model proposed by Estrup and Wolfgang⁷, the only difference being that hot-atom experimental data are not required.
6. One additional variable is difficult to evaluate. In the collision of a hot-atom with a molecule the molecular mass participating in the energy-transfer collision is probably not the total molecular weight. In the case of a T + CH₄ collision we are inclined to consider the ef-

fective mass of CH_4 as closer to 1.0 than to 16. When Br collides with CH_4 we have used 16 as the mass participating in the energy transfer process. In most systems, the exact choice of mass usually will not have an appreciable effect on the calculated product yield.

Results

T + H₂-D₂

Figure 1 contains data of Lee, Musgrave, and Rowland⁹. The solid line is calculated in terms of the model described above. The reason that the calculated curve is slightly lower than the experimental data could be due to a thermal isotope-exchange reaction which we did not include in the calculation.

T + CH₄

Extensive data of Wolfgang and coworkers indicate that the reaction of tritium with an excess of CH_4 results in approximately 36% CH_3T . Depending upon our choice of the effective mass of CH_4 we obtain values ranging from 31 to 46%.

T + CD₄

The paper by Cross and Wolfgang¹⁰ does not state a value for the percent CD_3T formed in the reaction of tritium with excess CD_4 . We have used the original data* of the inert-gas moderation of this reaction to construct four plots of $(A_{\text{CD}_3\text{T}}/A_{\text{S}}) \alpha/f$ vs. f/α . We plotted the data using the definitions of α and f given by Estrup and Wolfgang⁷. The variation in these plots was a result of two choices of the "collision" diameter of tritium: 1.1 and 2.4 Å were used. We prefer the larger value which is based on scattering measurements. In addition, we calculated one set of α values using a mass of CD_4 equal to 20; in another set, we used a mass of 2 corresponding to the atomic weight of deuterium. (Figs. 3, 5, 7, 9.)

* Kindly supplied by Professor Wolfgang.

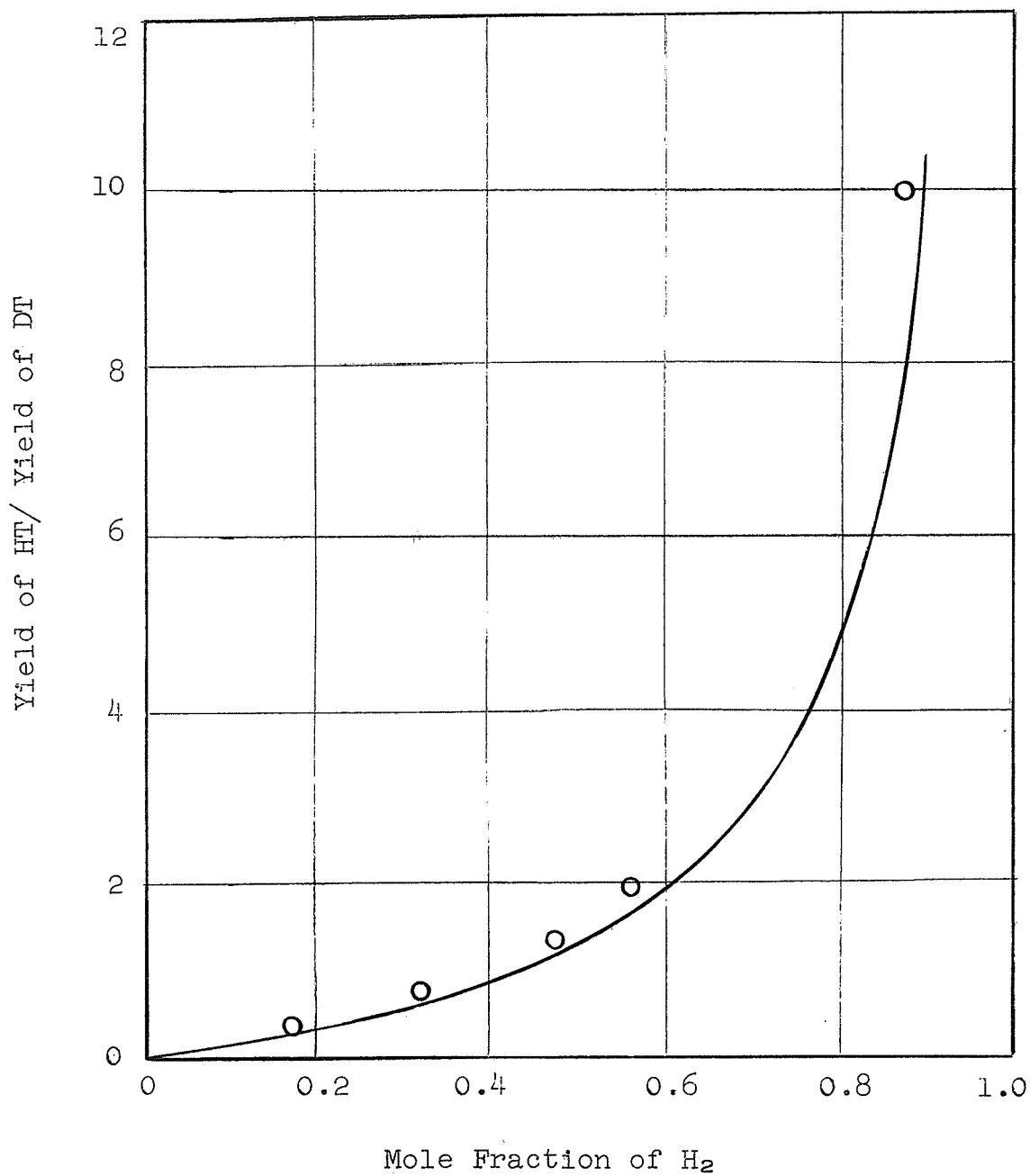


Fig. 1. Yield ratio of HT/DT as a function of the mole fraction of H₂ in H₂-D₂ mixtures. Data of Rowland, et. al.⁹; solid curve was calculated.

To determine the percent CD_3T in an essentially pure system, we extrapolated the data on each graph to the point where $f = 1$. From the corresponding value of $(A_{\text{CD}_3\text{T}}/A_S)(\alpha/f)$ we then calculated $A_{\text{CD}_3\text{T}}/A_S$. These values were 0.27, 0.28, 0.28, 0.30. It is not surprising that these values are all in reasonable agreement since the evaluation of this ratio at $f = 1$ results in a value of $A_{\text{CD}_3\text{T}}/A_S$ independent of the kinetic model and independent of the choice of the various parameters.

This percent CD_3T could also be determined by extrapolating data of $A_{\text{CD}_3\text{T}}/A_S$ vs. mole fraction CD_4 to unit mole-fraction CD_4 . From such a plot, (Fig. 11) a value of $A_{\text{CD}_3\text{T}}/A_S$ approximately equal to 0.31 is obtained.

For this reaction, we calculate a value of 25-35% CD_3T depending principally on our choice of the effective mass of CD_4 .
 CH_4 - CD_4 Isotope Effect

For various internally consistent choices of the effective masses of CH_4 and CD_4 we calculate an expected isotope effect in the tritium-methane reaction of $\% \text{CH}_3\text{T} / \% \text{CD}_3\text{T} = 1.2 - 1.3$. From Figs. 2-3, 4-5, 6-7, and 8-9, we calculate isotope effects of 1.1, 1.2, 1.1, and 1.1. From Figs. 10-11 we calculate 1.2. The agreement between theory and experiment appears excellent.

Cross and Wolfgang¹⁰ define the isotope effect as the ratio between the intercept values, I , in the Estrup-Wolfgang model. They quote¹⁰ an observed ratio of $I_{\text{CH}_4}/I_{\text{CD}_4} = 1.00 \pm 0.13$. We have re-examined their data for both CH_4 and CD_4 by constructing the four sets of curves mentioned above. From the intercepts, we calculate ratios of $I_{\text{CH}_4}/I_{\text{CD}_4} = 0.91, 1.01, 0.97, 0.86$. Figs. 2-3, 4-5, 6-7, and 8-9 are four sets of curves used in the calculations of both $\% \text{CD}_4$ and the intercept ratios. It should be noted that the uncertainty associated with these intercepts is probably at least $\pm 10\%$. The fact that intercept ratios for the pairs of data are approximately constant, suggests that the choices of the effective collisional mass of CH_4 and the choice of the collision diameter of tritium has little influence on the intercept ratio.

As stated above, we are able to calculate this intercept ratio, and this value is independent of our choice of the re-

action probability factor. The value does depend slightly on our choice of the effective collisional mass of methane. Given in Table V are the calculated intercept ratios. The agreement with the experimental data appears good.

Table V. Calculated Intercept Ratios

CH ₄ Mass	CD ₄ Mass	I _{CH₄} /I _{CD₄}
16	20	0.86
3	3.75	1.0
1	2	1.03

Other Non-Moderated Systems

Presented in Table VI are a few of the yields we have calculated for other non-moderated reaction systems where the target molecule is in great excess. Again, agreement between the calculated and experimental values appears surprisingly good. It should be emphasized that in these calculations, unlike the isotope-effect calculations, the choice of the effective collisional mass of the target molecule and the reaction probability factor can strongly affect the calculated yield.

Table VI. Yields of Hot-Atom Reactions

System	Product	Yields, %	
		Calculated	Experimental*
T + C ₂ H ₆	C ₂ H ₅ T	30	28
	CH ₃ T	4	5
	HT	51	43
Br + C ₂ H ₆	C ₂ H ₅ Br	12	4.0
	CH ₃ Br	2	5.6
Br + CH ₄	CH ₃ Br	12.3	13.3
I + C ₂ H ₆	C ₂ H ₅ I	4.4	1.4
	CH ₃ I	0.8	0.6
I + C ₃ H ₈	n-C ₃ H ₇ I	0.3	0.3
	i-C ₃ H ₇ I	0.0	0.5
	C ₂ H ₅ I	0.4	0.4
	CH ₃ I	0.5	0.4

* These data appeared in various journal articles.

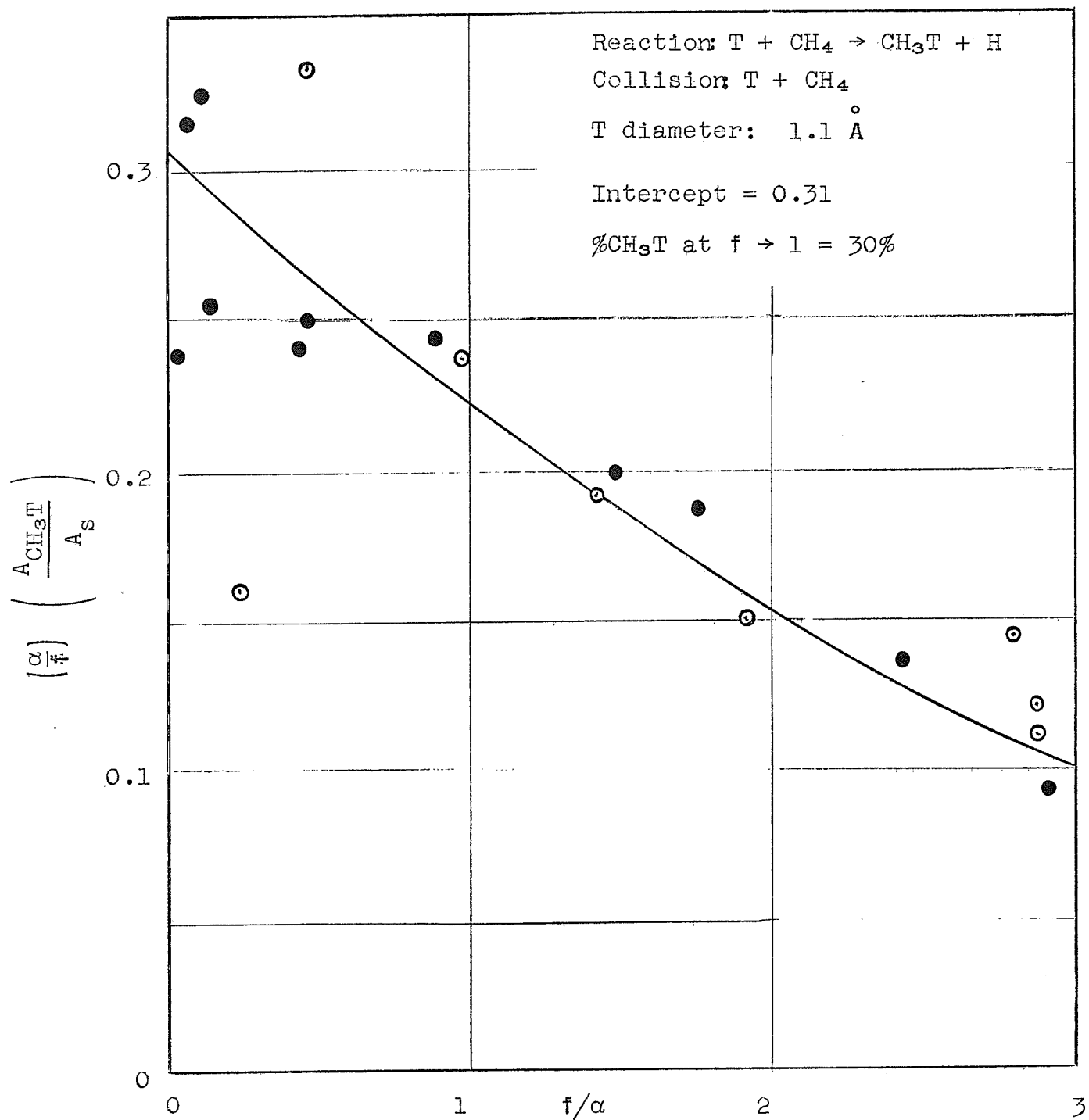


Fig. 2. Plot using the Estrup-Wolfgang equation:
 Data: Estrup and Wolfgang, ●, Cross and Wolfgang, ○.
 Only He moderation data are presented.

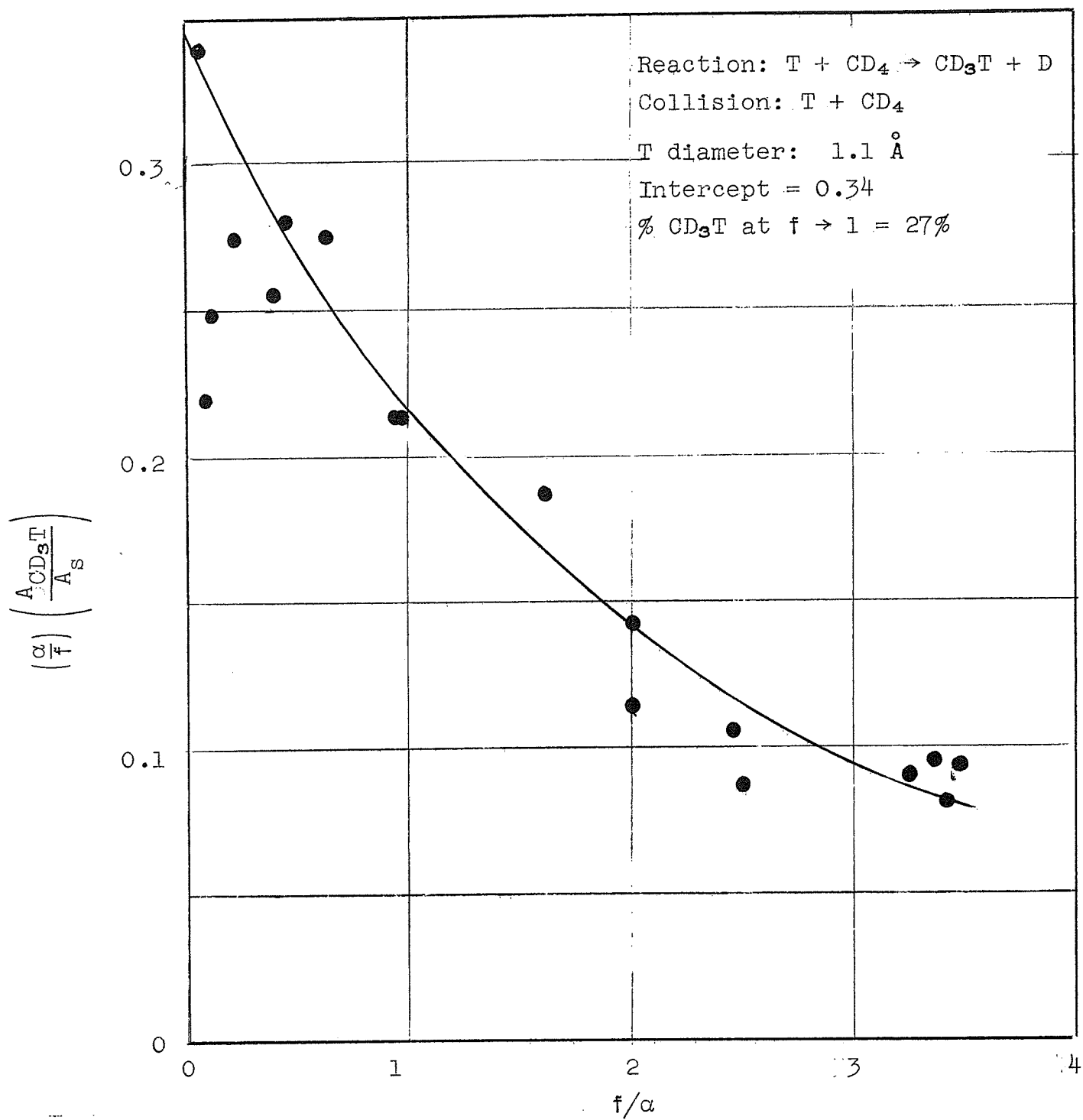


Fig. 3. Plot using the Estrup-Wolfgang equation
 Data of Cross and Wolfgang.
 Only He moderation data are presented.

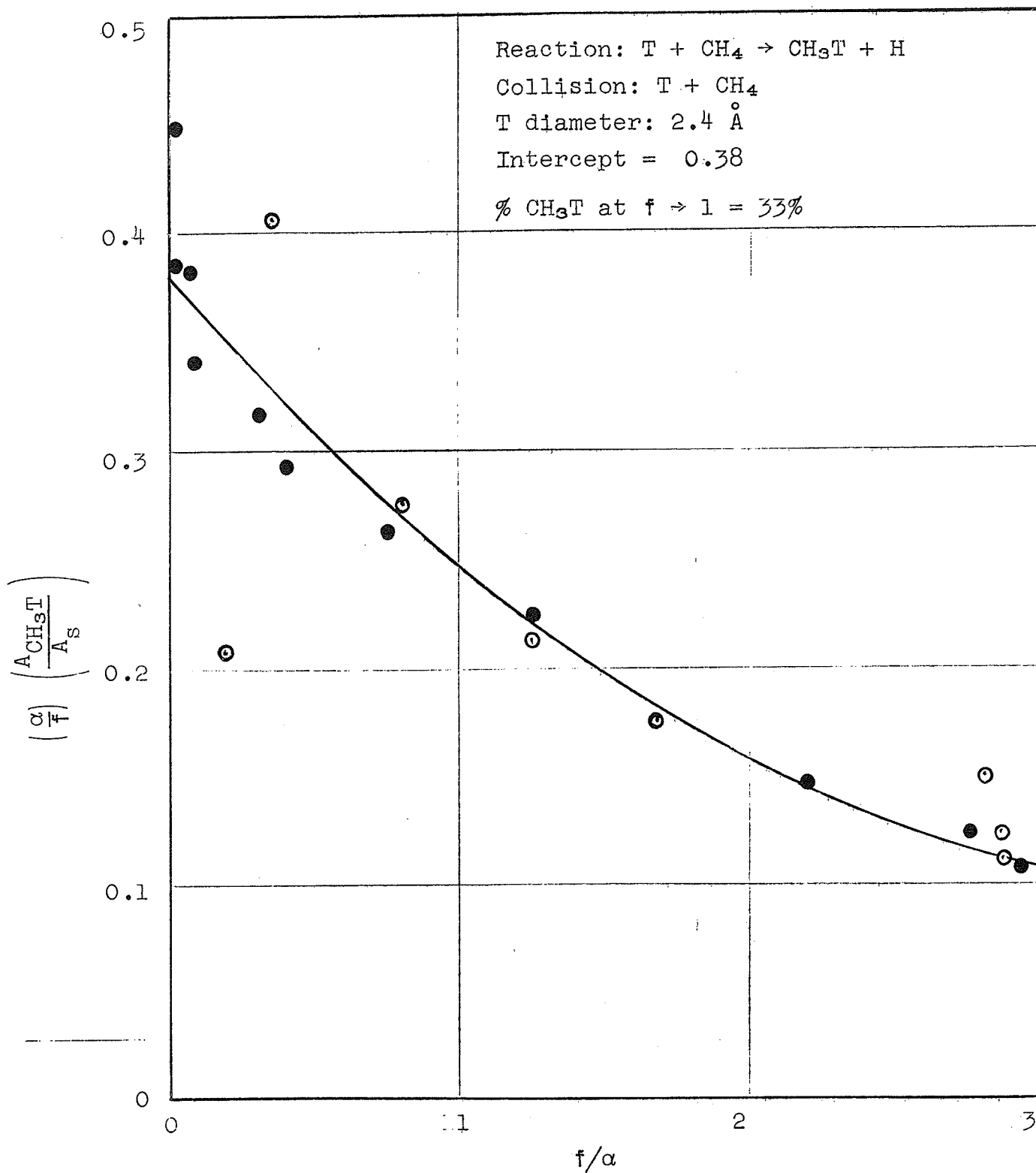


Fig. 4. Plot using the Estrup-Wolfgang equation
 Data: Estrup and Wolfgang, ●; Cross and Wolfgang, ○.
 Only He moderation data are presented.

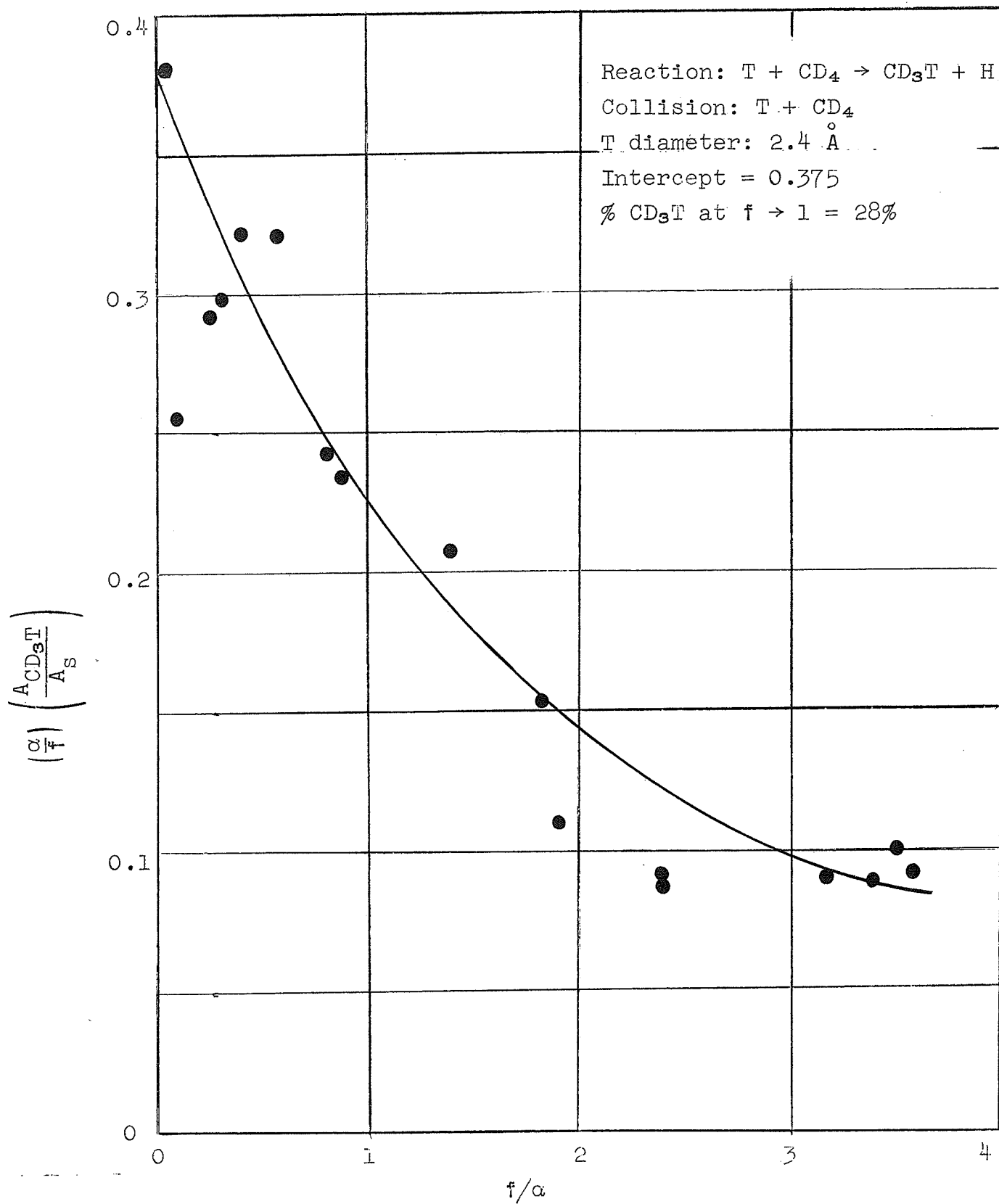


Fig. 5. Plot using the Estrup-Wolfgang equation.
Data of Cross and Wolfgang.
Only He moderation data are presented.

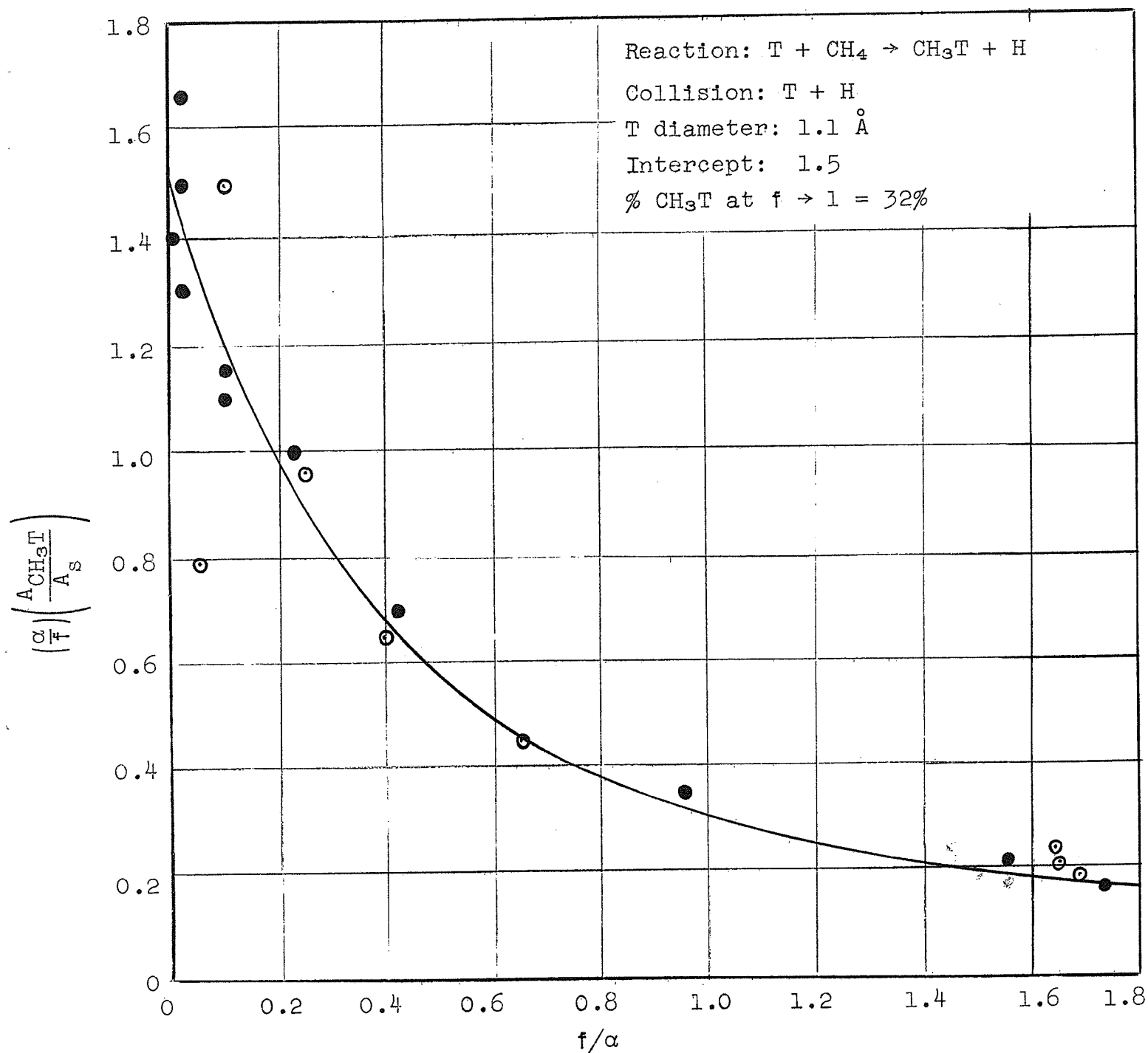


Fig. 6. Plot using the Estrup-Wolfgang equation:
 Data: Estrup and Wolfgang, ●, Cross and Wolfgang, ○.
 Only He moderation data are presented.

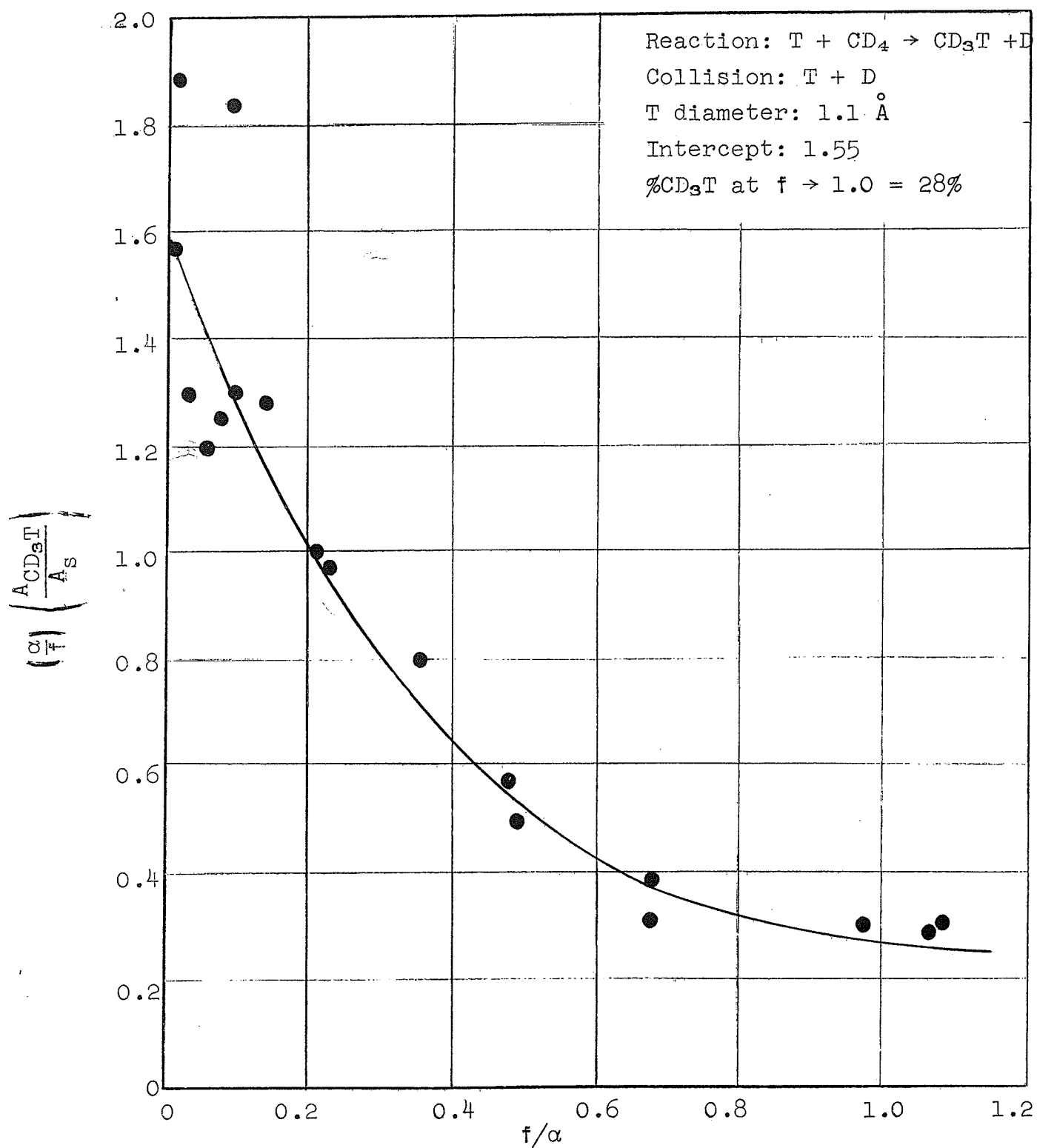


Fig. 7. Plot using the Estrup-Wolfgang equation.
 Data of Cross and Wolfgang.
 Only He moderation data are presented.

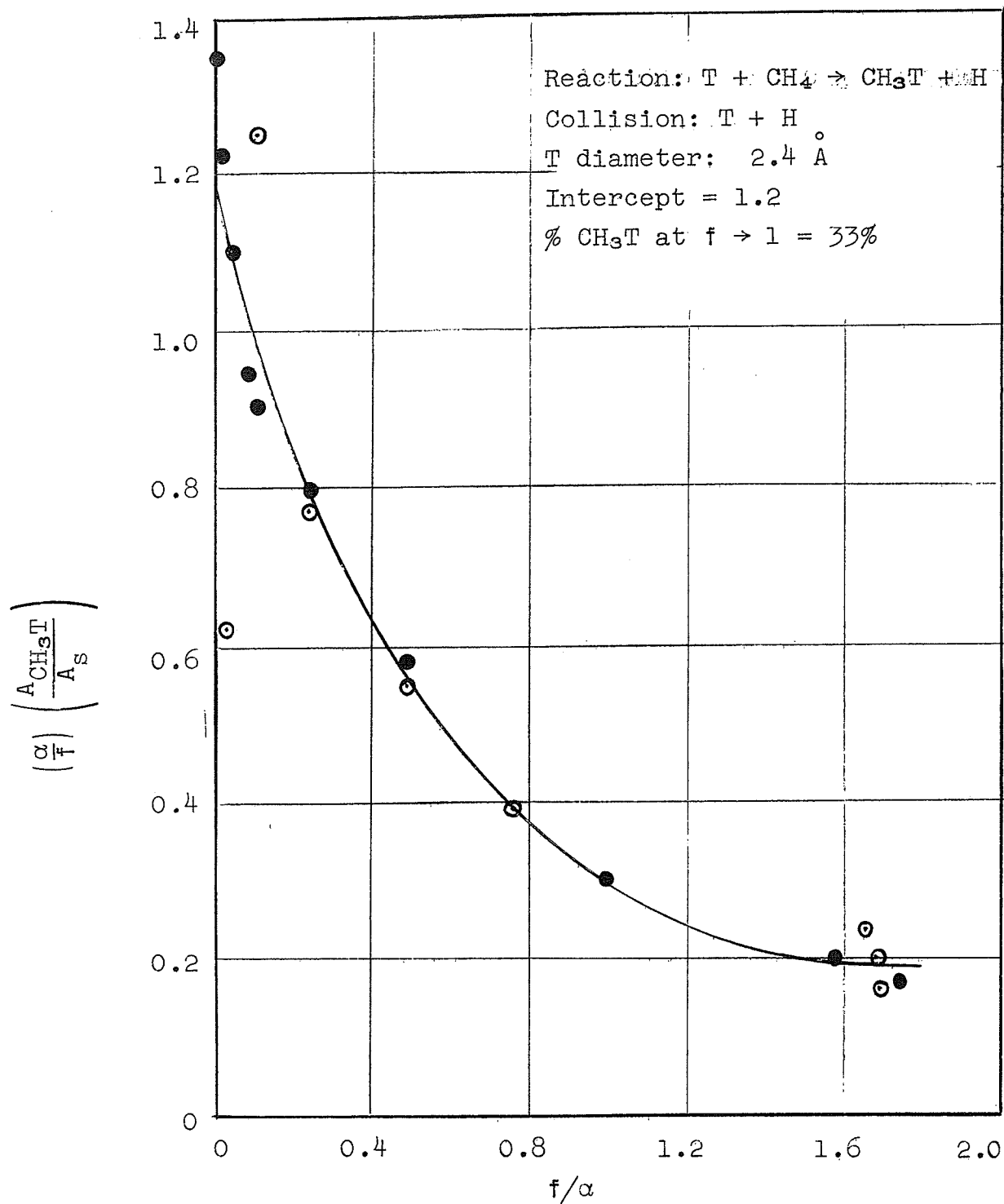


Fig. 8. Plot using the Estrup-Wolfgang equation:
 Data: Estrup and Wolfgang, ●, Cross and Wolfgang, ○.
 Only He moderation data are presented.

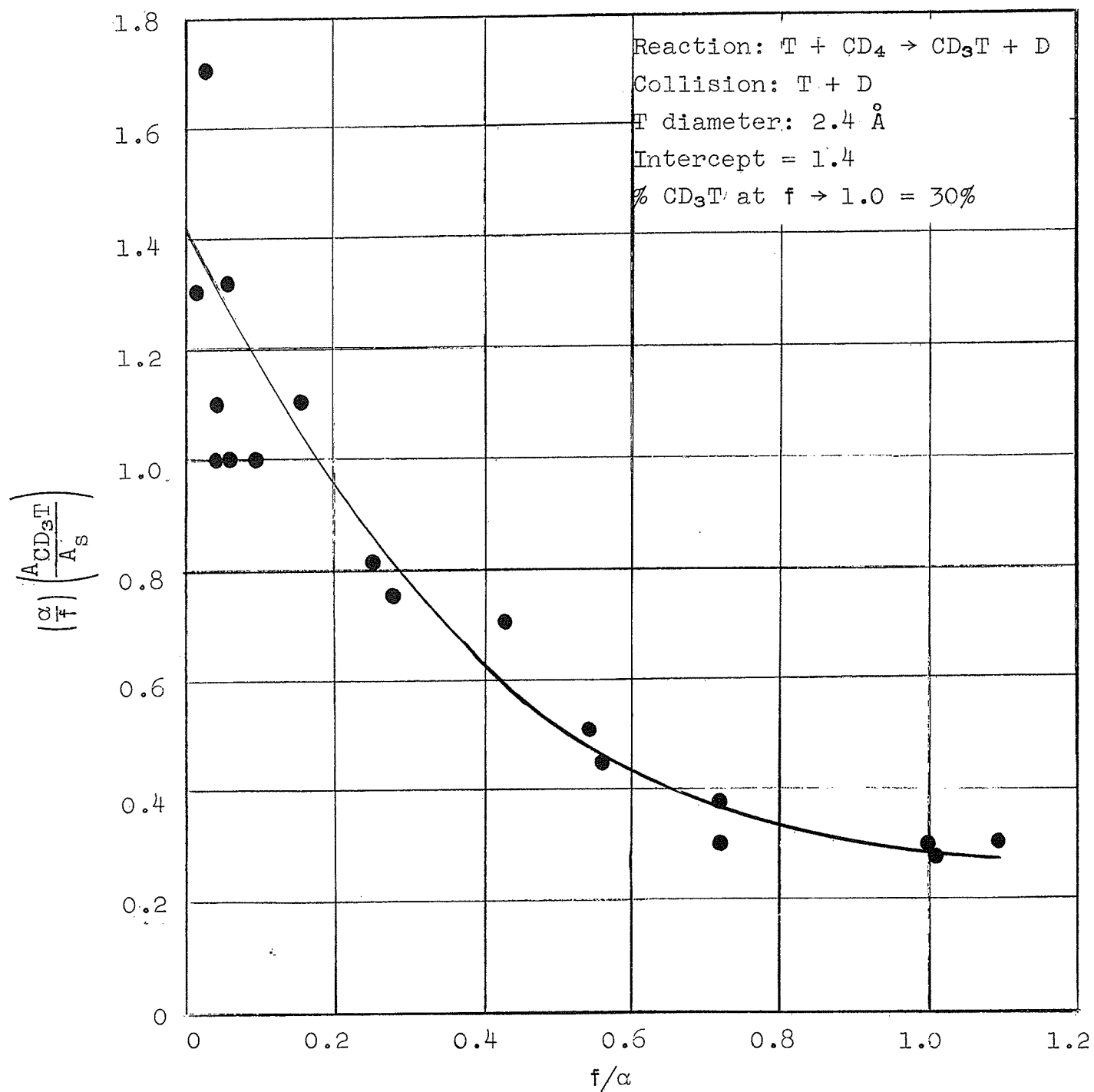


Fig. 9. Plot using the Estrup-Wolfgang equation
 Data of Cross and Wolfgang.
 Only He moderation data are presented.

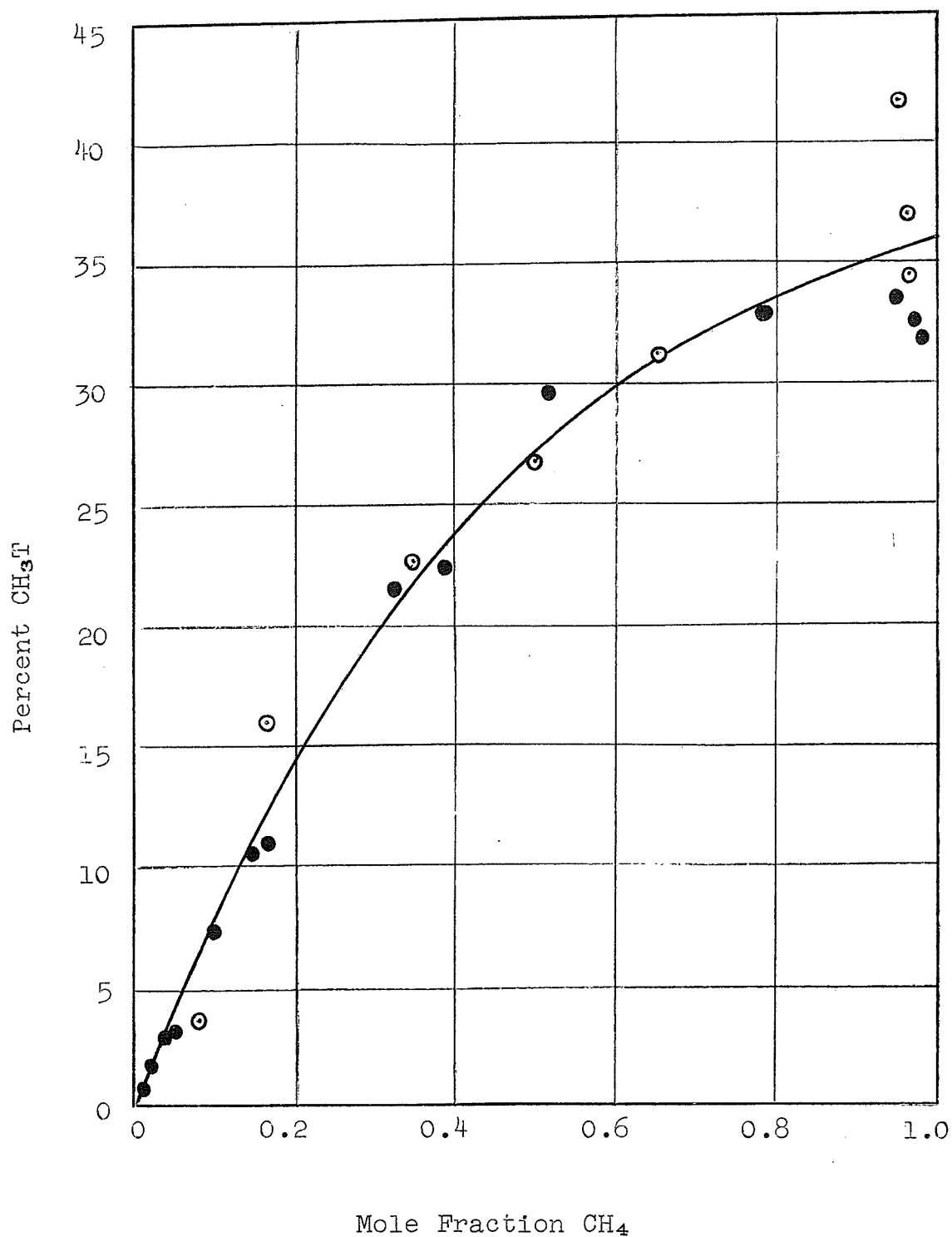


Fig. 10. Data: Estrup and Wolfgang, , Cross and Wolfgang, , Best visual curve drawn through data. Only He moderation data presented.

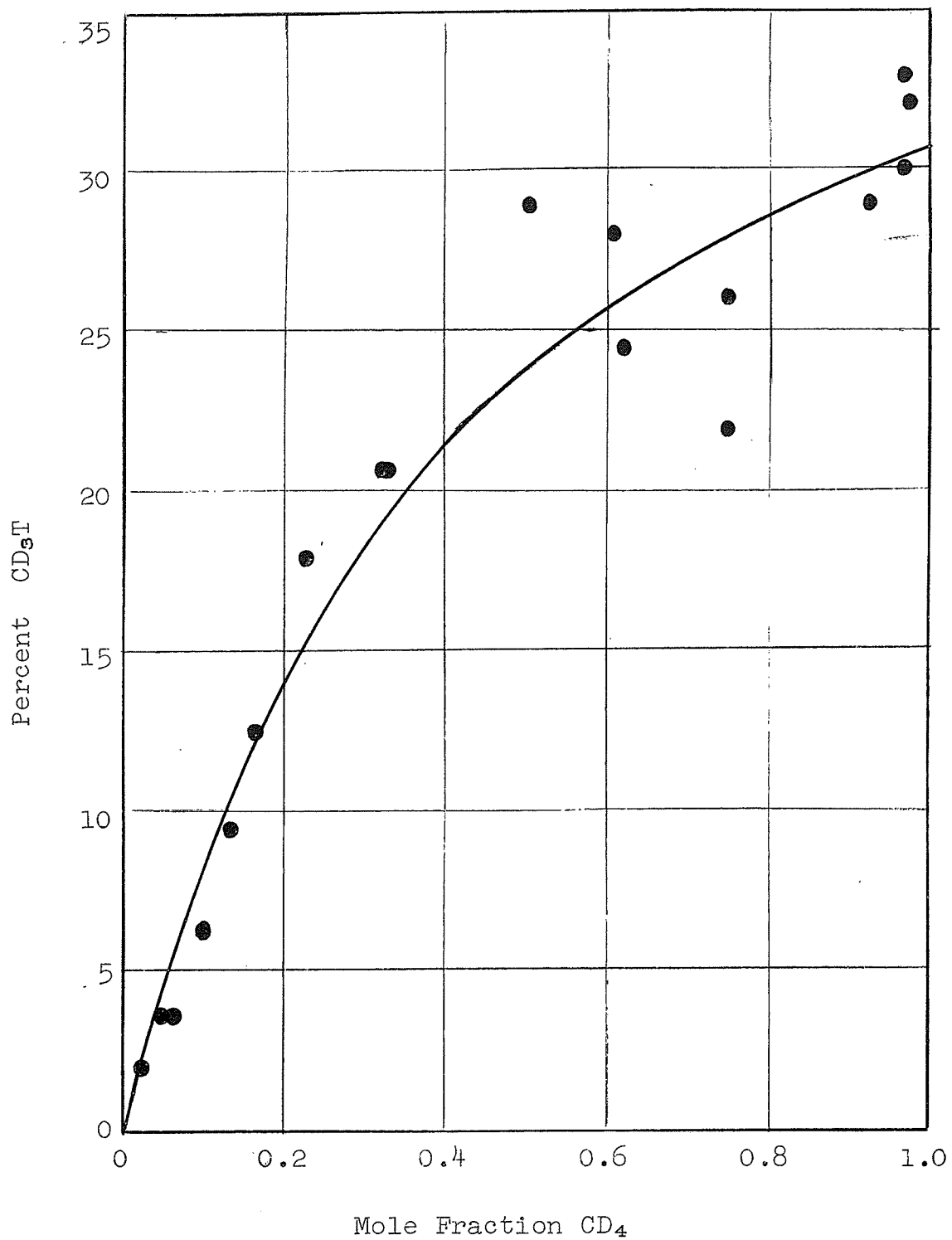


Fig. 11. Data of Cross and Wolfgang. Best visual curve drawn through data.

Only He moderation data are presented.

V. A MATHEMATICAL MODEL FOR THE EFFECTS OF ADDITIVES ON HOT-ATOM AND HOT-ION REACTIONS.

The effects of inert-gas and other additives on a hot-atom or hot-ion reaction can be accounted for by modifying slightly the mathematical model discussed in the preceding section. The inhibition of a reaction by an inert gas is the easiest to handle since the only effect of the inert gas usually will be to reduce the kinetic energy of the hot-atom or hot ion.

In the case of $I^+(^1D_2) + Xe$ collisions, we can introduce into the calculations a contribution for the charge-transfer process which yields $I + Xe^+$. If the additive is a reactive molecule, the calculation becomes relatively difficult and, as yet, we have not attempted to analyse mathematically such systems. If the additive molecule is assumed only to undergo charge transfer with a hot-ion and/or remove excess kinetic energy of the hot atom or hot ion, then the calculation remains relatively simple.

Calculations have been performed for a number of systems. Included are:

1. $T + CH_4 + He$
2. $Br + CH_4 + Kr$
3. $I + CH_4 + Kr$
4. $I + CH_4 + Xe$

$T + CH_4 + He$

As we have stated in the preceding section, we calculate a CH_3T yield ranging from 31 to 46% depending on our choice of the effective collisional mass of CH_4 . To calculate the helium moderation effect, we used a methane mass of 1.0 amu for one calculation and a mass of 16 amu for another calculation. Collision diameters of $T = 2.4 \text{ \AA}$, $CH_4 = 4.2 \text{ \AA}$, and $He = 2.2 \text{ \AA}$, were used in the energy range where both CH_3T and HT can be formed, we assumed that the fractional probability of formation of each molecule was 0.5. For methane mass of 1.0, we calculate that, in pure methane, 42.5% CH_3T would be formed. If a mass of 16.0 is used, we calculate 46.6% CH_3T .

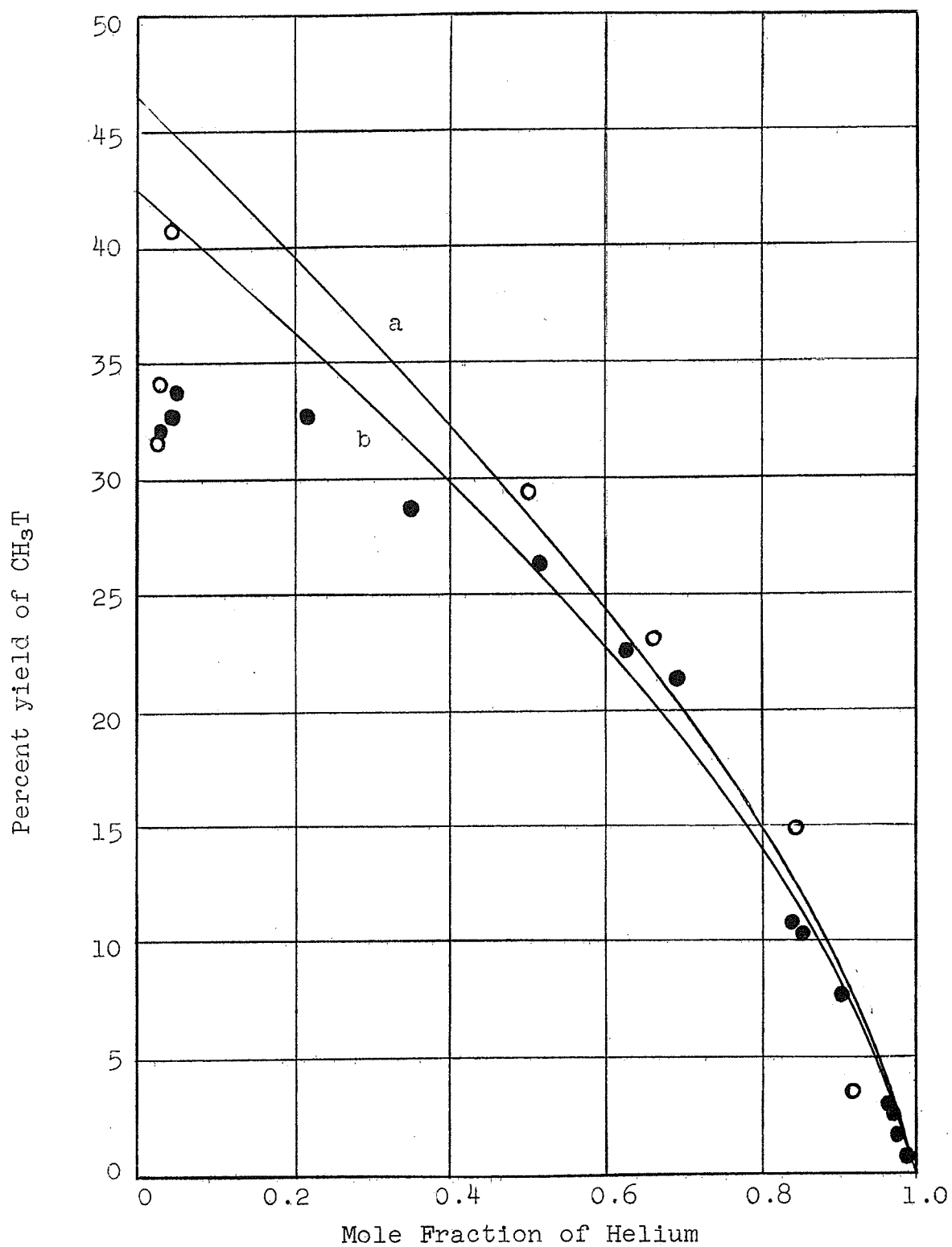


Fig. 12. Effect of helium in moderating the reaction of tritium atoms with CH_4 . Curve a: collisional mass of $\text{CH}_4 = 16$. Curve b: collisional mass of $\text{CH}_4 = 1$. Data: Estrup and Wolfgang, ●, Cross and Wolfgang, ○.

Presented in Fig. 12 are helium moderation curves calculated for the two choices of the effective collisional mass of CH_4 .

Br + CH_4 + Kr

The 12.3% yield of CH_3Br quoted in Section IV was based on the reaction of hot bromine atoms with CH_4 . We have not, as yet, calculated the expected yield of CH_3Br if the reaction involves hot bromine ions.

For the hot bromine atom reaction we calculated the expected moderation by krypton. This curve is presented in Fig. 13.

I + CH_4 + Kr

It has been demonstrated¹² that the reaction of (n, γ) activated I^{128} with CH_4 occurs principally as a result of hot-ion processes. We have calculated the yields of CH_3I or CH_3I^+ expected for each possible reaction. In these calculations it was assumed that the reaction stated was the only one occurring which will yield CH_3I . The reaction probabilities of CH_3I and HI were each assumed equal to 0.5. The results for essentially pure CH_4 systems are given in Table VII. The experimental¹² yield of CH_3I is 54.4%.

Table VII. $\text{I}^{128} + \text{CH}_4$ Calculated Yields

Reaction	Calculated Percent CH_3I
$\text{I}(^2\text{P}_{3/2}^0) + \text{CH}_4 \rightarrow \text{H} + \text{CH}_3\text{I}$	11.4
$\text{I}(^4\text{P}_{5/2}, \text{etc}) + \text{CH}_4 \rightarrow \text{H} + \text{CH}_3\text{I}$	45.7
$\text{I}^+(^3\text{P}_2) + \text{CH}_4 \rightarrow \text{H} + \text{CH}_3\text{I}^+$	60.5
$\text{I}^+(^3\text{P}_1, ^3\text{P}_0) + \text{CH}_4 \rightarrow \text{H} + \text{CH}_3\text{I}^+$	64.8
$\text{I}(^2\text{P}_{3/2}^0) + \text{CH}_4^+ \rightarrow \text{H} + \text{CH}_3\text{I}^+$	31.5

Given in Fig. 14 is the expected moderation by krypton of the various $\text{I} + \text{CH}_4 \rightarrow \text{CH}_3\text{I} + \text{H}$ reactions.

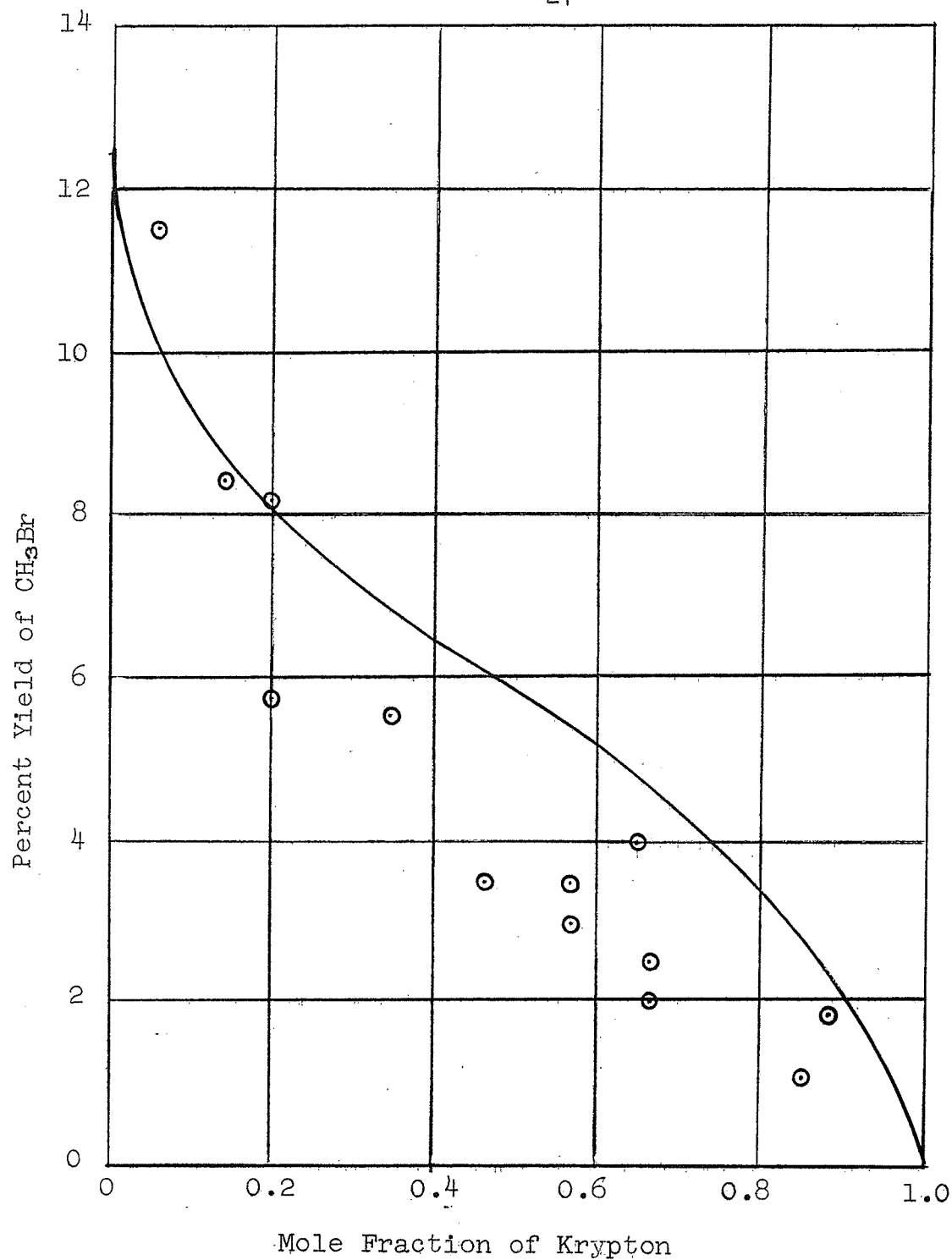


Fig. 13. Effect of krypton in moderating the hot-atom reaction: $\text{Br}^{80} + \text{CH}_4 \rightarrow \text{CH}_3\text{Br}^{80} + \text{H}$. Experimental data include those of Rack and Gordus¹¹ as well as recent unpublished data. Solid curve is calculated.

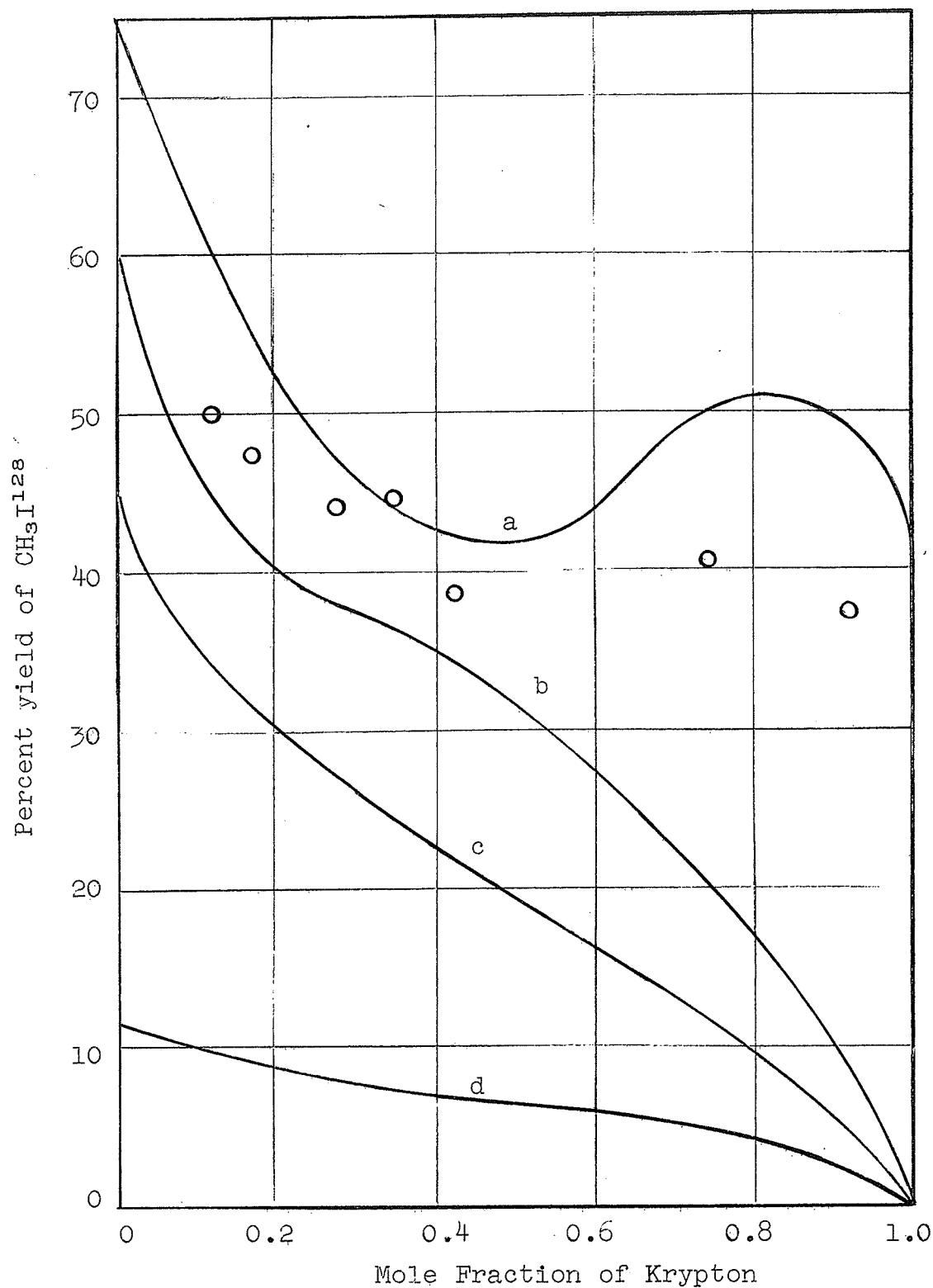


Fig. 14. Moderation by krypton of the reaction of I^{128} hot-atoms or hot-ions with CH_4 . Calculated curves are based on the assumption that the reaction indicated is the only one occurring. Reactions: (a) $\text{I} + ({}^3\text{P}_1, {}^3\text{P}_0) + \text{CH}_4$, (b) $\text{I}({}^1\text{S}_{1/2})$ or $\text{I}^+({}^3\text{P}_2) + \text{CH}_4$, (c) $\text{I}({}^4\text{P}_{5/2}, {}^4\text{P}_{3/2}, {}^4\text{P}_{1/2}) + \text{CH}_4$, (d) $\text{I}({}^2\text{P}_{3/2}^o) + \text{CH}_4$. Data are those of Rack and Gordus¹².

I + CH₄ + Xe

Figure 15 contains the calculated curves for the expected moderation of various I + CH₄ reactions. Curve e is not directly pertinent to the experimental hot-atom study although the curve is related to radiation chemistry processes.

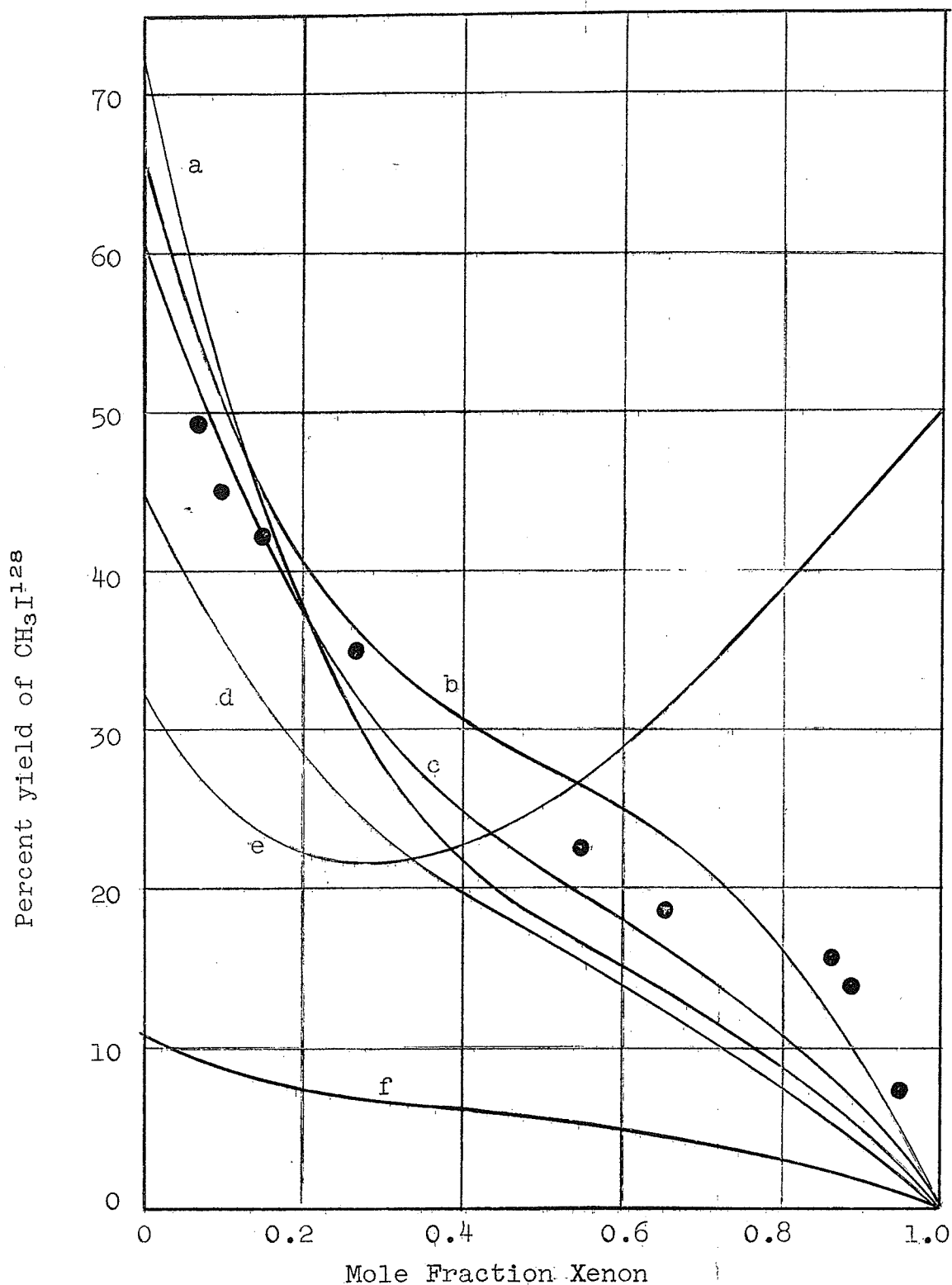


Fig. 15. Effect of xenon in moderating the reaction of I^{128} with CH_4 . Each curve was calculated assuming that the reaction indicated was the only one occurring. In all cases the product is CH_3I . Reaction: (a) $\text{I}^+(^1\text{D}_2) + \text{CH}_4$ or $\text{I}^+(^1\text{D}_2) + \text{Xe}$ charge transfer, (b) $\text{I}^+(^3\text{P}_1, ^3\text{P}_0) + \text{CH}_4$, (c) $\text{I}(^1\text{S}_2)$ or $\text{I}^+(^3\text{P}_2) + \text{CH}_4$, (d) $\text{I}(^4\text{P}_{5/2}) + \text{CH}_4$, (e) $\text{I} + \text{CH}_4^+$, (f) $\text{I}(^2\text{P}_{3/2}^o) + \text{CH}_4$. Data are those of Rack and Gordus¹².

VI. SPECIFIC SOLUTIONS FOR FIVE-STEP THREE-DIMENSIONAL RANDOM WALKS.

In Progress Report No. 1 we described a closed general solution of the probability distribution function for three-dimensional random-walk processes¹³. We listed the specific solution for all two, three, and four- step processes.

When four random steps are involved there exist 14 different complete solutions of the probability distribution function depending on the particular numerical values of the four vector lengths. Each of these fourteen solutions is divided into eight segments, each having an analytical solution. In many instances certain of the analytical solutions are common to more than one of the above cases. Because of this duplication, only 14 analytical solutions are needed for the $14 \times 8 = 112$ total segments.

We have found that for the case of five random steps there are 554 different complete solutions consisting of 16 segments per solution. Because of duplication, a total of 89 analytical solutions are needed for the $554 \times 16 = 8,864$ total segments.

We have determined the 89 analytical solutions and have assigned them to the 16 segments of each of the 554 complete solutions. These data will be tabulated and submitted to the Office of Technical Services for distribution to the U. S. Atomic Energy Commission depository libraries.

Because of the exponential increase in the number of solutions as the number of steps increases, it is apparent that a very large number of solutions will exist for the case of six random steps. We do not intend to attempt to tabulate further data since more than five gamma rays are emitted only infrequently in an (n, γ) reaction.

We do anticipate a need for closed general solutions of certain six, seven, and perhaps eight-step processes when we begin analysis of liquid-phase hot atom reactions. We suspect that it may be possible to analyse mathematically certain aspects of the liquid-phase reactions by considering three-dimensional random-walk kinetic diffusion processes.

VII. EFFECTS OF ADDITIVES ON THE REACTION OF METHANE WITH
 Br^{80} ACTIVATED BY ISOMERIC TRANSITION

Previous data¹⁴ suggest that the reaction of CH_4 with Br^{80} activated by isomeric transition proceeds as a result of translational kinetic energy acquired by the Br^{80} . This acquired energy has been ascribed¹⁴ to the coulombic repulsion which occurs in the highly charged Br^{80} parent molecule. Using helium and krypton moderators of the $\text{Br}^{80} + \text{CH}_4$ reaction it was observed that an increase in the mole-fraction of the inert-gas moderator results in a decrease in the $\text{CH}_3\text{Br}^{80}$ yield. As would be expected for Br^{80} kinetic-energy moderation, krypton was found to be a more effective moderator than helium.

VIII. WORK IN PROGRESS

The work in progress includes:

1. Further development of the mathematical models discussed in this report. We are attempting to apply these models to other activation processes such as photochemical activation.
2. An extension of the mathematical models to the liquid and solid phases.
3. Development of an automatic gas chromatography unit for use with radioactive compounds.
4. Determination of the hot-atom yields of systems as a function of temperature in the range: -78 to $+100^{\circ}\text{C}$.
5. Effects of Co^{60} gamma radiation on mixtures of tagged halogen, methane, and inert-gas.
6. Failure to bond-rupture of gaseous chlorocarbons.
7. (n,γ) activated failure to bond-rupture in liquid systems.
8. Reactions of Cl^{38} activated by the $\text{Cl}^{37}(n,\gamma)\text{Cl}^{38}$ process.
9. Effects of additives on such reactions as $\text{I}^{128} + \text{CHF}_3$.
10. Effects of inert-gas and molecular additives on the gas-phase reaction of CH_4 with Br^{80} activated by isomeric transition.

IX. PERSONNEL AND PUBLICATIONS

Personnel

1. Principal Investigator

Adon A. Gordus

2. Graduate Students (1/2 time)

Ruth (Chi-hua) Hsiung

Frank (Ta-Fang) Chai (as of June, 1961)

Basil Vassos (as of June, 1961)

Navanitray C. Kothary

John C. Whitmer (Summer, 1961)

Edward P. Rack (received Ph.D. in May, 1961)

3. Undergraduate Assistants (part-time, hourly)

William G. Rado

Allan M. Frew, Jr. (ended, Nov., 1961)

Richard E. Siemon

Wolf-Dietrich Blatter

R. Todd Powers (Summer, 1961)

Charles W. Haley (Summer, 1961)

Thomas R. Derleth (as of February 1, 1962)

Publications

A. Which have appeared during the period Feb. 1, 1961 to Feb. 1, 1962.

1. "Effect of Moderators on the (n,γ) Activated Reaction of Br^{80} with CH_4 " by E. P. Rack and A. A. Gordus, J. Phys. Chem. 65, 944 (1961).

2. "Effect of Inert-Gas Moderators on the (n,γ) Activated Reaction of I^{128} with CH_4 " by E. P. Rack and A. A. Gordus, J. Chem. Phys. 34, 1855 (1961).

3. "Reactions of High-Energy, Excited I^{128} Ions with Gaseous Molecules" by E. P. Rack and A. A. Gordus, J. Chem. Phys. 36, 287 (1961)

B. Which are in are press

4. "Momentum Transfer to an Atom in a Molecule: Internal Excitation and Bond Dissociation" by C. Hsiung and A. A. Gordus, scheduled for a February or March issue of J. Chem. Phys.

5. "Failure to Bond-Rupture and Nuclear Recoil Following (n,γ) Activation" by A. A. Gordus and C. Hsiung,

scheduled for a February or March issue of J. Chem. Phys.

- C. Which are in preparation
6. "Failure to Bond-Rupture Following Beta-Decay Recoil" by C. H. Hsiung and A. A. Gordus.
 7. "A Mathematical Model of Hot-Atom and Hot-Ion Reactions, I; Pure Gaseous Systems." by C. H. Hsiung and A. A. Gordus
 8. "A Mathematical Model of Hot-Atom and Hot-Ion Reactions, II; Effect of Moderators." by C. H. Hsiung and A. A. Gordus.
 9. "Feasibility of the Photochemical Enrichment of the Ca^{48} Content of Natural Calcium." by H. C. Hsiung and A. A. Gordus
 10. "Soft X-Ray Radiation Damage in n-Butyl Bromide." by A. A. Gordus and others.
 11. "Soft X-Ray Radiation Damage in an Organic Mercury Compound." by A. A. Gordus and others.
 12. "A Soft X-Ray Total Absorption Calorimeter." by A. A. Gordus and others.
 13. "Analytical Solutions of the Probability Distribution Function for all Three, Four, and Five Step, Three-Dimensional Random-Walk Processes."

Talks

A paper was presented at the Chicago meeting of the American Chemical Society, September, 1961.

Title: "Theory of Chemical Activation Resulting from Momentum Transfer to an Atom in a Molecule."

X. REFERENCES

1. Hsiung, C. and Gordus, A. A., both articles to appear in a Feb. or March issue of J. Chem. Phys.
2. (a) Wexler, S., and Hess, D. C., J. Phys. Chem. 62, 1382 (1958).
(b) Wexler, S., Anderson, G. R., and Singer, L. A., J. Chem. Phys. 32, 417 (1960).
3. Snell, A. H. and Pleasonton, F., J. Phys. Chem. 62, 1377 (1958).
4. Wolfgang, R., Anderson, R. C., and Dodson, R. W., J. Chem. Phys. 24, 16 (1956).
5. Miller, J.M., Gryder, J. W., and Dodson, R. W., J. Chem. Phys. 18, 579 (1950).
6. Capron, P. C. and Oshima, T. J., J. Chem. Phys., 20, 1403 (1952).
7. Estrup, P. J. and Wolfgang, R., J. Am. Chem. Soc. 82, 2661, 2665 (1960).
8. Urch, D and Wolfgang, R., J. Am. Chem. Soc 83, 2982 (1961).
9. Lee, J. K., Musgrave, B., and Rowland, F. S., J. Chem. Phys., 32, 1266 (1960).
10. Cross, R. J., Jr. and Wolfgang, R., J. Chem. Phys. 35, 2002 (1961).
11. Rack, E. P. and Gordus, A. A., J. Phys. Chem. 65, 944 (1961).
12. Rack, E. P. and Gordus, A. A., J. Chem. Phys. 34, 1855 (1961).
13. Hsiung, C., Hsiung, H., and Gordus, A. A., J. Chem. Phys. 34, 535 (1961).
14. Gordus, A. A. and Willard, J. E., J. Am. Chem. Soc. 79, 4609 (1957).