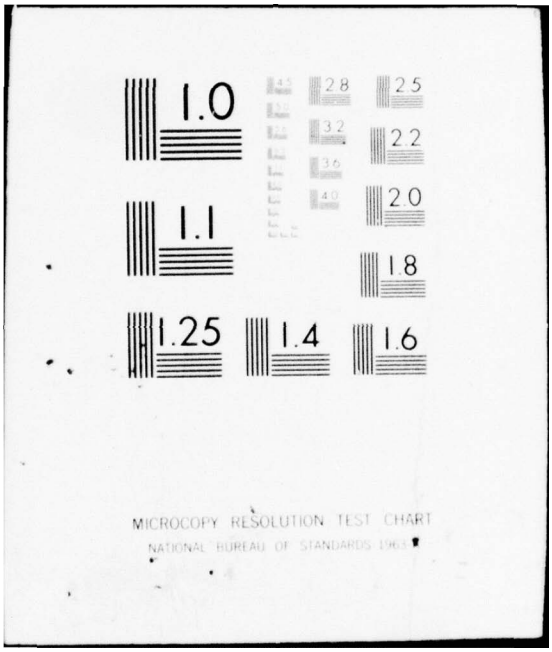
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by D. C. Tardy and B. S. Rabinovitch

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A comprehensive review of energy transfer in thermal unimolecular systems in the period from 1920 to 1976 is given. Continuing areas of interest are described and results from related techniques are correlated.

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Intermolecular Vibrational Energy Transfer in Thermal Unimolecular Systems

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Contents

I INTRODUCTION

A. Historical Background and Perspective
B. The Lindemann Mechanism. The Strong Collision Assumption
C. Early Experimentation: 1920-1950
D. The Post-War Period
E. Further Experimental and Theoretical Requirements

II MASTER EQUATION and SOLUTION

III COMPREHENSIVE EXPERIMENTAL TESTS OF COLLISION EFFICIENCY

A. Low Pressure Region. Constant Temperature and Dilution
B. Relative Cross-Sections for Vibrational Energy Transfer. Demonstration of Strong Collisional Behavior
C. Low Pressure Region. Dilution of Substrate
D. Low Pressure Region. Temperature Dependence of Efficiency
E. Variation of Collisional Efficiency with Degree of Fall-Off
F. Dependence of Collisional Efficiency on Structural Parameters of the Bath Gas and Substrate

IV VIBRATIONAL ENERGY TRANSFER PROBABILITIES

V RESULTS FROM OTHER TECHNIQUES. HIGH TEMPERATURE THERMAL SYSTEMS

A. Chemical Activation Systems
B. Hot Atom, Ion Molecule and Cross Beam Systems
C. Photoactivation. Photodecomposition and Fluorescence Studies
D. High Temperature Thermal Systems

APPENDIX I. Some $\langle \Delta E \rangle$ and $\beta_0(\infty)$ Relationships

I. INTRODUCTION

This review deals with collisional activation-deactivation of polyatomic molecules in thermal systems at the high levels of vibrational excitation characteristic of reaction. Only incidentally does it touch on the behavior of diatomic and small molecules, or results from other techniques – all of which have been more frequently and thoroughly reviewed, including low energy work.

A. Some Historical Background and Perspective

The study of unimolecular reactions provides both experimental information regarding a number of important fundamental physical processes and a test of related theoretical conceptions.[1] In the classical description, molecules must be prepared in a suitably excited condition in order that reaction may occur, i.e., they must be transported to a level of excitation equal to, or in excess of the critical energy threshold E_o for reaction. For clarity, we will refer to such critically energized molecules as activated molecules; our use of the term involves no reference to a transition state or activated complex. For a well-defined unimolecular reaction, the preparation time, τ_1, of the excited species, i.e., the duration of the exciting collision in a thermal system, should be short compared to the relaxation time for decomposition, τ_2, of the energized entity. The same condition also obtains between τ_1 and the shortest measuring time interval, τ_3, whereby the degradative relaxation process is monitored. In a thermal collisional system, τ_3 corresponds to an appropriately weighted time interval between collisions for the reactant molecules of the system. Implicit in the last statement is the understanding that the collision process effectively alters the energy state of the excited species; an elastic collision would not provide a useful measuring event. Thus a knowledge of the collision efficiency – whether between reactant molecules, in whatever states,

or between reactant and a bath species – is of great importance for an understanding of unimolecular reaction systems (and others, as well). It is essential to know, for example, whether a collision-induced transition of an activated molecule constitutes a deactivation event or corresponds, instead, to a new preparation event.

The above conceptions were first recognized by Lindemann[2] in 1922 and were developed more quantitatively by Hinshelwood[3] and by Rice and Ramsperger[4,5] and Kassel.[6] These workers provided the basic conceptual constructs which underlaid most of the experimental studies of unimolecular reactions – and virtually all of the thermal studies – for the succeeding half-century.

Paradoxically enough, although the thermal study of unimolecular reactions was the earliest, and has been the preponderant technique used, this method has not been successful in providing the earliest and most significant data concerning the collisional relaxation process. Rather, more recently developed methods, especially chemical activation,[7,8] photoactivation,[9] and cross-beam studies,[10] have furnished the most cogent results to date. This is due, in part, to the frequently unsuspected difficulty of successful experimentation by the disarmingly simple, but rather ponderous and demanding thermal method; in part, to the intrinsic averaging characteristic of thermal data; and, in part, to the absence during most of the period since the Lindemann formulation of a cogent rationale of thermal experimentation. Nonetheless, very considerable progress in the study of vibrational energy transfer has, in fact, been made <u>via</u> thermal studies in the

past decade. Indeed, this method has recently provided comprehensive data leading to new conceptions of the nature of energy transfer involving large molecules – as opposed to di- and triatomics – at high levels of vibrational excitation. This has been insufficiently appreciated, especially by devotees of more sophisticated techniques, and makes a review of the field worthwhile at this juncture. This seems all the more useful since it appears that progress in work at high temperatures, at least in the near future, will depend heavily on thermal methods.

B. The Lindemann Mechanism. The Strong Collision Assumption

The Lindemann-Hinshelwood formulation of unimolecular reactions involves a sequence of elementary steps:

$$A + M \xrightarrow{k_1} A^* + M \qquad (1)$$

$$A^* + M \xrightarrow{k_2} A + M \qquad (2)$$

$$A^* \xrightarrow{k_3} \text{products} \qquad (3)$$

In step (1), the reactant species A experiences an activating collision following a suitable collision with another molecule. The collision partner is represented for simplicity by the bath species M, as is appropriate for the case of infinite dilution of the reactant by bath molecules. Step (2) describes the collisional deactivation of A^* consequent on its next encounter with a bath molecule. Step (3) represents the degradative relaxation process that may intervene prior to Step (2).

The above formulation contains several grossly simplifying features.[11] One of these is that the eigenstate description of A, M and A^* is not given. A more precise description of reaction (1) is,

$$A_j + M_k \xrightarrow{k_{1jk}^{\ell m}} A_\ell^* + M_m \qquad (1')$$

where j, k, etc., are themselves summary quantum numbers that describe the internal states of A and M as well as their relative motion: Similarly, the deactivation step (2) is represented by $k_{2\ell m}^{jk}$. With the condition that averages over the detailed states should provide an operationally useful representation, one may rewrite the Lindemann scheme as,

$$A + M \xrightarrow{k_{1\ell}} A_\ell^* + M \qquad (1'')$$

$$A_\ell^* + M \xrightarrow{k_{2\ell}} A + M \qquad (2'')$$

$$A_\ell^* \xrightarrow{k_{3\ell}} \text{products} \qquad (3'')$$

where specification of the nature of M is provisionally omitted and $k_{3\ell}$ is averaged over the allowed states of the products that connect with A_ℓ^*. No further useful simplification may be made.

The Lindemann scheme, of course, led to the prediction of unimolecular fall off. As is well known, one can write the general expression for the specific reaction rate constant,

$$k_{uni} = \sum_\ell k_{1\ell} k_{3\ell} C_M / (k_{2\ell} C_M + k_{3\ell}) \qquad (4)$$

where C_M is the concentration of bath gas. For $C_M \longrightarrow 0$, the

limiting expression is

$$k_0 = \sum_\ell k_{1\ell} C_M \qquad (5)$$

While, for $C_M \longrightarrow \infty$,

$$k_\infty = \sum_\ell k_{1\ell} k_{3\ell} / k_{2\ell} \qquad (6)$$

which is the equilibrium expression that applies at sufficiently high pressures of the bath gas, whatever may be its collisional efficiency.

A second assumption contained in the original Lindemann scheme is that reaction (2) leads invariably to deactivation of A^*, i.e., to transport below the critical reaction threshold energy. This is one form of the "strong collision" assumption. Detailed balance then ensures that activated states arise by collision only from unreactive states of A below E_o whose populations are given by the Boltzmann distribution at all pressures.

At this point, some semantic matters relating to strong and weak collisions should be clarified. By strong collisions, in this paper we shall mean Markovian events whose outcome follows the probabilities given by the Boltzmann distribution, without reference to the initial conditions. This is the meaning of the simplified version of eq. (5) for the low pressure specific reaction probability,

$$k_0 = \omega \int_{E_o}^{\infty} B(\varepsilon) d\varepsilon \qquad (7)$$

where ω is a specific collision rate and $B(\varepsilon)$ is the Boltzmann probability distribution function.

It is evident that the collisional connection, $A_\ell^* \longrightarrow A$,

in the strong collision Lindemann scheme is the highly predominant, but not exclusive one at high values of the energy, E_ℓ ; moreover, even for strong collision conditions the naive Lindemann assumption fails drastically at low values of the threshold E_0, where E_ℓ approaches the level of the average energy of the relevant degrees of freedom. Obviously, no real system follows the strong collision description, but it is essential to realize that the experimental failure or success of this assumption is a pragmatic, operational matter defined by the nature of the system in question.[12] Thus, a strong collider bath gas is effectively one for which the experimental results are indistinguishable from those of the Boltzmann probability predictions – notwithstanding very large differences between the latter and the actual form of the collisional transition probabilities. Indeed, part of the problem has been to discover what practical requirements govern ostensible strong collision behavior in real systems.

Conversely, weak collisions and colliders are evidently those which fail to meet the Boltzmann criterion in the operational sense. It is quite possible that a given set of transition probability elements may conform to the strong collider description under some experimental conditions but fail the operational criteria under others.[12]

The above discussion has revealed an intrinsic, but not fatal, weakness of the thermal method. Collisional activation results in a Boltzmann, or perturbed Boltzmann input of reactant molecules to the activated levels. State selection is simply not possible and the results obtained in these systems refer always to suitable

averages over a distribution of states. However, as will be pointed out in detail in the body of this review, some variation in the weight and breadth of the active states may be achieved by suitable variation of experimental parameters, such as pressure or temperature. Moreover, in suitable systems, the number and nature of the bath gases M may be varied rather freely, and frequently much more so than is possible in the use of more elegant techniques; this advantage is a significant one. Finally, it transpires that some intrinsic control of the level of energy is possible in the study of a series of homologous molecules under the low pressure limiting conditions.

C. *Early Experimentation: 1920-1950*

We may, in retrospect, date the definitive period of experimental study of unimolecular reactions from the discovery by Daniels and Johnston in 1921 of the unimolecular nature of the thermal decomposition of N_2O_5.[13] This event was followed closely by the formulation by Lindemann[2] of the collisional character of the activation-deactivation process undergone by molecules in "quasi-unimolecular" systems. This was the prerequisite advance for the utilization of unimolecular reaction systems as subjects of experimentation for the characterization of collisional intermolecular transfer of vibrational energy (whether vibration-vibration or vibration-translation-rotation), as it concerns complex molecules (usually) at high levels of vibrational excitation.

The realization of this capacity did not spring up full-grown with the enunciation by Lindemann of his mechanism. At the same time that he proposed his theory, Lowry[14] pointed out that the

Radiation Theory had to be considered as unsupported because, in his view, there was simply no known authenticated example of a unimolecular reaction. It was two years more before J. J. Thompson[15] first suggested that the presence of inert gases could accelerate the rate of unimolecular reaction (in terms referring to what is now called the low pressure behavior); while F. O. Rice et al.,[16] were still noting the superfluity of theories of unimolecular reaction in the face of a possible total lack of examples of such.

Much of the early work either did not include the study of inert gas effects or included these only peripherally, as part of an investigation of mechanistic aspects. Naturally enough, much of the early emphasis and concern was focussed on the problem of whether or not bona fide examples of unimolecular reactions existed,[14,17-25] on the establishment of such, and on the reproducibility and reliability of experimental data. This concern was accentuated by the recognition of the importance of radical intermediates and chain carriers in many systems. Sickman and Rice[26] remarked in 1936 that, in their view, only two known organic reactions appeared to be free of radical-chain character. Later events reveal that even this pessimistic estimate may have been too sanguine and three years later, although most workers were convinced that unequivocal evidence existed in support of the Lindemann model, some scepticism still prevailed.[27]

An additional factor that hindered the development of interest in inert gas effects was the considerable preoccupation that existed with regard to the merits of the Radiation theory of Trautz (1918), and W. C. Lewis (1918), and Perrin (1919), and of the Energy

Chain theory of Christiansen and Kramers (1923).[28-30] This diversion persisted through the first decade of activity in the new field, but revealed a dearth of evidence in support of the general propositions of the two theories.[30-32] This, together with the formulation of the Rice-Ramsperger (1927)[4] and Kassel (1928)[6] theory, assisted in supporting lines of investigation more relevant for examination of collisional energy exchange phenomena.

A summary of most of the work of this period is given in Table I. Much of the presentation is qualitative in nature. The lack of quantification has two sources. In part it reflects the sometimes frustrating absence of experimental and numerical detail in some of the early reports. In part it is a question of judgment: it now appears that most early data retains little quantitative validity and much of it only a remnant of qualitative validity. In this circumstance, it would not be useful to convey excessive detail of studies whose significance is now largely historical. The results quoted below and in the table constitute a factual record and the citation or inclusion of any paper is not an endorsement of the correctness of the findings.

Much of the earliest thermal study of inert bath gas effects was indirect. It concerned the ability of the reaction products to maintain the magnitude of the observed rate constant during a run as the concentration of substrate declined toward zero with increasing extent of reaction. The first instance was reported in 1926 by Hinshelwood and Thompson[33] in a study of the decomposition of propionaldehyde to give CO, CH_4 and C_2H_6 products. Other examples quickly proliferated in which the same conclusion could be reached. Implicitly, this included most unimolecular

studies,[25] including N_2O_5, and, explicitly, the following systems: azomethane,[34] azoisopropane,[35] azoethane,[36] methyl ethyl ether,[23] methyl propyl ether,[23] di-isopropyl ether,[23] F_2O_2,[37] NO_2Cl,[38] and N_2O.[39]

The first demonstrations of a foreign inert gas effect was given for H_2 in the diethyl ether[22] and dimethyl ether[18] systems and in the propionaldehyde system[40] by Hinshelwood and co-workers. The collisional efficiency was stated to be close to unity, although the basis of the comparison is not clear and the data are not precise. The presence of sufficient hydrogen seemed to restore the rate constant measured in the fall-off region to its limiting value, k_∞, while excess hydrogen apparently did not cause k_∞ to be surpassed. By contrast, other simple inert gases such as He and N_2 were found to be almost without effect. Similar unique efficiency was not noted by later workers; indeed, some investigators reported zero[41] or even <u>negative</u>[24] efficiency. Interestingly enough, hydrogen was noted by the Oxford group itself to be without effect in the N_2O[42] and CH_3CHO[40] systems; but, at that time, this was regarded simply as an aspect of normal bimolecular behavior.

The erroneous proposition that H_2 is very efficient for the collisional activation-deactivation of complex organic molecules did provoke at least one spin-off of value. To explain this surprising finding, O. K. Rice[43] suggested that the active number of modes of the substrate molecule might be only a fraction of the total, so that it behaved like a small molecule. This idea of a restriction on the intramolecular relaxation of vibrational energy was not further exploited at that time and did not lead to useful interpretations of the existing data. However, in recent years,

one of the most important subjects of research on unimolecular decompositions has been the definition of the conditions of failure of the postulate of internal randomization of energy which is implicit in the present working theory of unimolecular reactions of Rice-Ramsperger-Kassel-Marcus.[44]

Most of the systematic work on inert bath gases during the early period (Table I) was carried out by a comparatively small number of research groups. Their interest was focused principally on variation of the nature of the bath gas. The Oxford group mainly studied the decomposition of aldehydes[33,40,45] and ethers.[18,22,23] After H_2, the gases He, N_2, CO, CO_2 and CH_4 were examined and were believed to have zero or low collisional efficiency. By contrast, C_2H_6 was assigned a higher efficiency, similar to H_2 and close to that of the substrate.

Ramsperger's work with azoalkanes led to analogous results. C_2H_6 was relatively efficient with azomethane,[36] while N_2 was not. Further detailed examination of azoalkanes was extended to another half-dozen gases by Sickman and O. K. Rice;[26,46,47] these included He, D_2, N_2, CO, CO_2, H_2O, and CH_4.

A concentrated study of N_2O decomposition was made by M. Volmer and co-workers.[39,48-51] They investigated some dozen gases in all: He, Ne, Ar, Kr, Xe, N_2, O_2, CO_2, H_2O as well as a few gases that proved reactive. Collisional efficiencies were ascribed relative to N_2O, for an assumed set of collision cross-sections, the least efficient being Xe (0.16) and the most, H_2O (1.5). As was mentioned

above, H_2 had been studied earlier by Hinshelwood who found it to have zero efficiency.

The group of H. J. Schumacher concentrated on small inorganic molecules. The decomposition of NO_2Cl was investigated[38] in the presence of H_2, O_2, Cl_2, N_2, CO and CO_2, which were rather equally inefficient, and of NO_2, which was more efficient. Ozone was examined[52] with He, N_2 and CO_2 whose efficiencies increased in that order. Decomposition of F_2O was studied[53] with He, Ar, O_2, N_2 and F_2, whose collisional efficiencies were all quoted as being 0.4-1.1 and with SiF_4 which had 0.9 efficiency. For the F_2O_2 system,[49] He was assigned a collisional efficiency of 0.07, with N_2 = 0.21, F_2=0.33, Ar=0.40, CO_2= 0.45, O_2=1.2, all relative to F_2O_2=1.0.

Inert gas effects in the N_2O_5 system were studied by a number of investigators. This led to no useful results relative to collisional efficiency because of the peculiarity of mechanism of this species which was clarified many years later by Ogg[54] and by Johnston.[55]

Heckert and Mack[32] investigated the ethylene oxide system in the presence of some 11 bath gases. This constructive effort was, unfortunately, completely negated by the complexities of the system and, except for H_2, <u>negative</u> efficiencies were found.

Efforts were made by several workers to rationalize the observed efficiencies of the various gases. Ramsperger[36] attributed the enhanced efficiency of ethane relative to N_2 in the azomethane system to the limited internal energy of the latter and to the fact that its vibration frequency is different from that of the substrate. By contrast, the more complex ethane

molecule has many near-resonances with the frequencies of the parent and an enhanced prospect for establishment of equilibrium between the internal degrees of freedom of the two molecules upon collision. In a later summary, Ramsperger[25] concluded that the collisional efficiency of inert gases, in general, is a specific property of both substrate and bath gas. No elaboration was offered. An explanation similar to that of Ramsperger was given by Hinshelwood[29] for the high efficiency of ethane in the methyl propyl ether system.

The idea that the internal degrees of freedom of the <u>bath</u> species, as well as those of the substrate, played an important role in energy exchange had been fostered by Fowler and Rideal[56] in an effort to explain the N_2O_5 anomaly. It was taken up again still later by Sickman and O. K. Rice[47] who employed the framework of the Zener theory which had been applied earlier to the interpretation of sound dispersion studies. The low efficiency of He in general was interpreted by them as being the consequence of inefficiency of vibrational-translation energy transfer, as compared to vibration-vibration for diatomic and polyatomic gas; such a relationship had been well known for many years from low vibrational energy, small molecule,acoustic studies. On the other hand, Sickman and Rice noted the disparity between absolute efficiency values found in sound dispersion work vis-à-vis unimolecular reaction, as well as the comparatively small range of magnitudes in the latter systems between the most and the least efficient gases. But this observation and the implicit dichotomy with the previous explanation lay fallow for many years.

In this period, the first (and only) refined interpretation of the nature of collisional efficiency in thermal systems came, not unexpectedly, also at the hands of O. K. Rice and Sickman.[46] They pointed out that the strong collision assumption was not apt for inefficient bath gases such as He. They applied a simple step ladder model with an assumed jump size of 1 kcal $mole^{-1}$ to the correction of the strong collider expressions for azomethane given earlier by Rice and Ramsperger.

Progress in other aspects of the study of collisional efficiency of inert bath gases in thermal systems was minimal. A theoretical interpretation and analysis of the relative collision efficiency quantity β_c and its dependence on experimental parameters was not forthcoming at this time. Correlations with variables such as region of fall-off, dilution and temperature were rather occasional and unsystematic. With the conceit of hindsight and the wisdom imparted by a perspective of forty years, it is evident that work of this period was somewhat confused in orientation and direction, control of other variables during specific tests of one variable being rather haphazard. A brief description, only, need be given of these further aspects which, again, are largely summarized in Table I.

A few studies were made of the effect of temperature on rate in inert gas systems. In principle, these should include investigation of both the change in the observed activation energy, ΔE_a, as between pure substrate system and inert gas system, as well as the variation of ΔE_a with temperature.

Volmer and Kummerow[48] made studies of N_2O decomposition over a range of temperatures for both the pure substrate and for a 10:1 dilution with CO_2; their data were inaccurate and they did not calculate ΔE_a. Volmer and Froehlich[50] made similar inconclusive experiments with He, Ar and O_2 inerts.

The acetaldehyde system [by now (1934) invested as a unimolecular reaction] was studied by Fletcher and Hinshelwood[45] at temperatures from 500° to 564°. They found that E_a was constant at 49.5 kcal $mole^{-1}$, both in the presence and absence of H_2, despite the fact that they also concluded that the collisional efficiency of hydrogen was significantly less than that of the parent substrate ($\sim$ 0.25 on a collision basis by our estimate).

Koblitz and Schumacher[53] made a more extensive investigation. They examined the temperature dependence of F_2O decomposition in the presence of a number of inerts (He, Ar, O_2, N_2, F_2, SiF_4), as well as the parent gas, but only over a very narrow temperature range, 250°-270°. Not unexpectedly, they found the same temperature coefficient for all gases within the limits of their precision.

Finally, in the azomethane system Rice and Sickman[46,47] took the collision efficiency of He to be constant with temperature, again over a narrow range (290° and 310°), which was consistent both with their narrow range and their experimental scatter.

A number of dilution studies involving variation of the relative proportion of substrate to bath gas, D, were made. These were often inadvertent and were usually unsystematic. They were sometimes incidental to the variation of total effective pressure of the system, so that variation of both k/k_∞ and D occurred simultaneously.

The earliest study with H_2 (and dimethyl ether)[18] covered a range of D from 1.5 to 15, but was grossly qualitative in nature. Dilution studies, especially with H_2, in the N_2O_5 system[57] were incapable of revealing useful information. A few casual results in the azomethane system[36] carried ethane over a narrow range from D = 0.4 to 2, with slowly increasing k/k_∞, but were of inadequate accuracy; helium was also investigated[46] at D = 5 and 10 over a range of fall-off of a factor of three.

The widest range of dilution employed and most systematic study was made by Volmer and Froehlich[50] for N_2O with He. D was varied at three temperatures from 625° to 670° over a range whose greatest extent was 0.7 to 10 at 670°; k/k_∞ varied by a factor 15 as well. Apart from the unresolved complexities of N_2O decomposition that existed at that time, and which inevitably affected the results, no use, other than averaging was made of these data.

Some unsystematic dilution studies were made in the F_2O[53] and F_2O_2[37] systems. The scatter in the data obscured any dependence of β_c on either dilution or magnitude of fall-off.

The above survey reveals somewhat anatomically why the thermal technique was relatively unproductive of refined information on intermolecular vibrational energy transfer in this period.

In the rest of this paper, β_c, or some suitable abbreviated designation, represents a collision-per-collision relative efficiency factor, while β with specific subscripts [such as ω, 0, ∞, ϕ], or superior designations [such as ' or $^-$], or parenthetic parameters [such as D, 0, (∞), T] will explicitly indicate the dependence of β_c on the quantity in question. In the interests of simplicity of notation, mathematical rigor in denoting the panoply of variables will frequently be sacrificed.

D. The Early Post-War Period.

A penetrating series of papers was presented in the early fifties by H. S. Johnston and his co-workers. These papers brought into focus a number of propositions relating to thermal energy transfer studies which, previously, either had not been understood or perceived, or had not been clearly expressed; they also clarified the meaning and statistical interpretation of the mechanical constants that characterize the physical processes embodied in the Lindemann mechanism.[11,58-60] Johnston[61] reinvigorated the proposition that the observed unimolecular rate in the low-pressure second order region is proportional to the rate of energy transfer between "normal" bath molecules and highly excited substrate species. Only by studying the reaction rate under these conditions, can the relative efficiencies of various foreign bath gases in energy transfer be determined most simply and directly.[3] Of course, this was not to say that the study of energy transfer in the fall off region should not and need not be utilized to provide useful and complementary information, as will be described in a later section.

Of the various systems which had been studied earlier in or near the second order region, including N_2O, N_2O_5, NO_2Cl, O_3, F_2O and F_2O_2 (Table I), the work of Johnston and co-workers now fixed N_2O_5,[61,62] and especially NO_2Cl,[63,64] as the only two reliable examples. The latter constituted a particularly exemplary and comprehensive study of energy transfer in a unimolecular system.

An even more important concept delineated by Johnston[61-64]

was the matter of the functional dependence of β_c on the hot molecule energy level, i, and on the bath species, M, involved. For the quantity $\beta_c(M,i)$, the question posed[61] was the strength of the dependence on i, and the specificity with regard to M. Even for strong dependence on i, the more important question was whether $\beta_c(M,i)$ is the same function for all M, i.e., $\beta_c(M,i) = \beta_c(i)$? An answer was forthcoming shortly in the study by Wilson and Johnston[62] of inert gas effects in the low pressure decomposition of nitrogen pentoxide for the series He, Ne, Kr, Xe and CCl_4 which, together with earlier data[61] for Ar, N_2, NO, CO_2 SF_6, and the parent N_2O_5, are tabulated in Table II. If deactivation occurred on every collision, or if $\beta_c(M,i)$ can be written as a universal function, $\beta_c(i)$, *then the identity holds*, $\bar{\beta}_c(M)/\bar{\beta}_c(N_2O_5) \equiv 1$, independent of M, where the bar quantities signify averages with respect to i. The ratios observed evidently depart markedly both from constancy and unity; furthermore, since possible errors in the collision cross section ratio, $[2s_{N_2O_5}/(s_{N_2O_5} + s_M)]^2$, cannot exceed the factor 4 for the smaller M gases (some modifications in accepted collision cross sections have, indeed, since occurred), no reconciliation of the ratio with unity is possible. Thus, the collisional efficiency is a function of M although its dependence on i remained moot at that time (the latter question will be taken up again later). Cordes and Johnston[63] came to a similar conclusion from a comparison of Ar and NO_2Cl efficiency in the low pressure decomposition of NO_2Cl.

The study by Volpe and Johnston[64] of some 16 bath gases in the NO_2Cl system (Table II; the data were corrected by these

workers for the (small) differential inert gas effect due to formation of product species) provided a signal advance in understanding of the variables that affect the efficiency of bath gases, M. Dependence of β_c on dipole moment and on the interaction potential was found. An empirical relation between β_c and boiling point was noted, so that collision efficiency is affected by molecular parameters that determine boiling point. A suggested correlation between β_c and "force of collision" may be considered more dubious. Volpe and Johnston pointed out that if $\beta(M,i)$ is a strong function of the energy states i, depending on the identity of the gas M, then the relative efficiencies of bath gases vary in general with the region of fall off and with the temperature, *since the range of energy states involved varies* strongly with both experimental variables.

Special attention should be called to an outstanding photochemical study by Russell and Simons[65] of third body efficiency in the photo-initiated I-atom recombination,[66] which was followed up by an important series of cognate investigations made by several groups.[67-71] The work of Russell and Simons included some 29 chaperone gases and independently revealed a general correlation between third body deactivation efficiency and boiling point and related parameters; study of the temperature dependence of the efficiency of some six gases He, Ar, N_2, CO_2, cyclo-hexane, benzene, was also made at 293° and 400°K. Both aspects of these results, and others from chemical activation systems, which is what these are, will be discussed further below.

The conclusions of Johnston and co-workers were an important advance in conceptual understanding of thermal energy transfer

systems. However, their contributions aroused a disappointing lack of response in concurrent or following work. What was needed for further progress was an approach to the operational design of experimental systems that would define and test the role of various efficiency parameters such as collisional cross section and dilution of substrate by bath gas, together with the pressure (fall off) and temperature dependence of the collisional efficiency. Still lacking, for another decade, was an explicit connection between the collisional transition probability elements p_{ji} for transitions from state i to j of the hot molecule (expressed both in terms of the form of the model for transition probabilities and in terms of the average energy jump $\langle\Delta E\rangle$) and the observed average inert gas efficiency, β_c. Both during the fifties and the first half of the sixties, with a few notable exceptions, many thermal studies of inert bath gas efficiency continued to be of a rather casual and fragmentary nature and were characterized by a notable lack of cogency of experimental design. We avoid invidious and unfruitful distinctions and simply cite some of the more important or historically interesting thermal work of this period in references 72-94 (Table III). Not all studies are uniformly reliable. Inconsistencies and incongruities may sometimes be discerned by casual inspection of data, but the bane of chemical kinetics – systematic chemical and mechanistic error – together with some experimental deficiencies noted in Part IE, acts upon us as a deterrent in the free use and systematization of much of this data.

E. Further Experimental and Theoretical Requirements

Obviously, the goal of thermal work on vibrational energy transfer involving highly excited polyatomic molecules in unimolecular reaction systems has been, and is a coherent theory of the phenomenon. Although significant progress has been made in this direction in the past decade, developments were at a rather rudimentary stage even in the middle sixties. Still lacking was an explicit connection between collisional behavior in thermal systems and the actual magnitudes of the energy amounts transferred between hot and cold molecules. Unknown from thermal evidence, also, was the form of the collisional transition probability distribution function, as well as the validity of a popular conception (derived probably from the Landau-Teller type of behavior observed in sound dispersion studies of diatomic molecules at low levels of excitation) that most collisions by weak collider bath molecules are completely inefficient. Also lacking from the thermal evidence was a demonstration of whether, and what bath species behaved like strong colliders. It had been postulated[75,76] earlier that large polyatomics are completely efficient; moreover, the parent molecule, especially, was frequently considered to display unit efficiency – a belief nourished on the rationale of favorable resonance conditions for interchange of energy between internal degrees of freedom of the collision partners. But a number of ambiguities, such as a lack of knowledge of appropriate collision cross sections for the phenomenon in question, as well as observed efficiencies which frequently appeared to exceed unity for some larger, complex bath gases[75,76,88,89,91] or, conversely, which showed large defects from unity by these,[75,91,93] obscured the

verification, if not the plausibility of the postulate. Very desirable was an independent criterion of strong collisional behavior in thermal systems and a coherent system of relative cross-sectional magnitudes.

Still another desideratum was control and mastery of the experimental variables: these include comprehensive variation of both molecule types and structures; variation of the characteristics of the substrate molecules in the sense of controlled variation of molecular parameters (as contrasted with indiscriminate comparison of subject molecules having simultaneous gross disparities in structure, vibrational and rotational parameters, reaction coordinate, critical energy threshold levels, region of fall off and temperature). Temperature dependence of collisional efficiency is obviously an important variable, and is fundamental in the theory and in the comparison of different systems. The degree of fall off of the system under investigation was also frequently subject to somewhat indiscriminate variation, sometimes within a single investigation. The degree of dilution of substrate by bath molecules was usually not systematically controlled and was treated very casually. Indeed, the lack of clear control of experimental conditions may be considered as a consequence of the lack of a clear operational definition of the collisional efficiency, β, and of the several alternative constructions that may be placed upon it.

In Section II, a quantitative formulation of energy transfer is presented. We largely follow the treatment of Tardy and Rabinovitch[95,96] who attempted to clarify the variables with specific relation to the needs of experimental design. Some aspects of

experimental and theoretical progress in the past decade are presented in Sections III and IV. Section V makes explicit connections between thermal work and results from other powerful techniques and suggests some important areas into which new work should extend.

II. MASTER EQUATION AND SOLUTION

The energy transfer information obtained in thermal unimolecular systems can be systematized by defining appropriate relative collision efficiencies. Due to the extensive "averaging" that occurs in thermal systems (from the large number of reacting states), these efficiencies cannot give the microscopic transition probabilities directly. Consequently, the experimental collision efficiencies must be compared with efficiencies obtained by computer experiments for a given set of transition probabilities.

Many definitions of collision efficiency have been used and as a result misunderstandings have resulted. Since the purpose of obtaining efficiencies is to make inferences as to the transition probabilities per collision for a particular set of collision partners, a knowledge of the collision frequency (ω) is nominally necessary. The associated experimental variable is the pressure, hence a transformation to collision frequency is made with the aid of the appropriate collision cross sections (s^2) and the reduced mass (μ) of the colliding pair. Since cross sections are not known exactly, associated errors may occur in the collision efficiency. These errors will be discussed in following sections along with methods of eliminating dependence upon s^2.

The appropriate relative collision efficiency is most easily defined in terms of the particular experiment. For simplicity and lack of information to the contrary, the substrate is considered to be a strong collider, at least at lower temperatures.

Thus, the rate constant k_{uni} as given by equation 4, increases linearly with pressure at low pressure and levels off at high pressure as shown in Figure 1. For a given initial pressure of substrate, addition of addend M (a weak or strong collider) causes an increase of k_{uni} as depicted in the Figure. For addition of a fixed amount of M, the increment in k_{uni} decreases with increase of the initial pressure of substrate. Likewise, the rate of increase in k_{uni} at a given substrate pressure increases nonlinearly with addition of large amount of M both in (Dilution effect), and outside of (Fali off effect) the p=0 region. Clearly, the efficiency of a given addend depends on dilution ($D = \omega_M/\omega_S$), order of reaction ϕ, or collision rate ω, and temperature.

Two types of collisional efficiencies can be defined:

a) a differential quantity, appropriate in the second order region or, in general, for small additions of M,

$$\beta_\omega(D) = \Delta\omega(sc)/\Delta\omega(wc), \text{ for } \Delta k(sc) = \Delta k(wc);$$

and

$$\beta'_\omega(D) = \Delta k(wc)/\Delta k(sc), \text{ for } \Delta\omega(wc) = \Delta\omega(sc);$$

b) an integral quantity which is more appropriate at higher dilutions, especially in the fall off region,

$$\bar{\beta}_\omega(D) = \omega(sc)/\omega(wc);$$

and

$$\bar{\beta}'_\omega(D) = k(wc)/k(sc).$$

Because of the linear nature of the dependence of rate constant on pressure in the low pressure region, $\beta_o(D) = \beta'_o(D)$.

In order to relate the "microscopic" collisional energy transfer probabilities p_{ij} to the observed reaction rates or collision efficiency, a Master Equation for the system is defined which describes the time evolution of each microscopic internal energy eigenstate,

$$\frac{dn_1}{dt} = f_1 + \omega\Sigma_j p_{ij} n_j - \omega n_1 - k_1 n_1 \; ;$$

$$\vdots$$

$$\frac{dn_i}{dt} = f_i + \omega\Sigma_j p_{ij} n_j - \omega n_i - k_i n_i \; ; \qquad (8)$$

where f_i is an "external" (non-collisional) input into the ith level, p_{ij} is the probability that after one collision molecules in internal energy state j are transported to internal energy state i; ω is the average number of collision that each molecule in state i undergoes per second and is taken to be a constant independent of i; k_i is the microscopic rate constant for reactant molecules which form products. The first two terms on the right-hand side generate input into the ith state while the last two terms give the rate at which molecules leave the ith state.

The p_{ij}'s must meet the requirements of completeness (equation 9) and detailed balance (equation 10):

$$\sum_j p_{ji} = 1 \; ; \qquad (9)$$

$$\frac{p_{ij}}{p_{ji}} = \frac{g_i}{g_j} e^{-(E_i - E_j)/kT} \; ; \qquad (10)$$

where g_i is the statistical degeneracy of the ith energy

level, k is Boltzmann's constant and T is the system temperature. For purposes of this review, the Marcus-Rice model will be used for the calculation of k_i. In this model k_i increases with an increase in energy. In theory the coupled equations in (8) can be solved. However, for calculational purposes the n microscopic energy levels comprising the system are grouped into N quasi-microscopic levels so that the number of levels can be reduced from an astronomic number to one hundred, say.

For ease of manipulation, the N coupled equation can be represented in matrix notation[97]

$$\dot{\vec{N}} = \vec{f} + \omega\overleftrightarrow{P}\vec{N} - \omega\overleftrightarrow{I}\vec{N} - \overleftrightarrow{k}\vec{N} \qquad (11)$$

where $\overleftrightarrow{I}$ is the unit matrix and the other symbols have the same meanings as before. The transition probabilities are not known a priori and the objective of the experiment is to obtain each of the actual transition probabilities from the data. However, in practice this is not directly realizable in a single experiment due to the averaging which occurs in thermal systems. Instead, the average collisional efficiency may be measured in terms of the observed rate constant for a particular chaperone molecule. Then the rate constant may be calculated for a particular set of assumed transition probabilities and collisional cross sections, and compared to the experimental value.

In a closed system $\vec{f}$ is identically zero and, formally, $\vec{N}(t)$ is:[98]

$$\vec{N}(t) = e^{(\omega\overleftrightarrow{P} - \omega\overleftrightarrow{I} - \overleftrightarrow{k})t}\,\vec{N}(0) = \left[\sum_{i=0}^{\infty} (\omega\overleftrightarrow{P} - \omega\overleftrightarrow{I} - \overleftrightarrow{k})^i \frac{t^i}{i!}\right]\vec{N}(0) \qquad (12)$$

$$\text{Rate}\,(t) = \sum_i k_i N_i(t)$$

The experimental conditions are usually such that time resolution is unimportant in thermal systems and it may be assumed that the interesting energy levels are in a quasi-steady state. These interesting levels are those which have energy in excess of $E_0-\Delta$, where Δ is a small energy interval determined by the transition probabilities and the temperature in question and E_0 is the critical energy for reaction. Under these conditions equation 11 reduces to

$$0 = \vec{f} + \omega\overleftrightarrow{P}\vec{N}^{ss} - \omega\overleftrightarrow{I}\vec{N}^{ss} - \overleftrightarrow{k}\vec{N}^{ss} \qquad (13)$$

Equation 13 can be solved directly for N^{ss} by matrix inversion,

$$\vec{N}^{ss} = (\omega\overleftrightarrow{I} + \overleftrightarrow{k} - \omega\overleftrightarrow{P})^{-1}\vec{f} \; . \qquad (14)$$

Then, Rate = $\sum k_i N_i^{ss}$ and,

$$k_{uni} = \frac{\Sigma k_i N_i^{ss}}{N_{tot}} \; ; \qquad (15)$$

the subscript uni, indicating pressure dependence, is dropped in the ratio k/k_∞. Alternatively, N^{ss} can be found by an iteration method[95,96] in which a $\overleftrightarrow{P}'$ matrix is formed from the $\overleftrightarrow{P}$ matrix by normalizing the sum of each column of $\overleftrightarrow{P}'$ to $\omega/(\omega+k_i)$; this factor is just the probability of a molecule undergoing collision from the ith level. $\overleftrightarrow{P}'$ then operates on $\vec{f}$ producing $\vec{f}^1$. This process is repeated until $f^n = f^{n+1}$. Physically this procedure corresponds to the shuffling of energy level populations by collision so that the net input flux into the interesting levels is equal to the flux of molecules leaving the system by reaction. Hence, for a given set of transition probabilities, k_{uni} can be computed from equation 15.

The "many shot" expansion technique of Serauskas and Schlag[100a] ie equivalent to these methods. The effect of non-equilibrium populations, for levels below the critical energy, on the rate has also been formalized by Schlag and Valance.[100b] Using matrix operations on the appropriate Master equation (equation 11) they showed that the rate will depend linearly on the ratio of weak to strong collider only if equilibrium is established below E_0.

Another approach to $\vec{N}^{ss}$ has been given by Troe;[101-103] this method is only useful in the low pressure second order region. The Master Equation is set up in terms of the energy level populations relative to the equilibrium Boltzmann Distribution at the reaction temperature,

$$\sum_j \omega p_{ij} h_j b_j - (\omega+k_i) h_i b_i \gtrsim 0 \; , \text{ for } E_i > E_0 \qquad (16a)$$

$$\sum_j \omega p_{ij} h_j b_j - \omega h_i b_i \gtrsim 0 \; , \text{ for } E_i < E_0 \; , \qquad (16b)$$

where b_j is the Boltzmann equilibrium population distribution and $h_j = n_j/b_j$. The energy levels are assumed to form a continuum so an integral equation results. The solution to the integral equation can be found for a given set of transition probabilities by using the method of Fourier transforms or, under certain circumstances, a second order differential equation obtained by differentiating equation 16. As a result, the solution (population distribution) is an analytic function of the transition probabilities. In the second order region, $h_i \approx 0$, for $E_i > E_0$, and thus,

$$h_i \approx \sum_{E_j<E_0} p_{ji} h_j \; , \text{ for } E_i < E_0 .$$

p.29a

Transferring to a continuous energy domain,

$$h(E) = \int_0^{E_0} P(E',E)h(E')dE' \quad , \text{ for } E < E_0 \ .$$

The corresponding second order rate constant, k_0, is

$$k_0 = \omega\int_{E_0}^{\infty} b(E')\left[\int_0^{E_0} P(E,E')h(E')dE\right]dE'$$

Troe assumed an arbitrary model of transition probabilities, $P(E',E)$, which simulated the statistical probabilities obtained by having a long-lived collision complex in which all modes are allowed to freely exchange energy. Three parameters α, β and γ define the probability distribution, such that α and γ are the average energy transferred down and up, respectively, as measured from a zero of reference which is the most probable energy transferred, β. This procedure results in an analytical function for the populations and for β_c. The conclusions are similar to those found previously by TR. We will concentrate on the results obtained by the TR iteration procedure which has been solved explicitly for a variety of experimental variables, including dilution, temperature and degree of fall off, for various forms of the transition probability models and for several operationally significant definitions of β_c.

Since relative efficiencies may be the experimental observables, we first review the behavior of strong collisions. For a strong collider, $p_{ij} = 0$ for all E_i, E_j greater than E_0; the equations 8, 11 and 13 are not coupled and can be solved exactly for the steady state populations. Specifically,

$$N_i^{ss}(sc) = N_i^{eq} \quad , E_i < E_0 \ ;$$

where N_i^{eq} is the equilibrium populations governed by the Boltzmann distribution at the temperature in question;

$$N_i^{ss}(sc) = \frac{\omega}{\omega+k_i} \ N_i^{eq} \quad , E_i > E_0 \ .$$

The rate becomes

$$\text{Rate} = \sum_i k_i N_i^{ss} = \sum_i k_i \frac{\omega}{k_i+\omega} N_i^{eq} ,$$

and

$$k_{uni} = \frac{\sum_i k_i \frac{\omega}{k_i+\omega} N_i^{eq}}{N_{tot}}$$

At high pressure, the steady state populations at all energy levels are given by the Boltzmann Distribution and the rate constant is simply

$$k_\infty = \frac{\sum k_i N_i^{eq}}{N_{tot}} .$$

Thus, the observed constant depends on the Boltzmann-weighted magnitudes of the k_i.

At low pressure, the energy level populations above E_0 are equal to $\frac{\omega}{k_i} N_i^{eq}$, so the rate constant is

$$k_o = \frac{\sum k_i \frac{\omega}{k_i} N_i^{eq}}{N_{tot}} = \frac{\omega \sum_{E_i>E_0} N_i^{eq}}{N_{tot}}$$

The observed low pressure constant is determined by the equilibrium fraction of molecules with energies in excess of the critical energy. The associated populations are illustrated in Figure 2 for a particular case. The decrease in the steady state population as the pressure is decreased accounts for the "fall off" of the "observed" rate observed in thermal unimolecular reactions (Figure 1).

Clearly, the reaction coordinate changes from predominantly

intramolecular energy transfer to predominantly intermolecular energy transfer as the pressure is decreased. The high and low pressure asymptotic limits are defined operationally by the conditions:

$$\omega >> k_i \quad \text{(high pressure)} ,$$

$$\omega << k_i \quad \text{(low pressure)} ,$$

for all levels above E_0 that contribute to the observed reaction. Due to the increase in k_i with energy, the limiting regions are reached at higher pressures as the temperature is increased. Thus, a "broader" fall off curve results as the temperature is raised.

For weak colliders, the complete set of coupled equations (8, 11 or 13) must be solved. Since the transition probabilities are not generally known from first principles, a pragmatic approach is used: various energy transfer models are assumed and the solutions to equations 14 and 15 are found. The models are chosen to represent extremes of physical cases, and it is felt that real models fall within these extreme limits. In general, any distribution is completely defined by all the moments of the distribution. However, for simplicity, two parameters are used to define the transition probabilities, namely, the step size <ΔE> (average energy removed on collision) and the form of the distribution. The calculations of TR were done in the above spirit. The test models ranged from step ladder (SL), in which a single unique amount of energy could be removed from the energized substrate by the chaperone in question (analogous to harmonic oscillator transition probabilities) to an exponential model (EXP) in which the probability for transfer decreases exponentially as the energy removed increases

(i.e., a high probability for zero energy transfer). Intermediate models were those corresponding to the gaussian and poisson statistical distribution functions. For present purposes, only the step ladder (SL) and exponential (EXP) models will be discussed. The low pressure results of Troe are comparable to those of TR if a conversion between $\langle \Delta E \rangle_{TR}$ used by TR and $\langle \Delta E \rangle_{T}$ used by Troe is made. This is described in Appendix I.

Calculations for various reactants (N_2O, NO_2Cl, CH_3NC, cyclo-C_3H_6 and dimethyl cyclopropane) in which energy transfer data exists were performed with the various energy transfer models mentioned above. As expected, the calculations show that for a given collision frequency, ω , the steady state populations of substrate activated by weak collisions are always less than those for strong collisions. For comparative purposes, relative populations, Γ_i and R_i are defined as,

$$\Gamma_i = \left. \frac{N_i^{ss}(wc)}{N_i^{eq}} \right|_{\omega} \quad , \quad R_i = \left. \frac{N_i^{ss}(wc)}{N_i^{ss}(sc)} \right|_{\omega}$$

respectively, where the ω is the appropriate collision frequency. From Γ_i and R_i, the effect of population on the collision efficiency can be evaluated. Both Γ_i and R_i decrease as the average energy removed decreases. The deficiency starts at an energy of approximately $E_0 \sim \frac{RT}{\langle \Delta E \rangle}$. Γ_i and R_i naturally increase as ω increases, since collisional processes contribute less to the reaction coordinate at higher pressures and the steady state populations for a strong or weak collider converge to the equilibrium population. At all finite pressures, Γ_i and R_i << 1 for the high

energy levels, since the high energy levels are more difficult to reach with the small step size of a weak collider. For a given average step size, the exponential model has larger values of Γ_i at all pressures due to finite probability for a large (strong collision) step. This effect is exhibited in Figure 3 for the case of methyl isocyanide.

Populations may also be compared at the collision frequencies for the weak and strong colliders such that k(wc) = k(sc). In this case, the weak collider has a few energy levels directly above the critical energy which have populations exceeding the equilibrium values; the other levels are depleted from the strong collider model. This follows from the fact that the higher energy levels are depleted and that this depletion must be made up by an increase in the population at the lower levels so that k(wc) = k(sc). An illustration of the deficiency for this condition is shown in Figure 4.

Thus the calculated rate constant which is determined by the steady state populations is also affected by the ratio of chaperone to substrate, the degree of fall off (i.e., reaction order, ϕ) and the temperature. At low D, the populations below the critical level are determined by the Boltzmann distribution, since most collisions are with the substrate (usually a strong collider); while at high D these populations are depleted from the Boltzmann distribution, since the predominant energy transport of the substrate is determined by weak colliders. As D increases, the average energy jump size decreases with D in a linear fashion; however, the observed rate constant for a given weak collider model is not a linear function of D or $\langle \Delta E \rangle$.

Calculations for various D values have been carried out with a mixed $\overleftrightarrow{P}$ matrix composed from strong and weak collision matrices having weights equal to their respective collision fraction.[46] The effect of dilution can be quantitatively interpreted by factoring $\beta'_\omega(D)$ into two parts. Specifically,

$$\beta'_\omega(D)=\Delta k(wc)/\Delta k(sc)=[\Delta k(wc)^{ss}/\Delta k(wc)^{eq}][\Delta k(wc)^{eq}/\Delta k(sc)^{eq}]$$
$$= \gamma'_N(D)\gamma'_K$$

where the two factors γ'_N *and* γ'_K *are related to the steady state* populations (ss) and transition probabilities, respectively. $\gamma'_N(D)$ is defined as the ratio of rate constant increments for the particular weak collider, under steady state conditions, to that for equilibrium conditions below E_0, while γ'_K is the rate constant increment for the weak collider to that of the strong collider under equilibrium conditions.

In the low pressure limit, the reaction coordinate is the collision coordinate and $\beta'_0(D) = \beta_0(D) = \gamma_N(D)\gamma_P$, where

$$\gamma_P = \frac{\Sigma P^{wc}_{ji} N_i^{eq}}{\Sigma P^{sc}_{ji} N_i^{eq}} \quad ; \quad \gamma_N(D) = \frac{\Sigma P^{wc}_{ji} N_i^{ss}}{\Sigma P^{wc}_{ji} N_i^{eq}} \quad ;$$

where $\overleftrightarrow{P}^{wc}$ and $\overleftrightarrow{P}^{sc}$ refer to transition probability matrices for weak and strong collisions and $\vec{N}^{ss}$ and $\vec{N}^{eq}$ are steady state and equilibrium population vectors below E_0. For low D, $\gamma_N(D) = 1$, since $N^{ss}(sc) = N^{ss}(wc)$, and $\beta'_0(0) = \gamma_P$; similarly, for high D the measured $\beta'_0(D)$ depends on both $\gamma_N(D)$ and γ_P. Hence, at low dilution $\beta'_0(D)$ is a measure of γ_P and, as D increases, $\beta'_0(D)$ also depends on γ_N. The behavior of $\gamma_N(D)$ as a function of D is shown in Figure 5 for a particular system, for the SL and EXP models. The functional

dependence for the EXP and SL models are unique; the $\gamma_N(\infty)$ decreases as $\langle\Delta E\rangle$ decreases.

For high dilution, $\bar{\beta}'_\omega(\infty)$ increases with pressure while $\bar{\beta}_\omega(\infty)$ decreases (Fig 6). The $\bar{\beta}_\omega(D)$ quantity, which stresses the collision process, exhibits the fact that the high energy levels are not being efficiently populated, while $\bar{\beta}'_\omega$ which stresses the efficiency related to the reaction coordinate indicates that the collision process is becoming less important at higher pressures.

The behavior of $\bar{\beta}'_\omega(\infty)$ with model (SL or EXP) is summarized in Figure 7 for various reactants at different regions of falloff. By using a dimensionless parameter, E', (defined as $E'=\langle\Delta E\rangle/\langle E^+\rangle$, where $\langle E^+\rangle$ is the Boltzmann average energy of the reacting molecules in the second order region), all reactants form a universal curve for a particular model distribution function. The use of this criterion firmly ties these β_c quantities to the Lindemann-Hinshelwood operational criterion of a strong collider, *namely* one which can bring about the collisional deactivation of a critically energized molecule in one collision. Because of the universal nature of these plots, from the measured value of β_c at any value of ϕ, E' i.e., $\langle\Delta E\rangle$, can be read off once the model is specified. At all values of ϕ, and for the step ladder model, $\beta_c \to 1$ for $E' \geq 5$; the corresponding exponential model condition is more severe, namely, $\langle\Delta E\rangle$ must be larger, and $E' > 10$ or more. A universal relation between $\bar{\beta}_\omega(\infty)$, or $\bar{\beta}'_\omega(\infty)$, and E' is found for all regions of the fall off as exhibited in Figure 8.

By measuring $\bar{\beta}_\omega$ or $\bar{\beta}'_\omega$ over the complete fall off range, all three parameters (s^2, $\langle\Delta E\rangle$ and model type) may in principle be

determined, since each parameter has a different functional dependence with pressure. However, experimental difficulties are rather severe. A somewhat more optimal and sensitive method is to measure the effect of dilution on $\beta_0(D)$ at low pressure. The cross section cancels in the ratio $\beta_0(0)/\beta_0(\infty)$. The various transition probability models for a particular E' have distinctive shapes when $\beta_0(D)/\beta_0(0)$ is plotted as a function of D (Fig. 5). Thus, data of high precision and accuracy can in principle be deconvoluted to give $\langle\Delta E\rangle$ and the model.

Finally, we compare Troe's calculational method[101-103] with that of TR. Troe[102] undertook an analytical treatment of fall off and energy transfer behavior for weak collisional behavior. He used the three-parameter model mentioned above for transition probabilities, together with various approximations for the depletion of steady state concentrations and for representation of the fall off in terms of the Kassel integral and some defined parameters. This treatment is attended by a rather large array both of limits of utility and nature of the approximations involved which tends to deprive it of practical or conceptual advantage relative to the allegedly "time-consuming" RRKM treatment.

Troe's definition of average energy transferred ($\langle\Delta E\rangle_T$) is the average for all collisions (up and down); that of TR ($\langle\Delta E\rangle_{TR}$) follows the Lindemann criterion and is the average energy removed per down collisions. The transition probability function used by Troe follows Detailed Balance only in special cases and must be brought into concordance both with it

and the completeness requirement. TR defined their collisional transition probabilities in terms of specific, simple functional forms-(step-ladder, gaussian, exponential, poisson) - all of which have many counterparts in physical and spectroscopic theory and which involve natural characteristic parameters. They are set up to obey detailed balance and completeness *ab initio*.

The temperature dependence of $\langle\Delta E\rangle_{TR}$ (presently unknown) depends on the nature of the energy transfer process and on the specific parameters which govern it; $\langle\Delta E\rangle_T$ involves in addition the temperature dependence dictated by Detailed Balance and differs from that of $\langle\Delta E\rangle_{TR}$. The dependence of $\langle\Delta E\rangle$ on specific model type (Troe was able to roughly change from EXP to gaussian by allowing β to take a non-zero value) also depends on the treatment used. The functional dependence of β_c on temperature, $\langle\Delta E\rangle_T$ and $\langle\Delta E\rangle_{TR}$ is described in Appendix I. With $\langle\Delta E\rangle_T$, little difference between SL (or gaussian) and Exp models is observed. However, $\langle\Delta E\rangle_{TR}$ exhibits a definite difference which is physically appealing and reasonable. Under conditions where the definitions of $\langle\Delta E\rangle$ become equivalent, both Troe's and TR's treatments give comparable values for β_c and related aspects. $\langle\Delta E\rangle_{TR}$ is preferred here since it is closest to fundamental definitions of strong collisions and its use has been extended to all pressure regions. One may, of course, insert an analytical definition for $\langle E^{\dagger}\rangle$ into E'.

Troe[101] has reported that calculated values of $\langle\Delta E\rangle$ by Tardy and Rabinovitch obtained from experimental collision efficiencies in thermal systems were larger by 50% than those which he has calculated. The apparent discrepancy is easily removed

by cognizance of the differences in definition of $\langle\Delta E\rangle$ (case $\beta \neq 0$):

$$\langle\Delta E\rangle_{TR} = \alpha = \langle\Delta E\rangle_{down}$$

$$\langle\Delta E\rangle_{T} = \frac{\alpha^2}{\alpha+kT} .$$

For low temperature external activation studies for which $\alpha > kT$, $\langle\Delta E\rangle_T \approx \alpha = \langle\Delta E\rangle_{TR}$; while for thermal studies (high temperature with a moderately weak collider), $\alpha < kT$,

$$\langle\Delta E\rangle_{T} = \frac{\alpha}{1+\frac{kT}{\alpha}} < \alpha = \langle\Delta E\rangle_{TR}$$

Likewise, the temperature dependence of $\langle\Delta E\rangle_{TR}$ depends only on the (unknown) temperature dependence of α, while that for $\langle\Delta E\rangle_T$ also has an additional dependence caused by the $\frac{1}{1+\frac{kT}{\alpha}}$ term; hence for low temperatures (chemical activation studies)

$$\frac{d\langle\Delta E\rangle_T}{dT} \approx \frac{d\langle\Delta E\rangle_{TR}}{dT} ,$$

while for thermal activation studies

$$\frac{d\langle\Delta E\rangle_T}{dT} \not\approx \frac{d\langle\Delta E\rangle_{TR}}{dT}$$

Troe[103] has examined the temperature dependence of $\beta_0(\infty)$ for weak colliders ($\beta < 0.3$). He concluded that the quantity $\beta_0(\infty)$ as defined by him (called β^T) goes as T^{-y} where $y \geq 1$. The quantity $\beta_0(\infty)$ as used by TR (β^{TR}) goes as T^{-x} where $x \geq 2$. The discrepancy between these two conclusions arises because Troe did not include the correct temperature dependence for $\langle\Delta E\rangle^T$. For low $\beta_0(\infty)$, when $\langle\Delta E\rangle_{down} \ll RT$ (small step size

and/or high temperature), β^T has the temperature dependence, $1/T^2\ f(T)$, while β^{TR} goes as $1/T^2\ g(T)$, where f(T) and g(T) are functions of T. The temperature dependence due to f(T) and g(T) is related to the change of the effective heat capacity of the molecules (and thus of their average excitation energy) with temperature and is a weaker function for smaller molecules. These terms are explicitly defined in the appendix. When $\beta_0(\infty)$ approaches unit efficiency (i.e., $\langle\Delta E\rangle_{down} = \gamma >> RT$), β^T and β^{TR} have similar temperature dependence since $\beta^T \sim (1-2RT/\gamma)g(T)$ and $\beta^{TR} \sim (1-C'T)f(T)$, where C' is a constant depending on the particular model.

III. Comprehensive Experimental Tests of Collision Efficiency

A. Low Pressure Region. Constant Temperature and Dilution.

The most ostensibly simple and direct method of determining collision efficiencies is to measure the absolute rate of reaction at constant dilution at fixed temperature in the low pressure region. The experimental collision efficiency, β_c , may be obtained from the measured rate with use of a value for the collision cross section, s^2 ; β_c can then be related to an average energy jump size by the calculational techniques of Section II. Two assumptions seriously affect the result: first, is the value of s^2 which is required to obtain β_c; and second, is the form of the collisional transition probability function which is required to obtain $\langle\Delta E\rangle$. Unfortunately, the correct magnitudes of s^2 for this energy transfer phenomenon have not been known. Moreover, for every assumed form of the transition probability function, a different value of $\langle\Delta E\rangle$ results, as is shown in Fig 7; in addition, all values of $\langle\Delta E\rangle$, i.e., of E', coalesce in the region around $\beta_c = 0.2$, where the several curves cross, so that the sensitivity to the form of the p_{ij} is particularly low in this region even for the two most diverse models, the step ladder and the exponential. A lesser source of error in obtaining β_c from the experimental rate is a requisite knowledge of the proper molecular parameters, rotational[104,105] and especially vibrational, which appear in the Boltzmann distribution; however, this problem is minor here relative to the calculational error that can affect β_c in externally activated systems, such as chemical or photoactivation,[106-109] and which arises in the theoretical Rice-Ramsperger-Kassel-Marcus

calculation of k_ϵ values which are necessary for the deconvolution of absolute experimental rates.

The moral of the above is, of course, that one should avoid use of the absolute rate method for the determination of collisional efficiency quantities, whenever possible.

In order to eliminate the sensitivity of the deduced values of β_c on the absolute errors of both measurement and calculation of k_o, the relative comparison method described in sections I and II has also been used. The relative rates of reaction for the "unknown" bath gas and for a standard substance, usually the substrate, are measured. This procedure replaces the assumptions of the absolute method by two new ones: first, relative collision cross-section must be assumed for the standard reference, as well as for the unknown gas; second, the efficiency of the standard must be assumed and the value is taken to be unity (i.e., strong collisions) if the standard is the parent substrate, as is usually the case.

The design of an experimental test of the latter assumption and the development of a consistent scheme of relative cross sections for energy transfer has been a significant development of the last decade. Moreover, experimental methods for eliminating or lightening the dependence of the derived results on either of the sets of pre-assumptions described above have also been devised; these will be outlined immediately below. In following parts of this section, a series of comprehensive experimental tests designed to bring in evidence

some of the important variables that govern the magnitudes of the collisional transition probabilities, will be described; they refer principally to results obtained in the study of the isocyanide isomerization system, RNC → RCN, which is presently the most intensively and extensively examined system. In a later section dealing with other techniques such as externally activated systems, reference will be made to still other and more powerful methods for eliminating energy transfer dependence on a knowledge of collision cross sections.

B. Relative Cross-Sections for Vibrational Energy Transfer. Demonstration of Strong Collisional Behavior.

In previous work, the magnitudes of the collision cross sections for vibrational energy transfer involving polyatomic molecules at high levels of internal excitation have not been known. It was common practice to transfer values derived from transport or virial data, but no justification for the propriety of this custom was offered. In 1967, Rabinovitch, Lin and Chan[110] described a technique for the determination of a self-consistent set of relative cross-sections based on the properties of homologous series of bath gases and extensible to any molecule more complex than some determinable minimum criterion. Furthermore, study of a homologous series, such as alkanes or alkenes, admits the possibility of varying a single parameter (the number of structural units, CH_2), and of examining its effect on the efficiency of energy transfer. The rationale of their method was as follows.

The relative efficiencies of inert activators M, compared with the parent substrate A, generally tend to increase with

molecular size. For the closely related species of a homologous series, the relative efficiency β_μ, derived from the observed pressure-per-pressure efficiencies β_p and corrected for reduced mass effects on collision rates, but not for relative cross sectional sizes, is expected to increase with chain length. Beyond some critical size, further increase in β_μ was postulated to depend primarily on the increase in effective collisional diameter, s_{AM}, and not on an increase in intrinsic efficiency. For molecules of critical complexity, no operationally significant enhancement of number, frequency distribution or range of vibrational and internal rotational degrees of freedom results from further elaboration of the molecule. On this basis, at low pressures,

$$\beta_{\mu(n+i)}/\beta_{\mu n} = (s_{AM_n} + i\Delta s_{AM})^2/s^2_{AM_n} \qquad (1)$$

where i is an increment to n, the number of carbons in the homologous chain, and Δs_{AM} is the average increment in diameter per CH_2 increment. Then,

$$R_{ni} = [\beta_{\mu(n+i)}/\beta_{\mu n}]^{1/2} - 1 = i\Delta s_{AM}/s_{AM_n} \qquad (2)$$

and a linear relation between R and i, of slope $\Delta s_{AM}/s_{AM_n}$, is predicted for $n > n_{critical}$. Justification for the use of a constant average increment Δs_{AM}, at least over a limited increase in $\underline{i}$, is found in the theoretical relation[111] $r_{rms}=1.023n$, where r_{rms} is a calculated root mean square end-to-end distance of alkanes and n is the number of skeletal bonds; this relation holds to well above C_{10}.

Fig. 9 shows plots of R_{ni} vs i for alkanes, alkenes and alkynes measured at infinite dilution of the substrate in the CH_3NC isomerization system at 280°.[112] The expected relation was found; $n_{critical}$ is 4 for alkanes and alkenes and is 5 for alkynes. Similar behavior was found[113] for perfluoroalkanes for which n_{crit} is 3. For highly polar aliphatic nitriles as the inert bath gas molecules in conjunction with the highly dipolar methyl isocyanide ($\mu \sim 4D$), a novel dipolar orientation effect also was found[114] whose nature was confirmed by crossed beam nonreactive scattering cross section measurements for homologous series of nitriles and hydrocarbons.[115] The experimental evidence thus reveals a constant value of the intrinsic efficiency for all higher members of the five homologous series studied. Since no bath molecule exceeds the parent substrate molecule in efficiency on the basis of a consistent set of relative cross-sections, the most reasonable and consistent assumption to be made is that β_c is equal to or close to unity. This postulate accords with the independent measurement of energy transfer magnitudes in externally activated systems. The postulate may be circumscribed somewhat by the corollary that parent gases and complex bath molecules may approach strong collisional behavior only at not-too-high temperatures.

With the adoption of a single value of the Lennard-Jones constant σ as standard for bath gases, chosen by these workers[113] at $\sigma_M = 5.23$ Å for n-butane (a value almost identical with the viscosity-derived value[116]), a connected interdependent set of relative collision cross sections s^2 was constructed and related to the Lennard-Jones force constants σ, through the use of the

equation[116], $s^2_{AM} = \sigma^2_{AM}\,\Omega^{(2,2)*}_{AM}$, whose employment for the interpretation of reaction kinetics data had been suggested earlier by Kohlmaier and Rabinovitch.[7] The collision integrals $\Omega^{(2,2)*}_{AM}$ may be based on the Lennard-Jones potential for systems where one or both of A and M are nonpolar, while angle-averaged reduced integrals based on the Stockmayer potential were used for two polar partners. The average increments in σ per CH_2 group were found to be 0.54 Å, 0.56 Å and 0.62 Å for n-alkanes, n-alkenes and n-alkynes, respectively, and 0.54 Å for perfluoroalkanes.

Good agreement of these relative cross sections for a homologous series was found between these values and viscosity-derived values insofar as the latter are available. This confers *a posteriori* sanction on the frequent use of the latter values, although not for use of constant or arbitrary values of σ in lieu of temperature-dependent s values, and not necessarily for proper account of the effects of branching and structural isomerization.

In a later study,[117] this method was applied to another substrate system, ethyl isocyanide isomerization at 231°. Homologues of n-alkanes and n-alkenes up to C_6 were investigated. The system is of particular interest since variation of the relevant experimental parameters, in comparison with methyl isocyanide, were closely controlled and permitted sharp focus on changes due simply to the altered molecular vibration-rotation parameters of the substrate. In this system, enhanced collisional efficiences were found relative to methyl isocyanide so that $n_{critical} = 2$ for both homologous series. A mean value of Δσ per CH_2 increment of 0.64 Å was measured, and is in reasonable agreement with values found with the methyl

substrate. Explanation of the enhanced efficiency cited is postponed for later discussion.

Spicer and Rabinovitch[118] further extended the domain of the technique to an examination of collision efficiency in the methyl isocyanide system for a series of C_5 and C_6 hydrocarbons isomers whose intrinsic efficiencies were taken, a priori, to be constant. In such case, for two bath species 1 and 2, $\beta_{\mu 1}/\beta_{\mu 2} = (s_{A1}/s_{A2})^2$. These authors were able to develop their findings into a general correlation which allows fairly accurate deduction of suitable cross-sections for which viscosity or other data are not available: the bath molecules may be treated as spheres whose diameters are proportional to their end-to-end geometric lengths. Suitable increases for side branching, cyclization and other specific structural features were described. These correlations were strengthened in chemical activation studies of a number of perfluoroalkane inert gases in the butyl radical decomposition system;[119] quantitative effects on collision cross sections due to branching cyclization and double bond insertion were reported. The results emphasize that a liquid drop model central force treatment does not apply to this phenomenon although appropriate for diffusion data[120] and probably for the non-reactive scattering data. This difference in behavior, it has been pointed out,[115] lies with the range and nature of the interactions involved for the various phenomena. The energy transfer data depend on stronger, shorter-range and more specific [121] interactions. However, the general magnitudes of the energy transfer efficiencies, which group between 0.1-1 at lower temperatures, reveal that attractive interactions are primarily involved for this phenomenon, also.

Illustration of the applicability of these developments may be made to the isomerization of 3-methylcyclobutene.[90] Table IV shows some reported values for β_c for pentanes which are improbably much larger than unity. The amended values group more suitably around unity for all isomers.

C. Low Pressure Region. Dilution of Substrate

In this section, dilution of substrate by the inert is the variable of interest and β_c is denoted as $\beta_0(D)$. From Section II, $\beta_0(D) = \beta_0'(D) = \gamma_N(D)\gamma_P$, and $\beta_0(\infty)/\beta_0(0) = \gamma_N(\infty)$ since $\beta_0(0) = \gamma_P$. The ratio is independent of collision cross section. The calculations of Tardy and Rabinovitch provide universal curves of $\gamma_N(D)$ as a function of D for several models of the collisional transition probability function (e.g. Fig 5) as well as of the variation of $\beta_0(D)$ with E' (e.g. Fig 7). For an assumed form of the transition distribution function a particular value of $\langle\Delta E\rangle$ results. The detailed shape of the variation of $\beta_0(D)$ between D=0 and D=∞ can, in principle, reveal the form of $\overleftrightarrow{P}$, although very accurate data is required.

Rabinovitch, Tardy and Lin[122] studied the low pressure CH_3NC isomerization at 280.5°C in the presence of helium over the range of dilutions of CH_3NC from D=0.1 to 340, on a pressure basis. The values of $\langle\Delta E\rangle$ measured were 0.8 kcal mole^{-1} for both SL and EXP models. The precision was not adequate to distinguish between the models because, as was mentioned in Section IIIA, the two curves for $\beta_0(\infty)$ vs E' cross in the near vicinity, namely, at $\beta_0(D) = 0.15$. As a consequence, the curves of $\beta_0(D)$ vs D are closely parallel for both models.

In a later study, Lin and Rabinovitch[123] amplified these dilution studies for helium and extended them to ethane and pentene-1 diluents. The ratios $\beta_o(\infty)/\beta_o(0)$ for helium, ethane and pentene were 0.62, 0.85 and 0.92, respectively. These studies contained a combined cross section-temperature-analytical error[113] of 17% in the absolute values of $\beta_o(D)$ which did not, however, affect the relative dilution ratios. Values of γ_P as well as $\gamma_N(D)$ were extricated from the data and values for $\langle\Delta E\rangle$ reported: > 6 kcal for pentene-1 and 5 kcal for ethane, both on a SL model, and 1 kcal for helium on an EXP model.

These studies were further extended in an examination of dilution and fall-off effects for He, Ne, Ar, Kr and Xe in the ethyl isocyanide system.[124] The dilution range on a collision basis extended from 18 to 196 for He, 15 to 176 for neon, 48 to 258 for Ar, 25 to 145 for Kr and 18 to 123 for Xe. In this case, both dilution and degree of fall off change as the system rises in the fall off region to ϕ values less than 2 (1.81). The resulting behavior is more complex, of course, but, in principle, provides a more stringent experimental test of the magnitude of $\langle\Delta E\rangle$ and of the appropriate model. The various relationships are depicted in Fig 10 which is a three-dimensional plot of $\bar{\beta}_\omega(D)$ and $\bar{\beta}'_\omega(D)$ vs D and k/k_∞ for a particular model (SL) and value of E' (0.80): two surfaces – one for $\bar{\beta}_\omega(D)$ and the other for $\bar{\beta}'_\omega(D)$ span all regions of D from 0 to ∞ and all regions of fall-off from 0 to 0.5. Both surfaces converge at $k/k_\infty \to 0$ (i.e. $\phi \to 2$) for all values of D; they also converge on unity for D=0, at all values of k/k_∞; they diverge at values of $k/k_\infty > 0$ (i.e., $\phi < 2$), for all $D > 0$. The detailed shapes of these curves are a function of E'.

As $\beta_\omega(D)$ approaches unity, the surfaces become more shallow and closer to a plane at a value of unity. The various β-relationships are summarized in Table V.

The best fits to the ethyl isocyanide data corresponded to ΔE (kcal mole^{-1}) and model values as follows: He: 1.42, EXP; Ne: 1.56, EXP; Ar: 1.82, P; Kr: 2.0, P; Xe: 2.0, P; where the Poisson model is intermediate in characteristics between EXP and SL models. The efficiencies of these bath molecules are all enhanced for C_2H_5NC relative to CH_3NC. This is considered in a following section.

Evidently, necessary corrections may arise in earlier literature data in which dilution D and order of reaction were not closely controlled. Illustration is made for the important NO_2Cl system, studied by Volpe and Johnston.[64] In this system, only the dilution correction enters because $\phi = 2$. The dilutions used were neither uniformly the same nor uniformly close to either limiting condition, $D = 0$ or $D = \infty$. They have all been brought to the same constant dilution for comparison purpose. Table VI shows the corrected, and the original observed efficiency values β_{obs} which were measured over various dilution intervals, given on a collision ratio basis. The collisional dilution was on the low side and varied from the extremes of 0.026-5.0 so that the correction-reference is chosen here as $D = 0$, on both an SL and EXP basis; the former model has been found plausible for the stronger colliders and the latter (or a Poisson model) for weaker collider basis. The change in β_{obs} varies from 2% to 40%. The <u>differential</u> in the correction is, of course, the significant indicator of the errors that can arise when comparisons of collisional efficiency are made on other than a strictly controlled dilution basis.

D. Low Pressure Region. Temperature Dependence of Efficiency

A limited amount of work has been done on the temperature dependence of collisional efficiency. It has been studied both for polyatomic molecules of conventional unimolecular systems as well as for simpler triatomic and diatomic molecules.

It is expected on the basis of the development given in Section II that the collisional efficiency of weak bath gases should decline with rise of temperature and produce a corresponding decrease in the observed activation energy. This is for the reason that E' declines as $\langle E^+ \rangle$ increases with temperature. Apart from that, the quantity $\langle \Delta E \rangle$ may also vary in temperature.

Consider the low pressure situation.[125] $\beta_0(\infty)$ is given by the expression

$$\beta_0(\infty) = \frac{k_0(M)}{k_0(A)}\left(\frac{\mu_{AM}}{\mu_{AA}}\right)^{\frac{1}{2}}\left(\frac{s_{AA}}{s_{AM}}\right)^2$$

where μ and s are reduced mass and cross section quantities. Then the observed activation energy differs from the parent strong collider value by

$$\frac{\partial}{\partial(1/T)} \ln \beta_0(\infty,T) = \frac{1}{R}\,(E_{aA} - E_{aM})$$

The collisional activation cross sections are not constant but actually vary with the temperature dependence of the collision integrals, i.e., as $\frac{\partial}{\partial(1/T)} \ln\left(\Omega_{AA}^{(2,2)*}/\Omega_{AM}^{(2,2)*}\right)$, where the ratio is a tabulated function[126] of $T^*(kT/\epsilon)$ and of $\delta_{max} = \mu_A^2/2\epsilon_A\sigma_A^3$. This feature itself produces a decrease in the observed activation

energy in the helium-methyl isocyanide system of 0.4 kcal mole^{-1}.[125]

In this system, values of $\beta_0(\infty,T)$ were measured over a range of temperatures from 210° to 326°. They decline from 0.29 to 0.21 (Table VII). This arises largely from the increase in $\langle E^+ \rangle$ from 400 to 500 cm^{-1} over the temperature range. The corresponding decrease in E_a was 1.1 kcal so that the total decrease was (1.1 + 0.4) = 1.5 kcal mole^{-1}.

The variation of $\langle \Delta E \rangle$ with temperature may also be determined from the dependence of $\beta_0(\infty,T)$ on E':

$$\frac{\partial}{\partial(1/T)} \ln\beta(\infty,T) = \frac{\partial \ln\beta(\infty,T)}{\partial(\langle \Delta E \rangle)} \cdot \frac{\partial(\langle \Delta E \rangle)}{\partial(1/T)} + \frac{\partial \ln\beta_0(\infty,T)}{\partial(\langle E^+ \rangle)} \cdot \frac{\partial(\langle E^+ \rangle)}{\partial(1/T)}$$

$$= (E_{aA} - E_A^M)\, R$$

Now the first factor of the first term on the right side, and all quantities in the second term are calculable or known since $\beta_0(\infty)$ is a known function of E' (Section II). Thus, $\partial(\langle \Delta E \rangle)/\partial(1/T)$ may be determined from experiment and Table VII reveals a very modest decline of $\langle \Delta E \rangle$ with temperature over the rather narrow range investigated.

Further information on the variation of $\langle \Delta E \rangle$ with temperature is available from studies of externally activated systems (chemically activated methyl cyclopropane, cyclopropane, butyl radical, halogenated ethanes and photoactivated cycloheptatriene) but discussion of these is postponed to Section V.

A few other studies of temperature dependence of collisional efficiency in complex molecules systems have been made. In the hydrogen peroxide system[82] an ostensible lowering of the activation

energy of 5.6 kcal mol^{-1} (48.1 to 42.5 kcal mol^{-1}) was found upon adding helium. This is surprisingly large. The temperature was only varied over a range of 40° (431-470°), and the Arrhenius plots show very bad scatter. This observed activation energy decrease may not be reliable.

Bell, Robinson and Trenwith[80] studied the temperature dependence with SO_2, CF_4 and CO_2 in the N_2O system. Over a range from 650 to 750°, they observed an increase in the activation energy for pure substrate of 14, 3.6, and 2.3 kcal mol^{-1} upon adding SO_2, CF_4 and CO_2, respectively. The first value is suspiciously large as the authors themselves suggested. The data are suspect for the two remaining smaller increases, also, since the system is complex and, in addition, substrate-inert gas dilution effects may be prominent. But if the qualitative direction of the change were correct, this would suggest that the thermal decomposition of nitrous oxide, which is a small molecule, cannot be described by a quasistatistical model of vibrational energy transfer which seems appropriate for large molecules at high levels of excitation (Section IV) and which, as we have seen, predicts a decrease in activation energy. A qualitative criterion of the expected behavior is the relative collisional efficiencies of noble gases in this system; helium was found by these authors to be the most efficient of these. This is in accord with experimental findings[127] at low energy levels for small molecules and also with general predictions derived from the Landau-Teller theory.[128,129] Indeed, Nikitin claimed to find a good fit[130a] between the experimental rate constant and that calculated via the Schwartz-Herzfeld equation[129] for the pure substrate system. Further experimental

work is desirable; Barton and Dove[130b] have described some inconsistencies in shock tube studies. Other triatomic molecules other than N_2O, have been investigated and it is appropriate to consider some work on a few small molecules at this point.

In the I-atom recombination system of Russell and Simons,[65] a decrease in k_{recomb} of a factor of roughly 2.5 was found for He, Ar, N_2, CO_2, cyclo-C_6H_{12} and benzene in measurements at 20° and 127°, which is interpretable as representing a decrease in collisional efficiency of stabilization of I_2^* with rise of temperature. The experimental data on the dissociation of diatomic molecules has been reviewed by Troe and Wagner[131] and Johnston and Birks.[132] In general, the observed Arrhenius activation energies are less than the bond dissociation energies, D_0°. Some investigators have used the Arrhenius activation energy and the critical energy barrier synonymously. Since E_a is just the temperature dependence of the rate constant, it depends on the energy level populations, the microscopic rate constants for each level and on D_0°.

The dissociation of a diatomic in an inert gas heat bath can be considered as a unimolecular reaction in the second order region in which the reaction coordinate is the transfer of energy from the heat bath to the diatomic. Johnston and Birks[132] have performed model calculations and concluded that the observed low activation energies, which decrease with an increase in temperature, can only be reconciled by models which allow dissociation to occur by direct promotion of molecules from any vibrational level. Ladder-climbing models which produce dissociation only from the top vibrational level could not explain the experimental findings.

Pritchard[133] recently has reviewed the importance of network effects (interconnections of the various levels) in the dissociation of a diatomic gas and the microscopic reverse process, the combination of atoms. A master equation was set up for all the microscopic energy levels (rotational and vibrational) and then approximations were made to reduce the complexity and still retain a realistic system so the coupled equation could be solved. Various models for the transition probabilities were assumed, and it was observed that the populations became more depopulated as the temperature was increased; the Arrhenius activation energy was found to decrease as the temperature increased. It was also observed that for a given D_0^o the rate constant for dissociation increased as the number of microscopic levels increased. Consequently, D_2 has a higher rate constant for dissociation than H_2. The temperature dependence for the rate constant was found to be relatively insensitive to the particular assumed transition probabilities, which is a corollary to Carrington's[98] conclusion that accurate transition probabilities cannot be obtained from experiments which involve extensive averaging such as the temperature dependence of rate constants. Pritchard concludes that the basic cause of low Arrhenius activation energies in the dissociation of diatomic molecules is due to the increase of the apparent dissociation energy as the rotational energy is increased. Thus, as the temperature is increased, higher rotational levels are populated, and since these higher levels have a smaller microscopic rate constant, the observed rate constant does not increase as rapidly with an increase of temperature.

Penner and Forst[134] have also considered the importance of both rotational and vibrational levels in the transfer of energy.

They have solved a two-dimensional master equation (vibration and rotation) by two approaches:

i) fixed v – where the rate of rotational dissociation for a given vibrational energy is averaged over the appropriate non-equilibrium vibrational distribution.

ii) fixed J – where the rate of vibrational activation for a fixed J is averaged over the appropriate rotational distribution.

Using exponential transition probabilities for both rotation and vibration energy transfer, the fixed v approximation produced rate constants that were comparable to those observed for the thermal dissociation of H_2. In a second paper,[135] the treatment was extended to the thermal dissociation of polyatomic molecules in the second order region. Agreement with experimental results for the H_2O_2 system (which has inherently large experimental errors) was cited.

The low activation energy observed for the dissociation of CO_2 at 3000°C in a shock tube has been interpreted by Tardy[136] as due to population depletion caused by weak collider effects in the second order region. He showed, from the calculations of TR, that for low E' (either low $\langle\Delta E\rangle_{TR}$ or high temperature) that the activation energy decreases by ≈ 2 RT for any set of transition probabilities in which $\langle\Delta E\rangle$ remains constant. If $\langle\Delta E\rangle$ decreases with an increase of temperature, which is possible, then the observed activation energy will decrease by more than 2 RT.

It is evident that although considerable progress has been made, a unified treatment of collisional activation and energy transfer in systems of small molecules does not yet exist.

E. Variation of Collisional Efficiency with Degree of Fall Off

Measurement of the variation of the collision efficiency of bath gases with degree of fall off ϕ of a unimolecular reaction provides another dimension to the experimental determination of the form of the collisional transition probability function. For sufficiently extensive and accurate data the results are independent, in principle, of the collisional cross section.

Variation of $\beta_\omega(D)$ with ϕ, of course, signifies a change in fall off shape of the substrate as between strong and weak colliders. Buff and Wilson[137] first gave a general discussion of fall off behavior for weak colliders; however, they employed a highly simplified collisional transition probability model in their practical example. TR's treatment in Section II uses more realistic forms of the transition probability distribution function. They have predicted quantitatively both the extent to which a weak collider shifts the fall off behavior to higher collision rates and also broadens the range of pressures over which the reaction order changes (Figs. 1,6,8); the pressure displacement factor increases with increasing collision rate and with decreasing bath efficiency. The method of TR has been applied to supply a general illustration of the variation of $\bar{\beta}_\omega(D)$ and $\bar{\beta}'_\omega(D)$ with increase of the fall off parameter k/k_∞ in a typical system, ethyl isocyanide, at all dilutions from 0 to ∞ for a particular choice of weak collider (Fig 10).

In Section IIIC, we previously described dilution studies[125] with ethyl isocyanide which extended into the lower part of the fall off region. Fujimoto, Lin and Rabinovitch[138] studied

several medium-efficiency gases in the methyl isocyanide system. They investigated C_2F_6, propane and propylene at 280°C at much higher k/k_∞ values – from 0.3 to 0.9. The collisional efficiencies $\bar{\beta}_\omega(\infty)$ were found to decline with increasing pressure as $\phi \to 1$, in good quantitative agreement with the predictions of TR. The comparison is shown in Table VIII for an SL model of transition probabilities. The data support the original low pressure energy transfer parameters of Chan, et al.[139]

The only extensive study of the variation of $\beta_\omega(D)$ with fall off in thermal systems has been made by Wang and Rabinovitch in the He-CH_3NC system[140] which was studied at 245° at $D=\infty$. These authors anticipated that helium, being the weakest collider, would provide the most accessible and strongest test of the variation. In order to strengthen the comparison of the helium behavior with the strong collider reference work of Schneider and Rabinovitch,[141] the fall off behavior in the presence of n-butane, which had previously been shown to display unit collisional efficiency (Sect. IIIB), was also examined over a fairly wide range of fall off.

The fall off curve of methyl isocyanide in the presence of helium at 245° is illustrated in Figure 11. Also shown is the fall off curve for parent substrate and for the n-butane-CH_3NC system.

The relative collisional efficiencies of helium at different positions of fall off were obtained from the smoothed data of Figure 11. The pressure displacement factor is just the reciprocal of the integral quantity $\bar{\beta}_\omega(\infty)$. Results are tabulated in Table IX

A value of $\beta_\omega(\infty)$ was not measured above $k/k_\infty \approx 0.775$ because experimental error rises rapidly in comparing the pressure displacement between curves which asymptotically approach $k/k_\infty = 1$.

The calculated behavior of $\bar{\beta}_\omega(\infty)$ as a function of the degree of fall-off is exhibited in Figure 12 for both the SL and EXP models at three different assumed step sizes. The calculations were made for the CH_3NC system at 245°K.

For high values of $\langle\Delta E\rangle$, i.e., for $E' > 1$, it has been established (Section II) that in the second-order region the number of molecules transported above the critical threshold E_0 on the basis of an SL model of collisional transition probabilities is greater than the transport provided by an EXP model. At sufficiently large values of $\langle\Delta E\rangle$, the steady-state population vector $\vec{N}_1^s$ below E_0 approaches the equilibrium vector $\vec{N}_1^e$ for both models, and all the more as k/k_∞ increases toward unity. But the EXP model is less efficient in pumping molecules above E_0 due to the fact that the exponential distribution has a head which corresponds to high probability for small jumps of size much less than $\langle\Delta E\rangle$. On the other hand, for a given initial value of E', the long tail of the EXP distribution, which gives finite probability for long jumps of size greater than $\langle\Delta E\rangle$, becomes more important as the average energy of reacting molecules $\langle E_r{}^+\rangle$ increases ($\langle E_r{}^+\rangle_{\omega=0} = 1.27$ kcal mol^{-1} and $\langle E_r{}^+\rangle_{\omega=\infty} = 3.09$ kcal mol^{-1} for CH_3NC) with increasing collision rate ($k/k_\infty \to 1$). Thus, the relative efficiency of the EXP model increases as $k/k_\infty \to 1$, and this results in the efficiency curves for the two models converging with increase of pressure (Figure 12, curves A).

For small values of $\langle\Delta E\rangle$ for which $E' < 0.5$, it has been shown that in the low-pressure region the steady-state concentration of reactant molecules below E_0 is greater for the EXP than for the SL distribution, due to the tail of the EXP distribution which permits some fraction of the more-efficient large steps. As the collisional rate increases, the average energy possessed by reacting molecules again increases toward the high-pressure value and further accentuates the role of the tail of EXP distribution in reaching further. Hence, as k/k_∞ approaches unity, the relative efficiency of the EXP model is enhanced and the EXP and SL curves spread apart (Figure 12, curves C).

At intermediate step sizes, the behavior falls between the limits described above. The SL model starts off at $\omega = 0$ as the more efficient one of the two, but crosses over at higher values of k/k_∞ to become less effective in replenishing the energized molecules above the reaction threshold (Figure 12, curves B).

Now, in principle, for sufficiently accurate data, the variation of the shape of the efficiency curve with fall-off should be able to reveal the parameters and model for energy transfer. In practice, this is probably not feasible from thermal data. Instead, the values of $\bar{\beta}_0(\infty)$ and $\bar{\beta}_0(0)$ may be used to suggest alternative values of $\langle\Delta E\rangle$ for the several models and the fall-off data then applied to these in order to make a selection of fall off shape. The best estimate from all of the data in this system are the values for the SL and EXP models given in the footnote of Table IX for $p = 0$.

The variation of $\bar{\beta}_\omega(\infty)$ with the degree of fall off, interpolated from the calculated curves for the step sizes deduced for

helium, are shown in Figure 13. The two curves are not distinguishable experimentally at the lower end of the fall off regime, say at $k/k_\infty < 0.05$, because of the convergence of behavior at $p = 0$ for the two models, for these values of E'. However, the curves diverge at higher pressures and illustrate the discriminatory power gained by the extension of the experimental testing to the fall off region. The measured behavior for CH_3NC-He fall off lies in between the two extreme models; at higher values of k/k_∞ it follows the SL model more closely. The ratio of $\bar{\beta}_{0.005}(\infty)/\bar{\beta}_{0.775}(\infty)$, which describes the accessible experimental range of variation of k/k_∞, equals 1.47 for the EXP case, and 2.13 for the SL. The experimental observed value of 2.08 is intermediate in behavior but indicates that a SL model is closer for helium. This work also provides a comprehensive experimental demonstration of the variation of fall off shape in the presence of a weak bath gas, i.e., of a decrease of collisional efficiency with increase in the k/k_∞ ratio, as predicted by the theory.

F. Dependence of Collisional Efficiency on Structural Parameters of the Bath Gas and Substrate

The question of vibrational energy transfer efficiency and its relation to molecular parameters of the bath gas was touched on in the Introduction. Both Russell and Simons[65] (I atom recombination) and Volpe and Johnston[64] (NO_2Cl decomposition) noted a general correlation between efficiency and boiling point of the bath gas. As the latter workers remarked, a number of structural parameters interrelate with boiling point; indeed, Rabinowitch and Wood[142] earlier had cited molecular complexity as a significant parameter. The important dispersion term of the average intermolecular potential is

$$V_{dis} = -\frac{3}{2} I_{red} \alpha_A \alpha_M / r^6$$

where I_{red} is the reduced ionization potential and the α are polarizabilities. For α_A constant, the dependence of the intermolecular interaction on polarizability follows α_M. In a system related to that of I atom recombination, namely, the deactivation of very highly vibrationally excited photo-activated I_2 molecules, a relationship between efficiency and polarizability has been observed.[143-5] Volpe and Johnston also proposed the dependence of β_c on dipole moment and on force of collision, $24\epsilon/\sigma$, where ϵ and σ are the 6-12 potential force constants. Trenwith[146] also claimed a similar correlation.

Most of the above studies involved a significant, but limited range of bath gases. A very comprehensive investigation of bath

gas efficiency has been made in the methyl isocyanide isomerization system.[139] Over one hundred molecules were examined at 280°C and $\beta_0(\infty)$ varies only over the modest range from 0.24 to 1.0.

A plot of $\beta_0(\infty)$ vs collisional forces does not provide a good correlation, nor does the plot against dipole moment alone. However, a good correlation with polarizability exists (Fig 14) which is all the more interesting because a systematic deviation from monotonicity is exhibited which reveals a contributory effect due to the dipole moment of the bath gas.

The correlations with polarizability and dipole moment verify that the longer range interaction is important. A molecular property which depends on total intermolecular attractive energy should reveal a general correlation with efficiency for all bath molecules. Boiling point, a universally available parameter, is a convenient quantity. Figure 15 shows a plot of β_μ vs boiling point for 102 gases. Considering the diversity of the gases studied, the correlation is very good.

Figure 16 shows the same plot for $\beta_0(\infty)$; some uncertainty is introduced in the assignment of collision diameters, but the general correlation is apparent: β_c increases with boiling point and levels off near unity for more complex molecules. Three classes of molecules may be discerned within the general correlation: I, monatomics; II, diatomic and small linear molecules; III, nonlinear polyatomics. The monatomics include the widest range of boiling points from He^{139}(4°K) to Hg^{147}(630°K). A limited number of deviations may readily represent experimental error, error in collision diameter assignment, or some possible special feature. The number of transitional vibration modes in the collision

complex, i.e., modes that correlate with rotation and relative translation of the collision partners, are three, five, and six, respectively, for the three groups. Chan et al.[139] proposed that the relative magnitudes of the efficiencies as between the three classes are explicable in terms of the increase in the number of transitional modes which are postulated to participate in efficient quasi-statistical[147] energy relaxation with the internal modes of A, as well as a decrease in the effective restrictions to such energy sharing that are imposed by conditions of angular momentum conservation. These ideas have been developed in more detail by Lin and Rabinovitch;[148] insofar as energy partitioning with transitional modes can play the single most important role in vibrational energy transfer of the present kind, then simple dynamical considerations related to angular momentum conservation comprise a very important aspect of the theoretical treatment. These aspects are considered in Section IV.

Chan, et al., discussed the detailed evidence from their data for the possible role of internal degrees of freedom of the bath molecules in the energy sharing process. They concluded that these may play a minor role but that, in general, efficiency increases somewhat with bath molecular complexity and with the number of internal degrees of freedom; at the low vibrational energy density of cold bath molecules, however, it is plausible, but by no means unequivocally evident from the various comparison tests that these authors were able to make, that only the lower frequency modes are (sometimes) active. It was clearly demonstrated from comparisons of similar and isotopic species that a resonance transfer phenomenon has no evident role. There seemed to

be some evidence for enhanced efficiency due to strengthened substrate-collider interaction brought about by the hydrogen bonding between CH_3NC and bath species.

Pavlou and Rabinovitch[149] examined some two dozen inert gases in the ethyl isocyanide system. The efficiency $\beta_0(\infty)$ was plotted against boiling point and again revealed a clear distinction between the same three classes of molecules (Fig. 17).
In fact, the same correlation may be detected in the work of Russell and Simons[65] on I atom recombination. A replot of the recombination rate constant k_R vs boiling point reveals a rough delineation of the same three classes (Fig 18). Despite the fears of these workers that quantum effects complicate the results for H_2 and He, Fig 18 reveals no peculiarities. Additional evidence for the existence of the three classes of bath molecules, although less clearly delineated because of the less comprehensive array of bath gases studied, may be found from some of the data reported in Table III, namely, for N_2O_5[62], cyclobutene[89] and sec-butoxyl.[93]

It is one of the advantages of thermal unimolecular systems that, in the p = 0 region, the magnitude of $\langle E^+ \rangle$ tends to follow classical statistical behavior ($\langle E^+ \rangle \approx RT$) and is only weakly dependent on substrate complexity.[150] Thus, the pragmatic operational test of bath molecule activation efficiency is virtually invariant in low pressure studies of a homologous substrate series for which E_0 is also nearly invariant; this is the case for CH_3NC and C_2H_5NC.[151]

The work on EtNC[117,124,149] permitted, for the first time, a

refined determination of the variation of the efficiency of a given bath gas with change in structure of the substrate molecule as between CH_3NC and C_2H_5NC. Both the moments of inertia and the number and dispersion of low-lying torsional and bending vibrational frequencies are altered between these two species. It is important to note, however, that such comparisons tend only to be confusing if indiscriminate comparison of bath gas efficiency is made between two substrate systems for which the critical thresholds E_0 (and the reaction temperature) differ, with a resulting concomitant change in the operational nature and severity of the experimental test of efficiency. Pavlou and Rabinovitch compared the efficiencies of the noble gases and a number of diatomic and polyatomic gases for the two isocyanide systems. Despite the naive expectation that the larger heat sink C_2H_5NC might correspond to decreased efficiency for collisional deactivation, most bath gases were more efficient in this system, both as demonstrated by measurement of $\beta_0(\infty)$ values and also as revealed by the R_{ni} plots for homologous series described in Section IIIB. These authors were able to rationalize the differential changes in efficiencies observed in terms of angular momentum conservation considerations and of a change in the effective number of transitional modes involved (increased by one for C_2H_5NC relative to CH_3NC).

Figure 19 reveals, for a number of systems, the disparate β_c trends observed in a variety of systems just for the sequence of noble bath gases. No complete explanation is at hand for the detailed relative efficiencies of many gases in many systems.

IV. VIBRATIONAL ENERGY TRANSFER PROBABILITIES

Sound dispersion work on very small molecules at low levels of vibrational excitation led early to quantitative accomplishment[143,144] and to theoretical treatment. A model of hard, non-adiabative repulsive collisional interaction was used, with emphasis on vibrational resonance and harmonic oscillator selection rules as crucial to high transfer efficiency. A concomitant postulate was that of inefficient transfer between vibration and translational degrees of freedom. These precepts also tended to dominate the intuitive conception of energy transfer in unimolecular reaction systems.

As pointed out in the Introduction, Sickman and Rice[47] first noted that the magnitudes of the efficiencies in unimolecular studies were relatively higher than in acoustic studies, as well as the fact there is a relatively small dispersion in efficiencies between bath species of differing complexity or structure. Volpe and Johnston[64] also pointed out that relative efficiencies tend to be of order of magnitude 0.1 - 1, even for atomic bath molecules, with no evidence for resonance effects on energy transfer: for the high-energy, high-density vibrational levels that are involved in reactive molecules, the potential energy function is strongly anharmonic and harmonic oscillator selection rules are inappropriate.

We briefly review these developments and the extensions of the theoretical treatments to high energy polyatomic systems.

The transfer of vibrational energy involving small molecules at low levels of excitation has been reviewed by Amme,[152] Moore[153] and Callear and Lambert,[154] and a brief recapitulation will suffice here.

Both laser and ultrasonic methods have provided most of the experimental information; shock tube data has also been useful for high temperature information. The early theoretical treatments used simple physical models for transfer, corresponding to the head-on collision of a diatomic molecule (described by a harmonic (usually) or anharmonic oscillator potential energy function) and a monatom, together with an exponential interaction potential. Efficient transfer of energy corresponds to a short impulsive collision along the repulsive part of the intermolecular interaction potential. This model initially presented by Landau and Teller[155] was expanded by Schwartz, Slawsky and Herzfeld.[156] They were fairly successful in predicting the exchange of translation and vibrational (T-V) energy. The functional relation between mass of the three particles and the energy level spacing and probability for transfer is correct. At higher levels of excitation the probabilities increase linearly with the vibrational quantum number, $P_{v,v-1} = vP_{10}$ and $\Delta v = \pm 1$. The calculated temperature dependence for the transition probabilities is typically in reasonable agreement with that determined experimentally. The probabilities ($\sim 10^{-6}$) increase as the temperature increases ($\log P_{ij} \propto T^{1/3}$).

An extension of three dimensional Schwartz-Slawsky-Herzfeld theory to polyatomics was made by Tanczos.[157] His calculation of the vibrational relaxation time for methyl chloride was in good agreement with the experimental value.

Further calculations of vibrational energy transfer probabilities in these small molecule systems have been extensive, ranging in complexity from simpler classical mechanical description[158] to a full-time dependent perturbation quantum mechanical[159] analysis.

In principle, the probabilities can be calculated from a knowledge of the intermolecular and intramolecular potential energy functions, using either classical or quantum mechanics. Adequate intermolecular potentials are not available although molecular beam measurements corresponding to single collision events are beginning to provide such information. Some developments associated with vibrational energy transfer calculations were reviewed by Rapp and Kassal.[160] They dealt primarily with the vibrational energy transfer between simple molecules at low levels of excitation. The one dimensional problem of vibrational energy transfer involving a harmonic oscillator can be considered solved. Mies[161] has solved the He + H_2 problem for all collisional orientations, while Benson and Berend[162] have made two dimensional calculations using a Morse potential for the A + BC system, at various rotational energies of BC. Approximations to the three dimensional case have been made with a breathing sphere model.[163-165] This model is appropriate for rapidly rotating molecules; however, the model cannot be used for systems in which the rotational period is less than the duration of the collision.

For TV transfer involving polyatomic molecules at low vibrational levels, Lambert and Salter[142b,166] have shown a correlation of relaxation time with ν_{min} (where ν_{min} is the smallest vibrational frequency of the energized molecule); as ν_{min} increases, the probabilities decrease. Two distinct classes of molecules were distinguished: those which contain H atoms have a higher probability than do molecules which do not contain hydrogen atoms. This distinction between classes may be due to rotational effects or the larger vibrational amplitudes associated with hydride bonds.

Vibrational-vibrational (V-V) energy transfer, both on an inter- and intra-molecular level have higher probabilities than the V-T counterpart. Not until 1962 had these probabilities been measured directly.[154] The theory shows that energy transfer is optimized when a resonance is available such that the residual which goes to translation is minimized. Dipole-dipole and other multipole interactions dominate at low temperature and the transfer probabilities decrease with an increase of temperature as the temperature rises to about 1200°K. Above 1200°K the probabilities increase since impulsive collisions are important. Thus, at low temperatures the long range attractive potential is important while at high temperature the short range repulsive potential is of prime importance, which also is observed at all temperatures for VT transfer.

Shin[167] has calculated the effect of temperature on the intermolecular V-V transfer probabilities for HF with HF. Below 500°K, dimers are prevalent due to the strong hydrogen bonding and the probability exhibit a negative temperature dependence; while at higher temperature repulsion dominates and a positive temperature dependence is predicted. Calculated probabilities are in good agreement with experimental values.

Smith[168] has recently reviewed the collisional relaxation of vibrationally excited molecules with potentially reactive atoms. Obviously, for this case the interaction potential is less repulsive than if the collider were inert. Experiments and computer calculations for diatomic and monatomic have been interpreted. The importance of the number and nature of accessible electronic states was related to the different types of potential energy surfaces. For normal T-V transfer involving a non-reactive chaperone, transfer

occurs on a single electronic surface (electronically adiabatic) and the traditional Landau-Teller treatment is adequate. When the species has an electronic ground state with non-zero angular momentum, vibrational energy transfer can then occur through either adiabatic or nonadiabatic electronic transitions; this will be particularly efficient for nonadiabatic collisions if the electronic splitting corresponds to the difference of the initial and final vibrational energies. For this case, $-\log P_{10} \propto \frac{1}{T}$, $\Delta v > \pm 1$, and $P_{v,v-1} > P_{1,0}$. Efficient energy transfer is interpreted as an encounter in which the transition state crosses the transition state region an odd number of times; reaction occurs when the transition state region is crossed an even number of times.

The importance of an attractive potential for efficient transfer of energy is illustrated by calculations performed by Gait.[169] For orbiting collisions, the collision time is enhanced, resulting in a larger probability for energy transfer. For hydrogen halides (CH, HCl, HI) colliding with excited $CO_2(C,0,1)$, the calculated probabilities were in good agreement with those experimentally determined. The effect of orbiting collision was significantly more important than transfer by a mechanism involving multiple moments.

In contrast to the behavior at low levels of excitation for small molecules, the transfer of energy has been reported to be very efficient for CO[170], I_2[143-146] and NO_2[171] excited to high rotational and vibrational levels. This behavior resembles that for large molecules as described in Section III. In general, for molecules at levels of excitation which are comparable to critical energies for chemical reaction, much less is known about theoretical transition probabilities for energy transfer. Various approaches have been used to gain information

about these transition probabilities. Four of the approaches which have provided insights into the form of the transition probabilities are:

i. Statistical accommodation distribution

ii. Limited statistical accommodation distribution or quasi-accommodation

iii. Trajectory analysis

iv. Information theory

These will be considered serially.

The simplest treatment, in which dynamic aspects are ignored, simply assumes that the collision complex between chaperone and reactant is long lived so that the energy is randomly distributed according to a quantum statistical model[23] in all of the internal modes of the collision complex.[100-101] The probabilities, P(E,E'), are given by

$$P(E,E') = \frac{D_I(E_T-E)D_R(E)}{\sum_{E=0}^{E_T} D_I(E_T-E)D_R(E)}$$

where E_T is the total energy of the complex, and $D_I(E)$ and $D_R(E)$ are the densities of states for the inert and reactant, respectively. These probabilities give calculated values of $\langle\Delta E\rangle$ which are larger than that which is experimentally observed. Also, the predicted dependence on the complexity of the inert is larger than what is experimentally observed.[139]

Their simple statistical model was later modified by Serauskas and Schlag[172a] on grounds of collision time restrictions on the intra-complex relaxation of energy and of the uncertainty principle. Their conclusion that only limited statistical accommodation occurs was correct even though the basis alleged was not as secure; the

question of collision lifetime restrictions on intra-complex relaxation of vibrational energy is considered again below and in Section VB. Later, Von Weyssenhoff and Schlag[172c] measured vibrational relaxation in electronically excited β-naphthylamine and concluded that a modified phase-space theory may be a satisfactory model for vibrational energy transfer. Very recently, Bhattacharjee and Forst[173] re-examined the simple statistical energy transfer model as applied to thermal and chemical activation systems but with consideration of restrictions imposed by conservation of angular momentum. They found that the average amounts of energy transferred $\langle \Delta E \rangle$ were still much higher than those experimentally determined; the angular momentum conservation did not adequately limit the amount of energy transferred if all internal modes are taken as active.

Lin and Rabinovitch[148a] followed up earlier conceptions of Stevens[148b] and successfully modified the statistical model by focusing on the transitional modes which appear when the collision complex between substrate and bath molecule is formed; these modes correlate with translational and rotational modes of the isolated species and lead to the distinction between monatomic, linear and polyatomic-nonlinear bath gases. A statistical intramolecular energy relaxation process is assumed only for energy redistribution among internal modes of the excited substrate and the transitional modes. The internal modes of the bath species are excluded from relaxation in the formal calculation, although a minor contribution to energy transfer due to these degrees of freedom was recognized to occur with the most efficient bath gases. Resonance energy transfer to internal modes of the bath species plays no special role. This model was applied in a semi-empirical fashion to experimental data obtained in the CH_3NC system. Upper limits for transfer of energy in the transition bending modes were obtained by invoking restrictions due

to conservation of angular momentum. The stretching transition mode removed an amount of energy which was adjusted to give the experimental efficiency. The calculated probability distributions for this model were quasi-exponential for inefficient colliders and became Gaussian as the efficiency increased, in agreement with the experimental observations.[139] A coherent account could be provided of the change in efficiency of bath molecules with change of substrate from CH_3NC to C_2H_5NC. Troe[106] has sought a relation between β and total number of atoms in the bath molecule. However, the sense of such a relation is that the internal modes of the bath gas share significantly in the energy relaxation – which is evidently not the case.

Wilson and co-workers[174] performed a variety of trajectory calculations for collisional partners having a 6-12 interaction potential and involving: i) a pair of Morse function diatomic molecules; ii) a Morse function linear triatomic and an atom; iii) a Morse function diatomic and an atom. Only colinear motion was allowed; thus, restrictions on their conclusions may be necessary relative to full 3-D analysis. In general, the Lennard-Jones 6-12 potential does not lead to efficient T-V or V-V transfer. The efficiency of transfer was found to increase as the mass of the transferring atom decreases; this is contrary to most experimental results for the family of inert gases. The simulated collision of C-C and C-H mass combination do not efficiently exchange energy. The efficiency of transfer increases as the initial relative translational energy increases.

By contrast, Steinfeld and Klemperer[144] have correlated the cross-sections for vibrational quenching of electronically excited I_2 ($v' = 25$) with reduced mass and polarizabilities of the collision

partner; the correlation also holds for cross sections[143] for v' = 15. The cross sections were found to be proportional to the polarizability and to the duration of collision (i.e. $\mu^{\frac{1}{2}}$) and to be independent of permanent electric dipole moment.

Insight into the importance of the collision dynamics has also been obtained by trajectory "experiments" performed by Bunker and Jayich.[175] They followed the intermolecular transfer of energy between CH_3NC and He, Xe, H_2 or N_2. They attempted to address the question of whether energy is removed all over the CH_3NC molecule, or is only one part of the molecule the initial site of the energy transfer. Trajectory calculations by integration of the appropriate equations of motion, were performed by the using potential energy functions of Bunker and Hase.[176] Pure repulsive pairwise interactions between the collider and the hit atom of CH_3NC were used. Representative sampling of the initial states was done by orthant sampling. They concluded that the energy loss distribution was nearly exponential for all the colliders, which is also in agreement with experimental findings for this system. The vibrational distribution of energy in the quasi normal modes was found to be non-random; the lowest levels were most easily excited.

Procaccia and Levine[177] have related experimental and computer vibrational relaxation times of molecules in selected internal states with the aid of Information Theory. This method demonstrates that a single dynamic constraint can be used to relate the transition probabilities involving the whole manifold of vibrational states. A "surprisal" constant, related to the discrepancy of the calculated and observed probabilities, was found to be independent of E'. This approach may also be useful in categorizing transition probabilities obtained from thermal and chemical activation systems.

Surprisal analyses have also been performed for the quenching of electronically excited iodine by rare gas atoms.[178] Large surprisal constants for rotational and vibrational quenching indicate that there is weak coupling between the internal and translational degrees of freedom. The surprisal constants were also found to be independent of the initial rotation and vibration quantum numbers.

In summary, the theory of vibrational energy transfer involving highly excited polyatomic molecules is in a more tentative and fragmentary condition than is the case for the better studied small molecule – low energy phenomena. There is strong evidence for a collisional complex of sufficient lifetime to provide efficient relaxation between a subset of the total number of internal degrees of freedom. Experimentation by other techniques (Section V) provides some further illustration of this matter.

V. RESULTS FROM OTHER TECHNIQUES. HIGH TEMPERATURE THERMAL SYSTEMS.

In this section relevant information obtained by other techniques is summarized and related to the thermal behavior described above. The coverage of this material is illustrative rather than comprehensive and is further restricted to behavior most closely related to thermal systems. Finally, some high temperature thermal studies and newer techniques and approaches are discussed.

A. Chemical Activation Systems.

The most quantitative and broadest range of data on collisional vibrational deactivation of highly excited polyatomic molecules has been obtained by application of the method of chemical activation of molecules.[179] By this method molecules are inserted directly into high levels of vibrational excitation by a chemical reaction which simultaneously forms and excites them. If the excitation level is above a critical threshold, unimolecular reaction may occur. Collisional quenching to levels below E_0 results in stabilization.

The first use of the method was reported in 1960 by Harrington, Rabinovitch and Hoare,[8] and a detailed analytical description of the technique was given a little later.[7, 97] In these earlier studies, the average experimental rate constant k_a was studied as a function of pressure in the presence of various inert gases; k_a is defined as $k_a = \beta_c \omega D/S$, where ω is the collision rate of the excited species; β_c is an effective collisional efficiency which is unity for strong collisions and approaches zero for very weak or elastic collisions; D and S are the respective amounts of decomposition (reaction) and stabilization of the chemically activated species. Two regions of pressure were distinguished:

a) High pressure (D << S). In this region the absolute magnitude of k_a is constant and independent of ω, but varies with collider M. If the appropriate collision cross-sections are known, then β_c may be evaluated both on an absolute basis and, also, relative to the behavior of some gas, usually the chemical precursor of the activated species, known to behave as a strong collider (see (b) below). The magnitude of $\langle \Delta E \rangle$ is found by a stochastic method of deconvolution from β_c.[7,95-97] This method is not optimal for two reasons: first, the resulting value of $\langle \Delta E \rangle$ depends sensitively on the magnitude of assumed collisional deactivation cross-section; second, a different value of $\langle \Delta E \rangle$ is found for every assumed form of the collisional transition probability distribution function; however, the uncertainty in $\langle \Delta E \rangle$ never involves more than a factor of two over the extreme range of assumed weightings of the P_{ij} – from the stepladder to the exponential model.

b) Low pressure (D >> S). In this region, k_a increases with decrease in pressure of (weak) colliders. The plot of k_a vs S/D is characteristic of the value of $\langle \Delta E \rangle$ and of the form of the probability distribution function and is independent of a knowledge of the collision cross sections. This method is quite powerful in this region, therefore. Furthermore, the conclusions derived from studies at low pressures can be applied to the calculation of the absolute value of k_a in the high pressure region and provide a method of verifying the correct collisional cross sections for vibrational activation-deactivation of molecules.

For strong colliders, k_a is independent of pressure and this characteristic permits recognition of molecules that meet the operational test for the system in question. Moreover, this behavior

permits the determination to be made as to whether weak bath molecules remove a small amount of energy on the average on each collision ($p_{ii} \to 0$), or whether a large amount of energy is removed only in rare collisions, while $p_{ii} \to 1$. In the latter case, no change of k_a with pressure in this region is expected since $\langle \Delta E \rangle$ is large and the form of the distribution function, with $p_{ii} \to 1$, simply connotes low collisional deactivation cross sections.

The above remarks refer to single reaction channel systems. The method was extended several years later by Tardy, Larson and Rabinovitch[180,181] to the study of collisional vibrational energy transfer from chemically activated molecules which undergo reaction by i competitive reaction channels each characterized by a threshold energy E_0^i. The various threshold energies index the energy levels of the hot species, while the various reaction events act as transducers of the populations of the various levels. Thus, a type of "competitive chemical reaction spectroscopy" is provided. This method has several virtues: since only comparative product yields need be measured within a given system, the experimental accuracy is, in principle, improved over that available by measurement of total reaction rates; moreover, the competition confers independence from collisional cross section information upon the deduction made from the data respecting $\langle \Delta E \rangle$ and the form of the model of transition probabilities; finally, these advantages obtain even in the high pressure region, although it has been shown desirable to measure relative product yields over as wide a range of pressures as possible.

It may be noted that the methods and calculational procedures described here for chemical activation systems apply

to other methods of external (as contrasted with internal collisional) activation, such as hot atom or photo-activation, provided the quantities S and D can be independently evaluated.

Results from various studies are summarized in Table X. The following conclusions are noted. They complement and are supported by the results noted previously for thermal systems:

a) The values of $\langle \Delta E \rangle$ range from $\sim$ 0.5 kcal to $\sim$ 12-15 kcal $mole^{-1}$ in all systems studied.

b) The values of p_{ij} follow a stepladder (gaussian) distribution for the more efficient bath gases and an exponential or poisson distribution for the less efficient colliders.

c) The value of p_{ii}, i.e. occurrence of elastic collisions, has no special weighting; energy transfer takes place on virtually every collision and weak bath gases are such because $\langle \Delta E \rangle$ is small and not because p_{ii} is close to unity.[182]

d) *The magnitudes of collision cross-sections conform to conventional* gas kinetic-transport magnitudes,[108,183] within some uncertainties of the absolute theoretical values of rate constants as calculated from Rice-Ramsperger-Kassel-Marcus (RRKM) theory. However, errors in RRKM magnitudes and arbitrariness in selection of molecular and calculational parameters are considerably restrained when theoretical values are fitted to a related or homologous series of molecules having closely related reaction coordinates.[183,184]

e) In the homologous series of chemically activated alkyl-2 radicals from butyl-2 to octyl-2, $\langle \Delta E \rangle$ is quasi-constant.[184]

f) The value of <ΔE> seems to increase with increase in total energy of the excited species as evidenced at room temperature by butyl-2 radicals having energies from 41.6 to 45.9 kcal $mole^{-1}$;[185] other, and stronger tests are desirable. In fact, the butyl radical system[7] and the cyclopropane and dimethyl cyclopropane systems[186,187] have been studied at temperatures from -78° to 25° and from 25° to 400°, respectively. Since the thermal energy of the species increases with temperature, these systems ostensibly provide further examples of the dependence of <ΔE> on the magnitude of <E>. However, the variation of temperature itself introduces another significant variable that vitiates the usefulness of these systems for the test in hand.

g) Experimental collisional efficiency varies with the nature of the pragmatic operational test. Thus, the hydrogen efficiency β_c for ethyl radical deactivation at room temperature declines from $\beta_c = 0.9$ for ethyl activated by the reaction, $H+C_2H_4$, and having zero minimum excess energy above threshold ($\langle E^+ \rangle = 1.9$ kcal $mole^{-1}$), to $\beta_c = 0.4$ for ethyl activated by the reaction, $D + C_2H_4$, and having minimum excess energy of 1.7 kcal $mole^{-1}$ ($\langle E^+ \rangle = 3.8$ kcal $mole^{-1}$).[12] Carter and Tardy[188] have performed calculations which show that in external activation systems, $\bar{\beta}'_{\omega}(\omega)$ first increases as $\langle E^+ \rangle$ increases from 0 and then slowly decreases with further increase of $\langle E^+ \rangle$. This maximum in $\bar{\beta}'_{\omega}$ is accounted for by the rapid increase in k_E with E, for values of $\langle E^+ \rangle$ near zero. Thus, decomposition results for very weak colliders in which up jumps are likely (approaching 50%).

h) The dependence of <ΔE> on temperature may be inverse in nature. A modest, or no decrease in <ΔE> with increase of temperature from -78° to 250° was found in the butyl system[7] and a possible decrease of a few kcal in <ΔE> between 25° and 450° in the cyclopropane-dimethyl cyclopropane systems[VA11,12] systems. Marcoux, Siefert and Setser[189] found indeterminate changes in the 1,1,1-trifluoroethane system (Table VA1) between 196°K and 298°K for H_2, N_2, CO_2, SF_6 and C_2F_6. More work on this aspect of the behavior is highly to be desired.

i) Some of the chemical activation data reveal the existence of the same three classes of bath molecules shown by thermal systems.[7,189,190] Figure 20 gives a plot of data from the butyl system[7] and from the better documented trifluorethane system.[189] Since <ΔE> is plotted, rather than β_c, a leveling of the P-NL curve, similar to that in Figs. 16 and 17, does not occur, but the curves have the same significance. Much of the data in the literature is too sparse or erratic to serve as a good criterion.

j) In a clear demonstration, Setser and Seifert[191] showed that there was no isotope effect on the collisional transition probabilities for deactivation of excited C_2H_4Cl and $C_2D_4Cl_2$; but Frank and Rowland have concluded otherwise in a fluoroethyl radical system.[192]

Finally, some conclusions with regard to general aspects of collision efficiencies that were noted for thermal systems were, in fact, discovered first in chemical activation systems.[193] The general behavior is in contradistinction to the predictions of the theories of Landau and Teller, and later extensions (Section IV), appropriate for small molecules at

low levels of vibrational excitation. These theories may not be used to predict vibrational energy exchange behavior for polyatomics at high levels of excitation: briefly put, helium is not the most efficient of the monatomic bath gases and the efficiency does not (usually) decrease with increasing atomic mass; collisional efficiency decreases, rather than increasing with rise of temperature; finally, even for weak monatomic colliders, elastic collision are infrequent events and energy transfer occurs on virtually every collision.

B. Hot Atom, Ion-Molecule and Cross Beam Systems.

There are several different techniques for bringing about vibrational excitation of species in each of hot atom, ion-molecule and cross beam systems. However, chemical activation has been the method of excitation in the comparatively few studies in which vibrational deexcitation has been studied.

Higher levels of excitation than are easily accessible in chemical activation systems, i.e., above 5 e.v., are readily attained in hot atom nuclear recoil systems. The activation process e.g., $c\text{-}C_4H_8 + T^* \rightarrow c\text{-}C_4H_7T^* + H$, is actually a chemical activation process involving a highly translationally excited atom reactant. In the past, some difficulties in defining the energy distribution function for the excited species, and also in sorting out chemical complications such as alternative modes of production of decomposition products, have hindered the utilization of these systems for the study of collisional vibrational energy transfer. Progress in that direction is now being made. Nogar, Dewey and Spicer[194] have carried out a quantitative study of collisional deactivation of $c\text{-}C_4H_7T$ for several bath gases (Table X)

with results that cohere with conclusions from conventional chemical activation systems.

Up to now, there have been only a few explicit and quantitative studies made of the collisional deactivation of vibrationally excited ions at higher energy levels although qualitative deductions concerning collisional efficiencies as derived from reactions such as ion-molecule recombination have been more common.[195]

The first explicit study was the work of Gill, Inel and Meisels[196] on chemically activated $C_4H_8^{+*}$ formed by the combination, $C_2H_4^+ + C_2H_4$, and having $\sim$ 60 kcal mole^{-1} of internal energy. In this system, decomposition to give $C_3H_5^+ + CH_3$ competed with charge exchange and collisional vibrational deactivation. Although involving a number of assumptions concerning chemistry and energetics, these authors deduced that on a stepladder model ethylene bath gas removed $\leq$ 2 kcal mole^{-1} per collision while the corresponding value for Ne was 0.7 kcal mole^{-1}. This comparative inefficiency was alleged to be due to inefficient energy transfer in an ultra short-lived complex at the large impact parameters predominantly involved.

Anicich and Bowers[197] studied the low pressure third order combinations

$$CF_2CH_2^+ + CF_2CH_2 \rightleftharpoons C_4H_4F_4^{+*} \xrightarrow{M} C_4H_4F_4^+$$

and

$$C_6H_6^+ + C_6H_6 \rightleftharpoons C_{12}H_{12}^{+*} \xrightarrow{M} C_{12}H_{12}^+$$

in the presence of He, Ne, Ar, Kr, Xe, N_2, CO and the parent species as inert neutral bath gases. The relative efficiencies for the ethylene ion dimer are normal, while those for the benzene ion dimer are very low (Table X). A linear relation was found between

collisional efficiency and reduced mass and was taken as evidence for a duration of collision determined by a "fly-by" time.

Hot ions were also produced[198] by chemical activation of $C_5H_9^+$ according to the scheme

$$C_3H_5^+ + C_2H_4 \rightleftharpoons C_5H_9^{+*}$$

Reaction of $C_5H_9^{+*}$ competed with collisional stabilization. Unlike the studies just cited, Miasek and Harrison suggested that a "long-lived" ion-bath molecule complex is formed similar to that proposed by Lin and Rabinovitch[148] for neutral-neutral systems. The results were consistent with a relaxation process between the internal modes of $C_5H_9^+$ and the transitional modes of the complex, with only minor involvement of the internal degrees of freedom of the bath molecule. The data of Miasek and Harrison also shows segregation of bath molecules into three classes – monatomic, diatomic-linear and polyatomic-nonlinear – when β is plotted against bath boiling points. The relative efficiencies found for some twenty bath molecules in this system closely parallel those found for the CH_3NC[139] and C_2H_5NC[149] thermal systems.

An illuminating series of experiments have been carried out by Fisk and co-workers using a tandem crossed beam technique. Diatomic KBr was chemically activated to an average level of vibrational excitation of 41 kcal mole^{-1} by the reaction, $K+Br_2 \rightarrow KBr^*$. The angular and velocity distribution arising from inelastic scattering of the KBr^* beam was studied. The first experiments[199] were made with small inert polar ($\mu \sim 1.7$D) scatterers, H_2O, NH_3 and CH_3OH, at initial relative translational energies of $\sim$ 1 kcal mole^{-1}. The dipole moment of KBr is very large (17D) and an

electrostatic interaction of $\sim$ 20 kcal mole^{-1} was estimated in these cases. The workers found that the behavior followed an intermediate complex model with quasi-statistical or quasi-accommodation relaxation of energy, similar to that of Lin and Rabinovitch, with effective internal relaxation involving the transitional modes and the vibration of KBr. A complex life time of $\sim 10^{-12}$ sec (0.3 of a rotational period) is adequate for internal randomization between the active modes. In this rather unusual case, where 41 kcal is originally in 1 vibrational degree of freedom, the vibrational decrement was $\sim$ 34 kcal mole^{-1}.

A particularly interesting study[200] was one in which the scattering partner, CH_3NO_2, was itself highly polar (μ = 3.5D). The number of relaxing modes in this case exceeded the number of transitional modes. The electrostatic interaction energy binding of a collision complex is $\sim$ 40 kcal. The lifetime of the complex is longer ($\sim 4 \times 10^{-12}$) and the data were understood if the three lowest vibrational modes of CH_3NO_2 (< 650 cm^{-1}) relaxed along with the transitional modes.

Results for small nonpolar scatterers,[201] Ne, Ar, N_2, CO and CO_2, differed considerably. The collision cross sections for transfer of vibrational energy were smaller (1/15) than those for the polar gases. The long range forces are less important and an impulsive model of energy transfer was invoked. Large amounts of energy (5-35 kcal mole^{-1}) were transferred with evidence that CO_2 and CO were internally excited.

The scattering molecules, C_3H_8, $(CH_3)_2O$ and $C_2H_5(OH)$, were also studied.[200] The last two molecules have dipoles similar to those of CH_3OH and H_2O. Although the behavior for non-polar C_3H_8

is similar to that described previously for CO_2, the observations for the polar gases could not be explained as satisfactorily as for CH_3OH, etc., although some variant of the quasi-accommodation model still seems indicated.

We call attention to, but must forego discussion of a host of other results of a related nature from molecular beam studies. These include the reverse type of inelastic scattering experiments to that studied by Fisk et al., namely, vibrational excitation consequent on collision of translationally hot atoms with target molecules (usually diatomic), e.g.[202] $Ar^*+CsI \rightarrow Ar+CsI^*$, which, despite its ostensible direct bimolecular character, nevertheless displays behavior different from that of Landau-Teller and involves a quasi-bound complex, [ArCsI].[202] They also encompass the study of intramolecular vibrational relaxation in reactive, association complexes (ion-neutral or neutral-neutral), a phenomenon obviously related to aspects of the intermediate collision complex model for intermolecular vibrational energy transfer. These reactive complexes provide a continuum of behavior that includes those whose lifetimes may be much longer than the period of rotation and whose decomposition is "unimolecular" in spirit (e.g. $C_2H_4^+ + C_2H_4 \rightarrow [C_4H_8^+]^* \rightarrow C_3H_5^+ + CH_3$[203]), as well as those that are traditionally thought of as elusively transient, i.e. simple, direct bimolecular processes in nature (e.g.[204,205] $Cs+SF_6 \rightarrow [SF_6Cs] \rightarrow CsF+SF_5$), and which actually may display internal statistical randomization of energy in the reaction complex.

C. Photoactivation. Photodecomposition and Fluorescence Studies.

We consider now some related results, first from photochemical and then from photoemission systems. Much of the work has dealt with low vibrational energies or small molecule substrates and our coverage is abbreviated.

The analysis of collisional quenching in steady state photochemical reaction systems follows the same principles as in any externally activated system. Direct and unequivocal interpretation of collisional deactivation in photoactivated systems is possible only if the role of vibrational excitation in the subsequent reaction processes is clearly defined. This is the case if a statistical vibrational relaxation process for unimolecular degradation is involved in the reaction of the excited electronic state; or if internal conversion to a highly vibrationally excited level of the ground electronic state precedes decomposition.

Srinivasan[206] studied the vibrational deactivation of electronically excited cyclopentanone (3130 Å) in the presence of a number of inert gases. On the assumption that the vibrational manifold of the first excited singlet state are the initial states of interest, the following relative efficiencies (pressure basis) were found: Ar, 0.21; H_2, 0.25; CO_2, 0.26; CH_4, 0.36; c-C_3H_6, 0.55; c-C_4H_8, 0.67.

G. B. Porter and co-workers made a quantitative analysis of the relationships for vibrational deactivation efficiencies in photochemical systems. The gas phase decomposition of ketene[207] from the excited singlet state competes with collisional deactivation by ground state molecules. The latter was interpreted to follow strong collision behavior and to go by a

vibrational cascade with an estimated downstep $\geq$ 6 kcal mole^{-1}. The decomposition of perfluoroacetone was also studied.[208,209] Again, a competition exists between the vibrational deactivation and the decomposition of a vibrationally and electronically excited singlet state. Strong collision behavior, ostensibly represented by the linearity of a plot of inverse quantum yield, ϕ^{-1}, *vs* concentration of bath (ground state substrate) molecules, was deduced. It must be emphasized, however, that this method is comparatively insensitive. The deviation from linearity involves a difference between two quantities of comparable magnitude – the total light energy absorbed and the total amount of equivalent decomposition. Techniques or systems that provide a direct measure of the collisional stabilization of the excited species are intrinsically more powerful in the sensitive low-pressure region where the decomposition is approaching 100%. In the particular case of perfluoroacetone, mechanistic uncertainties may also intervene. Kutschke and co-workers[210,211] concluded that emission from the higher vibrational levels of the excited singlet state invalidates the significance of the ϕ^{-1} *vs* Conc. plot used by Porter, and others,[210] as a diagnostic of collisional behavior. A modified treatment led them to the contrary conclusion-that a weak collisional vibrational cascade occurs.

Halpern and Ware[212] studied the fluorescence decay of hexafluoroacetone excited at several wavelengths between 2977 and 3577 Å over a wide pressure range, 0.1-700 torr. They used a time-correlated photon counting technique rather than the steady state method. They concluded that intersystem crossing occurs and that a vibrational cascade of the excited singlet is supported.

Collisional deactivation in photolysis of azoethane at several excitation wavelengths around 3600 Å and at temperatures from

-37° – 20°C was analysed by Worsham and Rice.[213] The data bear interpretation as supporting strong collisional behavior by the ground state molecule at all energies of excitation.

Data on perfluoromethane photolysis[214] at 3600 Å was analysed in the manner of Porter and co-workers.[208] Perfluoroethane and the substrate were equally effective deactivators but possible mechanistic complications and obscurities frustrated quantitative interpretation. A similar difficulty was encountered in the 2-pentanone photolysis system.[215]

Thomas and Steel[216] described a very novel photoactivation – chemical activation system in which the vibrationally excited species is not the original substrate. The reactions were:

2,3-diazabicyclo[2.2.1]heptene-2(I)

$$\xrightarrow{h\nu} I^{*} \longrightarrow \text{bicyclo[2.1.0]pentane}^{*}(II^{*}) + N_2$$

$$II^{*} \longrightarrow \text{cyclopentene}^{*}(III^{*})$$

$$\longrightarrow 1,4\text{-pentadiene(IV)}$$

$$III^{*} \longrightarrow \text{cyclopentadiene(V)} + H_2$$

The collisional deactivation of vibrationally excited II^{*} and III^{*} (excited to average levels of 76 and 104 kcal mole^{-1}, respectively) competes with decomposition. The following relative efficiencies were measured:

	Ar	CO_2	C_3H_6	C_8H_{18}	I
II	0.080	0.19	0.57	1.10	(1.00)
III	0.17	0.26	0.38	0.87	(1.00)

Quantitative energy transfer amounts were not found.

The few studies already described illustrate a general feature of these systems. The required knowledge of the positions and relations of the singlet and triplet excited state manifolds, and the attendant difficulties in mechanistic possibilities and

interpretations can place severe restraints on quantitative and qualitative energy transfer interpretations in conventional photochemical systems. More favorable circumstances are offered by the study of systems which undergo specific state excitation – usually laser induced – although usually feasible only for simple substrate molecules. An elegant technique of photoactivation, that leads, in principle, to simpler interpretations, utilizes the process of internal conversion to produce highly vibrationally excited molecules in their ground electronic states. Ideally, this method permits the preparation of monoenergetic species of variable energy. However, for most successful utilization it cannot escape the requirement of a knowledge of the intersystem crossing and internal conversion mechanisms and/or of a diagnostic chemistry that permits discrimination of the amounts of decomposition and stabilization that arise from the excited ground electronic state.

An early study[217] of the collisional deactivation of internally converted species represented a bold attempt to test the upper limits of $\langle\Delta E\rangle$. The reactions of internally converted 1,3-butadiene and 1,3,5-cycloheptatriene, excited to vibrational levels as high as 115 kcal mole^{-1}, were inhibited by increasing pressures of the bath gases, cyclobutane and cyclobutene. These latter molecules have thresholds for reaction at approximately 64 and 34 kcal mole^{-1}, respectively. No evidence for their induced decomposition was found.

Lee and Lee[218] studied the collisional deactivation of internally converted cyclobutanone excited to 93 kcal mole^{-1}. Decomposition to ethylene plus ketene competes with collisional stabilization.

Quantitative energy transfer interpretations were not made, however, but relative efficiencies of bath gases, β, were as follows: C_3H_6, (1.00); He, 0.06; Ne, 0.13; Ar, 0.50; Kr, 0.48; Xe, 0.45; D_2, 0.11; O_2, 0.12; N_2, 0.45; C_3H_8, 0.8. A correlation of β with the Lennard-Jones constant ϵ, gave general concordance but with marked negative deviations for the monatomics. Comparison with the plot of Fig 14 is of interest, as well as the related references and discussion in Section IIIF.

A later study[219] of vibrational deactivation of the initial excited singlet state of cyclobutanone clarified some errors of interpretation of the earlier work and illustrated the refinement that is possible (e.g., dependence of β on the level of rotational excitation and on the total energy level), in principle, although not attained in this work. In another study,[220] $\langle\Delta E\rangle$ for C_3H_6 bath gas was measured at vibrational excitation energies of 93 and 115 kcal mole^{-1}. Values of 3 kcal and 6 kcal mole^{-1}, respectively, were found on a stepladder model although $\Delta\langle\Delta E\rangle$ is obviously so large as to be unreliable; the basis of measurement of $\langle\Delta E\rangle$, unfortunately, was fit of the observed rate of decomposition of cyclobutanone to the absolute RRKM calculated value of k_E – a method whose defects were described in Section IIIA.

The quantitative study of energy transfer in the cycloheptatriene system was taken up again by Thrush and co-workers.[221,222] Internally converted cycloheptatriene isomerizes to toluene with an energy threshold of $\sim$ 50 kcal mole^{-1}. These workers measured energy transfer amounts by various bath gases, as calculated on a stepladder model. Corrected calculations have been compared with results in chemical activation systems.[223] Measurements in this

system at 2600 Å were further extended by Luu and Troe [106] who studied some 43 bath gases and correlated the relative efficiencies with N, the number of atoms in the bath molecule. The absolute rate method of comparison was used by these workers for the determination of energy transfer amounts and the errors involved, and their correction, in part, have been described in ref 108.

In a later paper,[224] Luu and Troe extended their system to the much-needed temperature dependence of efficiency. They worked in the range from 293°-673°K for a number of gases including He, N_2, CO, CO_2, CH_4, C_3H_8, C_6H_{14}, C_8H_{18}, CF_4, C_3F_8, and, most extensively, Ar. The variation of $\langle\Delta E\rangle_T$ with temperature was very weak and the sign of the dependence varied both positively and negatively.

To summarize, the internal conversion method is one of great potential. Since it can involve reaction from three electronic states, it is still intrinsically complex with regard to interpretation of the meaning of product yields with pressure, and several pre-conditions must be established and met for its optimal utilization.

Preceding much of the photo-decomposition work just described was an early series of papers by several workers on the collisional enhancement of fluorescence from the electronically excited singlet state of complex aromatic molecules. Neporent[225] suggested in 1950 that this phenomenon could be used to study vibrational energy transfer. This work led to some of the earliest useful information of a qualitative and quantitative nature on the vibrational deactivation of polyatomic molecules. With use of a steady state method, a number of species including aniline, β-napthylamine and several

diaminophthalimides were investigated by this author and co-workers in a series of papers.[225-227] The vibrational excitation of the excited singlet state could be varied by changing the excitation wavelength and extended from 5 - 30 kcal $mole^{-1}$, although not uniformly so. A range of a dozen bath molecules from He to complex hydrocarbons was examined and the collision efficiency increased markedly with energy. The importance of the attractive nature of the collisional interaction was stressed by Neporent.

Other workers[228] adopted this technique, adding more work on β-napthylamine,[148b,229,230] perylene[231] and perfluoroacetone.[232]

Some quantitative reinterpretation of the data of Neporent as well as a modest amount of new data in the β-napthylamine system was given by Boudart and Dubois.[229] However, their calculations of $\langle\Delta E\rangle$ suffered from lack of knowledge of the energetics of decomposition from the excited state and from some error in the model used, notably neglect of up-transitions. Nonetheless, the values of $\langle\Delta E\rangle$ so estimated agree well in magnitude with those found in chemical activation studies. Stevens[148b] made some penetrating deductions regarding the physical nature of the transfer process involved in these systems. These were corroborated in the later quantitative treatment of the thermal isocyanide system.[148a]

An early theoretical treatment of transients in fluorescence spectra was given by Wilson.[233] In later work, phase sensitive methods were introduced.[172b,212] We consider next some recent technical innovations of related interest.

Developments in laser technology and high speed infrared detectors have continued to open new techniques for obtaining information on vibrational energy transfer. Steinfeld[234a] has recently reviewed these techniques. Applications have tended to concentrate on lower vibrational levels of small molecules, principally diatomics and triatomics, but have not been limited to these. Laser-excited infrared fluorescence and other emission studies have been used to provide cross-section for diatomics and triatomics; while resonance fluorescence techniques provide unique information on both the initial and final state of the relaxation process. Emission intensities and delay times, as measured by phase shift (or lag) methods, have also provided information on quenching cross sections. Double Resonance methods – perturbing an energy level by intense pumping and monitoring the relaxation at another frequency – have provided both rotational and vibrational relaxation times for a range of species from diatomic to complex molecules like propylene oxide.[234b] A brief description of a few of the systems and methods reported in the literature will now be presented.

Steinfeld and co-workers[235,236] have used the infrared double resonance technique to obtain the temperature dependent near-resonant vibration-rotation energy transfer for $BCl_3(\nu_4)$ and HCl ($v = 0$). The measured probabilities, which show an inverse temperature dependence between 220 and 340°K, suggest the importance of long range attractive forces. The intramolecular V-V relaxation of $^{11}BCl_3$ and $^{10}BCl_3$ followed by V-T relaxation for a series of 14 deactivators was also reported.[236] Infrared-microwave double resonance techniques were also used by Steinfeld[237]

to estimate the rotational energy transfer in $^{14}NH_3$.

Laser-induced infrared fluorescence studies have provided relaxation times for N_2O, HCl, CH_4, etc.[234a] The relaxation of excited $CH_4(\nu_3)$ into other modes of CH_4 (VV transfer) and into translation with various deactivators has been reported.[238,239] Similar studies have been made for CO_2.[240] The reported cross-sections[241] for the transfer of vibrational energy from HCl are: noble gases, 10^{-5} Å^2: diatomics, 10^{-4}-10^{-1} Å^2; and CH_4, 0.4 Å^2. In general, it is observed that for polyatomics energized in a specific mode, relaxation first occurs by rapid collision-induced intramolecular V-V which is then followed by slower V-T processes from the lower v levels.

Resonance fluorescence spectrophotometry has been used for I_2,[144,242] Li_2[243] and H_2.[244] Steinfeld,et al have provided extensive data on energy transfer for electronically excited I_2 ($B^3\Pi_{0^+}$) (v'' = 15, 25, 43 and 50); $\Delta v''$ = +5 to -8 have been observed for all collision partners while ΔJ up to $\pm$ 12 have been obtained. The energy transfer cross-section (larger than kinetic cross sections) increase with an increase in reduced mass and with an increase in initial vibration energy (v'') and then decrease as the dissociation energy is approached. This decrease in cross section has been interpreted as a direct collisional dissociation process. Large cross sections ($s^2 \sim 120$ Å^2) have been measured for quenching by iodine atoms. A long lived I_3 complex is probably involved; however, no vibrational relaxation was observed.

Laser induced fluorescence and shock tube techniques have been used to measure the temperature dependence of vibrational energy transfer from HF (v=1) and DF (v=1). The deactivation of DF by infrared active molecules[245] (i.e., with a dipole moment)

exhibits a negative temperature dependence, indicating that the collisional V-V energy transfer involves the attractive part of the potential, while homonuclear diatomics (D_2, N_2 and O_2) exhibit a positive temperature dependence which is appropriate for a short range repulsive interaction. The HF decay times for diatomics[245] were found to correlate with the energy discrepancy of the two vibrational frequencies. A linear relation was obtained when the log of the decay time was plotted as a function of the energy discrepancy. Two distinct families were found; homonuclear diatomics had a lower probability for deactivation than did heteronuclear diatomics.

The deactivation of H_2O by H_2O, He, Ar and N_2 has been observed by monitoring the infrared emission of the bending and stretching modes of H_2O between 1800° and 4100°K.[247] Intramolecular vibrational energy transfer was rapid as the decay of the two modes gave similar relaxation times. Due to the strong attractive interactions, H_2O was found to self-deactivate 100 times faster than either helium, argon, or nitrogen. The relaxation times for all four deactivators showed a Landau-Teller temperature dependence. The H_2O relaxation times, extrapolated to low temperature, agree with sound dispersion and absorption experiments.

The temperature dependence of V-V energy exchange between vibrationally excited CO and COS was determined by observing the quenching of the CO fluorescence between 195° and 370°C.[248] A slight inverse temperature dependence was noted. Model calculations indicated that both long range dipole-dipole interaction and orbiting collision were necessary for agreement with the experimental data.

Polanyi and co-workers[249] have extended the infrared chemiluminescent method to obtain information on the transfer of rotational energy (J=0-16, v=1, for HCl or HF) to translational energy as a function of collision energy; T-V transfer is insignificant for these experiments. At low collision energies (1 kcal mole^{-1}) a net transfer from high J into low J is observed, while at high collision energies ($\sim$ 10 kcal mole^{-1}) transfer from low J to high J occurs. T-R transfer is efficient (cross-sections similar to those for elastic processes) with $\Delta J \geq 1$; the shape of the transition probabilities are probably exponential and the average T-R energy transferred increases with collision energy.

The relaxation of HF (v=1 and v=2) by methane, ethane, propane, acetylene and ethylene has been measured by observing the decay of the rotational-vibrational emission in a fast flow system.[249] Approximately 250 collisions were necessary for deactivation for v=1 with the polyatomics, while 1000 collisions was necessary with H_2. This inefficiency of homonuclear diatomics has been observed in other systems. The deactivation rates for v=2 were 3.3 to 5 times faster than those observed for v=1.

Nachson and Coleman[170] have measured the probabilities for exchange between excited CO molecules:

$$CO(\ ) + CO(v) \xrightarrow{P_{v',v'-1}^{v,v+1}} CO(\ -1) + CO(v+1)$$

The excited CO was formed by a short electrical pulse followed by the reaction of oxygen atoms and CS. The decay of various CO emissions were monitored and $P_{v',v'-1}^{v,v+1}$ for r and v $\sim$ 10 was found to be greater than 0.3. This method could also be used for NO, HF, HCl and HBr.

The quenching of the infrared emission of CO has also been observed for various deactivators at 298°K by Smith and co-workers;[250] CO was formed by the reaction of O + CS → CO + S. $P_{v,v-1}$ was measured for $4 \leq v \leq 13$. For helium (the most inefficient of the deactivators), $P_{v,v-1}$ increased with v and was approximately 10^{-6} while OCS (the most efficient deactivator) had probabilities which decreased with v and were approximately 10^{-2}. All diatomic and polyatomic deactivators produced linear relations when the logarithm of the probability for energy transfer was plotted as a function of the energy discrepancy.

Recently Streit and JOhnston[251] have reported rate constants for the quenching of vibrationally excited OH ($4 \leq v \leq 9$). The quenching cross-sections, determined from overtone emission intensities, as a function of v went through a slight maximum at v=7.

The phase shift method has been used by Schlag and co-workers[172b,252] to measure the cross sections for vibrational energy transfer from electronically excited β-napthylamine. For propylene[23] as the deactivator, the cross section was found to be independent of vibrational energy and apparently only 10% of the normal gas kinetic cross section. This surprising result merits further examination. In a later study[172b] helium was found to be 3 times less efficient than propylene and independent of excitation energy. Argon was observed to have an efficiency slightly less than propylene.

Fluorescence lifetimes and intensity measurements for electronically excited NO_2 have been made as a function of excitation wavelength.[171] Using the phase shift method, the amount of energy lost per gas kinetic collision for ground state NO_2 was found to

be ≈ 1200 cm^{-1} (at least one vibration quantum) over the whole excitation region 12,500-25,000 cm^{-1} above the ground state. It appears that energy transfer cross sections for this system are comparable to gas kinetic and large amounts of energy are transferred per collision. Apparently NO_2 is behaving as a large molecule for energy transfer processes. Other deactivators would be helpful in confirming this interpretation.

D. High Temperature Systems

Most studies on the subject of this review have been carried out at low temperatures, usually below 500°K and, with only a few exceptions, below 500°C. The past decade has seen a great increase of interest in high temperature kinetic studies, mainly by the technique of shock waves. In view of the almost complete absence of information on appropriate high temperature values, shock tube workers have usually transferred lower temperature values of β, without change, to higher temperatures. If this drastic simplification is incorrect, it can obviously lead to serious errors or misinterpretation of data in some cases. On a more fundamental level, it is important to learn how $\langle \Delta E \rangle$ varies with temperature as a prerequisite for firm theoretical advances.

In this section we first discuss some pragmatic features of the theoretical analysis of high temperature data and then go on to the consideration of some experimental systems. Infinite dilution will be assumed throughout if dilution is not otherwise indicated.

An understanding of the behavior of k_{uni} with temperature, particularly at high temperatures, is needed for the interpretation of experimental data. Calculations using the RRKM model exhibit quasi-Arrhenius behavior, i.e., $k_{uni} = A(T)e^{-E_a/RT}$, where A(T), a weak function of temperature is frequently treated as constant. However, some experimental systems show non-Arrhenius behavior; the rate-constant at high temperature does not change as predicted by low temperature Arrhenius parameters. Aside from mechanistic features, this deviation can be attributed to two other known factors:

1) increase of reaction order with increase in temperature

ii) decrease of collision efficiency with increase in temperature.

The first factor can easily be calculated from the definition of reaction order ϕ,

$$\phi = 1 + \left.\frac{\partial \ln \frac{k_{uni}}{k_\infty}}{\partial \ln \omega}\right|_T$$

and the explicit expression for k_{uni}/k_∞,

$$\frac{k_{uni}}{k_\infty} = \frac{\int_{E_0}^{\infty} \frac{\omega}{\omega + k_E} k_E B_E dE}{\int_{E_0}^{\infty} k_E B_E dE} = \omega\left(\overline{\frac{1}{\omega + k_E}}\right) = \frac{\omega}{\left(\overline{\frac{1}{\omega + k_E}}\right)} .$$

Then,

$$\phi = 2 - \frac{\omega \int_{E_0}^{\infty} \left(\frac{k_E}{\omega + k_E}\right)^2 B_E dE}{\int_{E_0}^{\infty} \frac{k_E}{\omega + k_E} B_E dE} = 2 - \frac{\omega \left(\overline{\frac{1}{\omega + k_E}}\right)^2}{\left(\overline{\frac{1}{\omega + k_E}}\right)}$$

$$= 2 - \omega\left(\overline{\frac{1}{\omega + k_E}}\right) ;$$

and

$$\left.\frac{\partial\phi}{\partial T}\right|_{\omega} = -\frac{\omega}{RT^2}\left[\frac{\int_{E_0}^{\infty}\frac{Ek_E}{(\omega+k_E)^2}B_E dE}{\int_{E_0}^{\infty}\frac{k_E}{\omega+k_E}B_E dE} - \frac{\int_{E_0}^{\infty}\frac{k_E}{(\omega+k_E)^2}B_E dE\int_{E_0}^{\infty}\frac{Ek_E}{\omega+k_E}B_E dE}{\left(\int_{E_0}^{\infty}\frac{k_E}{\omega+k_E}B_E dE\right)^2}\right]$$

$$= -\frac{\omega}{RT^2}\left[\frac{\left(\overline{\frac{E}{(\omega+k_E)^2}}\right)}{\left(\overline{\frac{1}{\omega+k_E}}\right)} - \frac{\left(\overline{\frac{1}{\omega+k_E}}\right)^2\left(\overline{\frac{E}{\omega+k_E}}\right)}{\left(\left(\overline{\frac{1}{\omega+k_E}}\right)\right)^2}\right]$$

$$= -\frac{\omega}{RT^2}\left[\left(\overline{\overline{\frac{E}{\omega+k_E}}}\right) - \overline{\overline{E}}\left(\overline{\overline{\frac{1}{\omega+k_E}}}\right)\right];$$

where $\bar{x}$ and $\bar{\bar{x}}$ represent the average of x over the distribution functions $k_E B_E dE$ and $\frac{k_E}{\omega+k_E} B_E dE$, respectively.

In general, for a given collision frequency, the order increases as the temperature increases. In fact, for reactions ranging from the decomposition of CO_2 to the isomerizations of methyl isocyanide and cyclopropane, $\left.\frac{\partial\phi}{\partial T}\right|_{\omega}$ is $2 \pm 1 \times 10^{-4}$ for $1.2 < \phi < 1.8$ and $T < 4000°K$. An increase in ϕ will appear as a decrease in k_{uni}/k_∞ and thus k_{uni} will not increase as strongly as it would otherwise as the temperature increases. For the decomposition of CO_2, the difference between the high and low pressure Arrhenius activation energy ranges from 1 to 20 kcal mole^{-1} as the temperature increases from 500°K to 4000°K. For larger reactants the difference is increased. For example, the spread in activation energy for the isomerization of methyl isocyanide is 2 kcal mole^{-1} at 500°K and 34 kcal mole^{-1} at 4000°K. Analogously, for cyclopropane isomerization the range is 3 to 64 kcal mole^{-1} over the above temperature limits. Thus, for cyclopropane experiments performed in the high or low pressure limit (< 10 torr) at 500°K the activation energy will be ∿ 64 kcal mole^{-1} greater than for the same reaction carried out at 4000°K at a pressure of 0.1 torr (i.e., $\phi \sim 2$). These reaction order corrections to the activation energy can be large but are easily calculated for a specified activated complex.

We now continue and expand the discussion presented in Section IIID for the relations between E_a, T, E' and β in the helium-methyl isocyanide system. The change of collisional efficiency with temperature can be formulated but cannot be explicitly calculated without a specific model for energy transfer. To obtain k_{uni}^{wc}, $\bar{\beta}'_\omega(T)$ is a convenient representation of the collision efficiency,

$$\bar{\beta}'_\omega(T) = \frac{k_{uni}^{wc}(T)}{k_{uni}^{sc}(T)}, \quad \omega^{sc} = \omega^{wc},$$

where T is explicitly exhibited. It follows that

$$\frac{k_{uni}^{wc}(T_2)}{k_{uni}^{wc}(T_1)} = \frac{k_{uni}^{sc}(T_2)}{k_{uni}^{sc}(T_1)} \; e^{\int_{T_1}^{T_2}\frac{\partial \ln\bar{\beta}'}{\partial T}dT}$$

and any deviation with temperature of weak collider behavior from strong collider behavior depends only on the exponential factor. From the calculations of TR, $\bar{\beta}'_\omega(T)$ was found to be dependent on the dimensionless variable E', on falloff, and on dilution. Both E' and ϕ depend on temperature and at infinite

dilution the factors which determine the temperature dependence of $\bar{\beta}'_\omega(T)$ are a) ϕ, b) $\langle E^+ \rangle$ and c) $\langle \Delta E \rangle$ for down transitions. Then

$$\frac{d\ln\bar{\beta}'_\omega(T)}{dT} = \left.\frac{\partial\ln\bar{\beta}'_\omega}{\partial\phi}\right|_{E'} \frac{d\phi}{dT} + \left.\frac{\partial\ln\bar{\beta}'_\omega}{\partial\ln\langle E^+\rangle}\right|_{\langle\Delta E\rangle,\phi} \frac{d\ln\langle E^+\rangle}{dT} + \left.\frac{\partial\ln\bar{\beta}'_\omega}{\partial\ln\langle\Delta E\rangle}\right|_{\langle E^+\rangle,\phi} \frac{d\ln\langle\Delta E\rangle}{dT}$$

The first two terms are negative while the last term takes the sign of $\frac{d\ln\langle\Delta E\rangle}{dT}$, which is not known, although from some physical arguments may also be expected to be negative. Values for these derivatives at various values of ϕ and E' can be calculated from the quasi-universal curves of TR; a few values derived from Figures 7 and 8 are tabulated in Tables XI and XII. The above expression can be written symbolically as

$$\frac{d\ln\beta'_\omega(T)}{dT} = \Phi + EA + ED$$

For a reactant such as CH_3CN, at T=500°K and $\langle\Delta E\rangle$ = 1.1 kcal mole^{-1}, i.e., (E=1) an illustrative set of numerical relations is:

ϕ	Φ	EA	ED
1.2:	-1×10^{-3}	-1.3×10^{-3}	$0.7 \frac{\partial\ln\langle\Delta E\rangle}{\partial T}$
1.8:	-0.2×10^{-3}	-2.6×10^{-3}	$1.3 \frac{\partial\ln\langle\Delta E\rangle}{\partial T}$

Transition probabilities for vibrational energy transfer are not known a priori, but some estimates of the value of ED can be made by considering two simple hypothetical transition probability models: 1) step ladder and ii) statistical (classical) redistribution in the collision complex.

For a simple step ladder (harmonic oscillator), $\langle\Delta E\rangle$ does not change with temperature

$$(\langle\Delta E\rangle = \frac{\sum_{j<i} P_{ji}\Delta E_{ij}}{\sum_{j<i} P_{ji}} = \frac{P_{ji}\Delta E_{ij}}{P_{ji}} = \Delta E_{ij}$$

and ED is zero.

For the simple statistical model, a reactant (number of vibration modes = n_R) with assumed energy of $E_0 + RT$ collides with a deactivator with internal energy $n_I RT$. Then, if the energy is statistically distributed among the $n_R + n_I$ oscillators, the average down step is

$$\langle\Delta E\rangle = \frac{n_I}{n_R+n_I}\,[E_0+RT(1-n_R)]$$

which for $n_I \ll n_R$ reduces to

$$\langle\Delta E\rangle = \frac{n_I}{n_R}\,(E_0-n_R RT).$$

Also,

$$\frac{d\ln\langle\Delta E\rangle}{dT} = \frac{-n_R R}{E_0-n_R RT},$$

$$= \frac{-n_R R}{E_0}, \quad \text{for low T;}$$

and

$$= \frac{1}{T}, \quad \text{for high T.}$$

The ED correction, assuming statistical equilibrium for the methyl isocyanide system, is thus 0.2×10^{-3} and 0.4×10^{-4} for ϕ = 1.2 and 1.8, respectively. Hence, the ED term will be ignored in further discussions. At high pressure where $\phi \sim 1$, $\Phi > E$ and

$\frac{\bar{\beta}'_\omega(T_2)}{\bar{\beta}_\omega(T_1)} = e^{\phi\Delta T}$; while for low pressure $\phi \to 2$ and $\frac{\bar{\beta}'_\omega(T_2)}{\bar{\beta}'_\omega(T_1)} = e^{ER\Delta T}$.

For this particular case when T is doubled to 1000°K, the corrections are approximately $e^{1.15}$ for $\phi = 1.2$ and $e^{1.14}$ for $\phi = 1.8$. In general, the correction due to Φ is maximal as $\phi \to 1$, but the EA and ED terms are at their minimum; while as $\phi \to 2$, the Φ term is minimal and ED and EA are maximal. The maximum correction is when $E' < 0.3$ in which case both $\frac{\partial \ln \bar{\beta}'_\omega}{\partial \ln \langle \Delta E \rangle}$ and $\frac{\partial \ln \bar{\beta}'_\omega}{\partial \ln \langle E^+ \rangle}$ are equal to 2.0, or

$$\frac{\bar{\beta}'_\omega(T_2)}{\bar{\beta}'_\omega(T_1)} = e^{2.0 \frac{\partial \ln \langle E^+ \rangle}{\partial T} \Delta T}$$

These corrections will be evaluated for a few experimental systems in the next section. For classical statistical systems, $\frac{\partial \ln \langle E^+ \rangle}{dT} = \frac{1}{T}$, and $\frac{d \ln \langle E^+ \rangle}{d \ln T} = 1$. However, for real molecules which obey quantum statistics these derivatives are greater than their classical analog, as is shown in Table XII. Both Tardy[136] and Bhattarcharjee and Forst[253] have shown (assuming that $\langle \Delta E \rangle$ is independent of temperature) that for small molecules (3 or 4 atoms) with $\phi \to 2$, the Arrhenius activation energy for a weak collider is approximately 2RT less than that for a strong collider. For larger molecules and/or high temperatures, the correction is $2RT \frac{\partial \ln \langle E^+ \rangle}{\partial \ln T}$. Quantitatively the difference in activation energy for a weak and strong collider is

$$\Delta E_{a\omega}(T) = E^{sc}_{a\omega}(T) - E^{wc}_{a\omega}(T) = RT^2 \frac{\partial \ln \beta}{\partial T}$$

when

$$\phi \to 2 \text{ and } E' < 0.3, \quad \Delta E_{a\omega}(T) = 2RT^2 \left[\frac{\partial \ln \langle E^+ \rangle}{\partial T} + \frac{\partial \ln \langle \Delta E \rangle}{\partial T} \right]$$

and

$$\text{at } 1000°K, \quad \frac{\partial \ln \langle E^+ \rangle}{\partial T} \sim 0.15 \times 10^{-2}, \quad \text{so } \Delta E_{a\omega}(T) \geq 6 \text{ kcal mole}^{-1}$$

The remainder of this subsection will be concerned with the examination of some high temperature experimental systems.

Most experiments involving unimolecular reactions at high temperatures are carried out in a shock tube where the reactant is diluted with an inert gas such as helium, argon or krypton. As a result weak collider effects are expected to be important. Unfortunately, these effects cannot be evaluated in an "absolute" manner as is done for low temperatures where collision efficiencies for various colliders including the substrate have been measured. Two methods of evaluating the effect of weak collisions are available: i) First, one can calculate an efficiency by assuming the known behavior of the rate constant for a strong collider which is evaluated from low temperature parameters. The deduced high temperature efficiency ($\beta_{calc} = k^{wc}_{expt}/k^{sc}_{calc}$) can then be compared to the known efficiency at low temperature. ii) First obtain the activation energy $E^{wc}_{a\omega}(T_1)$ for a particular weak collider at ω_1, T_1 (either by direct measurement or by calculation using the procedure outlined in the previous section with an assumed $\langle \Delta E \rangle$). This activation energy can then be extrapolated to a different set of experimental conditions, ω_2, T_2 , by the above method. This calculated value $E^{wc}_{a\omega_2}(T_2)$ can then be compared to the measured value, $E^{meas}_{a\omega_2}(T_2)$. The difference $E^{meas}_{a\omega_2}(T_2) - E^{wc}_{a\omega_2}(T_2)$ is a measure of $\frac{\partial \ln \langle \Delta E \rangle}{\partial T}$.

The first method has been used by Troe[103] in interpreting the decomposition of a variety of triatomic and small polyatomic reactants (N_2O, CO_2, COS, CS_2, NO_2, BrNO, O_3, HNO_3, C_2N_2, etc.). By finding the best fit values of β_0 and E_0 he concludes that β_0 behaves as $T^{-x}(\frac{1}{2} \leq x \leq 1)$ and $\beta_0 = 10^{-1.5 \pm 0.5}$ for $1000 \leq T \leq 3000$. This method supports the idea that energy transfer is inefficient at high temperature but suffers from the fact that k^{sc} is highly dependent on E_0. As mentioned before, when some experimental findings are compared to strong collider calculations, as in some photochemical activation systems, large errors may be involved.

The second method depends to some extent on calculational results but more importantly any systematic error in the data which is independent of temperature will not appear in E_a. However, this method depends on obtaining activation energies with a standard deviation smaller than 0.1 RT.

A few reactions which are representative of shock tube experiments will now be considered.

Triatomics. The decomposition of ozone has been studied by Center and Kung[254] behind incident shock waves between approximately 1000 and 3000°K. At 3000°K, the rate constant was a factor of 2-3 smaller than predicted by Arrhenius parameters in the 200-900°K temperature region. RRKM theory in its low pressure limit was consistent with the experimental data. The calculation was performed by taking β_0 for argon as independent of temperature and equal to 0.25 as suggested by Johnston.[255] Thus, either method suggests that β_0 is independent of temperature. Any differences in the rates due to dilution (1%, 2%, 5%) were masked by experimental error. Previously, Troe and Quack[256] had reported $\beta_0 = 0.01$

at 900°K. Michael[257] also obtained the rate constant for decomposition from 988 to 1144°K. He concluded that krypton has an efficiency of 0.053 between 1000-1060°K while that of argon is 0.066. Above 1060°K the rate constant showed a negative deviation from RRKM behavior; in fact, at 1400°K, the rate constant was too small by a factor of five. Michael attributes this deviation to the population of high vibrational quantum states as rate determining for the reaction. This data and explanation do in fact agree with the predicted weak collision behavior mentioned earlier; a factor of five in the rate constant corresponds to an activation energy difference of 1.6 RT. This particular reaction may not be representative of other triatomics since $E_0 = 22$ kcal mole^{-1} and low energy transition probabilities might be required.

The laser schlieren technique has been used by Kiefer[258] to measure the dissociation rate constant of SO_2 between 2900 and 5200°K in a shock tube with krypton as the diluent. His measured activation energy was reported as 112 ± 4 kcal mole^{-1}. An Arrhenius plot exhibits slight curvature; the rate at 5500°K was less than a factor of 1.4 smaller than that for the low temperature extrapolation while SO_2 gave a calculated rate constant 3.4 larger than that for Kr but with the same E_a. On the other hand, Olschewski, Troe and Wagner[259] (OTW) monitored the absorption of both SO_2 and SO and found a strong dependence of k on the mole fraction of SO_2, indicating the reaction may be complex; in fact, E_a for a 30% SO_2 argon mix was 70 kcal mole^{-1} for $3000 \leq T \leq 4500$°K while a 3% SO_2 mix was 110 kcal mole^{-1} for $4500 \leq T \leq 7500$°K. If these values are taken at face value, then SO_2 would be a weaker collider than Ar. The activation energy determined by Kiefer is in accord with an RRK model

with s = 4. The Kiefer's data indicate that β_0 is independent of temperature, while Troe has concluded $\beta_0 = 0.01$ at 3000°K from the data of ref. 259.

Dean[260] has recently reported the dissociation of CO_2 by monitoring the infrared emission from dilute CO_2/Ar mixtures for temperatures between 3700-5500°K. The effect of hydrocarbon impurities, which has plagued previous reports, were minimized and calibrated at known impurity levels. The E_a was 84.7 ≠ 2 kcal mole^{-1} for this temperature region; as in the SO_2 system, the dissociation energy for this reaction is approximately 130 kcal mole^{-1}. RRKM calculations predict the activation energy to be 112 kcal mole^{-1} in this temperature region. Hence, the data suggests a weak collider correction would be appropriate; such a correction will bring E_a down to 92 kcal mole^{-1} since $\frac{\partial \ln \beta_0(T)}{\partial \ln \langle E^+ \rangle} = 2$. This is in fair agreement with the observed value. Troe[1] has interpreted other shock tube data using method 1 and determined that $\beta_0(T) \approx T^{-\frac{1}{2}}$. However, further inspection of the data suggest that $\beta_0(T) \simeq T^{-2}$ is also acceptable within the range of experimental error.

Troe[103] has also analyzed the published data for the dissociation of N_2O and concluded that $\beta_0(T) = 10^{-1.5}$ at 2000 with $\beta_0(T) \geq 1/T^x$ $0.5 \leq x \leq 1.0$. Unfortunately, as in other shock tube systems, the data is not of sufficient accuracy to determine the temperature dependence of $\beta_0(T)$. One can, however, conclude that a weak collider correction is necessary at high temperatures.

Polyatomics. Some unimolecular dissociations and isomerizations in the fall off region which have been studied in shock tubes have recently been reviewed by Rabinovitch and co-workers.[261] As stated above, rate constants for reaction at pressures less than the high pressure limit need to be corrected for both fall off and weak

collision effects. If these corrections are not made, erroneous conclusions can result. Bott and Jacobs[262] have proposed that SF_6 decomposition represents an example of the breakdown of the intramolecular energy randomization postulate of RRK-RRKM theory. This conclusion was based on shock tube studies ($1650 \leq T \leq 2050$°K) in which the unimolecular fall off was shifted to an ostensibly anomalous high pressures due allegedly to the fact that not all internal modes were active and with use of the classical RRK model with s = 6 and $\beta_0 = 0.25$, log A = 12.95 and E_a = 75.9 kcal mole^{-1}. Smaller values of β_0 were rejected since they led to higher values of s. The frequency factor, log A = 12.95, appears low for a simple decomposition reaction which breaks the S-F bond. Moreover, the value os s = 6 is unreasonably low at these high temperatures for a molecule having a total of fifteen vibrational degrees of freedom. The fall off data may be fitted reasonably well by an RRKM model with use of a β_0 value of 0.03; in this case, the high pressure rate is summarized as log k = 14.11 - 86.0/2.3 RT. Rabinovitch et al[261] interpreted the data of this study, if taken at face value, as constituting evidence in favor of effectively lower values of β_0 for argon at these elevated temperatures than have usually been assumed or measured at lower temperatures.

A closely parallel situation exists for the decomposition of $SF_4 \rightarrow SF_3 + F$ at temperatures from 1650°-1950°.[263]

The thermal isomerization of cyclopropane,[264,265a] cyclobutane[264,265a] and ethane[266] have been carried out using a single pulse shock tube between 1060-1870°K. Two independent studies have revealed that above 1300°K the activation energy is substantially decreased. Previous explanations have included a proposal

that an intermediate reaction of low excitation energy was involved, and that a breakdown of unimolecular reaction theory occurs.[15b]

Rabinovitch and co-workers[261] have calculated values of $\beta_0(T)$ and $\bar{\beta}_\omega(T)$ for cyclopropane. If the value of $\beta_0(T)$ is 0.1 at 750°K, then the value declines to around 0.01 at higher temperatures, and similarly for cyclobutane. The application of these revised values of $\bar{\beta}_\omega(T)$ to the data of ref. 265a) results in a distinct reduction of the curvature, although it by no means eliminates the phenomenon. However, studies using optical detection[267-269] technique did not reveal the curvature and there may be experimental problems mixed in with these phenomenonological characteristics.

The shock tube studies on the isomerization of cis-butene[270] at 1200°K have also produced confusing results and suggests a marked decline of $\bar{\beta}_\omega(T)$ with temperature. It appears that the correct understanding and estimation of $\bar{\beta}_\omega(T)$ at high temperatures will also be necessary to interpret this system.

The isomerization of cycloheptatriene to toluene has been studied both in static and stirred reactors[271,272] between 600-700°K and in a shock tube between 900-1300°K.[273] The rate constants behave in a quasi-Arrhenius manner. This is indicative of a molecule in or near the high pressure limit where neither fall off nor energy transfer corrections are significant.

From the shock tube examples cited above, it becomes clear that the observed rate constants and their temperature variation depends on fall off and energy transfer probabilities. The data seem to lack consistency. In any case, it is evident that one of the important areas for future work is the study of energy transfer at higher

temperatures characteristic of the shock work: there is almost a complete dearth of reliable quantitiative data in this region. For this purpose it is desirable to devise and utilize other techniques, as well, so as to eliminate the existing, almost exclusive dependence on the shock tube method. Several alternative possibilities have been described in recent years.

Very low pressure pyrolysis (VLPP) has also provided higher temperature data on energy transfer.[274] In essence, the pressure dependence of the rate constant is determined at flows such that the number of gas-gas collisions are comparable to gas-wall collisions. The total collision rate which is fitted to the expression for k_{uni} is calculated as $\omega_{tot} = \beta_w\omega_w + \beta_g\omega_g$, where ω_w and ω_g are the collision rates for gas-wall and gas-gas collisions, respectively, and the β's are the corresponding efficiencies. β_w is assumed to be unity; however, this assumption is untested at high temperatures. β_g may then be calculated by fitting rate constants that are determined for various values of k/k_∞. For cyclobutane pyrolysis[275] ($k/k_\infty \sim 0.08$) β_g fell between 0.1 and 0.2 for both SF_6 and cyclobutane. This appears to be somewhat low for cyclobutane. Recently, the VLPP technique has been used to study the isomerization of cycloheptatriene[276] in the range of 819 to 902°K and $k/k_\infty \sim 0.1$. The collisional efficiency of the substrate cycloheptatriene was found to be anomalously low, less than 0.05, while efficiencies for other gases was inconsistent: hexane was 0.15 and octane $\sim$ 0.05. These results are contrary to those of Troe's photochemical studies (vide supra) at higher energies. Thus far, VLPP has provided only qualitative or semi-quantitative energy transfer information.

Shaub and Bauer[277] have shown that some of the complications and difficulties of interpretation involved in the reactions of laser pumped complex molecules may be avoided by an alternative technique that can provide a Boltzmann distribution of complex molecules at high temperature. The method takes advantage of the large infrared absorption cross section of a few stable molecular bath species and their relatively fast V-T relaxation. By use of large laser fluxes high bath temperatures may be achieved with millisecond rise times. Reactant molecules, imbedded in the bath gas, are thus effectively heated and may react in homogeneous fashion over a useful time up to 10 sec. Thus, laser-powered homogeneous pyrolysis (LPHP) can provide a technique complementary to shock tubes. In actual applications, SF_6 bath gas was heated by absorption of 10.6 μ CO_2 radiation, and various reactants such as cyclopropane, butene-2 and dihaloethylenes were studied at temperatures of 700-1000°K. Comparison reactions may be used as standards. While LPHP is still under improvement and exploration, it should prove valuable for many purposes, including those under review.

Still another thermal technique is termed "competitive" collisional activation spectroscopy (CCAS). This method was originally suggested by Chow and Wilson[278] and was first applied by Waage and Rabinovitch.[279] The aim of CCAS is twofold: on the one hand, to circumvent the need for a knowledge of collision-cross sections for the study of vibrational energy transfer in thermally activated systems; on the other, to eliminate experimental error associated with absolute rate measurements by substitution of the measurement of product rates produced via concurrent

competitive channels. Thermal flow systems may be extended in their range of accurate usefulness down to reaction times of the order of 0.01-0.1 sec.

Thus, in the low pressure limit, the relative amounts of products produced provides a direct measure of relative amounts of excitation of substrate from levels below the lowest reaction threshold to the regions above. The several reaction thresholds index the energy levels, while the several reaction processes act as transducers of the populations of the various energy intervals so indexed. Quantitative information regarding the form of the collisional transition probability distribution can be obtained with use of a stochastic model; the precision increases with the number of competitive channels.

The first system studied[279] was the competitive cis-trans geometrical isomerization and structural isomerization of trans-cyclopropane-d_2. This is not a favorable case for reasons described by the authors, although qualitative demonstration of the weak collision character of He bath gas was made. More recently, Klein, Jung and Rabinovitch[280] have studied the competitive processes of H and D atom migration in the structural isomerization of 1,1,-cyclopropane-d_2. The quasi-strong collider character of the parent was demonstrated at 770°K and $\langle \Delta E \rangle$ was evaluated for He bath gas as $\sim$ 300 cm^{-1}, on both an SL and EXP model. A marked decrease in efficiency of the parent becomes evident when the temperature is raised to $\sim$ 1000°K. Extension to the three-channel 1,1-d_2,2-t-cyclopropane system is being made.

Finally, one of the last virtually unexplored areas of study of unimolecular reactions is the transient time region in the

heating interval before the establishment of the steady state corresponding to the final temperature. Although much studied in the thermal dissociation of diatomics, mean first passage times have not been measured for polyatomics, apart from the trivial case of constant temperature systems. The only significant results reported so far are by Dove and co-workers[134b] in a shock tube study of N_2O decomposition at temperatures 2160°-3600°K. An "incubation" period of 4 to 7 vibrational relaxation periods preceded the establishment of steady state dissociation. All four vibrational modes relax together.

Still another technique – the diffusion cloud method – has recently been proposed for the study of energy transfer and of transients in the low pressure region of unimolecular reaction at higher temperatures.[281]

Preliminary results have also been obtained with an improved VLPP method for the study of the transient wall-activated region.[282]

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Appendix I: Some $\langle\Delta E\rangle$ and $\beta_0(\infty)$ Relationships

A comparison in the low pressure region between Troe's expression for the collision efficiency (Eq. I.1) and TR's

$$\beta_0^{T}(\infty) = \frac{\alpha^2}{(\alpha+RT)^2}\,\frac{1}{I^T} = \frac{\langle\Delta E\rangle_T}{\alpha+RT}\,\frac{1}{I^T} \qquad (I.1)$$

expression (Eq. I.2) for weak colliders ($\beta_0(\infty) \leq 0.03$)(or for

$$\beta_0^{TR}(\infty) = k'\,\frac{\langle\Delta E\rangle_{TR}^2}{\langle E^+\rangle^2} = k'\frac{\langle\Delta E\rangle_{TR}^2}{(RT)^2}\,\frac{1}{(E^+/RT)^2} = \frac{\langle\Delta E\rangle_{TR}^2}{(RT)^2}\cdot\frac{1}{I^{TR}} \qquad (I.2)$$

[k' is a constant close to unity (0.86 ± 0.05, depending on the model)] exponential distribution of down jumps, more generally, so β – Troe's energy parameter, and not the efficiency symbol! – is zero), can easily be made once the relation between $\langle\Delta E\rangle_T$ and $\langle\Delta E\rangle_{TR}$ is established. Starting at initial energy E, these quantities are defined as,

$$\langle\Delta E\rangle_T = \frac{-\int_0^\infty (E'-E)P(E',E)dE'}{\int_0^\infty P(E',E)dE'} = \alpha^2/(\alpha+RT), \qquad (I.3)$$

and

$$\langle\Delta E\rangle_{TR} = \frac{-\int_0^E (E'-E)P(E',E)dE'}{\int_0^E P(E',E)dE'} = \alpha \quad ; \qquad (I.4)$$

where E and E' are the initial and final energies of reactant (i.e., the energy before and after collision); $\langle\Delta E\rangle_T$ is the average energy transferred per collision; and $\langle\Delta E\rangle_{TR}$ (or α) is the average energy removed per "down" collision. Thus, $\langle\Delta E\rangle_T = \langle\Delta E\rangle_{TR}^2/(\langle\Delta E\rangle_{TR}+RT)$, which for steps larger than RT (i.e.,

Appendix (contd)

$\alpha = \langle\Delta E\rangle_{TR} >> RT$) reduces to $\langle\Delta E\rangle_T = \langle\Delta E\rangle_{TR}$. However, at relatively high temperature ($\langle\Delta E\rangle_{TR} << RT$), where $\int_E^\infty P(E',E)dE'$ is significant due to Detailed Balance,

$$\langle\Delta E\rangle_T = \langle\Delta E\rangle_{TR}^2/RT \ .$$

The expressions for I^T and I^{TR} are,

$$I^T = \int_{E_0}^\infty \frac{\rho_E}{\rho_{E_0}} e^{-(E-E_0)/RT} \frac{dE}{RT} \simeq 1 + (s-1)RT/E_0 \ , \qquad (I.5)$$

and

$$I^{TR} = k'(\langle E^+\rangle/RT)^2 = \left[\frac{\int_{E_0}^\infty (E-E_0)\rho_E e^{-E/RT} dE}{RT\int_{E_0}^\infty \rho_E e^{-E/RT} dE}\right]^2$$

$$= (1+sRT/E_0+\ldots)^2 \sim 1+2sRT/E_0 \ , \qquad (I.6)$$

where ρ_E is classical density of vibrational states, and s is the classical equivalent number of oscillators. Equation I.5 can be related to the relative population of molecules which have energy in excess of E_0, while I.6 relates to the average energy of molecules whose energies are in excess of E_0. The latter expression has a somewhat stronger dependence on temperature, especially for high temperatures and large molecules. The magnitudes of I^T and I^{TR} are similar and close to unity for lower temperatures.

Thus, at moderate temperatures where $\alpha < RT$, and $\beta_0(\infty) < 0.03$, (i.e., $E' < 0.3$), $I^T \approx I^{TR}$, $\beta_0^T \simeq \beta_0^{TR}$ (in the linear region of TR's quasi-universal plot) and both have similar temperature dependence:

Appendix (contd)

$$\beta_0^T \simeq \frac{\alpha^2}{(\alpha+RT)^2 I^T} \simeq \frac{\alpha^2}{(RT)^2} \cdot \frac{1}{I^T} = \frac{\langle\Delta E\rangle_{TR}^2}{(RT)^2 I^T}$$

$$\beta_0^{TR} = \frac{\langle\Delta E\rangle_{TR}^2}{(RT)^2 I^{TR}} \ .$$

For large α and β, (i.e. $\langle\Delta E\rangle_T = \langle\Delta E\rangle_{TR} = \alpha >> RT$), Troe writes

$$\beta_0^T \sim 1-\tfrac{1}{2} \exp(-\beta/\alpha)$$

which is not generalizable to the exponential model. Moreover, in this region the difference from unity of the quantity β_0^{TR} is strongly dependent on the assumed model of the transition probabilities (stepladder, exponential, etc.) so that analytical comparisons between β^T and β^{TR} are not appropriate for the case of efficient bath gases.

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Table I. Summary of Early Investigations of Inert Gas Effects in Thermal Systems

System	Inert	k/k_∞	D	ΔT	Remarks or Conclusions	Ref
C_2H_5CHO	reaction products CO, CH_4, C_2H_6	near unity	—	—	products sustain k_{uni}	33
C_2H_5CHO	H_2	near unity	5-14, irrelevant	—	β_p "high"[a]	40
CH_3CHO	H_2	—	—	—	$\beta_p \sim 0$	
CH_3CHO	H_2	$\Delta p = 19$[b]; $\Delta k/k_\infty = 6$	constant at ~ 1	500°-564°	E_a same in pure and diluted system; $\beta_p = 0.5$	45
	H_2O	—	~ 1	—	$\beta_p \sim 0.1$	
$(CH_3)_2O$	H_2	near unity	1.5-15, irrelevant		β_p "high"	18
	He, N_2, CO, CO_2, CH_4	—	—		$\beta_p \sim 0$	
$(C_2H_5)_2O$	He	near unity	~ 2	—	$\beta_p \sim 0$	22
	N_2	near unity	1.5-4, irrelevant		$\beta_p \sim 0$	
	H_2	near unity	1.5-7, irrelevant		β_p high	
$CH_3OC_2H_5$	reaction products, CO_2, CH_4	—	—	430°-460°, irrelevant	products sustain k_{uni}; $\beta_p(CH_4) < \beta_p(C_2H_6)$	23
	H_2		1.4-7, irrelevant		β_p "high"	
	C_2H_4	—	—	—	β_p "high"	
$CH_3OC_3H_7$	reaction products, CO, CH_4, C_2H_6	—	3	—	products sustain k_{uni}	23
	CO	—	4	—	$\beta_p \sim 0$	
	H_2	—	—	—	β_p "high"	
	C_2H_6	—	—	—	β_p "high"	

Table I. (contd), page 2

System	Inert	k/k_∞	D	ΔT	Remarks or Conclusions	Ref
$CH_3N_2CH_3$	products	$\Delta p=2400; \Delta k/k_\infty=4.5$, irrelevant	—		products sustain k_{uni}; efficiency equals parent	34
$CH_3N_2CH_3$	N_2	∿ 0.2	2-14	—	β_p increases from 0.06 to 0.19 with dilution; contrary to expectation from later theory.	36
	C_2H_6	∿ 0.2	0.4-2	—	β_p varied randomly with D from 0.55-1.2	
$CH_3N_2CH_3$	He	$\Delta k/k_\infty = 3$	5,10	290°, 310°	β_p ∿ 0.12 independent of T	46
$CH_3N_2CH_3$	D_2	—		290°, 310°	β_p = 0.66, indep. of T	47
	N_2	—	5,10	—	β_p = 0.19	
	CO	—		—	β_p = 0.12	
	CO_2	—		—	β_p = 0.20	
	CH_4	—		—	β_p = 0.23	
	H_2O	—	1	—	β_p = 0.41	
$\underline{i}$-$C_3H_7N_2\underline{i}$-C_3H_7	products	—	—	—	products sustain k_{uni}; effic. equals parent	i
$CH_3N_2NHCH_3$	products	—	—	—	products sustain k_{uni}; effic. equals parent	ii

Table I. (contd), page 3

System	Inert	k/k_∞	D	ΔT	Remarks or Conclusions	Ref
ethylene oxide	H_2	—	—	—	low efficiency	32
	He, Ne, Ar, CO, CO_2, CH_4, C_2H_6, C_3H_8, i-C_4H_{10}	—	—	—	negative effect on rate	
$C_3H_7NH_2$	He	—	1	—	$\beta \sim 0$	24
	H_2	—	0.25-2, irrelevant	—	$\beta \sim 0$	
	N_2	—	0.25-2, irrelevant	—	$\beta \sim 0$	
dimethyl maleate	H_2	$k/k_\infty \sim 1$	2-6	—	$\beta \sim 0$	41
	N_2	$k/k_\infty \sim 1$	3-6	—	$\beta \sim 0$	
	C_3H_8	$k/k_\infty \sim 1$	4	—	$\beta \sim 0.1$	
cyclopropane	H_2	$k/k_\infty \sim 1$	1.6	—	no significant effect	iii
	C_2H_4	$k/k_\infty \sim 1$	∿ 1	—	"	
	C_3H_6	$k/k_\infty \sim 0.8$	1	—	"	
N_2O	H_2	—	—	—	$\beta \sim 0$	iv
N_2O	N_2	k^∞ not known; $\Delta p_{tot} \sim 3$	2.4-13, irrelevant	—	β values not calculated. From the data $\beta_p \sim 0.45$	48,49
	O_2	p_{tot} constant	7-34, irrelevant	—	$\beta_p \sim 0.36$	
	CO_2	p_{tot} constant	1-24, irrelevant	temperature dependence measured. E_a not calculated.	$\beta_p \sim 1.25$	

Table I. (contd), page 2

System	Inert	k/k_∞	D	ΔT	Remarks or Conclusions	Ref
$CH_3N_2CH_3$	products	Δp=2400; $\Delta k/k_\infty$=4.5, irrelevant	—		products sustain k_{uni}; efficiency equals parent	34
$CH_3N_2CH_3$	N_2	~ 0.2	2-14	—	β_p increases from 0.06 to 0.19 with dilution; contrary to expectation from later theory.	36
	C_2H_6	~ 0.2	0.4-2	—	β_p varied randomly with D from 0.55-1.2	
$CH_3N_2CH_3$	He	$\Delta k/k_\infty$ = 3	5,10	290°, 310°	β_p ~ 0.12 independent of T	46
$CH_3N_2CH_3$	D_2	—		290°, 310°	β_p = 0.66, indep. of T	47
	N_2	—	5,10	—	β_p = 0.19	
	CO	—		—	β_p = 0.12	
	CO_2	—		—	β_p = 0.20	
	CH_4	—		—	β_p = 0.23	
	H_2O	—	1	—	β_p = 0.41	
$\underline{i}$-$C_3H_7N_2\underline{i}$-C_3H_7	products	—	—	—	products sustain k_{uni}; effic. equals parent	i
$CH_3N_2NHCH_3$	products	—	—	—	products sustain k_{uni}; effic. equals parent	ii

Table I. (contd), page 3

System	Inert	k/k_∞	D	ΔT	Remarks or Conclusions	Ref
ethylene oxide	H_2	—	—	—	low efficiency	32
	He, Ne, Ar, CO, CO_2, CH_4, C_2H_6, C_3H_8, i-C_4H_{10}	—	—	—	negative effect on rate	
$C_3H_7NH_2$	He	—	1	—	$\beta \sim 0$	24
	H_2	—	0.25-2, irrelevant	—	$\beta \sim 0$	
	N_2	—	0.25-2, irrelevant	—	$\beta \sim 0$	
dimethyl maleate	H_2	$k/k_\infty \sim 1$	2-6	—	$\beta \sim 0$	41
	N_2	$k/k_\infty \sim 1$	3-6	—	$\beta \sim 0$	
	C_3H_8	$k/k_\infty \sim 1$	4	—	$\beta \sim 0.1$	
cyclopropane	H_2	$k/k_\infty \sim 1$	1.6	—	no significant effect	iii
	C_2H_4	$k/k_\infty \sim 1$	~ 1	—	"	
	C_3H_6	$k/k_\infty \sim 0.8$	1	—	"	
N_2O	H_2	—	—	—	$\beta \sim 0$	iv
N_2O	N_2	k^∞ not known; $\Delta p_{tot} \sim 3$	2.4-13, irrelevant	—	β values not calculated. From the data $\beta_p \sim 0.45$	48,49
	O_2	p_{tot} constant	7-34, irrelevant	—	$\beta_p \sim 0.36$	
	CO_2	p_{tot} constant	1-24, irrelevant	temperature dependence measured. E_a not calculated.	$\beta_p \sim 1.25$	

Table I. (contd), page 4

System	Inert	k/k_∞	D	ΔT	Remarks or Conclusions	Ref
N_2O	He	Δp=29; Δk=15, maximum range	0.74 and 10, each constant over pressure range	670°	β_p = 1.0; nominally, one of most complete studies, but no derivative results	49,50
			3.4-12	640°		
			0.7-7	625°		
	Ar		4,10	670°	β_p = 0.1	
			0.7, 7	625°		
	O_2				β_p = 0.21	
N_2O	Ne	Δp ≳ 4, irrelevant	2	variable	β_p = 0.44	51
	Ar	Δp ∿ 4, irrelevant	2		β_p = 0.18	
	Kr	Δp ∿ 4, irrelevant	2		β_p = 0.24	
	Xe	Δp ∿ 4, irrelevant	2		β_p = 0.15	
	Hg	Δp ∿ 6; Δk ∿ 3	10	465-670	E_a(Hg) less than $E_a(N_2O)$ but catalysis proposed.	
	H_2O	p fixed	5.5		β_p = 1.62	
N_2O	products, N_2+O_2	—	—	938,955°K	E_a = 57,500 but too inaccurate for any conclusion	39
N_2O	Ar	Δp_{N_2O}=25	2,4	—	β_p declines from lower to higher press where $\beta \sim 0$	v
	N_2		2	—	same as Ar	
	CO_2		2	—	β_p constant with press. region $\beta_p(N_2O) > \beta_p(CO_2) > \beta_p(N_2) > \beta_p(Ar)$	
N_2O_5	N_2	Δp=2800; Δk=0	15	—	β_p = 0	vi
N_2O_5	Ar	—	—	—	β_p = 0	vii

Table I. (contd), page 5

System	Inert	k/k_∞	D	ΔT	Remarks or Conclusions	Ref
N_2O_5	H_2	p_{tot} const	0.05-2	—	β = 0 for all	57
	CO, Br_2, Cl_2		2-4	—	gases	
NO_2Cl	decomp products, $NO_2 + Cl_2$	—	—	—	same efficiency as substrate	38
	H_2	$\Delta p_{tot} \sim 1$-2	2	—	$\beta_p \sim 0.22$	
	N_2		2	—	$\beta_p \sim 0.22$	
	CO		2	—	$\beta_p \sim 0.29$	
	O_2		2,5.5	—	$\beta_p \sim 0.28$	
	Cl_2		0.5-4, irrelevant	—	$\beta_p \sim 0.27$	
	CO_2		4	—	$\beta_p \sim 0.28$	
	NO_2		0.6-4, irrelevant	—	$\beta_p \sim 0.42$	
O_3	He	—	—	—		52
	N_2	—	—	—	$\beta_p(He) < \beta_p(N_2) < \beta_p(CO_2)$	
	CO_2	—	—	—		
F_2O	He	—	Variable; between 0.1-7	250°-270°	β_p=0.68 } All gases in this study gave same temperature coeff as parent	53
	Ar				β_p=0.43 }	
	N_2				β_p=0.96	
	O_2				β_p=0.96	
	F_2				β_p=0.99	
	SiF_4				β_p=0.87	

System	Inert	k/k_∞	D	ΔT	Remarks or Conclusions	Ref
F_2O_2	Decomp. prods $F_2 + O_2$	—	—	—	same effic. as parent	37
	He	—	22,45	—	β_p=0.11	
	Ar	—	7	—	β_p=0.25	Scatter in data;
	N_2	Δp_{tot}=3.5	7.5-150		β_p=0.15	no evidence for
	O_2	—	5.5-10	—	β_p=0.28	variation of β
	F_2	—	—	—	β_p=0.22	with k or D.
	CO_2	—	4-17	—	β_p=0.30	

a) β_p is recorded since it is an objective magnitude, whereas β_c depends on particular choices of collision cross-sections.

b) Δ always signifies a multiplication factor, in this table.

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Table II. Averaged Collisional Efficiency in the Second Order Region

A. N_2O_5 System[62,a]

M	$\beta_c(M)/\beta_c(N_2O_5)$
N_2O_5	1.000
He	0.065
Ne	.086
Ar	.154
Kr	.208
Xe	.189
N_2	.228
NO	.300
CO_2	.387
CCl_4	.673
SF_6	.443

B. NO_2Cl System[64] (476.5°K)

M	β_p	s, Å	β_c
NO_2Cl	1.00	6.7	1.00
He	0.247	2.6	0.15
Ne	.179	2.8	.22
Ar	.211	3.4	.30
Kr	.209	3.6	.36
Xe	.265	4.0	.46
H_2	.341	2.9	.15
N_2	.286	3.7	.34
O_2	.261	3.5	.34
Cl_2	.335	4.4	.50
HCl	.513	(4)	.63
CO_2	.382	4.1	.49
N_2O	.409	4.6	.48
NO_2	1.24	(5)	1.38[b]
SiF_4	0.456	6.3	0.51
SF_6	.358	5.5	.49
CCl_2F_2	.489	4.9	.71

a) Temperature unspecified in this reference; presumably 323.7°K.[61]

b) Considered unreliable by the present authors.

Table III. Some Representative Studies, 1950-1967.

Substrate	Temp	Inert Gases	Ref
Cyclobutane	449°	H_2, N_2, NO, CO_2, C_3H_6, toluene	72
	445°	H_2, C_2H_4, C_2H_6	73
	449°	He, Ne, Ar, H_2, N_2, H_2O, CH_4, C_2H_4 toluene, mesitylene, benzotrifluoride	76
Cyclobutene	150°	He, H_2, N_2, CO_2, CH_4, C_2H_4, C_3H_8, n-C_4H_{10} cis-, trans-, cyclo-C_4H_8	89
3-methylcyclobutene	~137°	CO_2, n-, iso- and neo-C_5H_{12}	90
Cyclopropane	492°	He, Ar, H_2, N_2, CO, H_2O, CH_4, C_3H_6 toluene, mesitylene, benzotrifluoride	75
Methylcyclopropane	465°	He, Ar, H_2, N_2, CH_4, C_2H_6, C_4H_8-1, toluene	85
butene-2	469°	He, Ne, Ar, Kr, Xe, N_2, CO_2, CH_4, H_2O, D_2O, toluene	87
1,1-dimethyl cyclopropane	477°	CO_2	84
	459°	He, Ar, H_2, N_2, CO_2, CH_4, C_2H_4, CF_4, SF_6, toluene	88
1,2-dimethyl cyclopropane	431°	CO_2	86
dichloroethane	433°	He, N_2, HCl, C_2H_4, C_2H_3Cl	74
N_2O	720°	Ar, N_2, CO_2, CF_4	77
	673°-750°	He, Ne, Ar, Kr, Xe, CO_2, SO_2	80
O_3	~100°	He, N_2, O_2, CO_2	79
C_4-C_7 paraffins	~500°	Ar, N_2, CO_2, SO_2, NH_3, CF_4, C_2H_5, SF_6	78

Table III. (continued)

H_2O_2	432°	O_2, H_2O	82
	432°-469°	He	
t-butyl peroxide	160°	N_2, CO_2, CCl_4, SF_6	81
	160°	N_2, N_2O, CO_2, CCl_4, CF_4, SiF_4, SF_6 acetone, n-C_6H_{14}	83
C_2H_6	600°	He, Ne, Ar, Kr, N_2, CO_2, H_2O	92
isopropoxyl	200°	Ar, H_2, N_2, CO, NO, CO_2, N_2O, SF_6, CH_4, C_2H_6, C_3H_8 n-, iso-C_4H_{10}, n-C_5H_{12}, cyclopropane, dimethyl ether, isopropanol, isopropyl nitrite	91
sec-butoxyl	170°	Ar, H_2, N_2, CO, NO, CO_2, N_2O, SF_6, cyclopropane n-, iso- C_4H_{10}, neo-C_5H_{12}, sec-butanol, dimethyl ether, sec-butylnitrite	93
dimethyl ether	248°	CO_2	94

Table IV. Inert Gas Efficiency in 3-Methylcyclobutene (A) Isomerization (~ 137°)

M	s_{AM}, Å [a]	β_c(lit) [a]	s_{AM}, Å [b]	β_c(corr) [b]
A	7.0	(1.0)	5.6	(1.0)
CO_2	4.1	0.48	4.1	0.37
n-C_5H_{12}	5.8	1.32	5.8	1.07
iso-C_5H_{12}	5.3	1.25	5.6	0.98
neo-C_5H_{12}	5.2	1.12	5.2	0.94

a) Literature values, ref. (90).

b) Revised values, based on method in the text.

Table V. Relationships of Relative Collisional Efficiencies at Various Regions of Falloff and Dilution [a]

Dilution	Second order	Falloff	First order [c]
0	$\bar{\beta}_0'(0)=\bar{\beta}_0(0)=1$	$\bar{\beta}_\omega'(0)=\bar{\beta}_\omega(0)=1$	$\bar{\beta}_\infty'(0)=\bar{\beta}_\infty(0)=1$
	$\bar{\beta}_0'(0)=\beta_0(0)$ [b]	$\beta_\omega'(0)=\beta_\omega(0)<\beta_0(0)$	$\beta_\infty'(0)=\beta_\infty(0)<\beta_\omega(0)$
D	$\bar{\beta}_0'(D)=\bar{\beta}_0(D)<1$	$\bar{\beta}_\omega'(D)>\bar{\beta}_\omega(D)$ [d]	$\bar{\beta}_\infty'(D)=\beta_\infty'(D)>\bar{\beta}_\infty(D)=$
	$\beta_0'(D)=\beta_0(D)<\beta_0(0)$	$\beta_\omega'(D)>\beta_\omega(D)$	$\beta_\infty(D)<\beta_\omega(D),\beta_\infty(0)$
∞	$\bar{\beta}_0'(\infty)=\bar{\beta}_0(\infty)=\beta_0'(\infty)$	$\bar{\beta}_\omega'(\infty)>\bar{\beta}_\omega(\infty)$	$\bar{\beta}_\infty'(\infty)=\beta_\infty'(\infty)=1>\bar{\beta}_\infty(\infty)$
	$=\beta_0(\infty)<\beta_0(0)$	$\beta_\omega'(\infty)>\beta_\omega(\infty)$	$=\beta_\infty(\infty)<\beta_\omega(D),\bar{\beta}_\omega(\infty)$

a) From ref. 124

b) Magnitude less than unity, in general, and may be obtained from quasiuniversal curves given by TR and depend only on E' for a particular collisional transition probability model.

c) $\omega \to \infty$; $k/k \to 1$; this region is not experimentally useful.

d) $\beta_\omega'(D_i)>\beta_\omega'(D_j)>Q<\beta_\omega'(D_k)....<\beta_\omega'(D_\infty)$ and $\beta_\omega(D_i)>\beta_\omega(D_j)....>\beta_\omega(D_\infty)$; *where $i<j<k$, and Q is a minimum value. The same trend is observed* for $\bar{\beta}'$ and $\bar{\beta}$ quantities.

Table VI. Collisional efficiency NO_2Cl[a] (476.5°K; $\langle E^+ \rangle$ = 377 cm^{-1}).

Inert gas	p(inert)/p(parent)	ω(i)/ω(p)	β_{obs}[b]	$\beta_0(0)$ SL	$\beta_0(0)$ EXP
NO_2Cl			1.00		1.00
He	0.37-1.7	0.61-2.8	0.15		0.20
Ne	0.46-2.3	0.37-1.9	0.22		.26
Ar	0.28-2.2	0.20-1.5	0.30		.34
Kr	0.19-1.8	0.11-1.0	0.36		.40
Xe	0.046-0.46	0.026-0.26	0.46		.47
H_2	0.46-2.2	1.0-5.0	0.15		.21
N_2	0.28-2.4	0.23-2.0	0.34		.38
O_2	0.093-2.3	0.071-1.8	0.34		.36
Cl_2	0.37-1.0	0.25-0.67	0.50	0.57	
CO_2	0.37-2.4	0.29-1.9	0.49	0.58	
N_2O	0.46-2.3	0.39-2.0	0.48	0.57	
SiF_4	0.28-2.2	0.25-2.0	0.51	0.62	
SF_6	0.28-2.3	0.20-1.7	0.49	0.58	
CCl_2F_2	0.46-2.3	0.37-1.6	0.71	0.78	

a) Data of Ref. 64

b) Collision cross sections of Volpe and Johnston were retained for these comparisons.

Table VII. Summary Values of β_0, $\langle E^+ \rangle$, and $\langle \Delta E \rangle$[a] at Different Temperatures in the CH_3NC-He System.

Temp, °C	$\beta_0(\infty)$	$\langle E^+ \rangle$ cm^{-1}	$\langle \Delta E \rangle$,[b] cm^{-1}
210	0.29	400	460
220	0.28	410	460
280.5	0.24	470	450
315	0.22	510	450
326	0.21	500	447

a) Data of ref. 125

b) Values are based on the exponential form for the collisional transition probability distribution; the change with temperature has only qualitative significance.

Table VIII. Some collisional efficiency parameters at various k/k^{∞} in the CH_3NC system.[a]

	$\beta_0(\infty)^b$ obs	E'	$\langle\Delta E\rangle$ (cm^{-1})	$\bar{\beta}_{0.3}(\infty)$ theor.	$\bar{\beta}_{0.3}(\infty)$ obs.	$\bar{\beta}_{0.6}(\infty)$ theor.	$\bar{\beta}_{0.6}(\infty)$ obs.	$\bar{\beta}_{1.0}(\infty)$ theor.
C_3H_8, C_3H_6	0.63	2.0	850	0.56	0.49	0.50	0.43	0.47
C_2F_6	0.45	1.6	680	0.37	0.35	0.31	0.28	0.27

a) From ref. 138

b) The subscript on $\bar{\beta}$ refers to k/k^{∞} value

Table IX. Measured and Theoretical Values of Collisional Efficiency for He at Various k/k_{∞} (245°)[a]

	$\bar{\beta}_{\omega}(\infty)$									
k/k_{∞}	0	0.005	0.01	0.05	0.10	0.50	0.775	1.0	$\bar{\beta}_{0.005}/\bar{\beta}_{0.775}$	$\bar{\beta}_0/\bar{\beta}_{1.0}$
Exptl	(0.203)[b]	0.199	0.194	0.170	0.154	0.112	0.096		2.08	
EXP[c]	0.198	0.196	0.195	0.178	0.168	0.141	0.133	0.128	1.47	1.55
SL[d]	0.200	0.196	0.190	0.163	0.149	0.108	0.092	0.084	2.13	2.38

a) Data of ref. 140

b) Extrapolated value

c) $\langle\Delta E\rangle$ = 400 cm^{-1}; E' = 0.90.

d) $\langle\Delta E\rangle$ = 350 cm^{-1}; E' = 0.80.

Table X. Inert Gas Effects in Chemical Activation Systems

System	Inert Gas[a]	T(°K)	Method[b]	$\beta_0(\infty)$	$\langle\Delta E\rangle$ (kcal mole^{-1})	Preferred Model	Ref
1. butyl-2(H+cis-butene)	cis-butene	298	SC,LP	1.0	≥ 8.5	SL	8
2. butyl-2(H+cis-butene)	He	195	SC,LP	0.55	2.1	EXP	7a
	Ne			--	--		
	Ar			0.59	2.1	EXP	
	Kr			0.59	2.0	EXP	
	cis-butene	300		1.0	≥ 9	SL	
	He			0.35	1.5	EXP	
	Ne			0.40	1.9	EXP	
	Ar			0.41	2.6	EXP	
	Kr			0.46	2.3	EXP	
	He	373		0.28	1.5	EXP	
	Ne			0.30	1.7	EXP	
	Ar			0.30	2.0	EXP	
	Kr			0.34	2.3	EXP	
3. butyl-2(H+cis-butene)	H_2	195	SC,LP	0.48	1.3	EXP	7b
	D_2			0.48	1.3	EXP	
	N_2			0.67	2.7	SL	
	H_2	300		0.30	1.3	EXP	
	D_2			0.35	1.3	EXP	
	N_2			0.54	2.7	SL	
	CO_2			0.83	4	SL,EXP	

a) Dilution usually close to infinite
b) SC, single channel; MP, multiple channel; LP, low pressure; HP, high pressure; AP, all pressure; Rec, recombination stabilization.

Table X. (continued)

System	Inert Gas	T(°K)	Method	$\beta_0(\infty)$	$\langle\Delta E\rangle$ (kcal mole^{-1})	Preferred Model	Ref
3. (continued)	CH_4			0.73	5	SL,EXP	
	CD_3F			0.75	-		
	CH_3Cl			0.82	≥ 7	SL	
	SF_6			1.00	≥ 9	SL	
	H_2	373		0.21	1.0	EXP	
	D_2			0.27	1.2	EXP	
	N_2			0.34	2.0	SL	
4. butyl-2(H+trans-butene)	He	300	SC,HP	0.35	1.25	EXP	
(H+butene-1)	He	300		0.36	1.8	EXP	185
5. cyclopropane(C_2H_4+$^1CH_2$)	C_2H_4	298	SC,LP	--	> 10[c]	SL	186
		598			≥ 10	SL	
		723			≥ 7	SL	
dimethyl cyclopropane (cis-butene+ $^1CH_2$)	cis-butene	298			> 12[c]	SL	
		583			≥ 12	SL	
		673			≥ 10	SL	
6. $C_2H_2D_3$(trans-$C_2H_2D_2$+H)	He	195	SC,HP	0.37			12
		300		0.26			
	D_2	195		0.52			
		300		0.38			
$C_2H_3D_2$(trans-$C_2H_2D_2$+H)	H_2	300		0.9			

c) quoted upper limit higher than value cited here.

Table X. (continued)

System	Inert Gas	T(°K)	Method	$\beta_0(\infty)$	$\langle\Delta E\rangle$ (kcal mole^{-1})	Preferred Model	Ref
7. cyclopropane ($C_2H_4+{}^1CH_2$)	C_2H_4	298	SC,LP		>10	SL	187
		423			12	SL	
		598			10	SL	
		723			7	--	
	He	298			∿ 4	EXP	
	Ar				6	EXP	
	N_2				6	EXP	
8. hexyl-3(trans-hexene-3+H)	H_2	300	MC,AP		1.2	SL,EXP	180
	CF_4				> 4.6	SL,EXP	
9. butyl-2(cis-butene+H)	H_2	300	SC,HP	0.21	1.3	SL	184
	N_2			0.48	2.3	SL	
	CH_4			0.81	4.3	SL	
	CF_4			1.0	> 8.6	SL	
pentyl-2(pentene-1+H)	H_2	300	SC,HP	0.22	approximately same as butyl-2 but $\langle\Delta E\rangle$ a little larger		
	N_2			0.53			
	CH_4			0.81			
	CF_4			1.0			
hexyl-2(hexene-1+H)	H_2	300	SC,HP	0.22	approximately same as pentyl-2 but $\langle\Delta E\rangle$ a little larger		
	N_2			0.57			
	CH_4			0.83			
	CF_4			1.0			
octyl-2(octene-1+H)	H_2	300	SC,HP	0.27	approximately same as for hexyl-2		
	N_2			0.53			
	CH_4			0.70			
	CF_4			1.0			

Table X. (continued)

System	Inert Gas	T(°K)	Method	$\beta_0(\infty)$	$\langle\Delta E\rangle$ (kcal mole^{-1})	Preferred Model	Ref
10. 3,3-dimethyl hexyl-2	H_2	300	MC,AP	--	1.4 or 1.1	EXP or SL	181
(3,3-dimethyl hexene-1+H)	CF_4				4.6	SL	
3-methyl hexyl-2	H_2				1.4 or 1.1	EXP or SL	
(3-methyl hexene-1+H)	CF_4				4.6	SL	
11. 1,2 dimethyl cyclopropane	cis-butene	300	SC,LP		11.4	SL	i
(cis-butene+${}^1CH_2$)	CO				4.6	EXP	
12. pentyl-2(pentene-1+H)	H_2	298	SC,LP	0.2	1.4	EXP	ii[d]
				0.19	1.15	EXP;SL	
	CH_4			0.58	2.6	SL	
				0.67	3.1	SL	
	CF_4			0.85	4.6	SL	
13. 2,4-dimethyl pentyl-2	H_2	298	SC,LP		1.5	EXP	183
(2,4-dimethyl pentene-1+H)	D_2				2.2	EXP	
	CF_4				4.6	SL	
14. $C_2H_4Cl_2$(CH_2Cl+CH_2Cl)	Ar	300	SC,LP		6	SL only used	iii
	N_2				6	SL only used	
	CH_3Cl				10	SL	
	CH_2Cl_2				10	SL	
	CF_4				10	SL	
15. $C_2H_4Cl_2$(CH_2Cl+CH_2Cl)	CO	300	SC,LP		6	SL only used	iv
	cyclo-C_4F_8				13	SL	
16. $C_2H_4F_2$(CH_2F+CH_2F)	CH_2ClF	300	SC,LP		11	SL	v
		475			11	SL	

d. This reference gives a summary of all work by different techniques on alkyl radical deactivation by H_2, CH_4 and CF_4.

Table X. (continued)

System	Inert Gas	T(°K)	Method	$\beta_0(\infty)$	$\langle\Delta E\rangle$ (kcal mole^{-1})	Preferred Model	Ref
17. $C_2H_4Cl_2(CH_2Cl+CH_2Cl)$	He	300	SC,LP		1.4	EXP	191
	Ne				2.9	EXP	
	CO				4	SL	
	CH_3Cl				6	SL	
18. $C_2D_4Cl_2(CHD_2Cl+CHD_2Cl)$	He	300	SC,LP		1.4	EXP	191
	Ne				2.9	EXP	
	CO				4	SL	
	CD_3Cl				6	SL	
19. $C_2H_4Cl_2(CH_2Cl+CH_2Cl)$	Ar	300	SC,LP		4.0	EXP	vi
	Kr				4.0	EXP	
	Xe				5.0	SL	
	N_2				4.0	SL	
	SF_6				7.0	SL	
	CF_4				$\sim$ 5		
	C_4F_8				12	SL	
20. $CH_3CF_3(CH_3+CH_3)$	C_2F_6	300	SC,LP		7	SL	vii
	$CF_3N_2CH_3$				7	SL	
	cyclo-C_4F_8				7	SL	
	n-C_6F_{14}				10	SL	
	n-C_8F_{16}				10	SL	
21. $CH_3CF_3(CH_3+CF_3)$	H_2	196	SC,LP		1.5	EXP	189
	N_2				1.0	EXP	
	CO_2				2.0	EXP	

Table X. (continued)

System	Inert Gas	T(°K)	Method	$\beta_0(\infty)$	$\langle\Delta E\rangle$ (kcal mole^{-1})	Preferred Model	Ref
21. (continued)	SF_6				7.0	SL	
	C_2F_6				6.0	SL	
	He	300			1.0	EXP	
	Ne				1.0	EXP	
	Ar				0.8	EXP	
	Kr				0.8	EXP	
	Xe				1.0	EXP	
	H_2				1.5	EXP	
	D_2				1.0	EXP	
	N_2				1.5	EXP	
	CO_2				2.0	EXP	
	CH_4				3.0	EXP	
	CH_3Cl				4.0	EXP	
	CF_4				5.0	SL	
	SF_6				6.0	SL	
	C_2F_6				6.0	SL	
	CH_3COCH_3				8.0	SL	
	CF_3COCF_3				8.0	SL	
22. $C_2H_5F(CH_3+CH_2F)$	CH_4	303	SC,HP		2.5	SL only used	viii
	CH_3F	313			5		
	CH_2CO	313			5		
	N_2	315			1[e]		
	N_2	363			1.75		
	N_2	433			2		
	N_2	508			4		
	N_2	557			5		

e. Temperature dependence of $\langle\Delta E\rangle$ for N_2 believed suspect.

Table X. (continued)

System	Inert Gas	T(°K)	Method	$\beta_0(\infty)$	$\langle\Delta E\rangle$ (kcal mole^{-1})	Preferred Model	Ref
23. $C_2H_5F(CH_3+CH_2F)$	He	300	SC,LP		0.8	EXP	ix
	N_2				3	SL	
	CO_2				3	SL	
	SF_6				7	SL	
24. $C_2H_4F_2(2CH_3F)$	He	300	SC,LP		1	EXP	
	N_2				3	SL	
	CO_2				3	SL	
	SF_6				7	SL	
25. $CH_3CF_3(CH_3+CF_3)$	C_2F_6	307	SC,LP		4.0	SL only	x
	C_2F_5H				6.3		
	CF_3CFH_2				4.0		
	$(CF_2H)_2$				5.2		
	CF_3CH_3				4.0		
	CF_2HCFH_2				4.0		
	CF_2HCH_3				4.0		
	CFH_2CH_3				4.0		
26. $NO_2(O+NO)$	He	295	Rec,LP	0.33[f]			190
	Ne			0.43			
	Ar			0.64			
	CO			0.61			
	N_2			($\sim$0.50)			
	CO_2			0.83			

f) Values relative to N_2 as basis

Table X. (continued)

System	Inert Gas	T(°K)	Method	$\beta_0(\infty)$	$\langle\Delta E\rangle$ (kcal mole^{-1})	Preferred Model	Ref
26. (continued)	CH_4			0.72			
	CH_6			0.58			
	c -C_3H_6			0.67			
	C_3F_8			1.07			
	SF_6			0.83			
	neo-C_5H_{12}			0.68			
	2,2-dimethyl butane			0.68			
	iso-propyl bromide			0.84			
27. $NO_3(O+NO_2)$	He	295	Rec	0.23[f]			190
	Ne			0.31			
	Ar			0.33			
	CO			0.47			
	N_2			(0.24)			
	CO_2			0.63			
	CH_4			0.62			
	C_2H_6			0.64			
	C_3H_8			0.54			
	c-C_3H_6			0.76			
	CF_4			1.05			
	C_2F_6			1.02			
	C_3F_8			1.70			
	SF_6			0.86			
	neo-C_5H_{12}			0.89			

Table X. (continued)

System	Inert Gas	T(°K)	Method	$\beta_0(\infty)$	$\langle\Delta E\rangle$ (kcal mole^{-1})	Preferred Model	Ref
27. (continued)	2,2-dimethyl butane			0.93			
	trimethyl butane			1.43			
	iso-propyl bromide			0.68			
28. INO(I+NO)	He	330	Rec	0.19			xi
	Ne			0.44			
	Ar			0.45			
	Kr			0.52			
	Xe			0.49			
	H_2			0.18			
	N_2			0.65			
	CO			0.50			
	CH_4			0.59			
29. INO_2($I+NO_2$)	He	330		0.22			xi
	Ne			0.42			
	Ar			0.42			
	Kr			0.42			
	Xe			0.49			
	H_2			0.18			
	D_2			0.20			
	N_2			0.47			
	CO			0.49			
	O_2			0.56			
	N_2O			0.63			
	CO_2			0.63			
	CH_4			0.45			
	C_2H_4			0.58			

Table X. (continued)

System	Inert Gas	T(°K)	Method	$\beta_0(\infty)$	$\langle\Delta E\rangle$ (kcal mole^{-1})	Preferred Model	Ref
29. (continued)	SF_6			0.58			
	C_2F_6			0.58			
30. methyl cyclopropane(C_3H_6+$^1CH_2$)	C_3H_6	291	SC	--	1.5	SL only	xii
31. methyl cyclobutane(c-C_4H_8+$^1CH_2$)	c-C_4H_8	298	SC,LP		~ 5	SL only	xiii
32. C_2H_5(H+C_2H_4)	He	298	Rec,LP	0.28			xiv
	Ne			0.39			
	Ar			0.39			
	Kr			0.35			
	H_2			0.1			
	N_2			0.28			
	SF_6			(1.00)			
33. ClF_5(ClF_4+F)	He	303	SC,HP	0.18[h]			xv
	N_2			0.22			
	F_2			(1.0)			
	ClF_5			0.4			
33.(a) spiropentane(methylene-cyclopropane + $^1CH_2$)	CH_2-c-C_3H_6	300[g]	SC,LP		7.2	SL only	xvi

g) Not specified; approximately room temperature

h) Efficiency on a pressure basis

Table X. (continued)

System	Inert Gas	T(°K)	Method	$\beta_0(\infty)$	$\langle\Delta E\rangle$ (kcal mole^{-1})	Preferred Model	Ref
34.(a) $\underline{c}$-C_4H_7T($\underline{c}$-C_4H_8+T^*)	Ne	∿ 300[g]	SC,HP	0.32		SL only used	194a
	CF_4			1.05			
	$\underline{c}$-C_4H_8			(1.00)			
(b) $\underline{c}$-C_4H_7T(c-C_4H_8+T*)	He	∿ 300	SC,HP	0.14			194b
	Ne			0.23			
	Ar			0.24			
	Kr			0.31			
	Xe			0.39			
	N_2			0.40			

Table X. (continued)

System	Inert Gas	T(°K)	Method	$\beta_0(\infty)$	$\langle\Delta E\rangle$ (kcal mole^{-1})	Preferred Model	Ref
35. $C_4H_8^+$($C_2H_4^+$+C_2H_4)	Ne	∿ 300[g]	MC		< 0.7	SL only used	196a
	C_2H_4				≤ 2.0		
36. $C_4H_4F_4^+$($C_2F_2H_2^+$+$C_2F_2H_2$)	He	300	Rec,LP	0.14[i]			197
	Ne			0.19			
	Ar			0.39			
	Kr			0.45			
	Xe			.48			
	N_2			.40			
	CO			.42			
	CF_2CH_2			(1.00)			
37. $C_{12}H_{12}^+$($C_6H_6^+$+C_6H_6)	He	300	Rec,LP	0.033[i]			197
	Ne			0.0			
	Ar			0.058			
	Kr			0.09			
	Xe			0.13			
	C_6H_6			(1.00)			
38. $C_5H_9^+$($C_3H_5^+$+C_2H_4)	He	373	Rec,LP	0.19[i]			198
	Ne			0.21			
	Ar			0.24			
	Kr			0.19			
	H_2			0.17			

i) Relative values based on parent molecule set at unity.

Table X. (continued)

System		
38. (continued)	D_2	0.22
	N_2	0.33
	CO	0.33
	CO_2	0.53
	SO_2	0.62
	CH_4	0.57
	CD_4	0.58
	CF_4	0.76
	CH_3F	0.57
	CH_2F_2	0.71
	SF_6	0.83
	C_2H_4	(1.00)
	C_2H_6	1.02
	C_2D_6	0.98

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Table XI. Illustration of Variation of $\bar{\beta}'$ with ϕ

	$-\left.\frac{\partial \ln \bar{\beta}'}{\partial \phi}\right\|_{E'}$					$\frac{\partial \ln \bar{\beta}'}{\partial \ln \langle \Delta E \rangle} = -\frac{\partial \ln \bar{\beta}'}{\partial \ln \langle E^+ \rangle}$				
E'/ϕ	1.18	1.37	1.50	1.62	1.87	1.1	1.25	1.50	1.75	2.0
0.5	3.05	2.33	1.98	1.64	0.56	0.73	1.08	1.43	1.72	1.84
1.0	1.86	1.34	1.06	0.77	0.52	0.43	0.67	1.07	1.28	1.37
1.5	0.71	0.36	0.32	0.28	0.18	0.25	0.40	0.67	0.82	0.99

Table XII. Illustration of Variation of $\langle E^+ \rangle$ and ϕ with Temperature

T°K	CO_2	CH_3CN	C_3H_6
		$\frac{\partial \ln \langle E^+ \rangle}{\partial T}$	
250	0.446×10^{-2}	0.479×10^{-2}	0.482×10^{-2}
500	$.225 \times 10^{-2}$	$.260 \times 10^{-2}$	$.264 \times 10^{-2}$
1000	$.117 \times 10^{-2}$	$.155 \times 10^{-2}$	$.163 \times 10^{-2}$
2000	$.607 \times 10^{-3}$	$.993 \times 10^{-3}$	$.117 \times 10^{-2}$
4000	$.322 \times 10^{-3}$	$.519 \times 10^{-3}$	$.591 \times 10^{-3}$
		$\frac{\partial \ln \langle E^+ \rangle}{\partial \ln T}$	
250	1.11	1.20	1.21
500	1.13	1.30	1.32
1000	1.17	1.55	1.63
2000	1.21	1.99	2.34
4000	1.29	2.08	2.36
		$\langle E^+ \rangle$ (kcal mole^{-1})	
250	0.48	0.50	0.50
500	.97	1.10	1.12
1000	1.98	2.71	2.85
2000	4.08	8.74	10.47
4000	8.90	37.22	61.04
		$\left.\frac{\partial \phi}{\partial T}\right\|_{\omega}$ $(1.2<\phi<1.8)$	
250	0.12×10^{-3}	0.40×10^{-3}	0.50×10^{-3}
500	$.32 \times 10^{-3}$	$.48 \times 10^{-3}$	$.72 \times 10^{-3}$
1000	$.22 \times 10^{-3}$	$.36 \times 10^{-3}$	$.55 \times 10^{-3}$
2000	$.14 \times 10^{-3}$	$.28 \times 10^{-3}$	$.32 \times 10^{-3}$
4000	$.07 \times 10^{-3}$	$.12 \times 10^{-3}$	$.20 \times 10^{-3}$

Figure Captions

Figure

1 Calculated plots of k/k_∞ vs log ω (arbitrary units) for methyl isocyanide at (a) 353°K; (b) 546°K for 1) strong collision and for a 360 cm^{-1} SL model at dilutions of 2) 1, 3) 10 and 4) ∞ ; (c) for cyclopropane at 728°K for 1) strong collider, and for a 352 cm^{-1} SL model at dilutions of 2) 0.5, 3) 1, 4) 5, 5) 10, 6) 50 and 7) ∞ . Dashed lines represent experimental dilution paths.

2 Plots of vibrational level populations as a function of vibrational energy for a strong collider with a) $\omega = 1\times10^6$ sec^{-1}; b) $\omega = 1\times10^7$ sec^{-1}; c) $\omega = 1\times10^8$ sec^{-1}; d) $\omega = 1\times10^9$ sec^{-1}; e) $\omega = 1\times10^{10}$ sec^{-1}.

3 a) Calculated plots of Γ_i vs E for methyl isocyanide at 546°K for strong collision (solid curve) and 360 cm^{-1} SL (dashed curve) at relative collision rates of 1) 4×10^6, 2) 10^8, 3) 10^9, and 4) 10^{11} sec^{-1}; (b) Summary plots of R_i vs E for 360 cm^{-1} SL model (dashed) and 360 cm^{-1} Exp model (solid) for the above collision rates. Populations immediately above E_0 are not shown because of the finite graining. The energy scale is given with E_0 as the zero of reference. The above relative collision rates correspond to the following k/k_∞ for the strong collision case: 1) 0.058, 2) 0.48, 3) 0.83 and 4) > 0.99 .

4 a) Calculated plots of Γ_E vs E for methyl isocyanide at 546°K for strong collision (solid) and a 360 cm^{-1} SL model (dashed), at k/k_∞ of 1) 0.084, 2) 0.16, 3) 0.48, and 4) 0.82; (b) Summary plots of R_E vs E for 360 cm^{-1} SL model at the same values of k/k_∞.

5 Summary plots of population depletion function $\gamma_N(D)$ vs dilution for (a) a step ladder model and (b) an exponential model, p=0, as calculated for the NO_2Cl, CH_3NC and C_3H_6 systems at 476°, 546°, and 728°K, for the various values of E' shown on right hand side of the graph. The individual computational points which these quasiuniversal curves summarize are not shown. The limiting values for D = ∞ also include computational results for the N_2O and dimethyl cyclopropane systems (see caption, Fig. 3).

6a Calculated plots of $\bar{\beta}'_\omega(\infty)$ (solid) and $\bar{\beta}_\omega(\infty)$ (dashed) vs k/k_∞ for methyl isocyanide; 353°K, 1) 180 cm^{-1} SL, 2) 360 cm^{-1} SL, 3) 360 cm^{-1} Exp, and 4) 700 cm^{-1} SL, 546°K, 5) 180 cm^{-1} SL, 6) 360 cm^{-1} SL, 7) 360 cm^{-1} Exp and 8) 700 cm^{-1} SL.

6b Calculated plots of $\bar{\beta}'_\omega(\infty)$ (solid) and $\bar{\beta}_\omega(\infty)$ (dashed) vs k/k_∞ for cyclopropane; 728°K, 1) 352 cm^{-1} SL, 2) 704 cm^{-1} SL, 3) 1408 cm^{-1} SL and 4) 2112 cm^{-1} SL, and for ease of direct comparison methyl isocyanide at 353°K, 5) 180 cm^{-1} SL; and at 546°K, 6) 360 cm^{-1} SL. The subscript ω corresponds to a given k/k_∞ for a particular system and varies from system to system for a given k/k_∞ .

7 Plots of relative collisional efficiency vs the reduced parameter E' for five systems at p = 0 for the step ladder, Poisson and exponential models: N_2O, ○; NO_2Cl, ●; CH_3NC, □ ; C_3H_6, ▽ ; C_5H_{10}, ▼ . The abscissa refers to the SL curve; P and E have been arbitrarily displaced to the right by log 1.5 and log 2.25, respectively, to prevent crowding.

8 Quasi-universal summary plots of $\bar{\beta}'_\omega(\infty)$ vs E' on a SL model for all molecules at reaction orders of 1) 1.10, 2) 1.25, 3) 1.50, 4) 1.75, and 5) 2.00; cyclopropane, 728°K, ▽ ; methyl isocyanide, 353°K, ○, and at 546°K, ●. The dashed line is a more limited correlation on the exponential basis and detailed points are omitted to avoid confusing overlap.

9 Plot of R_{1i} vs. i for alkanes and R_{2i} vs. i for alkenes and alkynes for CH_3NC at 504°K (from data of ref. 112).

10 Calculated three-dimensional plots for $\bar{\beta}'_\omega(D)$, ---, and $\bar{\beta}_\omega(D)$, ——, vs. $(k/k_\infty)_{init}$ and D, for C_2H_5NC; 504°K, 385 cm^{-1} SL; the dashed and solid surfaces depict the behavior of the $\bar{\beta}'$ and $\bar{\beta}$ quantities, respectively. The horizontal curves lie on various dilution planes slicing the two surfaces along all values of k/k_∞, while the curves on vertical planes span values of the efficiencies for all dilutions on various intersecting k/k_∞ planes; (from ref. 124)

11 Pressure dependence of unimolecular rate constants at 518°K for CH_3NC with (a) C_4H_8 at infinite dilution (circles) and pure substrate (upper solid curve); (b) He at infinite dilution; the lower solid curve connects the experimental points. The pure substrate curve is transposed from ref. 141 at 230°. To facilitate the comparison, butane pressures were converted to equivalent pressures of CH_3NC; (from ref. 140).

12 Plots of $\bar{\beta}(\infty)$ vs. k/k_∞ for CH_3NC at 518°K with mean step sizes of (a) 560, (b) 340, and (c) 170 cm^{-1} on EXP (dashed line) and SL (solid) models; (from ref. 140).

13 Variation of $\bar{\beta}_\omega(\infty)$with fall-off k/k_∞ for CH_3NC at 518°K based on (a) calculated 400 cm^{-1} EXP model, (b) experimental data, and (c) calculated 350 cm^{-1} SL model, at 245° for CH_3NC-He system; (from ref. 140).

14 A plot of β_c vs. polarizability, for CH_3NC at 554°K. Polar molecules with dipole moments of other molecules are proportional to the filled area of their respective symbols. Numbering of molecules and figure follows ref. 139.

15 A plot of β_μ vs. boiling point for CH_3NC at 554°K; (from ref. 139).

16 A plot of β_c vs. boiling point for CH_3NC at 554°K; monatomic species, ⊡ ; diatomic and small linear molecules, ⧋; other molecules, ● ; (from ref. 139).

Fig. 1

17 Plots of $\beta_0(\infty)$ vs. boiling point for C_2H_5NC at 504°K; ○, monatomic molecules; ●, diatomic and linear molecules; ▨, *n-alkenes*; □, *n-alkanes*; ■, *alkyl nitriles, except* C_2H_5NC; (from ref. 149).

18 Plot of third-order rate constant k_R for iodine atom combination against boiling point of chaperon X; (from data of ref. 65).

19 Plots of relative collisional efficiencies of noble gases β quantities vs. boiling point for various unimolecular systems: CH_3NC, 504°K, ● ; C_2H_5NC, 504°K, □ ; N_2O_2, 223°K, ○ ; NO_2Cl, 546°K, △; sec-C_4H_9, 300°K, X ; cyclobutanone, 296°K, ▲; (from ref. 124).

20 Plots of <ΔE> vs. boiling point for inert gases in the butyl (data of ref. 7), closed symbols, and trifluoroethane (data of ref. 189) systems, open symbols: monatomic, ○ ; diatomic-linear, □ ; non-linear, ▲.

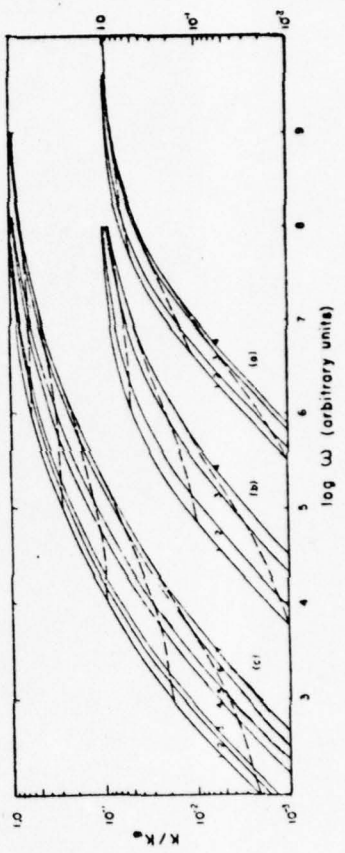


Fig. 2

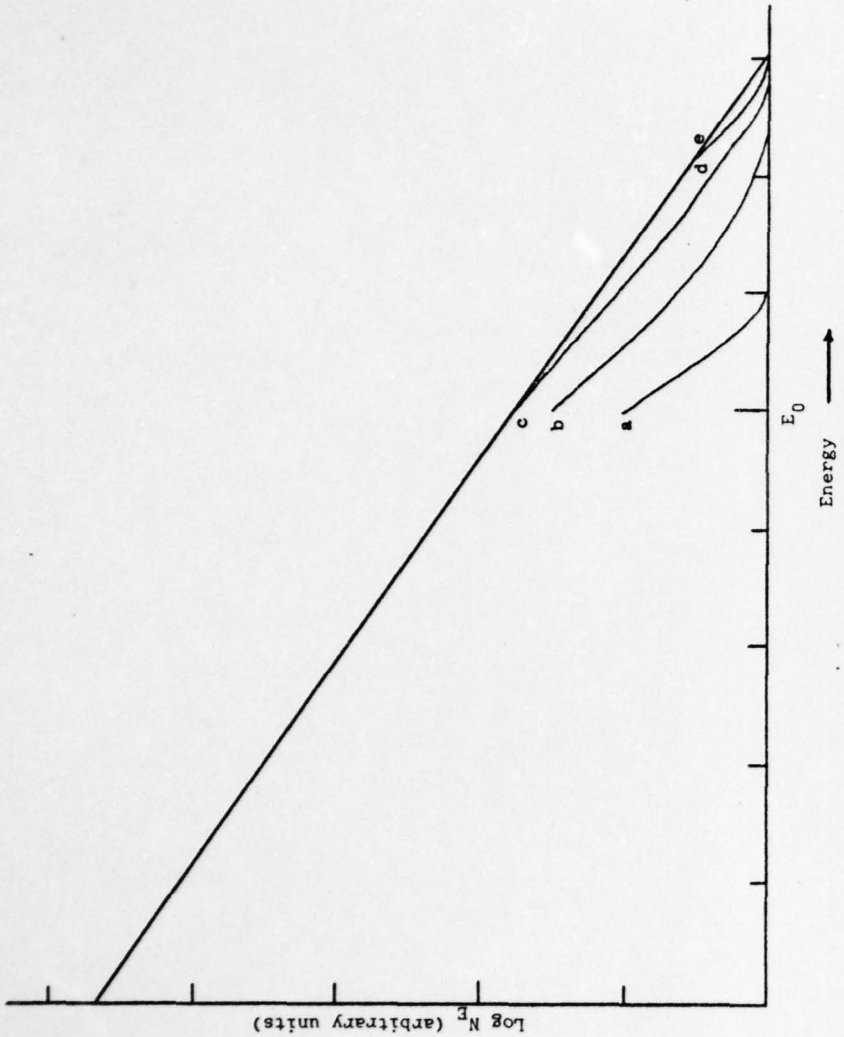

Log N_E (arbitrary units)
Energy
E_0
a
b
c
d
e

Fig. 3

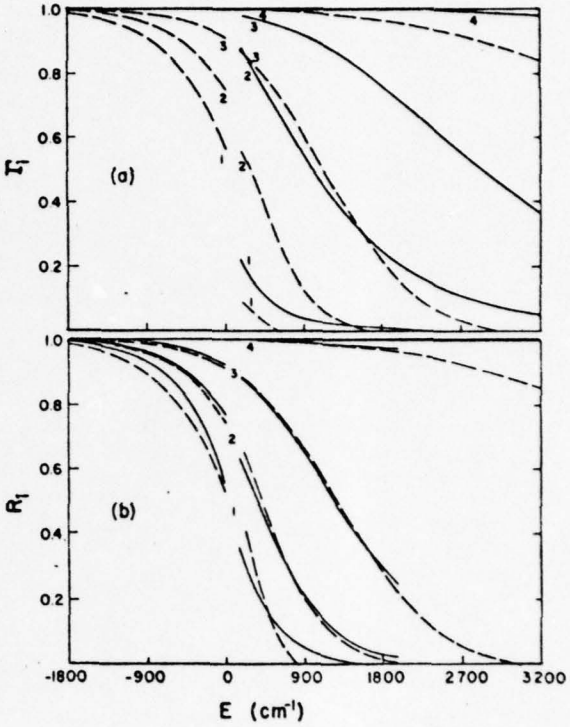

T_1
R_1
(a)
(b)
1.0
0.8
0.6
0.4
0.2
-1800
-900
0
900
1800
2700
3200
E (cm^{-1})

Fig. 5

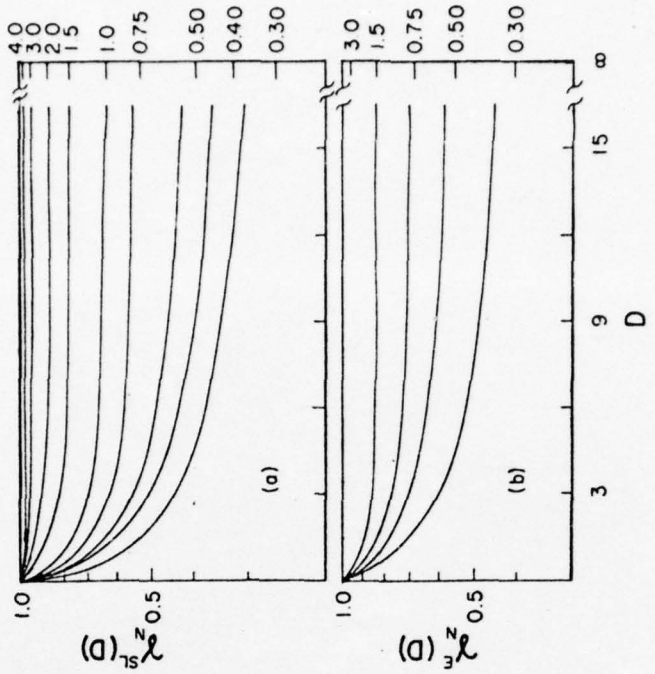

4.0
3.0
2.0
1.5
1.0
0.75
0.50
0.40
0.30
3.0
1.5
0.75
0.50
0.30
1.0
0.5
(a)
(b)
3
9
15
∞
D

Fig. 4

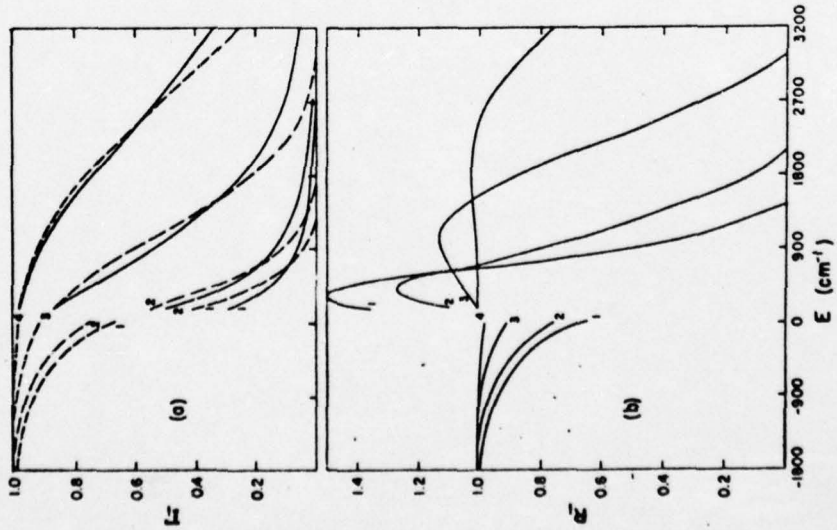

(a)
(b)
E (cm⁻¹)
-1800
-900
0
900
1800
2700
3200

Fig. 6a

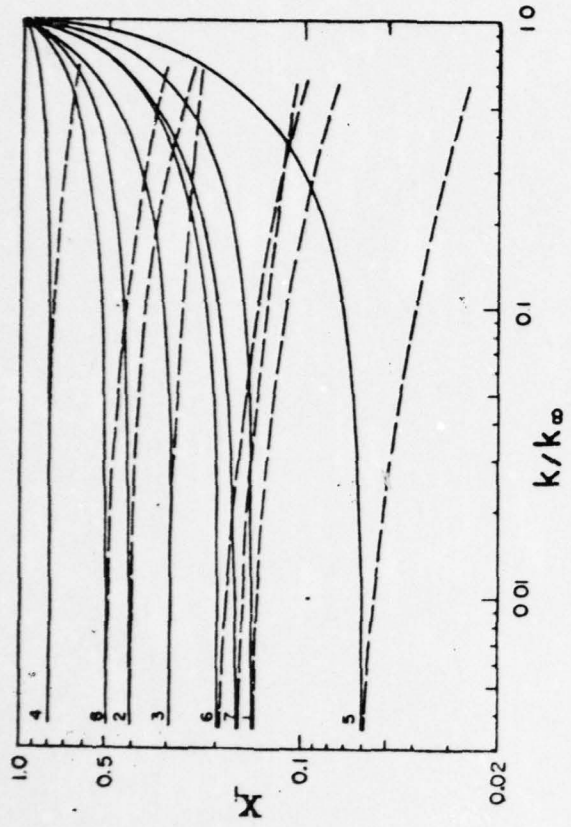

1.0
0.5
0.1
0.02
$\bar{X}$
1.0
0.1
0.01
0.001
k/k_∞
4
8
2
3
6
7
1
5

Fig. 6b

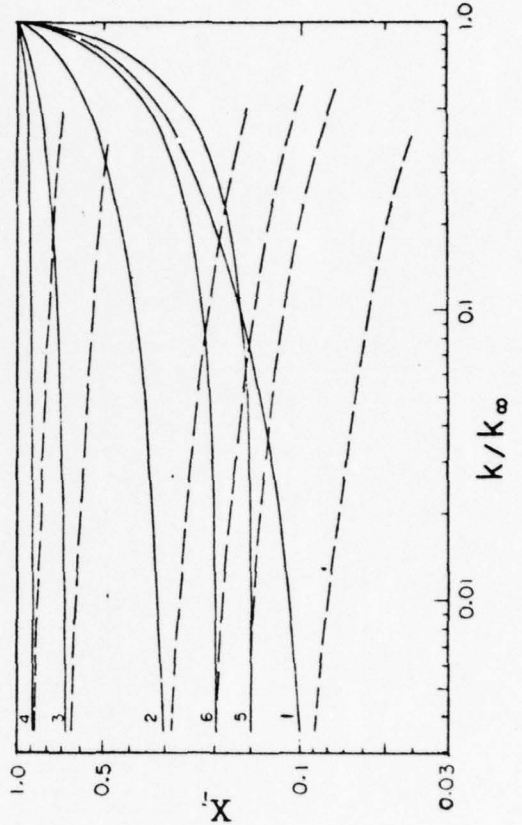

1.0
0.5
0.1
0.03
$\bar{X}$
1.0
0.1
0.01
k/k_∞
4
3
2
6
5
1

Fig. 7

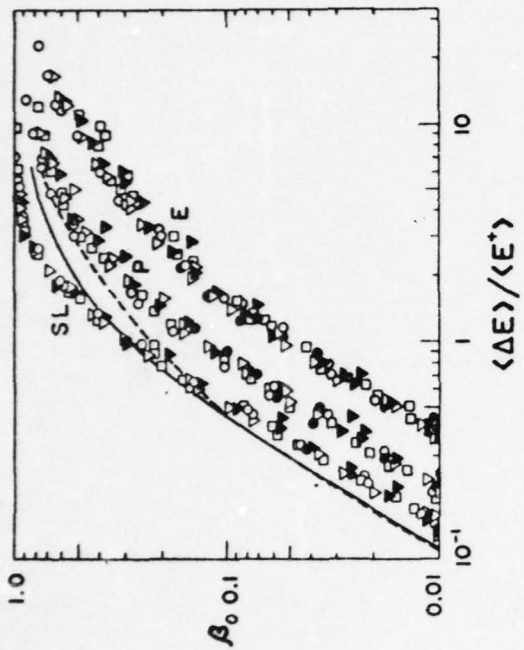
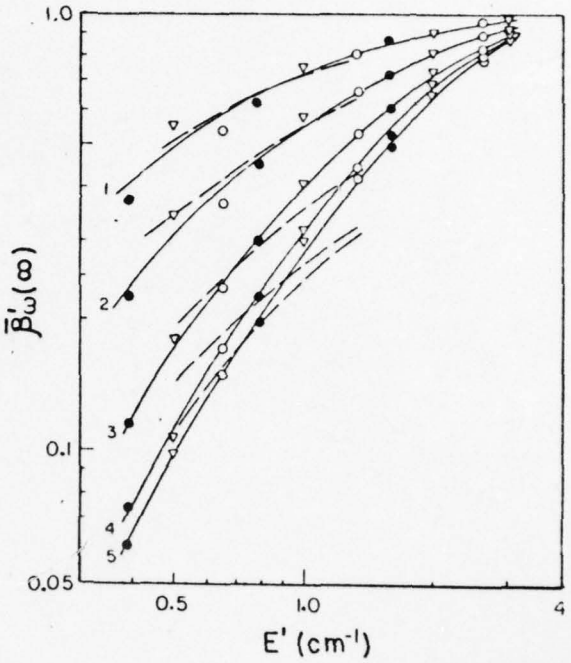
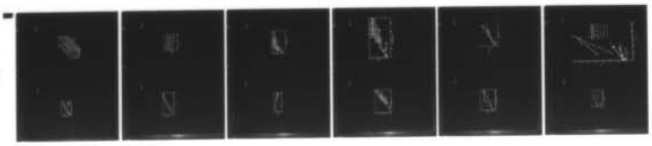

SL
E
P
1.0
0.1
0.01
β_0
10
1
10^{-1}
$\langle\Delta E\rangle/\langle E'\rangle$

Fig. 8


1.0
0.1
0.05
$\bar{\beta}'_\omega(\infty)$
1
2
3
4
5
0.5
1.0
4
E' (cm^{-1})

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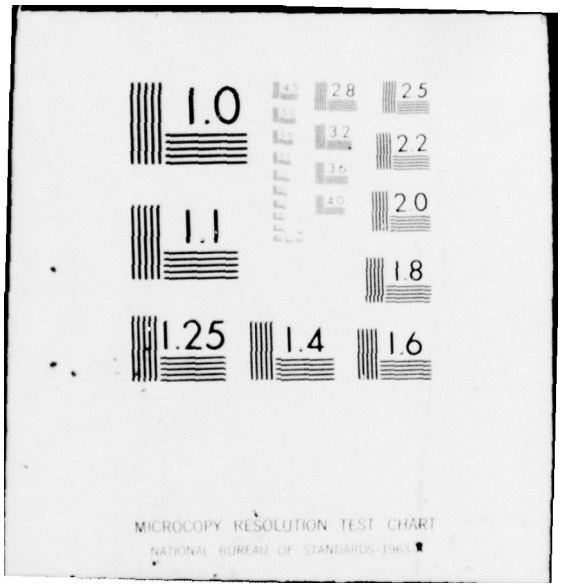

1.0
1.1
1.25
1.4
1.6
2.8
2.5
3.2
2.2
3.6
2.0
4.0
1.8
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963

Fig. 9

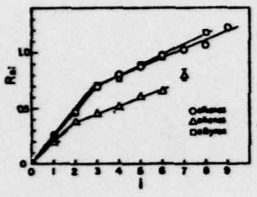


Fig. 10

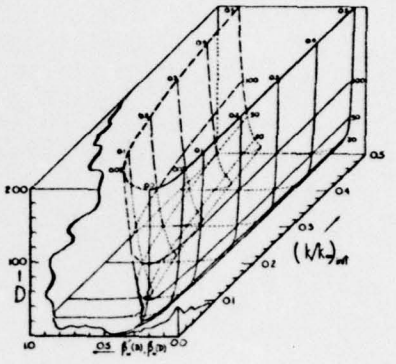


Fig. 11

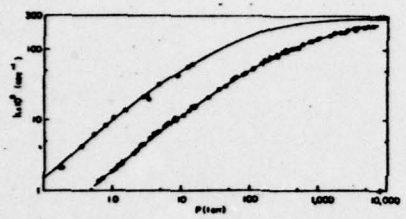


Fig. 12

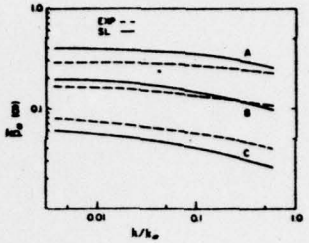


Fig. 13

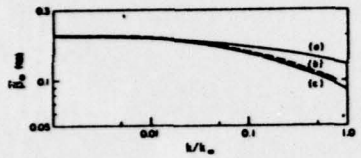


Fig. 14

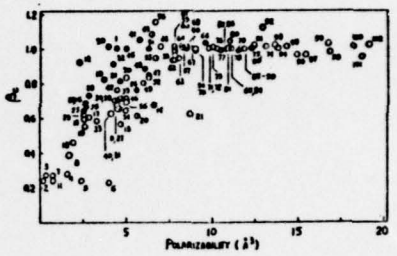


Fig. 15

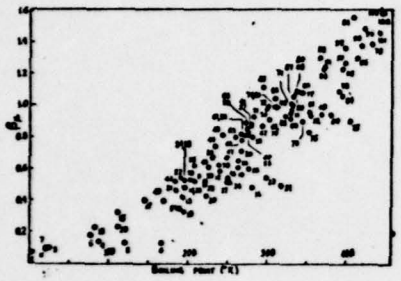


Fig. 16

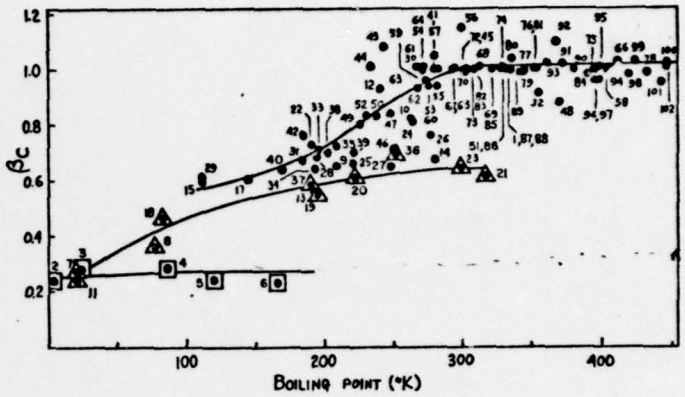


Fig. 17

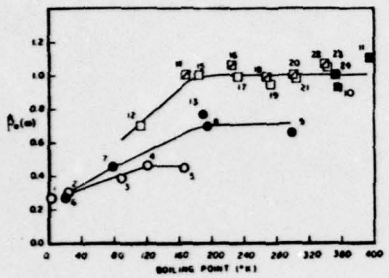


Fig. 18

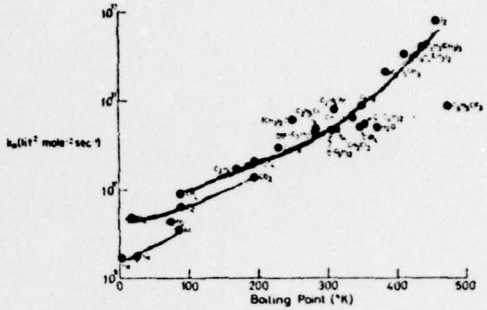


Fig. 19

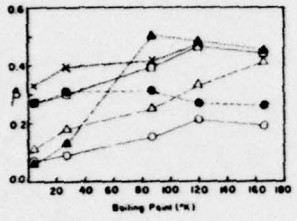
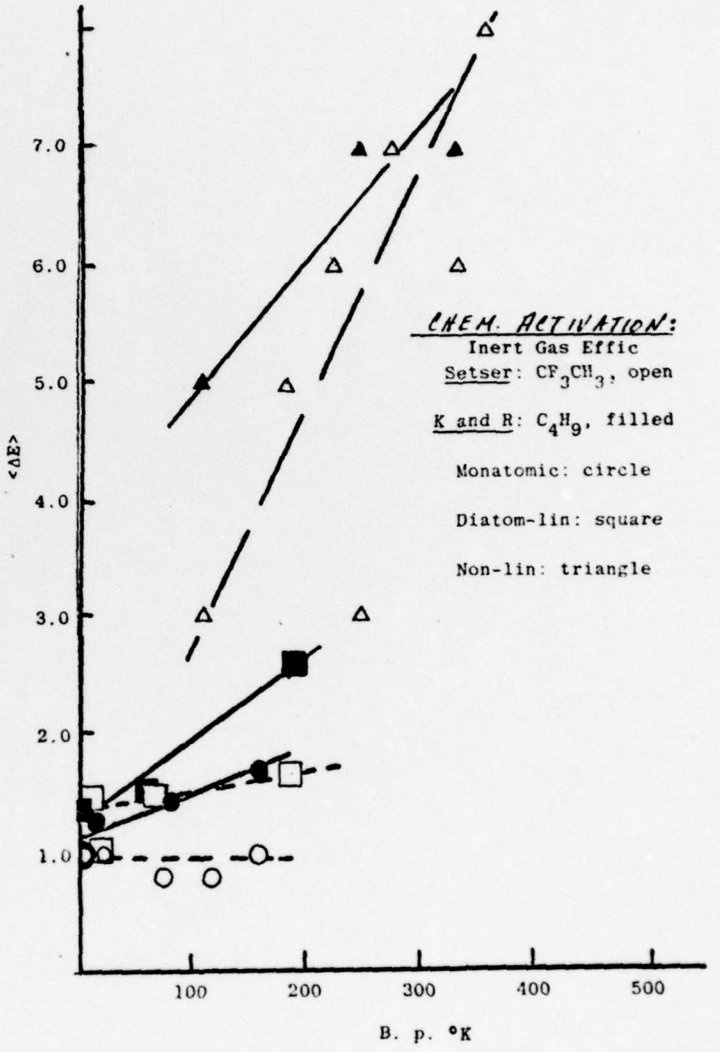

0.6
0.4
0.2
0.0
20 40 60 80 100 120 140 160 180
Boiling Point (°K)

Fig. 20


7.0
6.0
5.0
4.0
3.0
2.0
1.0
<εE>
100
200
300
400
500
B. p. °K
CHEM. ACTIVATION:
Inert Gas Effic
Setser: CF_3CH_3, open
K and R: C_4H_9, filled
Monatomic: circle
Diatom-lin: square
Non-lin: triangle