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In Memory of My Mother

Glossary of Terms

$A=Y_{m'}/Y_{m'}^{eq}$

$B=Z_{n'}/Z_{n'}^{eq}$

ΔE_o the heat of reaction

$E_{v'}$ the vibrational energy of reagent level, v′

$k \equiv (k^f N_A/k^{BC}_{10}N_M - k^r N_C N_{AB}/k^{BC}_{10}N_{BC}N_M)$.

$k^{AB}_{nn'}$ is the rate constant for (de-)activation of the diatomic molecule AB, from level n to n′,

k^{AB}_{10} (de-)activation of AB from v= 1 to v=0

$k^{AB'}_{n,n'} \equiv k^{AB}_{n,n'}/k^{BC}_{10}$

k^{BC}_{10} (de-)activation of BC from v=1 to v =0

$k^{BC}_{m,m\pm1}$ and $k^{AB}_{n,n\pm1}$ are the specific rate constants for the energy transfer processes

$k^{BC}_{m,m'}$ is the rate constant for (de-)activation of the diatomic molecule, BC, from level m to m′ $k^{BC'}_{m,m'} \equiv k^{BC}_{m,m'}/k^{BC}_{10}$

k_{exo} - Overall thermal rate coefficient for an exothermic reaction

$k_f(T)$ - Overall thermal rate coefficient

$k^{f'}_{m-n} \equiv N_A k^f_{n-m}/N_M k^{BC}_{10}$,

$k^{r'}_{n-m}=N_C k^r_{n-m}/N_M k^{BC}_{10}$

k^f_{m-n} is the rate constant for the forward reactive process from vibrational level m of BC to vibrational level n of AB

k^r_{n-m} is the rate constant for the reverse reactive process from vibrational level n of AB to vibrational level m of BC

k_f and k_r are the phenomenological rate coefficients for the reaction. k_f is for the forward reaction and k_r for the reverse reaction. k_f^{eq} and k_r^{eq} are values at thermal equilibrium. K_{eq}

Equilibrium constant $K_{eq} = k_f^{eq} / k_r^{eq}$

k_v - Rate constant for a vibrationally enhanced reaction

k^0_v Prior (statistically expected) rate constant

$k_{vv'}$ and $k_{v'v}$ The state-to-state reactive rate constants

k_0 Rate constant for v=0.

$K_T = Q = [AB][C] / [BC][A]$

m. and n. the single most important vibrational level of the reactants and products

N_m^{BC} Concentration of the diatomic molecule BC in vibrational level m

N_n^{AB} Concentration of the diatomic molecule AB in vibrational level n

N_A Concentration of A

N_C Concentration of C

N_M Concentration of all colliding species present in the system.

Y_m fractional level populations for BC molecule

Z_n fractional level populations for AB molecule

$\beta = k^r_{n\bullet} . Z_{n\bullet} . N_C / k^{BC}_{10} N_M$

$$\Phi = \frac{k^r_{n\bullet} . N_C}{n_\bullet . k_{10}^{AB} N_M} \left(1 - Z_{n\bullet}^{eq} + n_\bullet . Z_{n\bullet}^{eq} \sum_{k=1}^{n\bullet -1} \frac{e^{kv}}{k} \sigma_{k-1}\right).$$

$\gamma = k^r_{m\bullet} . Y_{m\bullet} . N_A / k^{BC}_{10} N_M$

$$\varepsilon = \frac{k^f_{m\bullet} . N_A}{m_\bullet . k_{10}^{BC} N_M} \left(1 - Y_{m\bullet}^{eq} + m_\bullet . Y_{m\bullet}^{eq} \sum_{i=1}^{m\bullet -1} \frac{e^{iu}}{i} S_{i-1}\right)$$

λ Eigenvalues for the matrix U, $\lambda = (k_f [H] / N_M k^{BC}_{10} - k_r [OH][O] / [N_M][O_2] k^{BC}_{10})$ (Chapter 2)

λ The slope, of plots of the surprisal versus (E_{τ} - ΔE_{o}) (Chapter 3)

$X = k^{BC}{}_{10} / k^{AB}{}_{10}$

ξ extent of the reaction

Abstract

The master equation describing the rate of the bimolecular reaction $A + BC \rightleftharpoons AB + C$ under steady-state conditions at the vibrational level of detail, is solved by a matrix technique. A computer program (MRBIM) has been written by the author to exploit the matrix technique as applied to the $H + O_2$ reaction. Reaction from levels v =0 to 15 for O_2 and from levels v =0 to 9 for OH are considered for, while vibrational-translational (V - T) energy transfer by O_2, H, OH, O and He is considered as the mechanism for equilibration. State-to-state rate constants are taken from the literature. The distortion to the rates of the reaction $H + O_2 \rightleftharpoons OH + O$ caused by the non-equilibrium vibrational population distribution is investigated in detail. It is found that the ratio of forward and reverse rate coefficients, (k_f/ k_r), does not equal the equilibrium constant, K_{eq}, when the reaction proceeds far from equilibrium; and this is because the individual rate coefficients are suppressed from their equilibrium values to different extents. Interesting details of the fractional level populations are discussed.

We have applied information theory to the HBr (v) + Cl $\rightleftharpoons$ HCl (v') + Br reaction over a wide range of temperatures, and we have thus extracted an extensive set of state-to-state rate constants from scattered literature data. We also made use of microscopic-reversibility to obtain the exothermic state-to-state rates. Our values for the rate constants fit and extrapolate all existing data. For example, k_0 (rate coefficient for v=0) for the endothermic reaction at 298 K agrees with Arnoldi's estimate, and with our calculated value using Douglas's exothermic rate and Pollak's microscopic-reversibility relation, thus ensuring consistency. This data base is then used to investigate the non-equilibrium effect for the reaction HBr (v) + Cl $\rightleftharpoons$ HCl (v') + Br .

Reaction from levels v' =0 to 9 of HCl and levels v =0 to 9 of HBr are considered, while vibrational-translationsl (V - T) energy transfer by HCl, HBr, Cl, Br, and Ar is considered. The measure of the non-equilibrium effect $(k_f/k_r) / K_{eq}$ is much more severe for reaction occuring far from equilibrium compared to reaction occuring close to equilibrium, where it is close to unity. The fractional population of higher vibrational levels is depleted for both extremes, but it is more severe for reaction occuring far from equilibrium.

For both reactions it is found that the kinetic mass action law breaks down, ie $(k_f/k_r) \neq K_{eq}$. When the forward reaction dominates ie $Q/K_{eq} < 1$ ($Q= [AB][C]/[A][BC]$), the non-equilibrium factor, $(k_f/k_r)/K_{eq} < 1$; whereas when the reverse reaction dominates it is >1. The deviation of k_f / k_r from K_{eq} becomes more severe as the reaction gets further from equilibrium. The temperature dependence of the non-equilibrium factor is complex.

An effort to solve the master equation analytically has resulted in closed form expressions for the rate law for reversible bimolecular reactions, as well as for the thermal rate coefficients, k_f and k_r , and for the ratio of k_f / k_r under highly reactive non-equilibrium conditions. They are improvements over the classical expressions commonly used by kineticist. They are in qualitative agreement with the exact numerical results, and under some conditions, also in quantitative agreement. Model calculations wherein are varied the molecular vibrational spacings, the state-to-state reactivities, the equilibrium constant, the energy transfer rate constants, and the molecular concentrations, indicate that our analytical expressions improving on the kinetic mass action law, can be best used when reactivity is from v >0, v' >0, and when $K_{eq} \approx 1$. The results present a challenge to experimentalists for confirmation. Whether analytical or experimental, the present results indicate that the commonly used kinetic mass action law must be used with extreme caution.

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CHAPTER 1

Introduction

1.0 $H + O_2 \rightarrow OH + O$

The branching chain kinetics of the combustion of hydrogen and oxygen has been studied extensively over the past 50 years in the temperature and pressure regions spanning the explosion limits. One property of the branching chain mechanism is the occurrence of an induction period during which practically no reaction occurs. The length of the induction period has been studied in detail as a function of temperature and of the H_2, O_2, and inert gas concentrations. The important reaction steps during and after the induction period are believed to be:

0) $H_2, O_2 + M \rightarrow H, O, \text{or } OH + M$,

1) $H + O_2 \rightarrow OH + O$,

2) $O + H_2 \rightarrow OH + H$,

3) $OH + H_2 \rightarrow H_2O + H$,

4) $H + O_2 + M \rightarrow HO_2 + M$,

5) $H, O, OH \xrightarrow{\text{wall}} H_2, O_2, H_2O$.

The chain branching step 1) is the critical one which determines the overall rate, the length of the induction zone and the first explosion limit. Hence there has been and there still is a great deal of interest in that reaction. A key study of this reaction to which we shall refer is that of Schott who measured the rate coefficient and activation energy for the $H + O_2 \rightarrow OH + O$ reaction [1, 2]. His Arrhenius expression was $k = 1.22 \times 10^{17}\, T^{-0.907} \exp(-8369/T)\ \text{cm}^3\,\text{mole}^{-1}\,\text{s}^{-1}$. For several years the most reliable description of the high temperature rate constant was this expression of Schott's. However, Frank and Just questioned the negative temperature dependence for the reverse reaction implied by the above expression [3]. Because of the importance of the reaction, the rate coefficient, k, has been measured and reviewed by several investigators [3-10]. These recent high-temperature experimental data agree with one another up to about 2000 K; however, above 2000 K the spread in the values increases to about a factor of 2 as the temperature increases to 2500 K. At even higher temperatures, this uncertainty in k increases to a factor of 5. The activation energy decreases from 16.9 to 12 kcal mol^{-1} over the temperature range 300 to 2500 K. At higher temperatures E_a increases to the expected limit of 17 kcal mol^{-1} as the reagents become more dilute in Ar. This is an unacceptable level of uncertainty for such a critical parameter. We have plotted log k vs 1/T for this reaction and we have included in Figure 1.1 recent work on this reaction. The negative deviation is contrary to transition state theory, which in this case predicts a positive deviation from Arrhenius behavior.

Fuji et al also questioned Schott's Arrhrenius expression at higher temperatures: " The present data support the long-suspected feeling of combustion modelers that there is some difficulty unappreciated so far with Schott's experiments". Schott offered an explanation for his observations: "One appealing hypothesis is that the dilution effect being seen is associated with a non-thermal vibrational condition of either the H_2 or the O_2 ......" [4].

1.1 $OH + O \rightarrow O_2 + H$

The reverse of our reaction of interest has been also extensively studied over the years [11-23].

We have plotted log k.vs 1/T for this reaction and included in Figure 1.2 recent studies. The rate constants are large and consistent with each other but the interesting feature in Fig 1.2 is that combined with existing low-temperature data, the work of Frank and Just [3] implies that the rate coefficient first decreases with increasing temperature and then starts to increase. We used their rate coefficient, k_f, for the forward reaction ($O_2 + H \rightarrow O + OH$) and the equilibrium constant K_{eq} to determine the high-temperature value of k_r for the exothermic reaction, ie $k_r = k_f / K_{eq}$ This result demonstrates a possible problem with making uncritical use of the kinetic mass action law.

1.2 Review of Experimental methods for $H + O_2 \rightarrow OH + O$

In this section we are going to examine Fig. 1.1 in greater detail. We are going to demonstrate that a non-equilibrium effect is playing a role for this reaction, and that not merely experimental errors are causing the discrepancies. We are going to compare the work of Just and Fuji [3,4] with the works of Schott and Yuan [2,6], since their works show the greatest deviations. The works of Just and Fuji agree with each other and the works of Schott and Yuan agree with each other. Yuan used a shock tube to measure this rate coefficient with various mixtures of H_2-O_2-Ar. The difference between the result of Schott's rate coefficient and Yuan's rate coefficient is less than 6%, within the experimental uncertainties. Yuan's Arrehenius expression, $k = 1.59 \times 10^{17} T^{-0.927} e^{-8493/T}$ $cm^3 mol^{-1} s^{-1}$ with one standard deviation of 0.05 for log k . Fuji also used a shock tube to determine the rate coefficient of this reaction. His work gave $k = 6.0 (\pm 3) \times 10^{14} \exp(-95 \pm 5$ $kJ/RT)$. At lower temperatures the Arrhenius expression given by Yuan agrees with Fuji's Arrhenius expression. At higher temperatures the deviation is large, as much as a factor of 2. For example, at 3000 K Yuan's expression gave $\log k = 12.75 \pm 0.05$ $cm^3 mol^{-1} s^{-1}$ and Fuji's expression gave log k = 13.11 ± 0.15. Even if we take the experimental error into account the deviation between the two values of k at 3000 K is 40%. This proves that experimental error alone does not explain the discrepancies in k measured over the years but rather that an explanation must be sought elsewhere. Non-equilibrium effects have to be taken into account. The difference between Fuji's experiment and Yuan's experiment is the initial concentration of O_2 and H_2. Yuan used in all his experiments O_2 concentrations which were 10 or 20 times the concentration of H_2. Fuji, on the other hand, varied the ratio of concentrations, covering more cases like when hydrogen was present 4 times as much as oxygen. Thus we conclude that the rate coefficient for this reaction depends on the chemical environment. Most importantly in Fuji's experiment, oxygen and hydrogen were more highly diluted in Argon. Essentially this means that equilibrating non-reactive collisions dominated, confirming that energy transfer processes play a role in the discrepancies.

1.3 Definition of Non-equilibrium Kinetics

It turns out that Schott was right about the observed dilution effect being associated with a non-thermal vibrational condition. This is a manifestation of non-equilibrium kinetics. Whenever a chemical reaction occurs via a specific excited quantum level of the reagent, that level population becomes selectively depleted. Just as for unimolecular reactions with a "weak" collider at low pressures, a bimolecular reaction will occur with a non-Boltzmann distribution of reagent levels. Products of reactions are also formed in non-Boltzmann distributions, and they are the reagents for subsequent steps in a complex mechanism. The Boltzmann distribution in terms of the fractions of molecules Y_i^{eq} in state i is:

$$Y_i^{eq} = \frac{e^{-\beta\epsilon_i}}{\sum_i e^{-\beta\epsilon_i}}$$

Here β is $1/k_BT$ and ϵ_i is the energy of the state I. During a real reaction highly reactive levels are relatively depleted so that the true fractional population distribution Y_i will not obey this equation. No general equation can be written to describe the non-Boltzmann distribution because the distribution depends on the particular reaction and reaction media.

Nonequilibrium effects on dissociation and unimolecular reactions have been widely studied [24-30]. Most work on non-equilibrium effects on nondissociation reactions has centered on translational disequilibrium [31-34], usually using approximate solutions of the Boltzmann equation. Internal-state disequilibrium effects may be addressed in terms of the discrete-index master equation. Eyring and co-workers presented early examples of such treatments for irreversible few-state first-order or pseudo-first-order models of reactions [35, 36]. Poulsen and Shizgal have presented more realistic examples for slow four-centered exchange reactions [37, 38]. There has been less work on atom-transfer reactions, but Finkelman and Dove studied vibrational state models [39, 40]. In addition to the papers presenting calculations, several authors have provided general discussions of the effect on reaction rates of non-equilibrium internal-state distributions of reactants or products [44-47].

The approach, considering non-Boltzmann distributions, can be termed, by definition, "non-equilibrium kinetics". Although this term encompasses all kinds of energy levels, including electronic and translational, this study is restricted to the case of chemical interest and does not consider plasma temperatures where electronic and translational effects become important [43]. What is known currently about vibrational / rotational non-equilibrium kinetics is restricted in the literature to the field of unimolecular reactions.

1.4 Comparison between unimolecular and bimolecular reactions

Non-equilibrium effect on dissociation and unimolecular reaction have been widely studied [24-30]. There has been relatively little work done, however, on non-equilibrium kinetics of bimolecular reactions. The same guiding principles successfully used for unimolecular reaction (competition between energy transfer and reactivity) apply in general to all reactions, and suggest that manifestations of this should be looked for in the case of bimolecular reactions. The following table illustrates the expected similarities and differences between unimolecular and bimolecular reactions.

	Unimolecular Reaction $BC + M \rightarrow B + C + M$	Bimolecular Reaction $A + BC \rightleftharpoons AB + C$
competition between energy transfer and reactivity	Yes	Yes
Distortion of population distribution	Yes	Yes
k	$< k_{eq}$	$< k_{eq}$
[BC's reactive partners]	[M]	[A]
[collider]	[M] = constant	[M](t) [M]= A, BC, AB, C, He..
E_o (barrier height)	$>> k_BT$	no restriction

Important levels which react	only those close to within k_BT of the dissociation limit	any level of product and reactant can react
$k_f/\ k_f^{eq}$	independent of concentrations	depends on the concentrations
Scientific activity	well-studied	hardly studied at all

Note that it is expected that k_f/k_f^{eq} depends on the ratio of reactive rates to energy transfer rates. For unimolecular reactions this is $k_{reactive}[BC]/k_{energy\ transfer}[BC][M] = k_{reactive}\ /\ k_{energy\ transfer}[M]$. For bimolecular reactions it is $k_{reactive}[BC][A]/\ k_{energy\ transfer}[BC][M] = k_{reative}[A]/\ k_{energy\ transfer}[M]$, a qualitatively different behaviour.

1.5 Kinetic Mass Action

Classical chemical kinetics is based upon two or three fundamental equations which are used (almost) universally without question. For

$$A + BC \rightleftharpoons AB + C \tag{1.1}$$

the rate can be written

$$\frac{d[BC]}{dt} = k_f[A][BC] - k_r[C][AB] \tag{1.2}$$

Here k_f and k_r (the thermal rate coefficients for the forward and reverse processes respectively) are considered to be pure constants depending only on the temperature. The kinetic mass-action law relates k_f and k_r by:

$$K_{eq} = \frac{k_f}{k_r} \tag{1.3}$$

where K_{eq} is the thermodynamic equilibrium constant K_C. These fundamental equations are predicated upon the implicit assumptions that the internal energies of BC and AB are described by Boltzmann distributions during the reaction. However, in actual fact, whenever a chemical reaction proceeds primarily via a specific level of the reagents and products, that level population becomes selectively depleted. Consequently if those levels are particularly important, the rate coefficients, k_f and k_r are depressed from the values they would have had under conditions of thermal equilibrium [41]. A bimolecular reaction will occur with a non-Boltzmann or "non-equilibrium" population distribution for reagents and products .

What is the origin of our ideas concerning the use of $k_f / k_r = K_{eq}$ for reaction 1.1? At any time t

$$\text{rate} = k_f[A][BC] - k_r[AB][C].$$

At equilibrium

$$0 = k_f^{eq}[A]_{eq}[BC]_{eq} - k_r^{eq}[AB]_{eq}[C]_{eq}$$

So

$$k_f^{eq} / k_r^{eq} = [A]_{eq}[BC]_{eq} / [AB]_{eq}[C]_{eq} = K_c^{eq}.$$

But does $k_f/k_r = k_f^{eq}/k_r^{eq}$ at all times? Generally not because k_f and k_r can depend on the concentration of all chemical species present, some of which change with time, and this is because the depression of k_f and k_r from their expected values is due to depletion of the population of important levels because of poor energy transfer processes which are highly dependent on the available collision partners.

Why do we need to use $k_f/k_r = K_{eq}$ and why not just measure k_f and k_r in the experiment simultaneously ? In most experiments either the forward reaction dominates or the reverse reaction dominates. Consequently, either k_f or k_r are determined, but not both. However, since both rate constants are needed to simulate complex reactions, there is a need to estimate the missing k. Therefore we need to use the kinetic mass action law. As we shall see below, this law in not always acceptable. Therefore, we need a better law.

The need to study the kinetics of reversible bimolecular reactions with their vibrational detail stems from two important observations: a) endothermic bimolecular reaction rates are enhanced by vibrational energy of the reagents; and b) exothermic bimolecular reactions often produce species which are vibrationally and rotationally excited [42]. Until now kineticists have simulated real reaction mechanisms, (consisting of several bimolecular reactions) by implicitly assuming that the vibrational and rotational levels of all multi-atomic species are distributed according to Boltzmann statistics. This is an approximation which is not justified particularly for fast chemical reactions or for species whose internal energy equilibrates ("relaxes") slowly. A given reaction will proceed under vibrational non-equilibrium conditions if the four following conditions are satisfied: (a) reaction is "fast" when compare to energy transfer; (b) the reagents/products relax "slowly" when compare to reaction, (c) the reaction is enhanced by vibrational energy; and (d) the temperature is high enough so that a significant fraction of vibrationally excited states is populated and can be potentially depleted. If some or all of these requirements are met, then eq.(1.2) is not valid under these non-equilibrium conditions; i.e, k_f and k_r are not true constants in concentration or time. Thus, it is generally true that the population of the high vibrational levels of reagents are depleted, whereas the high vibrational levels of products are overpopulated. Since the products of one reaction are sometimes the reagents for subsequent reactions, the whole process is rather complicated. Depending on the reaction conditions different scenarios can be envisaged. The 'rate coefficients', k_f and k_r, become distorted from the kineticist's expectation, k_f^{eq} and k_r^{eq} respectively. Indeed the whole concept of a rate constant comes into question. However, even if k_f and k_r are constants they are affected differently and their ratio is not necessarily equal to K_{eq}. The examples of reactions which show a non-equilibrium effect at least in the forward direction are: $O + HCl \rightleftharpoons OH + Cl$, $Cl + HBr \rightarrow Br + HCl$, $H + H_2 \rightarrow H_2 + H$ (and its isotopic variations) , $O + H_2$, and $OH + H_2$. These reactions are discussed in more detail in later sections.

1.6 Manifestations of the Failings of Classical Kinetics

It has already been mentioned above that k_f and k_r differ from k_f^{eq} and k_r^{eq}, by varying amounts depending on the temperature. This could result in non-Arrhenius behavior. Theories of chemical reaction rely on the equilibrium assumption and fine-tune themselves by trying to reproduce experimental results. Curvature of such plots might be falsely attributed to special features of the transition state or to quantum mechanical tunnelling rather than to simple non-equilibrium effects. Consequently theoretical approaches might be led astray.

Consequences for experimental kinetics are no less severe. One may legitimately ask if the rate coefficients for the elementary reactions in the literature are correct. Are they k_f^{eq} and k_r^{eq} or somewhat less than k_f^{eq} and k_r^{eq}? Were they determined under conditions where non-equilibrium effects were absent? May they be used to predict the behavior of complex systems such as combustion or atmospheric processes? In other words, even if k_f^{eq} and k_r^{eq} for an elementary process were properly extracted from well-designed experiments, is it appropriate to use them for simulating complex processes in which non-equilibrium effects are likely to show up? Certainly the chemical environment of such systems is highly varied. Furthermore, the products of elementary reactions may be produced in strongly non-Boltzmann distributions, especially if exothermic. Consequently, secondary reactions may not even proceed initially from a Boltzmann distribution. Each effect is compounded by a subsequent step, and each subsequent step's effect is compounded by the previous one's.

We are systematically investigating non-equilibrium phenomena for fast bimolecular reactions in the gas phase in our lab, and at the same time we are attempting to write improved analytical expressions for rate laws that can be readily used to replace the standard one (eqn(1.2)) whenever non-equilibrium effects might be important. A second problem with which we are concerned is the uncritical use of the kinetic mass-action law (eqn(1.3)). As we stated earlier, k_f and k_r are affected differently. Thus eqn (1.3) cannot be valid unless the non-equilibrium factor for the forward reaction equals the non-equilibrium factor for the reverse reaction at all times. However, since the concentrations of all chemical species change with time during a reaction, it would be coincidental if BC were to relax and react at the same rate as AB so as to ensure that the factors cancel. Therefore it is worth investigating this question in detail.

1.7 Non-equilibrium Kinetics of Reversible Bimolecular Reactions.

1.7.1 Previous Studies of the Phenomenological Rate Law

There has been very little work done which solves the problem for this class of reactions analytically. However, there are a number of studies which address the problem numerically.

The first study of this type was done by Snider and Ross [44] who investigated the validity of the phenomenological rate law for the case of exchange reactions of the form

$$X + YZ \rightleftharpoons XY + Z \qquad (1.4)$$

They concluded that a phenomenological rate law is valid for the above reaction only for two cases: i) when the chemical reaction is proceeding sufficiently slowly that it causes a negligible perturbation of the internal-state distributions, and ii) when one of the components, say YZ, is present in large excess so that the following conditions hold: a) the rate of the back reaction is insignificant; and b) essentially all inelastic collision suffered by X are X-YZ collisions. Snider and

Ross also considered what happens when reactive system (1.4) is displaced a small amount from equilibrium. They showed that even for this case, a phenomenological equation holds . They did not, however, explicitly consider what experimentally observable effects would occur in case a phenomenological rate equation was not obeyed.

Later, Widom [45] too addressed the validity of the phenomenological rate law. In the above reaction X and Z are structureless ground-state species, whereas YZ and XY are diatomic molecules. He found that the equilibrium approximation overestimates the phenomenological rate constant by a factor "that is typically about 2 and may often be much larger". In a later study Widom [46] concluded that the local equilibrium approximation would be accurate i) for a large excess of both atoms over molecules or ii) very close to equilibrium, if the activation energy is much greater than k_BT, which he assumed implied that the state-to-state reaction rate constants are much smaller than the relevant state-to-state vibrational energy-transfer rate constants. Unfortunately neither set of conditions i) or ii) is relevant for the usual conditions under which gas-phase rate coefficients are measured, let alone for real combustion conditions.

The validity of the phenomenological rate law for the above reaction is also addressed in a thesis by Finkelman [38]. A vibrational ladder model was employed in this study (in which reactive and non-reactive processes were considered) and rotational effects were not considered. The system was composed of structureless species (X), diatomic molecules (YZ), products (XY,Z) and an inert gas (M). The diatomic reactant was treated as a truncated harmonic oscillator with 4 or 7 vibrational levels. Landau-Teller scaling was used to obtain the energy transfer rates which were also assumed to be proportional to [M]. The latter implies either that (i) the mixture is so highly dilute in inert gas that V-V energy transfer is negligible and inert-gas collisions dominate the vibrational energy transfer rates or that (ii) reactants and products have approximately equal energy-transfer efficiencies. Thus the mechanism considered for (1.4) is

$$YZ(v) + M \rightleftharpoons YZ(v \pm 1) + M \qquad (1.5)$$

$$X + YZ(v) \rightleftharpoons XY + Z \qquad (1.6)$$

The set of differential rate equations for the system was integrated using a numerical integrator based on Gear's method [47]. Finkelman found that, after a transient period, the system obeyed a second-order phenomenological rate law, and that under some conditions the phenomenological rate coefficient, averaged over the course of the reaction, represented the observed rate coefficient whereas for extreme conditions (for example, high temperature) it did not. In the most extreme case he found that the final value of the phenomenological rate coefficients were almost 1000 times smaller.

Some of the results in Finkelman's thesis are included in a paper by Clark et al [40]. They reported substantial departures (factors of $3\text{-}10^3$) of the observable rate coefficient for (1.4) from the local equilibrium estimate, even for small [YZ]/[M], a case where the energy of activation is $9k_BT$.

Gutkowicz-Krusin studied a simple 3-component multi-state model of the exchange reaction (1.4) in order to illustrate how it gives rise to the phenomenlogical rate equation [48]. The reactant molecule YZ is assumed to have two internal states and the product molecule XY one.

Only collisions of the type X-YZ and XY-Z are considered, and all other collisions are assumed to contribute only to translational equilibrium and maintenance of local equilibrium for XY. For this model, Gutkowicz-Krusin found that the phenomenological rate equation always holds eventually, sometimes after a very short transient period, but in other cases only after macroscopically long transient times. The duration of the transient period and the magnitude of the rate constant were found to depend on the conserved quantities, i.e. [X] + [XY].

More recently Lim, and Truhlar [49] reported that the rate coefficients, for Cl + Hbr ⇌ Br + HCl were distorted by no more than 1%, though, under non-typical experimental conditions. The phenomenological rate coefficients for their reaction was calculated by numerical integration of the rate equations using a method derived from the work of Gear [47], as well as by iteration to a quasi-steady state and by eigenvalue analysis of a linearized master equation. Their differential rate equation accounted for state-to-state reactive processes and for simultaneous intramolecular vibration-rotation energy transfer as well as intermolecular vibration-vibration energy transfer processes and analogous processes for the reverse reaction. However, they chose a temperature of 300 K and they concentrated on the exothermic direction. Both these choices led to negligible non-equilibrium effects and coloured their conclusions prematurely.

All the above mentioned studies show that there is an important effect. At times the results are seemingly contradictory. However, when substantial effects <u>are</u> predicted these studies concentrate on only some of the relevant parameters. Furthermore, although an invalid phenomenological rate expression implies an invalid kinetic mass action law too, this seems not to have been addressed explicitly from a theoretical viewpoint. Such will be the innovation of the present study, with the aim being to present a usable improved expression.

1.7.2 Previous Studies of the Kinetic Mass Action Law

In 1922, Lindemann proposed a general theory for thermal unimolecular reactions which forms the basis for the current theory of thermal unimolecular rates. He proposed that molecules AB become energized by bimolecular collisions. The energized molecule might lose its excess energy by collision with another, or alternatively the excited molecule might decompose spontaneously and form products. According to these concepts, the mechanism for the unimolecular reaction may be written as

$$AB + M \rightarrow AB^{*} + M \quad k_1$$

$$AB^{*} + M \rightarrow AB + M \quad k_{-1}$$

$$AB^{*} \rightarrow A + B \quad k_2$$

Here, AB^{*} represents a molecule with sufficient energy to react and M is some collision partner. It is assumed that each AB^{*} + M collision transfers much energy and thus leads to de-energizing of AB^{*}: this is known as the "strong collision" assumption for de-energizing collisions. A major achievement of Lindemann's theory is its ability to explain the experimental finding that the reaction rate changes from first to second order in going from the high- to low-pressure limit. If the steady-state hypothesis is applied to the concentration of AB^{*}, the overall rate of reaction becomes

$$\text{rate} = k_{uni}[AB] = k_2[AB^*] = k_1k_2[AB][M]/(k_{-1}[M] + k_2)$$

The reaction rate is first order at high pressure, where [M] → ∞, and second order at low pressure, where [M] → 0. The transition from the high-pressure rate constant to the low-pressure linear decrease in k_{uni} is called the fall-off region. The theory predicts the fall-off in k_{uni} to occur at much higher pressures than what is observed experimentally.

One of the reasons for the discrepancy is that the Lindemann-Hinshelwood mechanism, fails to recognize that a specific excitation of the molecules may be required before reaction occurs. This is the approach used in the RRK (Rice-Ramsperger-Kassel) theory and its extension, which is referred to as the RRKM (Rice-Ramsperger-Kassel-Marcus) theory. These two theories picture a molecule as a collection of coupled harmonic oscillators which exchange energy freely under the assumptions that vibrational energy redistribution within the energized molecule is much faster than unimolecular reaction.

The Lindemann theory of unimolecular reactions lacks a detailed microscopic picture of the collision dynamics of intermolecular energy transfer. What is needed is an understanding of how intermolecular energy transfer from highly energized molecules is influenced by the energizing level, the partitioning of energy between vibration and rotation, and the relative translational energy between the colliding bath and energized molecules AB. The minimum requirement is an understanding of the dependence on the internal energy E of the dissociating molecule, recognizing the non-Boltzmann (or "non-equilibrium") nature of the energy distribution, $[AB(E)]$.

Non-equilibrium effects on dissociation and unimolecular reactions have been widely studied. The master equation of a dissociation-recombination system can be written, in continuous form,

$$\frac{d[AB(E)]}{dt} = +\int_{0}^{\infty} k(E/E')[M][AB(E')]dE' - \int_{0}^{\infty} k(E'/E)[M][AB(E)]dE' + k_{ass}(E)[A][B] - k(E)[AB(E)] \quad (1.7)$$

$k(E'/E)$ denotes the rate constant for collisional energy transfer between AB and M with AB's energy changing from E to E′; $k_{ass}(E)$ is the rate constant for association of A and B to AB in state E; $k_{diss}(E)$ is the rate constant for dissociation of AB in state E. The dissociation experiments are usually carried out under conditions $[AB] \ll [M]$ and $[AB] \gg [A]$ and $[B]$; and the association experiments are carried out under conditions $[A]$ and $[B] \ll [M]$, and $[AB] \ll [A]$ and $[B]$. Master equations are solved under the steady state assumption, i.e. $[AB]^{-1}\, d[AB(E)]dt \approx 0$, for dissociation and $([A][B])^{-1}d[AB(E)]dt \approx 0$, for recombination. For dissociation the non-equilibrium fractional population in state E is given by $[AB(E)]/[AB]$ and the equilibrium population in state E is $f(E) \equiv ([AB(E)]/[AB])_{eq}$. Hence, the non-equilibrium factor, $h_{diss}(E)$, is given by $[AB(E)]/[AB]/([AB(E)]/[AB])_{eq}$. For recombination the non-equilibrium fractional population is given by $[AB(E)]/[A][B]$ and the equilibrium population is given by the product of the equilibrium ratio $f(E)K_{eq}^{-1} = \{[AB(E)]/[A][B]\}_{eq}$. The non-equilibrium factor, $h_{rec}(E)$, is defined as the ratio of those 2 fractional populations. Using detailed balancing, $k(E/E')\, f(E) = k(E'/E)$ and $k(E)f(E) = K_{eq}k_{ass}(E)$, Equation 1 can be transformed into

$$k(E)\,h_{diss}(E) = \int_0^\infty k(E'/E)\,[M]\,[h_{diss}(E') \; - \; h_{diss}(E)]\,dE' \qquad (1.8)$$

for dissociation, and

$$k(E)\,[1 \; - \; h_{rec}(E)] = \int_0^\infty k(E'/E)\,[M] \;\; (1 \; - \; [h_{rec}(E')] \; - \; [1 \; - \; h_{rec}(E)])\;dE' \quad (1.9)$$

for recombination.

The solution of Equation 1.8 for $h_{diss}(E)$ and for of equation 1.9 for $[1\text{-}h_{rec}(E)]$ are nearly the same, and one has $h_{diss}\,(E) + h_{rec}\,(E) = 1$. We insert this into the expression for the rate constants, i.e. into

$$k_{rec} = \int_0^\infty \;(k_{ass} f(E)\;(1 - h_{rec}(E))\,K_{eq}^{-1} dE$$

and

$$k_{diss} = \int_0^\infty k(E)\;f(E)\;h_{diss}(E)\,dE$$

taking the ratio of k_{diss} to k_{ass} leads directly to the equilibrium relation, $k_{diss}\,/\,k_{ass} = K_{eq}$.

In the rate constant, k_{diss}, the nonequilibrium effects can be represented by a collision efficiency factor, β, that is given by the ratio of the weak collision nonequilibrium rate coefficient and the hypothetical strong collision equilibrium rate constant, $k_{diss} / k_{diss}{}^{SC} \equiv \beta$. This factor is given by

$$\frac{\beta}{1-\sqrt{\beta}} \simeq \frac{<\Delta E>}{F_E kT}$$

The collision efficiency factor β increases monotonically with increasing $-<\Delta E>/F_E\, kT$. $<\Delta E>/F_E\, kT$ measures how efficient the energy transfer process is. This term is analogous to k_{10}, the energy transfer rate constant for bimolecular reaction (see below).

Taking the ratio of k_{diss} to k_{ss} leads directly to the equilibrium relation for low pressure unimolecular reactions highly diluted in M. This is only true because the assumption is made that $h_{diss}(E) + h_{rec}(E) \simeq 1$. Even if this were true we must examine the term β more closely. It turns out that β is approximately given by $1/(1+\epsilon)$ for both unimolecular and bimolecular reactions, where ϵ expresses the competition between the reaction and the energy transfer processes. Kineticsits who use weak-collision theories for unimolecular reactions always make two assumptions. One is that $[AB] << [M]$; and the other is that reaction occurs from the level just above the threshold for dissociation. Hence ϵ for unimolecular reactions can be written qualitatively as $\epsilon = k_f[AB^*]/(k_{energy\ transfer}[AB^*][M])$ which can be simplified as $\epsilon = k_f / (k_{energy\ transfer}[M])$. The term ϵ is constant because [M] is constant and it is the same for both directions. Therefore the nonequilibrium factors for the forward and reverse unimolecular reactions cancel out. On the other hand ϵ, the ratio of reactivity to energy transfer rates, for the forward bimolecular reaction, is given qualitatively by $\epsilon = k_f[BC^*][A] / k_{10}[BC^*][M]$, where M can be A, BC, or an inert diluent; whereas, for the reverse bimolecular reaction it is given by k_r [AB][C] /k_{10} [AB][M], where M is essentially AB, C or an inert diluent. Therefore, not only will the non-equilibrium factors not cancel out when taking the ratio of k_f / k_r , but neither factor is even constant, as they depend on the chemical environment, ie on [A], [BC], [AB], [C] and [M]. Clearly, we cannot expect $k_{forward}$ / $k_{reverse}$ to equal to K_{eq}, at least for bimolecular reactions.

In contrast to the lack of theoretical attention to eq. (1.3) **observed** rate coefficients, k_f and k_r, for the reaction Cl + H_2 = HCl + H have been found not to obey the relation $k_f/k_r = K_{eq}$, where K_{eq} is the equilibrium constant for the reaction [35]. The observed ratio of rate coefficients is lower than K_{eq} by a factor of 2-3 over the temperature range studied. In the experiments the forward reaction was run in a large excess of H_2, while the reverse reaction was run in a large excess of HCl. It was noted that $k_f/k_r = K_{eq}$ held only if k_f and k_r were measured in large excesses of the same component. Various explanations have been offered to resolve this paradox. While it is always true that microscopic reversibility holds for individual state-to-state transitions, eq. (1.3) need not be valid for macroscopic rate coefficients unless the reactants and products are in thermal equilibrium. For example, Snider [50] and Clyne [51] suggested that the observed k_f could be smaller than anticipated if Cl($^2P_{1/2}$) is much more reactive than Cl($^2P_{3/2}$), so that its relative concentration would be significantly depleted by the reaction. Alternatively, Westenberg and de Haas [52] suggested that k_r could be larger than expected if HCl formed by the forward reaction has sufficient excess rotational energy to enhance the reverse reaction rate.

These explanations, which are based on a non-equilibrium distribution of states, have been discussed in detail by Galante and Gislason [53]. They have concluded that they are incompatible with much of the available experimental and theoretical evidence on the system. For example, if Snider's proposal were correct, the rate of the reverse reaction would be increased by the presence of a molecule, such as CCl_4, that efficiently interconverts $Cl(^2P_{1/2})$ and $Cl(^2P_{3/2})$. However, a measurement of k_r [54], yielded a value (1.4×10^{-14} cm^{3}molecule^{-1} s^{-1}) that was in substantial agreement with that obtained earlier by Westenberg and deHaas (1.3×10^{-14} cm^{3}molecule^{-1} s^{-1}). This agreement between the various measured values of k_r led Galante and Gislason to critically reexamine measurements of the reaction between atomic hydrogen and HCl. They noted that Westenberg and de Haas failed to detect the presence of all the atomic chlorine, and suggested a possible reason for this - namely, the occurrence of a fast wall reaction between atomic chlorine and atomic hydrogen:

$$H + Cl \xrightarrow{wall} HCl$$

They argued that, if this reaction were sufficiently fast, a second hydrogen atom would be consumed, and the value of k_r, estimated from the measured hydrogen decay rate, would be high by a factor of 2. The work of Spencer and Glass [55] showed no evidence for the wall reaction between H and Cl. However, they argued that secondary reactions do produce effects similar to those produced by the mechanism postulated by Galante and Gislason. Later work of Miller and Gordon confirmed, though, that wall reactions are important [56]. We therefore conclude that there is no non-equilibrium effect for this reaction. We do not expect one, anyway, because the H_2 vibrational levels are so far apart that few vibrationally excited molecules can possibly be involved and also because relaxation of H_2 is much faster than the reaction itself.

Recently, Teitelbaum [57] addressed the validity of the kinetic mass action law for the $O+HCl \rightleftharpoons OH + Cl$ reaction. He considered first $O + HCl$ to react in isolation from the reverse process, and then he considered $Cl + OH$ to react in isolation from its reverse process. In both cases he used experimental state-resolved rate constants which are related by microscopic reversibility, so that at least $k^f_{eq}/k^r_{eq} = K_{eq}$. These rate constants, along with the known energy transfer rate constants, were used as input data in the differential rate equations. This set of rate equations was then solved exactly in the limit where a steady vibrational energy level population distribution was established before the reverse reaction interfered. He calculated the forward thermal rate coefficients, k_f, and the reverse thermal phenomenological rate coefficient, k_r. It was demonstrated that the ratio, k_f/k_r, does not equal the equilibrium constant, $K_{eq.}$ when the reactions proceed far from equilibrium. The deviations are only about 5%. However, from a fundamental viewpoint this represents a breakdown of the kinetic mass action law.

Studies of the $Cl + H_2$ reaction and the $O + HCl$ reaction addressed the question whether the kinetic mass action law breaks down or not experimentally. The former study concentrated on measurements of k_f and k_r; while the latter concentrated on measurements of vibrationally state-selected rate constants (which were used to deduce k_f and k_r). However, both studies suffered from being unable to consider situations where forward and reverse reactions are simultaneously contributing significantly to the overall rate. The present study contributes to this issue by examining such realistic situations. We shall extend the theoretical approach initiated by Teitelbaum for uni-directional reactions, as described below.

1.8 Previous Studies of Non-equilibrium Irreversible Bimolecular Reactions.

Until the Teitelbaum group began focussing on the issue there was relatively little work which examined vibrationally disequilibrated bimolecular reactions. Shizgal calculated the decrease in the forward rate of the reaction

$$H_2 + H_2 \rightarrow \text{products}$$

due to perturbation of the vibrational distribution function by reaction, using a numerical solution of the nonlinear master equation [38]. Translational and rotational equilibrium were assumed, and a 3-state vibrational model involving only $H_2(v)$ with $v=0,1$ and 2, was used. Shizgal calculated k^f/k^f_{eq}, but he completely neglected back reaction. The value of k^f/k^f_{eq} deviating most from its equilibrium value of unity was 0.9979 at 3200 K, the highest temperature studied.

Porter et al. considered the reaction $Cl + HCl \rightarrow Cl_2 + H$ at 400K. They solved a vibrational-level master equation numerically, neglecting the back reaction [58]. They found that, although the local equilibrium model would predict that reaction proceeds predominantly through the $v=5$ state, this state cannot be regarded as being in local equilibrium, and actually about 50% of the reactive flux proceeds through $v=4$. Although this was an ominous sign, the authors did not report a value for k^f/k^f_{eq}.

Recently Teitelbaum developed a rate law for the uni-directional bimolecular reaction

$$\boldsymbol{A} + \boldsymbol{BC} \rightarrow \boldsymbol{AB} + \boldsymbol{C} \tag{1.10}$$

under conditions of translational-rotational equilibrium but vibrational disequilibrium [59]. An appropriate rate equation was shown to be of the form

$$Rate = k[A][BC]/[1 + f(T)[A]/[R]] \tag{1.11}$$

where k is a time- and concentration-independent constant, f is a temperature-dependent constant and [R] is the concentration of the molecules responsible for relaxing BC via T ⇔ V processes alone.

In deriving eq. (1.10) Teitelbaum assumed that the rotational population distribution is not disturbed by the chemical reaction. (Generally, rotational equilibrium occurs on the 1-10 collision time scale [60] so this assumption is justified). This limits studies to temperatures where the reaction rate coefficient is less than one tenth of the gas-kinetic collision value. Second, for an energy-transfer mechanism he considered only T⇔V processes and ignored V⇔V processes. Although the latter may be efficient they cannot replenish the vibrational energy of an ensemble of harmonic oscillators lost by reaction [61]. Anharmonicity allows for some energy replenishment, but only at the expense of efficiency [61]. Third, he formulated a model which treats the diatomic molecules, BC, as harmonic oscillators reacting from energy level, m_*, which contributes most to the reaction flux. It was discovered that m_* is usually quite low on the vibrational ladder (eg. $m_* = 1$ for $Br + HCl \rightarrow HBr + Cl$ [62]) i.e. in the region where the intra-molecular potential is essentially harmonic. The depleted population of level m_* is replenished by energy transfer from the reservoir levels $v \leq m_*$ containing most of the population. Furthermore, his study of the reaction $H + H \rightarrow H_2 + H$, established that there is practically no difference between a calculation which treats H_2 as an anharmonic oscillator and one which treats H_2 as a simple harmonic oscillator [63]. Finally, he considered only that portion of the reaction which is free of transient phenomena, i.e. he assumed that a steady-state population distribution is established before back reaction sets in. The criterion for validity of this assumption is $k_r k_f [A][BC] << k_{10}^2 [R]^2$ where k_r is the rate coefficient for the reverse reaction, $AB + C \rightarrow A + BC$ [64]. It is satisfied for the reactions he considered.

The first example examined was the reaction $Br + HCl \rightarrow HBr + Cl$. Depending on the initial reagent concentration it was shown that the rate is reduced (by factors ranging up to 11) from the equilibrium rate. Other series of reactions: $H + H_2$ (and its isotopic variations) [65], $O + H_2$, and $OH + H_2$ [17] also showed similar behavior, albeit not so dramatic. Teitelbaum then proceeded to eliminate the major approximation that reaction only take place from the vibrational level m_*. An exact analytical expression was obtained for the phenomenological rate of reaction and for the non-equilibrium vibrational population distribution of BC [59]. He also offered an alternative matrix method of solving the steady state master equation exactly. The validity of the simple approximate rate law (eq. (1.6)) was confirmed by comparing with the results of the numerical technique. The reaction of choice was $Br + HCl \rightarrow HBr + Cl$. The agreement between the approximate solution and the exact solution was good to excellent [63]. His systematic investigation examined most of the approximations made to solve the problem. However, he did not address the full role of the reverse reaction by allowing its state-selected components to proceed simultaneously with the forward reaction, a problem which was an order of magnitude more difficult. The novelty of the present study is to solve this problem.

1.9 Plan of Study

In order to see how seriously k_f/k_r deviates from K_{eq} it is important to investigate the kinetics at the microscopic level of detail for real (in distinction from model) reactions with known state-to-state rate constants. First, we shall solve the set of vibrational-level-dependent rate equations exactly using a numerical method. We shall improve upon the existing model by allowing the reverse reaction to participate. We also allow reaction to proceed from any vibrational level, m, of the reactants into any vibrational level, n, of the products. Next, we shall attempt to solve the set of vibrational-level-dependent rate equations by analytical means. This approach jumps off from and exploits all of Teitelbaum's previous findings. We allow reaction to proceed from the single most important vibrational level m_* of the reactants to the single most important vibrational level n_* of the products and vice-versa. If we can get a sufficiently good picture of the problem by solving the master equation approximately, there is no need to evaluate the exact solution (which requires us to know all of the state-to-state reactive rates). We nevertheless do offer the exact solution which makes use of numerical methods. However, the analytical solution has the advantage of physical transparency that closed form solutions always have. The numerical technique is more exact but it can be inconvenient for modelers of complex chemical systems in the sense that they cannot calculate the matrix eigenvalues by hand. Even a computer program would become unwieldy with the enormous number of terms that needed to be included in the rate expression. We shall check the validity of our analytical expression by comparing the results with those obtained using the numerical matrix technique. The first reaction of choice is $H + O_2 \rightleftharpoons OH + O$ because of its importance and because this is the only one in the literature for which the microscopic state-to-state rate coefficients are available over a wide temperature range.

We shall consider four general questions: i) After the initial transient period, does the phenomenological rate law hold with constant rate coefficients or do the rate coefficients change continuously? ii) If the rate coefficients do not depend on the extent of reaction during a single experiment, to what extent are they independent of the initial composition of the reactive system? (iii) To the extent that the phenomenological rate coefficients are independent of extent of reaction and initial composition, how do they compare to the equilibrium rate constants? (iv) If the rate coefficients do depend on the extent of the reaction, to what extent is k_f/k_r equal to K_{eq}? The first two questions examine the validity of the phenomenological rate law for bimolecular reactions, and the third question gives a quantitative estimate of the deviations of the phenomenological rate coefficients from their local equilibrium estimates. The last question examines the validity of the kinetic mass action law.

Although it is a very important reaction we do not want to limit our study to $H + O_2 \rightleftharpoons OH + O$. Rather we want to test our analytical expression on other reactions as well. The endothermic reaction $HCl + Br \rightarrow HBr + Cl$ is known to exhibit a profound non-equilibrium effect [66], and it is for this reason that we decided to re-examine it with its reverse process included. Unfortunately the data base was very limited. We had to apply information theory to extend our knowledge of microscopic state-to-state rate coefficients for $HBr + Cl \rightleftharpoons HCl + Br$ in order to advance towards our goals. We shall examine the above four questions for this reaction also.

To begin with, then, we consider the reaction $H + O_2 \rightleftharpoons OH + O$. As stated earlier, a given reaction will proceed with vibrational non-equilibrium populations if the four following conditions are satisfied: (a) reaction is "fast" when compared to relaxation of O_2 and OH (; (b) the reagents/products relax "slowly" when compare to reaction, (c) the reaction is enhanced by vibrational energy; and (d) the temperature is high enough so that a significant fraction of vibrationally excited states are populated and can be potentially depleted.

Before we start, we need to see if these conditions are actually satisfied by our reaction. We have summarized the rate constants for vibrationally enhanced reactivity for $H + O_2 \rightarrow OH + O$ in Table 1.1. Miller [67] used the Melius - Blint potential energy surface [68] for a quasi classical trajectory calculation of the effect of vibrational energy of O_2 on the rate of this endoergic reaction. He covered the range $v = 0$ to 4 and $T = 250$ to 2500 K. He provided analytical fits, and Teitelbaum used them to extrapolate to 8000 K [69]. The reaction changes from endoergic to exoergic at $v=4$. An earlier study by Gauss using an LEPS surface [70] complements Miller's, as it covers the range $v = 4$ to 6. Then Teitelbaum extended the work to higher vibrational levels using information theory [69]. The rate constants for the exothermic reaction $OH + O \rightarrow O_2 + H$ were calculated using microscopic reversibility. These results are summarized in Table 1.2.

From Table 1.1 and Table 1.2 one can see that as the temperature is raised the rate constants become larger. They also increase as the vibrational level increases. Thus our reaction satisfies the condition that reaction is "fast" (when compared with the relaxation of O_2 and OH) and also that the reaction is enhanced by vibrational energy. In order to see if the reactants and products relax slowly we need to compare the reactive rates with the relaxation rates of O_2 and OH. We have summarized the relaxation rate constants in Table 1.3 and Table 1.4. By comparing the reactive rate constants with the relaxation rate constants we see that reactive rates are larger and hence our reactants and products indeed relax "slowly" enough. The temperature also has to be high enough so that the higher vibrational levels are populated. The reason we need higher vibrational levels to be populated is so that these vibrational levels have a chance to become depleted and hence suppress the rate coefficients. Indeed, the Boltzmann population of O_2 for $v = 0$ to 5 at 300 to 4000 K (Table 1.5) demonstrates the significant amounts of excited O_2. OH is relatively less vibrationally excited, and this alone indicates different behaviours for the forward and reverse reactions.

Table 1.1 Rate Constants ($cm^3\ mol^{-1}\ s^{-1}$) for vibrationally enhanced reactivity of $H + O_2$ - $OH + O$.

v	300 K	500 K	1000 K	2000 K	4000 K	8000 K
0	1.05 (2)[b]	7.46 (6)	2.71 (10)	1.72 (12)	1.42 (13)	3.44 (13)
1	1.25 (5)	4.14 (8)	1.71 (11)	4.14 (12)	2.37 (13)	5.42 (13)
2	5.82 (7)	1.14 (10)	6.39 (11)	7.24 (12)	3.25 (13)	7.31 (13)
3	9.17 (9)	1.40 (11)	1.38 (12)	9.72 (12)	3.84 (13)	8.75 (13)
4	3.07 (11)	7.08 (11)	2.23 (12)	1.22 (12)	4.41 (13)	1.01 (14)
5	8.75 (12)	9.85 (12)	1.34 (13)	3.07 (12)	7.15 (13)	1.40 (14)
6	5.64 (13)	4.85 (13)	4.54 (13)	6.34 (13)	1.05 (14)	1.73 (14)
7	1.56 (14)	1.25 (14)	1.00 (14)	1.11 (14)	1.50 (14)	2.13 (14)
8	2.33 (14)	2.01 (14)	1.58 (14)	1.61 (14)	1.93 (14)	2.45 (14)
9	2.49 (14)	2.39 (14)	1.94 (14)	1.94 (14)	2.21 (14)	2.61 (14)
10	2.60 (14)	2.54 (14)	2.12 (14)	2.17 (14)	2.45 (14)	2.82 (14)
11	2.67 (14)	2.62 (14)	2.19 (14)	2.27 (14)	2.53 (14)	2.85 (14)
12	2.68 (14)	2.66 (14)	2.24 (14)	2.34 (14)	2.63 (14)	2.98 (14)
13	2.76 (14)	2.71 (14)	2.29 (14)	2.39 (14)	2.69 (14)	3.04 (14)
14	2.80 (14)	2.76 (14)	2.32 (14)	2.43 (14)	2.73 (14)	3.08 (14)

[a] Obtained from ref (68).[b] 1.05 (2) means 1.05 x 10^2 $cm^3\ mol^{-1}\ s^{-1}$

Table 1.2 Rate Constants ($cm^3mol^{-1}\ s^{-1}$) for vibrationally enhanced reactivity of $OH + O \rightarrow O_2 + H$.

v	300 K	500 K	1000 K	2000 K	4000 K	8000 K
0	2.02 (13)	1.65 (13)	1.26 (13)	1.31 (13)	1.71 (13)	3.06 (13)
1	3.05 (13)	2.88 (13)	2.26 (13)	2.23 (13)	2.53 (13)	3.82 (13)
2	3.17 (13)	3.05 (13)	2.45 (13)	2.46 (13)	2.75 (13)	3.96 (13)
3	3.28 (13)	3.16 (13)	2.53 (13)	2.53 (13)	2.70 (13)	3.66 (13)
4	3.40 (13)	3.27 (13)	2.61 (13)	2.55 (13)	2.57 (13)	3.16 (13)
5	3.50 (13)	3.35 (13)	2.66 (13)	2.54 (13)	2.46 (13)	2.70 (13)
6	2.86 (13)	2.85 (13)	2.24 (13)	2.06 (13)	1.87 (13)	1.77 (13)
7	8.59 (12)	1.19 (13)	1.05 (13)	1.06 (13)	9.51 (12)	7.85 (12)
8	6.03 (11)	1.75 (12)	2.21 (12)	2.99 (12)	2.96 (12)	2.30 (12)
9	-	9.22 (11)	2.06 (11)	4.75 (11)	5.79 (11)	4.63 (11)
10	-	1.99 (10)	9.53 (9)	4.52 (10)	7.51 (10)	6.73 (10)

[a] Obtained from ref (68).

Table 1.3 Rate constants ($cm^3mol^{-1}s^{-1}$) for vibrational de-excitation of O_2 by M= H, O_2, OH, O, He ; O_2 (v = 1) + M → O_2 (v = 0) + M.

T/K	$k^{O_2}_{10}$ [f]	k^{He}_{10} [c,f]	k^{O}_{10} [d,f]	k^{H}_{10} [e]	k^{OH}_{10} [e]
300	1.54 (6)[a,g]	5.98 (8)	8.07(11)	1.57(10)	8.07(11)
500	2.77 (7)[a]	4.07 (9)	1.36(12)	6.20(10)	1.36(12)
1000	1.06 (9)[b]	4.29 (10)	3.02(12)	3.50(11)	3.02(12)
2000	3.78 (10)[b]	3.93 (11)	8.07(12)	1.95(12)	8.07(12)
4000	9.36(11)[b,h]	3.30 (12)	2.58(13)[h]	1.10(13)	2.58(13)
8000	1.69(13)[b,h]	2.54 (13)	9.31(13)[h]	6.18(13)	9.31(13)

[a] From ref. (71). [b] From ref. (72). [c] From ref. (73). [d] From ref. (74). [e] See chapter 2 for more detail. [f] Measurement of relaxation times, pτ/atm s, were converted to rate constants using $k_{10} = 82.06T[1-\exp(-u)]^{-1} (p\tau)^{-1}(N_{av})^{-1}$. [g] 1.54 (6) means 1.54 x 10^6. [h] Data extrapolated from lower temperatures.

Table 1.4 Rate constants ($cm^3mol^{-1}s^{-1}$) for vibrational de-excitation of OH by M= H, O_2, OH, O, He; OH (v = 1) + M → OH (v = 0) + M.

T/K	k^{O2}_{10} [a]	k^{He}_{10} [a]	k^{O}_{10} [a]	k^{H}_{10} [a]	k^{OH}_{10} [a]
300	6.00(11)[b]	1.20(10)	6.00(12)	1.03(13)	1.08(13)
500[c]	1.30(12)	4.50(10)	6.00(12)	1.03(13)	1.44(13)
1000[c]	2.30(12)	1.98(11)	6.00(12)	1.03(13)	1.92(13)
2000[c]	4.50(12)	6.60(11)	6.00(12)	1.03(13)	2.40(13)
4000[c]	7.30(12)	1.62(12)	6.00(12)	1.03(13)	2.88(13)
8000[c]	1.10(13)	3.40(12)	6.00(12)	1.03(13)	3.36(13)

[a] From ref (75). [b] 6.00(11) means 6.00x10^{11}. [c] See chapter 2 for more detail.

Table 1.5 Fractional level population of O_2

T/K	v=0	v=1	v=2	v=3	v=4	v=5
300	0.99994	0.00057	3.266×10^{-7}	2.603×10^{-10}	2.090×10^{-13}	1.895×10^{-17}
1000	0.8932	0.09494	0.01044	0.00119	0.00010	1.715×10^{-5}
2000	0.67112	0.21879	0.07258	0.02449	0.00841	0.00294
4000	0.42217	0.24105	0.13883	0.08066	0.04727	0.02747

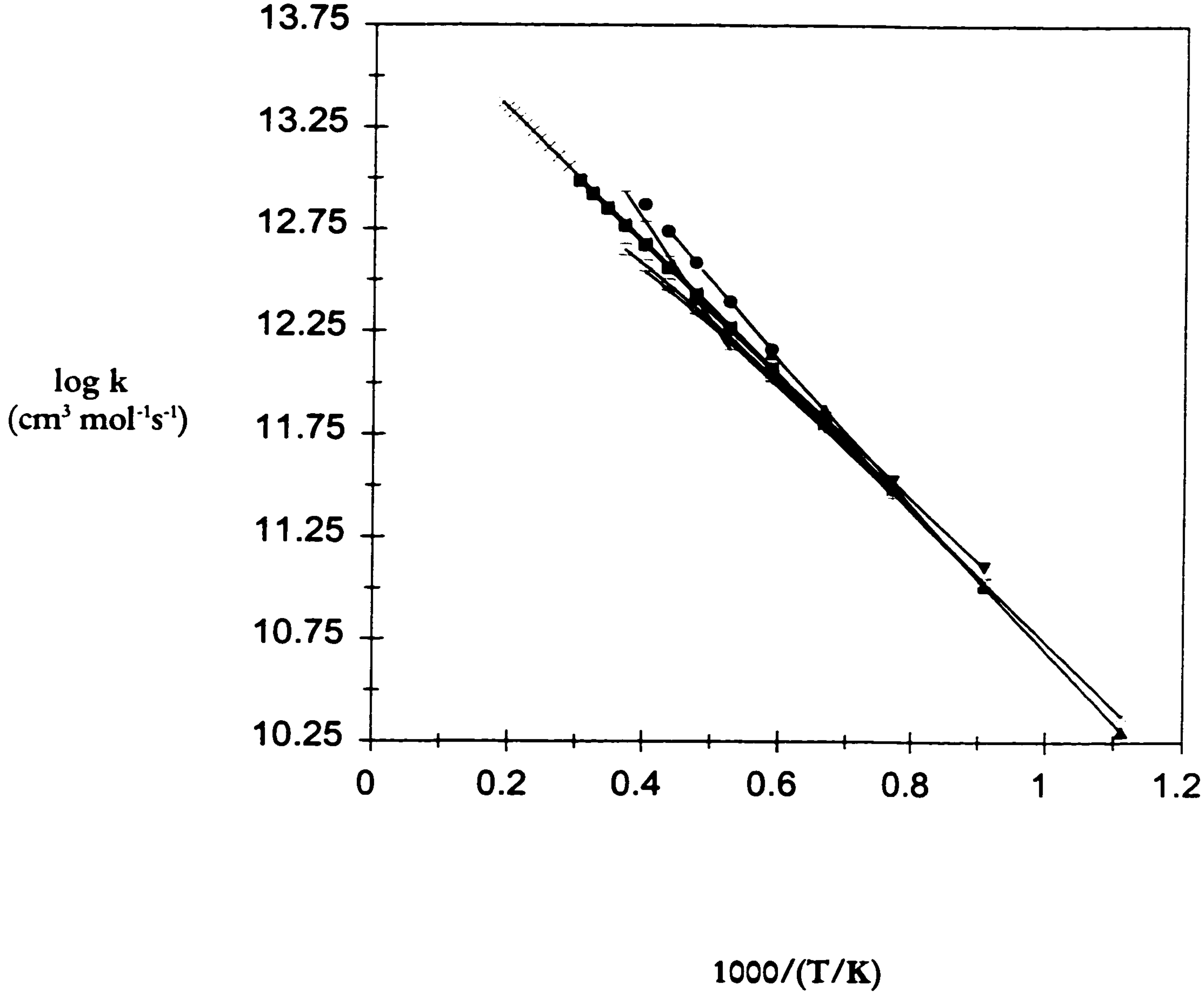

Fig 1.1: Thermal rate coefficient for H + O_2 → OH + O. + from ref. 2. ● from ref. 3. – from ref. 4. ■ from ref. 5. □ from ref. 6. ▲ from ref. 7. ▼ from ref. 8. × from ref 9

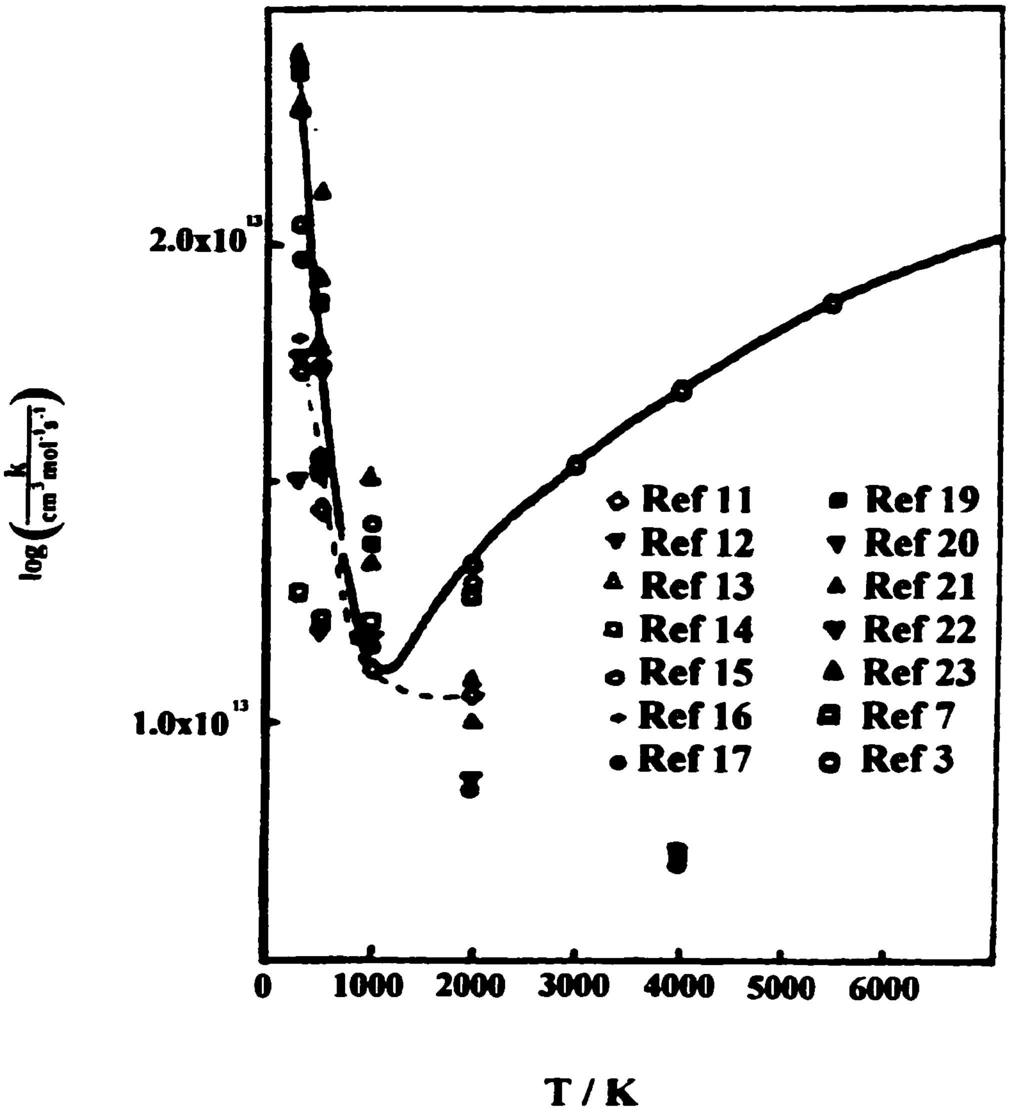

Fig1.2: Thermal rate coefficient for OH + O ➡ H + O_2

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CHAPTER 2

Exact solution of the Master Equation

2.1 Introduction

For the elementary bimolecular exchange reaction, A + BC = AB+C, we may write the set of differential equations describing the rate of change of the concentrations of the molecules AB & BC in specific vibrational states. The set is known as the " Master Equation". The reaction is said to be occurring "steadily" when the vibrational population distributions are invariant with time. Previous workers have attempted to solve the rate equations, but they did not include the reverse reaction [1-4] or did not consider appropriate conditions. In this chapter we shall offer a method of solving the master equation utilizing a matrix technique, which, for the first time, includes reverse reactions under extreme conditions.

2.2 The Steady-State Master Equation

For simple harmonic oscillators only those energy transfer processes are allowed for which the vibrational quantum number changes by ±1 (approximation A1). This is similar to optical transition rules. The rate of change of the concentration, N_m^{BC}, of the diatomic BC in vibrational level m is given by the following master equation:

$$\frac{dN_m^{BC}}{dt} = (-k_{m,m-1}^{BC} N_m - k_{m,m+1}^{BC} N_m + k_{m-1,m}^{BC} N_{m-1} + k_{m+1,m}^{BC} N_{m+1}) N_M - \sum_n k_{m-n}^{f} N_m^{BC} N_A + \sum_n k_{n-m}^{r} N_n^{AB} N_C \quad (2.1a)$$

and the rate of change of the concentration, N_n^{AB}, of the diatomic AB in vibrational level n is given by the following master equation:

$$\frac{dN_n^{AB}}{dt} = (-k_{n,n-1}^{AB}N_n - k_{n,n+1}^{AB}N_n + k_{n-1,n}^{AB}N_{n-1} + k_{n+1,n}^{AB}N_{n+1})N_M - \sum_m k_{n-m}^{r}N_n^{AB}N_c + \sum_m k_{m-n}^{f}N_m^{BC}N_A \qquad (2.1b)$$

where $k^{BC}_{m,m\pm1}$ and $k^{AB}_{n,n\pm1}$ are the specific rate constants for the energy transfer processes

$BC(m) + M \rightleftharpoons BC(m\pm1) + M$ (2.2a)

$AB(n) + M \rightleftharpoons AB(n\pm1) + M,$ (2.2b)

N_M is the concentration of all colliding species present in the system. $k^f{}_{m-n}$ is the rate constant for the forward reactive process and $k^r{}_{n-m}$ is the rate constant for the reverse reactive process: $A + BC(m) \rightleftharpoons AB(n) + C$. It is convenient to rewrite eq. (2.1a) and eq. (2.1b) in terms of fractional level populations, Y_m and Z_n, where

$$Y_m \equiv \frac{N_m^{BC}}{N_{BC}}, \quad N_{BC} = \sum N_m^{BC} \qquad (2.3a)$$

$$Z_n \equiv \frac{N_n^{AB}}{N_{AB}}, \quad N_{AB} = \sum N_n^{AB} \qquad (2.3b)$$

In this way we can decompose the disappearance and appearance of BC and AB into transient and non-transient components. Hence,

$$\frac{1}{N_{BC}}\frac{dN_m^{BC}}{dt}=\frac{Y_m}{N_{BC}}\frac{dN_{BC}}{dt}+\frac{dY_m}{dt} \qquad (2.4a)$$

$$\frac{1}{N_{AB}}\frac{dN_n^{AB}}{dt}=\frac{Z_n}{N_{AB}}\frac{dN_{AB}}{dt}+\frac{dZ_n}{dt}. \qquad (2.4b)$$

Were it not for the reactive processes and truncation of the harmonic oscillator ladder, perfect cancelation of the energy transfer terms upon summing $dN^{BC}{}_m/dt$ and $dN^{AB}{}_n/dt$ would lead to $dN_{BC}/dt=0$ and $dN_{AB}/dt=0$. We also note that the phenomenological rate law for this reaction, is just

$$\frac{dN_{BC}}{dt}=-k_fN_AN_{BC}+k_rN_cN_{AB} \qquad (2.5a)$$

$$\frac{dN_{AB}}{dt}=k_fN_AN_{BC}-k_rN_CN_{AB} \qquad (2.5b)$$

This serves as an experimentalist's definition of his observable. We now rewrite the master eq.(2.1a) and eq.(2.2b) in terms of Y_m and Z_n, respectively. This is accomplished by making use of eqs.(2.3)-(2.5): hence,

$$\frac{dY_m}{dt}=-Y_m(-k_fN_A+k_r\frac{N_CN_{AB}}{N_{BC}})-Y_mN_A\sum_n k^f_{m-n}+\frac{N_CN_{AB}}{N_{BC}}\sum_n k^r_{n-m}Z_n-N_M\sum_{m'}k^{BC}_{m,m'}Y_m+N_M\sum_{m'}k^{BC}_{m',m}Y_{m'} \qquad (2.6a)$$

$$\frac{dZ_n}{dt} = -Z_n\left(k_f\frac{N_A N_{BC}}{N_{AB}} - k_r N_C\right) - Z_n N_C \sum_m k^r_{n-m} + \frac{N_A N_{BC}}{N_{AB}} \sum_m k^f_{m-n} Y_m - N_R \sum_{n'} k^{AB}_{n,n'} Z_n + N_R \sum_{n'} k^{AB}_{n',n} Z_{n'} \qquad (2.6b)$$

where $k^{BC}_{m,m'}$ is the rate constant for (de-)activation of the diatomic molecule, BC, from level m to m' and $k^{AB}_{nn'}$ is the rate constant for (de-)activation of the diatomic molecule AB, from level n to n', and where k^f_{m-n} and k^r_{n-m} are rate constants for the forward and reverse reactive processes respectively; and N_M is the concentration of the colliding species.

After a short transient period during which the relative populations of the vibrational levels adjust to reactive conditions, the reaction is said to occur "steadily" at the observable rate. In the steady-state limit where the reaction proceeds with invariant (but non-Boltzmann) relative populations, eqs. (2.6) become the set of linear algebraic equations:

$$Y_m \sum_{m'} k^{BC'}_{m,m'} - \sum_{m'} Y_{m'} k^{BC'}_{m',m} + Y_m \sum_n k^{f'}_{m-n} - \frac{N_C N_{AB}}{N_A N_{BC}} \sum_n k^{r'}_{n-m} Z_n = k' Y_m \qquad (2.7a)$$

$$\frac{N_{AB}}{N_{BC}} \sum_{n'} k^{AB'}_{n',n} Z_{n'} - Z_n \frac{N_{AB}}{N_{BC}} \sum_{n'} k^{AB'}_{n,n'} + \sum_m k^{f'}_{m-n} Y_m - Z_n \frac{N_C N_{AB}}{N_A N_{BC}} \sum_m k^{r'}_{n-m} = k' Z_n \qquad (2.7b)$$

where $k^{BC'}_{m,m'} \equiv k^{BC}_{m,m'}/k^{BC}_{10}$, $k^{AB'}_{n,n'} \equiv k^{AB}_{n,n'}/k^{BC}_{10}$, $k^{f'}_{m-n} \equiv N_A k^f_{n-m}/N_M k^{BC}_{10}$, $k^{r'}_{n-m} = N_A k^r_{n-m}/N_M k^{BC}_{10}$ and $k' \equiv (k^f N_A/k^{BC}_{10} N_M - k^r N_C N_{AB}/k^{BC}_{10} N_{BC} N_M)$. Note that for $m=0$, $m' > m$, and for $n=0$, $n' > n$. Also, in practice we are limited to vibrational levels, M and N, beyond which the state-selected reactivity data k^f_{m-n} and k^r_{n-m} are not available (theoretically or experimentally) or beyond which there is no longer any contribution to the reactive flux. Thus for $m=M$ and $n=N$

upward transitions are neglected. Essentially we have transformed a series of coupled differential equations into (M+N+2) linear coupled algebraic equations involving (M+N+2) unknowns (Y_m and Z_n).

Eqs (2.7) can be written compactly as

$$\tilde{A}Y-\tilde{N}_fZ=k'Y \qquad (2.8a)$$

$$\tilde{O}Z-\tilde{N}_rY=k'Z \qquad (2.8b)$$

where the elements $a_{mm'}$ and $o_{nn'}$ of the matrices $\tilde{A}$ and $\tilde{O}$ are

$$a_{m,m'}=-k^{BC'}_{m',m} \qquad (m'\neq m)$$

$$a_{m,m'}=\sum_{m'}k^{BC'}_{m,m'}+\sum_{n}k^{f'}_{m-n} \qquad (m'=m)$$

$$o_{n,n'}=\frac{N_{AB}}{N_{BC}}k^{AB'}_{n'n} \qquad (n'\neq n)$$

$$o_{n,n'}=-\frac{N_{AB}}{N_{BC}}\sum_{n'}k^{AB'}_{n,n'}-\frac{N_CN_{AB}}{N_AN_{BC}}\sum_{m}k^{r'}_{n-m} \qquad (n'=n)$$

Also the elements of matrices $\tilde{N}_f$ and $\tilde{N}_r$ are given by

$$n_{\varepsilon_{n,m}} = k^{\varepsilon'}_{m-n}$$

$$n_{\varepsilon_{m,n}} = -\frac{N_C N_{AB}}{N_{BC} N_A} k^{\varepsilon'}_{n-m}$$

Eqns (2.8a) and (2.8b) can alternatively be written even more neatly as

$$\tilde{U}W = k'W \qquad \textbf{(2.9)}$$

where we consider the vectors Y and Z to be components of a longer vector W. Here the elements u_{ij} of the matrix $\tilde{U}$ are given by

$$u_{i,j} = -\frac{N_{AB}}{N_{BC}} \sum_{n'} k^{AB'}_{n,n'} - \frac{N_C N_{AB}}{N_A N_{BC}} \sum_{m} k^{\varepsilon'}_{n-m} \qquad (i=j \quad i \geq M+1-n, \quad j \geq M+1-N)$$

$$u_{i,j} = \sum_{m'} k^{BC'}_{m,m'} + \sum_{n} k^{\varepsilon'}_{m-n} \qquad (i=j, \quad i \leq M, \quad j \leq M)$$

$$u_{i,j} = -k^{BC'}_{m',m} \qquad (i \neq j \quad i \leq M, j \leq M)$$

$$u_{i,j} = \frac{N_{AB}}{N_{BC}} k^{AB'}_{n',n} \qquad (i \neq j, \quad i \geq M+1-N, j \geq M+1-N)$$

$$u_{i,j} = k^{\varepsilon'}_{m-n} \qquad (i \neq j, \quad i \geq M+1-N, j \leq M)$$

$$u_{i,j} = -\frac{N_C N_{AB}}{N_{BC} N_A} k^{\varepsilon'}_{n-m} \qquad (i \neq j, \quad i \geq M-N, \quad j \leq M+1-N)$$

$\tilde{U}$ is an $(M+N+2) \times (M+N+2)$ matrix. Certain blocks of this matrix involving pure energy transfer terms are tri-diagonal in the special case where nearest-neighbour transitions alone are permitted (as in the case of harmonic oscillators obeying the Landau-Teller scaling rules). In any case there are $M+N+2$ possible eigenvalues, k', of which only the smallest non-zero eigenvalue (whose corresponding eigenvector is real, positive and unitary) has a physical significance (the rate coefficient which we seek) . These eigenvalues can be obtained from standard matrix techniques by setting the determinant equal to zero and by solving the resultant $(M+N+2)$ order secular equation. Therefore, this rapid procedure gives us numerically the k', Y_m and Z_n.

2.3 Application: $H + O_2 \rightleftharpoons OH + O$

A computer program has been written by the author, MRBIM (Matrix technique applied to Reversible BIMolecular reactions), which allows for easy exploration of the non-equilibrium effect. (See Appendix A for a detailed description of MRBIM.) As described in the introduction, the reaction

$$H + O_2 \rightleftharpoons OH + O$$

is not only the most important elementary combustion reaction, it is also rather controversial. The role of non-equilibrium phenomena has never been investigated for this case. It is for these reasons that we apply our calculation to this reaction first. Fortunately the reactive state-to-state rate constants over the temperature range 300 - 8000 K have been calculated by Lifshitz and Teitelbaum [5] using information theory in order to scale and extend published data. They are summarized in

Appendix B. As input to our calculation we also require values for the relaxation rate constants k^{H}_{10}, k^{O}_{10}, k^{OH}_{10}, k^{O2}_{10} and k^{M}_{10} for both species of diatomic molecules, OH and O_2.

The notation used in the master equation, (eqn.(2.1)) $k_{i,j}N_M$ is not intended to refer to any particular relaxer, M, but rather to symbolize all possible equilibration processes, i.e.

$$k_{1,0}^{BC} N_M \equiv k_{10}^{H} N_H + k_{10}^{O_2} N_{O_2} + k_{10}^{OH} N_{OH} + k_{10}^{O} N_O + k_{10}^{Z} N_Z$$

where Z refers to any other species present in the mixture, such as an inert diluent. Dividing the above equation by the concentration of species A, i.e by N_H, converts all concentrations to relative concentrations. This has a certain advantage that we are not required to know the exact concentrations of species present in the equilibrium system but rather their relative amount. Thus,

$$k_{10}^{BC} \frac{N_M}{N_H} \equiv k_{10}^{H} + k_{10}^{O_2} \frac{N_{O_2}}{N_H} + k_{10}^{OH} \frac{N_{OH}}{N_H} + k_{10}^{O} \frac{N_O}{N_H} + k_{10}^{Z} \frac{N_Z}{N_H} \qquad (2.10)$$

A similar expression can also be written for k^{AB}_{10}.

k^{BC}_{10} has been measured over a broad temperature range (300 - 8000) with M = Ar, He and H_2 as collision partners. k^{BC}_{10} for OH and H atoms as collision partners are, as far as we are aware, unknown. In the absence of data we estimated k^{OH}_{10} as being approximately k^{O}_{10}. In the case of k^{H}_{10} we estimated this to be $1.393k^{H2}_{10}$, where 1.393 is the reduced mass ratio for H and H_2. Table 2.1 summarizes the rate constants, k^{BC}_{10}, which we used for the vibrational de-excitation of O_2. Measurements of the vibrational relaxation times, $p\tau$, of O_2, were made for M = O_2 by Kiefer [6] and by Holmes and Smith [7,] for M = He by Milkan and White [8], and for M = O by Breen and Glass [9] at shock-tube temperatures. We converted $p\tau$ to k^{BC}_{10} using the relation $(k_{1,0} - k_{0,1})[M] = 1/\tau$.

The vibrational relaxation rate constants for OH are considerably more problematical. Only sparse information is available for some collision partners. Kajimoto et al. [10] reported rate constants, k_{10}, for the de-excitation of OH($n'=1 \rightarrow n'=0$) by the relatively inert species H_2, He and Ar ~ 10^{-14} cm^3 molec^{-1} s^{-1}, by the more reactive species O_3 and O_2 ~ 10^{-12} cm^3 molec^{-1} s^{-1} , and by the reactive atom H = 1.8×10^{-11} cm^3 molec^1 s^1 at 300K. No information exists for OH and O as collision partners. We classified them as reactive species and assigned the same value as k^{H}_{10}. Finally, in order to estimate k^{AB}_{10} at higher temperatures we assumed that k_{10} was independent of temperature, a reasonable assumption considering the nearness to the gas-kinetic collision frequency. Our values of k^{AB}_{10} are the least accurate in the present study. Table 2.2 summarizes our estimates of k^{AB}_{10}. They are already quite large at 300K, generally larger than k^{BC}_{10}. Ours is a conservative estimate. Wih improved estimates our conclusions would not be changed in the qualitative sense.

The vibrational energies of O_2 and OH were determined accurately from spectroscopic constants. However O_2 and OH were treated as simple harmonic oscillators as far as energy transfer rate constants are considered: only V-T energy transfer processes were considered; and Landau-Teller scaling of energy transfer rate constants was employed [11]. The harmonic oscillators were truncated at $M = 14$ and $N = 9$ respectively, not due to lack of information but because higher levels did not contribute to the reaction flux. This conclusion was drawn by varying M and N and discovering that even $M=14$ and $N=9$ do not contribute much to the reaction flux at the highest temperatures.

The computation was performed on a UNIX machine named TESLA at the University of Ottawa. Using a standard double precision subroutine named DEVCRG, which is part of the IMSL math library, efficient and rapid calculations of eigenvalues and eigenvectors could be performed. Processing of the results was done using QUATRO-PRO 5 on a Pentium PC. We have summarized in Table 2.3 the running times of sample calculations for various concentrations.

2.4 Discussion of the Eigenvalue - Eigenvector results

In order to test the validity and demonstrate the use of the program a reaction system must be found for which appropriate input data is available and for which suitably detailed calculations have been done. There are not many systems for which state-to-state reactive rate constants and energy transfer rates constants are available. The $H + O_2$ system is one. Various procedures were carried out to test the validity of the program. In the first test we set the concentration of OH and O to nearly zero so that only the forward reaction plays a role, and then we calculated the value of k_f for the above reaction and compared the results to the known value of k_f which was calculated by previous workers for the forward reaction alone [5]. Our method gave k_f at 2000 K to be $2.100 \times 10^{12}\ cm^{-3} mol^{-1} s^{-1}$ while the previously used forward reaction matrix technique gave k_f to be $2.100 \times 10^{12}\ cm^{-1} mol^{-1} s^{-1}$. Thus, the two techniques gave essentially the same results. The second test was to set all the reverse microscopic rate constants to zero, thus isolating the forward reaction. Our method gave k_f to be $2.100 \times 10^{12}\ cm^{-3} mol^{-1} s^{-1}$, the same result as the other test. In yet another test we artificially made the energy transfer rate constants for OH and O_2 very large. Hence there should be very little or no non-equilibrium effect. We have summarized our results for this test in Table 2.4. We discovered that k_f and k_r were equal to their equilibrium values for all temperatures expected. Although shunting out reverse processes leads to correct results this does not prove that the reverse reactions itself is treated correctly by our program. We proved this latter point by setting forward microscopic rate constants to zero, and comparing the results with those expected from the technique for the uni-directional reaction, noting that what we call the reverse reaction in this study becomes the forward reaction when it is the lone reaction. The results again were identical to what was obtained using prior techniques. This confirms that our program works correctly.

Then the values of the microscopic reverse rate constants were slowly increased to their original values in order to observe system behaviour. A number of interesting features of MRBIM were observed:

1) Eigenvalues, λ , can be negative or positive, the sign of the eigenvalue corresponding to the direction of the net reaction flux. When λ changes sign the role of the forward and the reverse reactions are reversed. 2) The smallest non-zero eigenvalue with physical meaning was the one corresponding to a positive eigenvector, ie to Y_m and Z_n whose elements were less than unity. The magnitude of the eigenvalue corresponds to the overall rate.

2.5 Definitions of k_f and k_r

The phenomenological rate law for the reaction is

$$\text{Rate} = k_f[O_2][H] - k_r[OH][O]$$

Here k_f and k_r are the phenomenological rate coefficients for the reaction. The numerical calculation produces values for the eigenvalue $\lambda = (k_f [H]/N_M k^{BC}_{10} - k_r[OH][O]/[N_M][O_2] k^{BC}_{10})$ and for Y_m and Z_n. There are at least 2 (not necessarily identical) arbitrary ways to separate k_f from k_r. One corresponds to the way an experimental kineticist would do so in the lab when forward and reverse reactions are both occurring significantly, namely $k_f = 1/[H]\, \partial Rate/\partial[O_2]$ while keeping the concentration of [H], [O] and [OH] constant, and $k_r = -1/[O]\partial Rate/\partial[OH]$ while keeping the concentration of [O], $[O_2]$ and [H] constant. On the other hand an experimental dynamicist would prefer to define k_f and k_r as:

$$k_f = \sum_{m=0}^{M} \sum_{n=0}^{N} Y_m k^f_{m-n} \quad and \quad k_r = \sum_{n=0}^{N} \sum_{m=0}^{M} Z_n k^r_{n-m} \; .$$

Here $M = 14$, and $N = 9$, Y_m and Z_n are the fractional populations in levels m and n. Both methods use quantities calculated by MRBIM.

The initial conditions are in the range 2000-8000 K where the non-equilibrium effect is most profound; He is our choice of inert species, M, responsible for vibrational relaxation. We have calculated K_{eq} for this reaction at different temperatures. Once we knew K_{eq} for the reaction then we proceeded to calculate the equilibrium concentrations. These results are summarized in Table 2.5. We study the non-equilibrium effect for this reaction at two different extremes: when reaction is occuring close to equilibrium $[AB][C]/[A][BC] \approx K_{eq}$ and when reaction is occuring far from the equilibrium $[AB][C]/[A][BC] << K_{eq}$ or $>> K_{eq}$.

2.6.1 Conditions set Close to equilibrium

First the reaction was set close to equilibrium as in Table 2.5. The main trends observed in Table 2.6 and Table 2.7 are:

1) For [H]/ [He]= 0.001, $k_f/k_f^{eq} < 1$ and $k_r/k_r^{eq} > 1$ if $\lambda > 0$. When $\lambda < 0$ the behaviour is reversed.

2) k_f values (with [H]/[He] =0.001) are slightly inflated from their equilibrium values, while k_r values show little change from their equilibrium values.

3) k_f values (with [H]/[He] =0.1) are slightly suppressed from their equilibrium values, while k_r values show little change from their equilibrium values.

4) The non-equilibrium factor $(k_f/k_r)/K_{eq}$ is approximately 1.

5) The fractional populations for the products and reactants are only slightly disturbed from those of the Boltzmann distribution.

The non-equilibrium factor is approximately 1, which is understandable because we set our conditions close to equilibrium. However, the individual rate coefficients k_f and k_r differ from their equilibrium values because the forward and reverse rates are each much faster than the corresponding relaxation rates. The inflation or suppression in k are slight for the conditions of Table 2.5 because the fractional populations of the products and reactants are not disturbed seriously from the Boltzmann distribution by the reaction. When [H]/[He]=0.1 the k_f values show suppression; but when [H]/[He]=0.001 the k_f values show inflation. When the concentration of helium is decreased then helium is no longer the main solvent but rather the other more efficient species present in the environment are, depending on the initial concentrations of these species. The reverse reaction is showing very little non-equilibrium effect because relaxation of OH is more rapid than for O_2. Cancellation of the two non-equilibrium effects becomes more and more perfect the closer the reaction is to equilibrium. The fractional population of the ground level is slightly lower than the ground level population given by the Boltzmann distribution for both products and reactants in Table 2.7 simply because of conservation of mass $\sum_m Y_m = \sum_m Y^{eq}_m = 1$ and $\sum_n Z_n = \sum_n Z^{eq}_n = 1$. If the upper level populations are augmented then the lowest level population must correspondingly decrease.

2.6.2 Far from equilibrium

The reaction was set far from equilibrium as in Table 2.8. For reactions set far from equilibrium, the results are summarized in Table 2.9 and in Table 2.10 [Only representative results are shown in order to illustrate our main points]. The main trends observed in Table 2.9 and Table 2.10 are:

1) k_f values are inflated from their equilibrium values when [OH] and [O] are large. When [O_2] is large k_f values are suppressed form their equilibrium values.

2) k_r values show no change from their equilibrium values when [OH] is large, however they are suppressed when [O] is large and inflated when [O_2] is large.

3) The non-equilibrium factor $(k_f/k_r)/K_{eq}$ is greater than unity when [OH] and [O] are large and less than unity when [O_2] is large. Exceptions occur at 4000 K and at 8000 K when [OH] = [O_2] =[O]= [H].

4) The non-equilibrium factor $(k_f/k_r)/K_{eq}$ increases with increasing concentration of OH and O ie

when the reverse reaction dominates, and decreases with increasing concentration of O_2 and H ie when the forward reaction dominates.

5) The non-equilibrium factor approaches unity with increasing concentration of solvent, He.

6) Higher vibrational levels of products and reactants are more severely depleted while the ground level populations are relatively augmented under conditions where the forward reaction dominates.

When the reaction is taking place far from equilibrium the non-equilibrium effect is more severe than when reaction is taking place close to equilibrium. This can be seen by comparing the non-equilibrium factor for the two cases. Also, the higher vibrational levels are more severely depleted when the reaction occurs far from equilibrium than when reaction occurs close to equilibrium. The most severe non-equilibrium effect is reached at 2000 K, with the mixture [H]:[O_2]:[OH]:[O]:[Ar] = 1:1:1:100:10. The relative populations of excited states increase as the temperature increases and hence their potential contribution to the rate is more measurably repressed. However at higher temperatures, relaxation becomes more efficient, leaving the greatest effect to be manifested around 2000 K.

The non-equilibrium factor increases with increasing concentration of OH and O. The change in magnitude of the non-equilibrium factor is approximately the same whether [OH] is changed or [O] is changed. These efficient relaxer species tend to replenish the level populations. That is why the k_r values show little change from their equilibrium values while the k_f values are inflated from their equilibrium values. The k_f values are inflated from their equilibrium values because under these conditions when the reverse (exothermic) process is dominating, the reaction produces primarily vibrationally excited O_2. Therefore what little forward (endothermic) reaction is occuring is weighted by the highly reactive higher vibrational levels. Hence, the k_f values are larger than k_f^{eq} here. It is only when the forward reaction dominates that the reaction proceeds from essentially unreactive ground state O_2. Hence we see that as the concentration of O_2 increases, the non-equilibrium factor decreases. k_r values are inflated when $[O_2]$ is large because the forward reaction is producing more important vibrational levels of OH. Hence, the k_r values are lager than k_r^{eq}.

The non-equilibrium factor decreases with decreasing concentration of solvent [He]. Note that when the concentration of helium is decreased it is no longer the solvent but rather other species present in larger quantities in the mixture become the solvent. They are generally more efficient relaxers. The non-equilibrium factor is also temperature dependent, but in a complicated manner, as a result of its effect on the relative population distributions of O_2 and OH as well as on the $k^f_{m\text{-}n}$ $k^r_{n\text{-}m}$, and all of the k_{ij}.

2.7 Comparison between experimental results and results of simulations.

In Table 2.11 we have summarized the most recent research on $O_2 + H \rightarrow OH + O$. We have shown in this table the techniques and the typical concentrations that the experimentalists used. We have compared the experimental results and matrix results in Fig. 2.1, Fig. 2.2 Fig 2.3. In Fig. 2.1 we have plotted log k vs 1/T. This figure is similar to Fig. 1.1, but it also contains the results of simulations. This figure shows that there is no non-equilibrium effect up to 1000 K. Most importantly it shows that our results agree with the experimental values below 1000 K. In Fig 2.2 and Fig 2.3 each point on the experimental curve represents different experiments. By looking at the graphs we see that our matrix technique does not completely explain the discrepancies between the k values. In fact our technique, under these experimental conditions, predicts no non-equilibrium effect. We need to explain why our matrix technique does not account for the discrepancies. First we notice that we should use Ar as a bath instead of He, because most of the experiments were performed in Ar. The reason we used He as a solvent in our calculations is that the rate of relaxation of OH by argon is unknown ($k_{10}^{OH\text{-}Ar}$) . We realize that argon is a poor relaxer of O_2 compared to He. The non-equilibrium effect should be more profound when agron is used. We then proceeded to calculate k_f using the matrix the technique for an Ar bath. The comparison between the two solvents is made in Fig. 2.4. We see from the figure that indeed the non-equilibrium effect is larger when argon is used as a solvent. The second reason why our results do not agree with the experimental results is that there are experiment faults. The experiments which are designed to measure the concentration of OH, make the assumption that a Boltzmann distribution is maintained during the reaction. Our work has shown that this is not to be the case. Furthermore, these experimental faults get worse with increasing temperature. The third reason why our results do not explain the discrepancies is that we have made the assumption that a steady state exist for this reaction. In a later chapter we shall show that most of the reaction is over before the steady-state is established.

Our matrix technique shows that the maximum non-equilibrium effect is going to be around 2000 K. For energy transfer, ln k_{10} varies linearly with $T^{-1/3}$; whereas for reaction ln $k_{vv'}$ varies linearly with 1/T. When energy transfer rates are plotted on an Arrhenius type of graph the curve is concave. Thus at low temperatures the energy transfer rates are larger than the reactive rates; hence there is no non-equilibrium effect. At intermediate temperatures energy transfer rates are smaller than the reactive rates, and hence a non-equilibrium effect is observed. As the temperature increases the energy transfer rates increase and they eventually catch up to the reactive rates. Thus the non-equilibrium effect deceases. The maximum non-equilibrium effect occurs around 2000 K. Experiments, on the other hand, show increasing discrepancies with increasing temperature. Consequently the discrepancy with theory also appears to be worse as the temperature increases beyond 2000 K.

2.8 Summary

We have solved the steady-state master equation exactly, using a matrix technique. A computer program has been written by the author, MRBIM (Matrix technique applied to Reversible BIMolecular reactions) which allows for easy exploration of the non-equilibrium effect (See Appendix A) . We have tested our matrix technique on the $H + O_2 \rightleftharpoons OH + O$ reaction. A number of interesting features of MRBIM were observed: eigenvalues can be negative or positive; the sign of the eigenvalue indicates the direction of the reaction; and the magnitude of the eigenvalue is the overall rate coefficient.

The non-equilibrium effect is much more severe for reaction occuring far from equilibrium compared to reaction occuring close to equilibrium. The non-equilibrium factor is close to unity for reaction occuring close to equilibrium. The fractional population of higher vibrational levels is depleted for both cases, but it is more severe for reaction occuring far from equilibrium.

As far as the controversy is concerned regarding measured values of k_f , we see that indeed non-equilibrium effect are playing a role. Not only is $k_f < k_f^{eq}$ but the deviation is highly dependent on the experimental conditions. Although the effect is less than 20%, maximizing around 2000 K, we now understand why different laboratories have been obtaining different values of k_f for over more than 50 years.

Perhaps the most important discovery we have made in this chapter is that the non-equilibrium factor $(k_f/k_r)\ /K_{eq}$ becomes greater than unity with increasing concentration of AB (OH) and C (O), and less than unity with increasing concentration of BC (O_2) for reaction far from equilibrium under conditions when the reverse reaction dominates. In other words, the kinetic mass action law breaks down, and the deviation of k_f/k_r from K_{eq} becomes more severe as the reaction gets further from equilibrium. The temperature dependence of this non-equilibrium factor is complex. Commonly accepted usage of the kinetic mass action law must therefore be reconsidered.

Table 2.1 Rate constants ($cm^3mol^{-1}s^{-1}$) for vibrational de-excitation of O_2 by M= H, O_2, OH, O , He ; O_2 (v = 1) + M → O_2 (v = 0) + M.

T/K	$k^{O_2}_{10}$ [f]	k^{He}_{10} [c,f]	k^{O}_{10} [d,f]	k^{H}_{10} [e]	k^{OH}_{10} [e]
300	1.54 (6)[a,g]	5.98 (8)	8.07(11)	1.57(10)	8.07(11)
500	2.77 (7)[a]	4.07 (9)	1.36(12)	6.20(10)	1.36(12)
1000	1.06 (9)[b]	4.29 (10)	3.02(12)	3.50(11)	3.02(12)
2000	3.78 (10)[b]	3.93 (11)	8.07(12)	1.95(12)	8.07(12)
4000	9.36(11)[b,h]	3.30 (12)	2.58(13)[h]	1.10(13)	2.58(13)
8000	1.69(13)[b,h]	2.54 (13)	9.31(13)[h]	6.18(13)	9.31(13)

[a] From ref. (6). [b] From ref. (7). [c] From ref. (8). [d] From ref. (9). [e] See the text. [f] Measurement of relaxation times, pτ/atm s, were converted to rate constants using $k_{10} = 82.06T[1-\exp(-u)]^{-1} (p\tau)^{-1}(N_{av})^{-1}$. [g] 1.54 (6) means 1.54 x 10^6. [h] Data extrapolated from lower temperatures.

Table 2.2 Rate constants ($cm^3mol^{-1}s^{-1}$) for vibrational de-excitation of OH by M= H, O_2, OH, O , He; OH (v = 1) + M → OH (v = 0) + M.

T/K	$k^{O_2}_{10}$ [a]	k^{He}_{10} [a]	k^{O}_{10} [a]	k^{H}_{10} [a]	k^{OH}_{10} [a]
300	6.00(11)[b]	1.20(10)	6.00(12)	1.03(13)	1.08(13)
500[c]	1.30(12)	4.50(10)	6.00(12)	1.03(13)	1.44(13)
1000[c]	2.30(12)	1.98(11)	6.00(12)	1.03(13)	1.92(13)
2000[c]	4.50(12)	6.60(11)	6.00(12)	1.03(13)	2.40(13)
4000[c]	7.30(12)	1.62(12)	6.00(12)	1.03(13)	2.88(13)
8000[c]	1.10(13)	3.40(12)	6.00(12)	1.03(13)	3.36(13)

[a] From ref (10). [b] 6.00(11) means 6.00x10^{11}. [c] See the text.

Table 2.3 Running time for computation

Temperature (K)	[H]/[OH]	[H]/[O]	[H]/[O_2]	Running time (s)
2000	1.0	1.0	0.1	0.36
	1.0	1.0	0.01	0.41
	1000	1000	1 x 10^{-8}	15.35
4000				
	1.0	1.0	0.1	0.31
8000	1.0	1.0	0.01	0.34
	1.0	1.0	0.1	0.38
	1.0	1.0	0.01	0.33

Note:Compiling time for the program MRBIM is 8.05 s.
-Pentium Processor (INTEL - 90 Mhz CPU) was used to process the results calculated by a RISC System/6000 Model 390 - A1X 4.3.10

Table 2.4 Comparison of k_f^{eq} and k_r^{eq} with k_f and k_r respectively when relaxation rates for O_2 and OH are very large.

T/K	k_f^{eq}	k_f [a]	k_r^{eq}	k_r [a]
2000	3.1661(12)	3.1661(12)	1.3803(13)	1.3803(13)
4000	3.0096(13)	3.0095(13)	1.9560(13)	1.9561(13)
8000	9.9663(13)	9.9663(13)	3.5230(13)	3.5230(13)

[a] Obtained from MRBIM.

Table 2.5 Equilibrium Concentrations used for H + O_2 = OH + O at various temperatures.

T/K	$k^f_{eq}/k^r_{eq} = K_{eq}$[a]	$[H]/[O_2]$[b]	$[H]/[O]$[b]	$[H]/[OH]$[b]
2000	0.2294	0.02794	0.34905	0.34905
4000	1.5386	0.00695	0.06720	0.06720
8000	2.8289	0.00403	0.03776	0.03776

[a] Calculated using thermodynamics and data from JANAF. [b]Calculated from the knowledge of K_{eq}.

Table 2.6a Rate coefficients ($cm^3mol^{-1}sec^{-1}$) for H+O_2=OH+O obtained by the matrix technique. Relative concentrations were set close to equilibrium conditions as in Table 2.4. All mixtures were diluted in a He bath ([A]/[He] =0.001).

T/K	k_f	k_r	k_f^{eq}	k_r^{eq}	k_f/k_r	$(k_f / k_r)/K_{eq}$
2000	3.1749(12)	1.3808(13)	3.1661(12)	1.3803(13)	0.2293	1.0024
4000	3.0162(13)	1.9562(13)	3.0096(13)	1.9560(13)	1.5415	1.0018
8000	9.9789(13)	3.5204(13)	9.9663(13)	3.5230(13)	2.8346	1.0020

Table 2.6b Rate coefficients ($cm^3mol^{-1}sec^{-1}$) for H+O_2=OH+O obtained by the matrix technique. Relative concentrations were set close to equilibrium conditions as in Table 2.4. All mixtures were diluted in a He bath ([A]/[He] =0.1).

T/K	k_f	k_r	k_f^{eq}	k_r^{eq}	k_f/k_r	$(k_f/k_r)/K_{eq}$
2000	3.1645(12)	1.3804(13)	3.1661(12)	1.3803(13)	0.2292	0.9995
4000	3.0072(13)	1.9562(13)	3.0096(13)	1.9560(13)	1.5373	0.9991
8000	9.9624(13)	3.5196(13)	9.9663(13)	3.5230(13)	2.8306	1.0059

Table 2.7 Fractional populations of reactants (O_2) and of products (OH) obtained by the matrix technique. Relative concentrations were set close to equilibrium conditions as in Table 2.4 and T= 4000 K. All mixtures were diluted in a He bath ([H]/[He] =0.001).

Vibration levels	Y(m)	$Y^{eq}(m)$	Z(n)	$Z^{eq}(n)$
0	4.20992(-1)[a]	4.21800(-1)	7.14695(-1)	7.15475(-1)
1	2.40878(-1)	2.40991(-1)	1.98594(-1)	1.98252(-1)
2	1.39018(-1)	1.38889(-1)	5.86331(-2)	5.83928(-2)
3	8.09273(-2)	8.07432(-2)	1.84027(-2)	1.82819(-2)
4	4.75184(-2)	4.73497(-2)	6.14091(-3)	6.08418(-3)
5	2.81426(-2)	2.80091(-2)	2.18028(-3)	2.15230(-3)
6	1.68112(-2)	1.67130(-2)	8.24813(-4)	8.09326(-4)
7	1.01288(-2)	1.00596(-2)	3.30064(-4)	3.23492(-4)
8	6.15531(-3)	6.10772(-3)	1.40411(-4)	1.37443(-4)
9	3.77290(-3)	3.74067(-3)	6.34941(-5)	6.20730(-5)
10	2.33278(-3)	2.31096(-3)	3.05188(-5)	2.97990(-5)
11	1.45490(-3)	1.44015(-3)		
12	9.15309(-4)	9.05302(-4)		
13	5.80894(-4)	5.74053(-4)		
14	3.71921(-4)	3.67183(-4)		

[a] 4.20992(-1) means 4.20992 x 10^{-1}

Table 2.8 Concentrations set far from equilibrium

T/K	Q/K_{eq}	[H]/[OH]	[H]/[O]	$[H]/[O_2]$
2000	4.3592	1.0	1.0	1.0
	43.592	0.1	1.0	1.0
	435.92	0.01	1.0	1.0
	43.592	1.0	0.1	1.0
	435.92	1.0	0.01	1.0
	0.4359	1.0	1.0	0.1
	0.0436	1.0	1.0	0.01
4000	0.6499	1.0	1.0	1.0
	6.4990	0.1	1.0	1.0
	64.990	0.01	1.0	1.0
	6.4990	1.0	0.1	1.0
	64.990	1.0	0.01	1.0
	0.0650	1.0	1.0	0.1
	0.0065	1.0	1.0	0.01
80000	0.3535	1.0	1.0	1.0
	3.5350	0.1	1.0	1.0
	35.350	0.01	1.0	1.0
	3.5350	1.0	0.1	1.0
	35.350	1.0	0.01	1.0
	0.0353	1.0	1.0	0.1
	0.0035	1.0	1.0	0.01

Table 2.9: Part 1 Rate coefficients ($cm^3mol^{-1}s^{-1}$) for $H+O_2=OH+O$ obtained by the matrix technique. Relative concentrations were set far from equilibrium as in Table 2.7.

T/K	k_f [b]	k_r [b]	k_f/k_r [b]	k_f [c]	k_r [c]	k_f/k_r [c]
2000	3.3473(12)[a]	1.3803(13)	0.24251	4.1362(12)	1.3758(13)	0.30065
	4.6398(12)	1.3801(13)	0.33618	6.1395(12)	1.3782(13)	0.45852
	6.7961(12)	1.3803(13)	0.49237	7.3573(12)	1.3801(13)	0.53311
	4.6034(12)	1.3735(13)	0.33517	6.0354(12)	1.3508(13)	0.44682
	6.4212(12)	1.3501(13)	0.47561	6.7688(12)	1.3374(13)	0.50611
	3.1458(12)	1.3820(13)	0.22760	2.9413(12)	1.3820(13)	0.21264
	3.1250(12)	1.3900(13)	0.22482	2.7979(12)	1.3885(13)	0.20150
4000	2.9968(13)	1.9577(13)	1.5308	2.7900(13)	1.9574(13)	1.4254
	3.3010(13)	1.9562(13)	1.6875	4.1941(13)	1.9527(13)	2.1479
	4.3343(13)	1.9560(13)	2.2159	4.9134(13)	1.9554(13)	2.5127
	3.2948(13)	1.9484(13)	1.6910	4.0726(13)	1.9022(13)	2.1410
	4.1399(13)	1.8914(13)	2.1888	1.0526(14)	1.5227(13)	6.9125
	2.9608(13)	1.9696(13)	1.5033	2.3773(13)	1.9608(13)	1.2124
	2.9582(13)	2.0024(13)	1.4773	2.4852(13)	1.9778(13)	1.2566
8000	9.9476(13)	3.5464(13)	2.8050	8.6090(13)	3.5910(13)	2.3975
	1.0374(14)	3.5425(13)	2.9286	1.1875(14)	3.5329(13)	3.3612
	1.1759(14)	3.5432(13)	3.3188	1.3126(14)	3.5428(13)	3.7049
	1.0376(14)	3.5306(13)	2.9387	1.2353(14)	2.6858(13)	4.5994
	1.2210(14)	2.9566(13)	4.1297	1.4175(14)	1.0717(13)	13.227
	9.8996(13)	3.5745(13)	2.7695	8.0725(13)	3.6373(13)	2.2193
	9.9266(13)	3.6339(13)	2.7317	9.2254(13)	3.6544(13)	2.5245

[a] 3.3473 (13) means 3.3473×10^{13}. [b] All mixtures were diluted in a He bath ([A]/[He] =0.001). [c] All mixtures were diluted in a He bath ([H]/[He] =0.1).

Table 2.9: Part 2 Rate coefficient ratios for $H+O_2 \rightleftharpoons OH+O$ obtained by the matrix technique. Relative concentrations were set far from equilibrium as in Table 2.7.

T/K	$(k_f/k_r)/K_{eq}$ [a]	Y_0/Y_0^{eq} [a]	Z_0/Z_0^{eq} [a]	$(k_f/k_r)/K_{eq}$ [b]	Y_0/Y_0^{eq} [b]	Z_0/Z_0^{eq} [b]
2000	1.0573	0.9798	1.0006	1.3107	0.8515	1.0055
	1.4657	0.8533	1.0002	1.9991	0.6907	1.0024
	2.1466	0.6943	1.0001	2.3243	0.6585	1.0003
	1.4612	0.8560	1.0078	1.9480	0.7097	1.0338
	2.0735	0.7150	1.0344	2.2065	0.6896	1.0489
	0.9924	1.0015	0.9981	0.9271	1.0383	0.9967
	0.9802	1.0037	0.9890	0.8785	1.0619	0.9905
4000						
	0.9949	1.0020	0.9973	0.9264	1.0659	0.9979
	1.0967	0.9389	0.9997	1.3959	0.7422	1.0052
	1.4401	0.7426	1.0000	1.6331	0.6443	1.0009
	1.0990	0.9400	1.0117	1.3915	0.7686	1.0811
	1.4226	0.7745	1.0999	4.4927	0.3143	0.2214
	0.9770	1.0097	0.9791	0.7879	1.2006	0.9916
	0.9601	1.0102	0.9285	0.8167	1.1463	0.9653
8000						
	0.9912	1.0085	0.9974	0.8473	1.2091	1.0561
	1.0349	0.9614	0.9971	1.1878	0.7585	0.9896
	1.1728	0.7912	0.9984	1.3092	0.6118	0.9994
	1.0385	0.9613	0.9917	1.6253	0.7474	0.5314
	1.4593	0.7609	0.5619	4.6742	0.6106	0.4246
	0.9787	1.0138	0.9953	0.7828	1.2869	1.0900
	0.96953	1.0114	0.9613	0.8921	1.1027	0.9911

[a] All mixtures were diluted in a He bath ([A]/[He] =0.001). [b] All mixtures were diluted in a He bath [H]/[He]=0.1).

Table 2.10 Fractional level populations of reactants (O_2) and of products (OH) obtained by the matrix technique. Relative concentrations were set far from equilibrium conditions: [H]/[OH] = 1.0 [H]/[O] = 1.0, [H]/[O_2] = 0.01 and [H]/[He] 0.001 and T = 4000 K.

Vibrational levels	Y(m)	$Y^{eq}(m)$	Z(n)	$Z^{eq}(n)$
0	4.26105(-1)[a]	4.21800(-1)	6.6429(-1)	7.15475(-1)
1	2.42018(-1)	2.40991(-1)	2.28548(-1)	1.98252(-1)
2	1.38589(-1)	1.38889(-1)	7.26102(-2)	5.83928(-2)
3	7.99873(-2)	8.07432(-2)	2.30507(-2)	1.82819(-2)
4	4.64952(-2)	4.73497(-2)	7.53877(-3)	6.08418(-3)
5	2.71951(-2)	2.80091(-2)	2.57145(-3)	2.15230(-3)
6	1.60125(-2)	1.67130(-2)	9.08656(-4)	8.09326(-4)
7	9.49595(-3)	1.00596(-2)	3.07586(-4)	3.23492(-4)
8	5.67760(-3)	6.10772(-3)	1.08207(-4)	1.37443(-4)
9	3.42604(-3)	3.74067(-3)	4.11395(-5)	6.20730(-5)
10	2.08777(-3)	2.31096(-3)	1.76240(-5)	2.97990(-5)
11	1.28556(-3)	1.44015(-3)		
12	8.00157(-4)	9.05302(-4)		
13	5.03765(-4)	5.74053(-4)		
14	3.21101(-4)	3.67183(-4)		

[a] 4.26105(-1) means 4.26105 x 10^{-1}.

Table 2.11 Experiments for the reaction $O_2 + H \rightarrow OH + O$.

Researcher	Technique	[Ar] (mole/cm^3)	$[H_2]$%	$[O_2]$%	[H] (mole/cm^3)	k_f/k_f^{eq}
Yuan et al [12]	LAS	1.6×10^{-5}	0.5	1	3.3×10^{-13}	0.6254
Masten et al [13]	LAS / ARAS	1.0×10^{-5}	5	0.5	3.3×10^{-12}	0.7125
Du & Hessler [14]	LAS	6×10^{-6}	2 - 4	0.15 - 0.4	2.5×10^{-12}	0.7314
Pirraglia [15]	ARAS	3.3×10^{-6}	-	2.5	1.3×10^{-12}	0.9145
Shin & Michael [16]	LP-ST (ARAS)	5×10^{-6}	-	0.13	1.7×10^{-12}	0.6194
Schott [17]	Chemi-luminescence	3.3×10^{-5}	10	1	3.3×10^{-11}	0.5927
Frank & Just [18]	ARAS	1.3×10^{-5}	0.01	0.01	6.5×10^{-11}	0.9955
Fuji & Shin [19]	LAS	1.2×10^{-5}	0.025	0.25	3.3×10^{-13}	0.6240

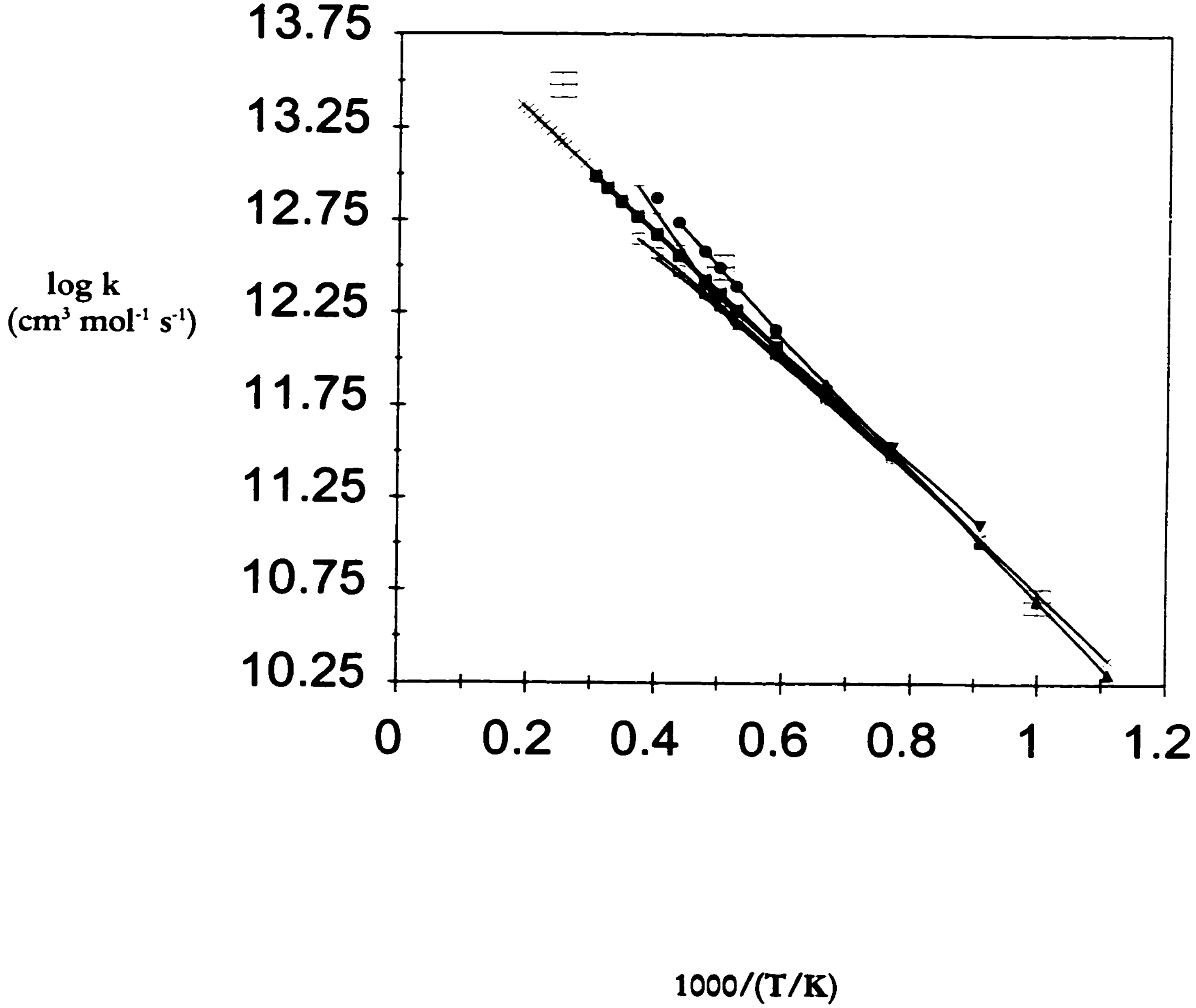

Fig 2.1: Thermal rate coefficient for H + O_2 → OH + O. + from ref. 2. ● from ref. 3. – from ref. 4. ■ from ref. 5. □ from ref. 6. ▲ from ref. 7. ▼ from ref. 8. × from ref 9

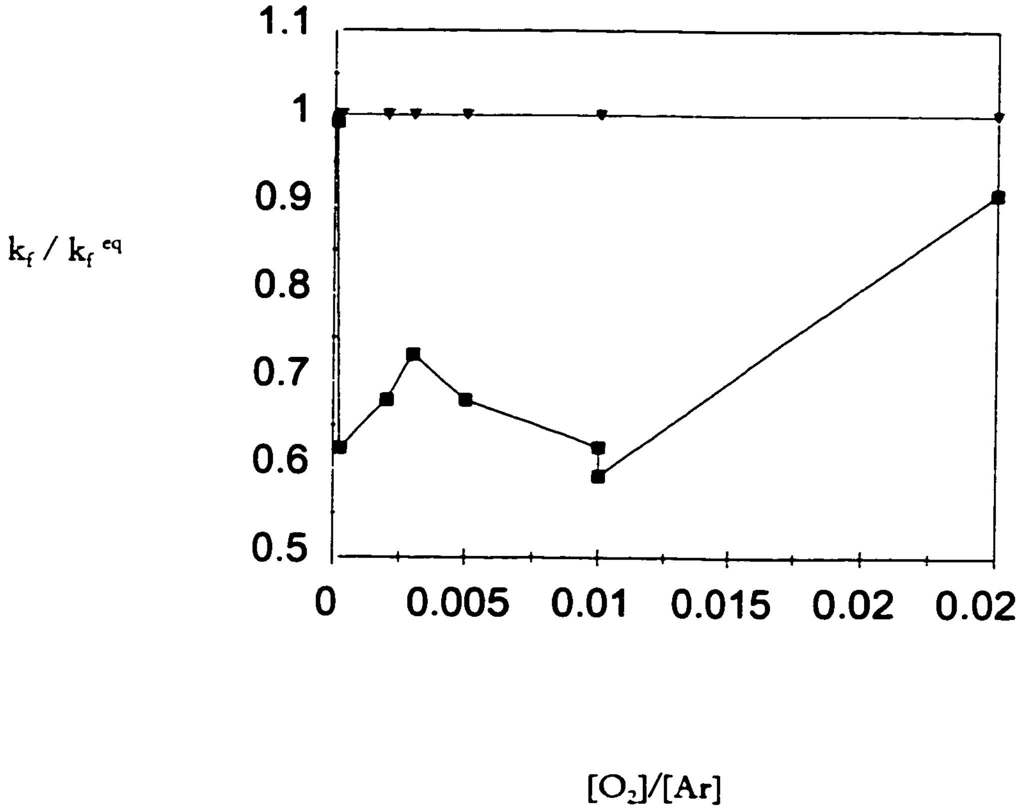

Fig. 2.2 The ratio of k_f / k_f^{eq} vs. $[O_2]/[Ar]$ at T = 2000 K. ▼ is for the matrix technique. ■ is for the experiments.

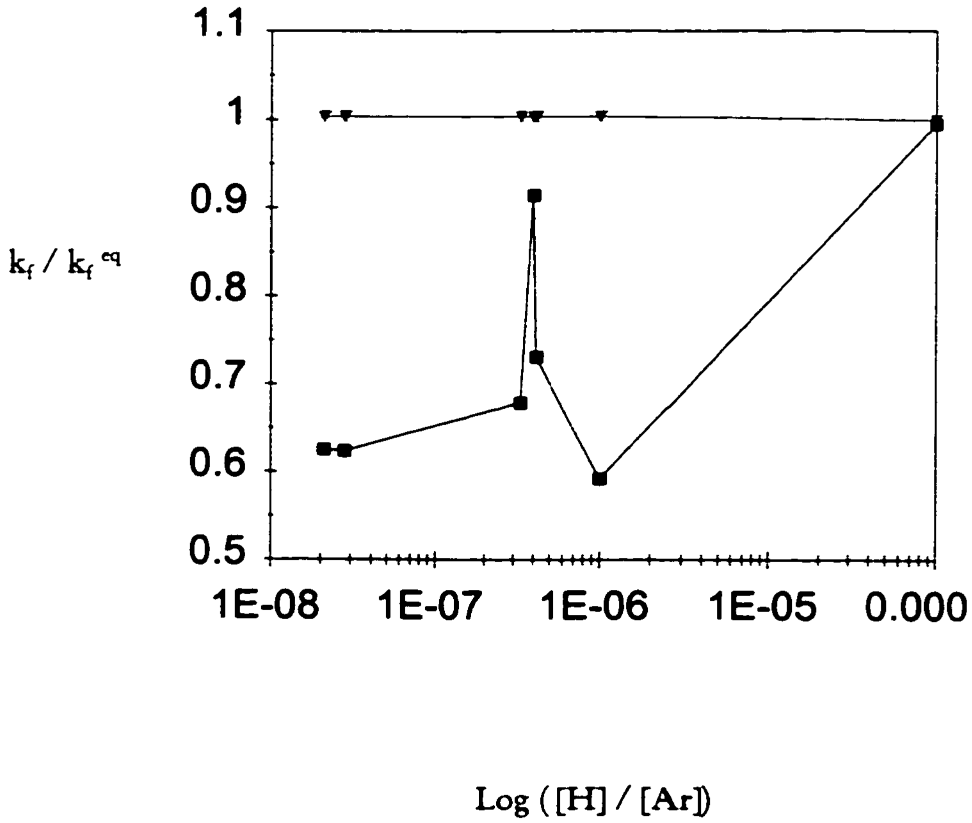

Fig. 2.3 The ratio of k_f / k_f^{eq} vs. log ([H]/[Ar]) at T = 2000 K. ▼ is for the matrix technique. ■ is for the experiments.

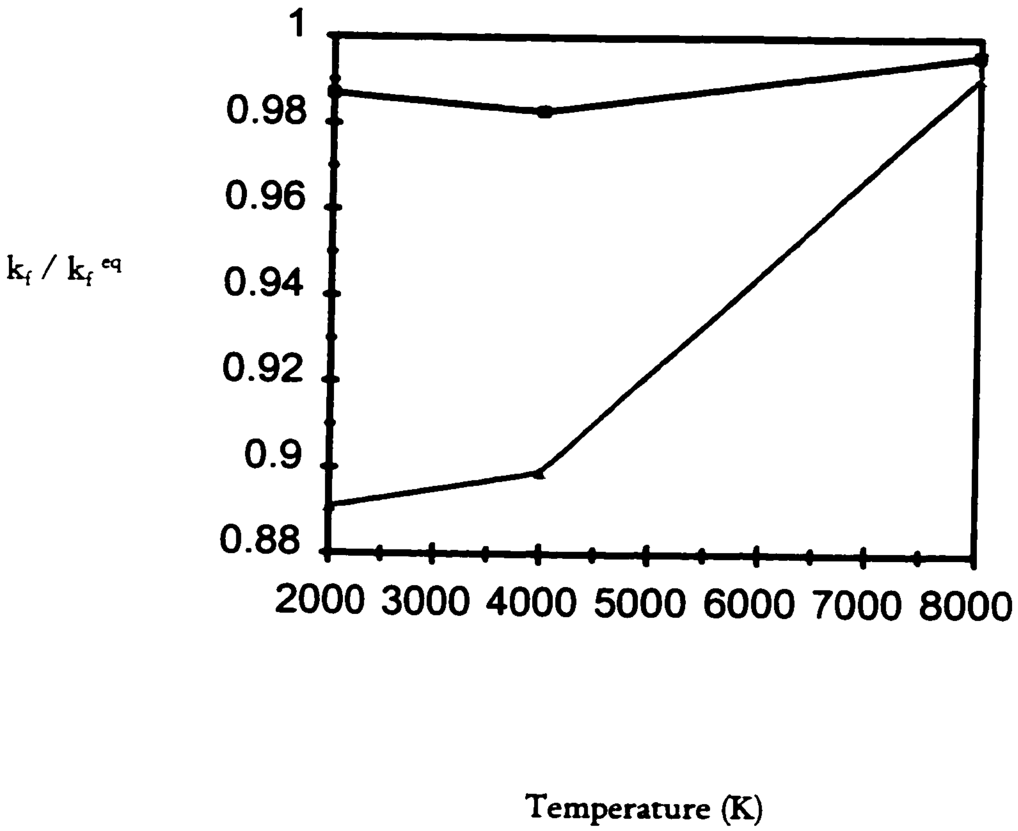

Fig. 2.4 The ratio of k_f / k_f ^{eq} vs. Temperature. ■ is for Helium ([H]/[He] =0.001). ▲ is for Argon ([H]/[Ar] =0.001).

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Chapter 3

Application of Information Theory to Cl + HBr(v) $\rightleftharpoons$ HCl (v') + Br

3.1 Introduction

In the previous chapter, the essential physics of the problem was addressed. We formulated a model which treated the diatomic molecules, BC and AB, correctly as fas as energetics and reactivity are concerned. We considered only vibrational disequilibrium and allowed only V- T energy-transfer processes (i.e. we ignored V-V processes). We solved the master equation in the steady-state limit ie where a steady vibrational population distribution is established before significant forward or reverse reactions set in. We have applied our matrix technique to the $H + O_2 \rightleftharpoons OH + O$ reaction and made predictions concerning the kinetic mass action law. In the next two chapters we shall examine another reaction for which state-to-state rate constants are partially available and for which high vibrational states are known to contribute to the reaction rate dramatically [1]. In this chapter we shall use information theory to obtain these state-to-state rate constants. In the following chapter we shall use these $k_{v\,v'}$ to examine the whole reaction.

The reaction of choice is

$$Cl + HBr(v) \rightleftharpoons HCl\,(v') + Br \qquad \Delta\bar{H}^0 = -65.6 \text{ kJ mol}^{-1} \tag{3.1}$$

Results reported in the literature for reaction (3.1) include experimental determinations of rate constants [1-4] and energy distributions among the products [5-7], and as well as results of threedimensional quasi-classical trajectory (QCT) calculations [8-10]. Thus the literature provides us with enough information to extract state-to-state rate constants. Furthermore, there has already been an attempt by Lim and Truhlar to extract state-to-state rate coefficients for this reaction [11,12]. They carried out a surprisal analysis at 300K, including vibrational levels and rotational levels of HCl. To find the rate constants for the reverse reaction they applied microscopic reversibility. We shall use their work as a guide for our contribution at high temperatures and for comparison purposes.

3.1.1 $Cl + HBr(v) \rightarrow HCl(v') + Br$

There is little information on the temperature dependence of k_v for this exothermic reaction. In the "forward", exoergic direction, the relative values of the detailed rate constants for reaction (4.1) into specific HCl vibrational levels [5-7] are: $k_f(v' = 2 | v=0;T) = 0.4$, $k_f(v' = 1 | v=0;T) = 1.0$ and $k_f(v' = 0 | v=0; T) = 0.6$. The relative value of $k_f(v' = 0 | v=0; T)$ was derived from a surprisal analysis [7]. The relative values of these detailed rate constants can be made absolute using recent measurements [13,14] of the overall thermal rate coefficients, $k_f(T)$. Theoretical results also exist. Broida used an LEPS potential energy surface [15] for a quasi-classical trajectory study of this exothermic reaction. He covered the range $T = 220$ to 500 K and $v = 0$ to $v = 1$; and those results would normally be quite useful. However, classical trajectory results depend sensitively on potential energy surfaces, and the LEPS surface is only approximate. Hence we prefer to rely on the experimental results. These results are summarized in Table 3.1.

Different techniques have been employed to study the kinetics of the thermal reaction as a function of temperature [13-21]. There seems to be a lack of consistency among the reported results. We shall have to determine which reported values are the most accurate. These results are summarized in Table 3.2. It can be seen from inspection of Table 3.2 that significant discrepancies exist in measured values of k_{exo}(298K). The recent work of Nicovich and Wine [21] reported k_{exo} (298) to be 3 time smaller than Rubin and Persky's results [18]. They concluded that their value for k_{exo} is small due to problems with a heterogeneous dark reaction between HBr and Cl_2. The relatively large rate coefficients reported by Rubin and Persky agree well with the results of Dolson and Leone [20]. We believe Rubin and Persky's results are the most accurate ones, and we shall employ them. They reported the following Arrhenius expression for $k_{exo} = 4.8 \times 10^{-11}e^{-454/T}$ cm^{3}molec^{-1} s^{-1}. We shall use the rate constants for this exothermic reaction in order to calculate thermal rate coefficients for the endothermic reaction using the equilibrium constant. We shall then compare them with our rate constants derived from a surprisal analysis.

3.1.2 HCl (v') + Br → Cl + HBr(v)

Douglas et al. [6,7] have measured the relative rates of removal of HCl from v' = 1 to v' = 4 using an "infrared chemiluminescence depletion" technique. In these experiments, the intensity of emission from HCl, that was formed in these levels by a "pre-reaction" between Cl and HI, was observed with and without Br atoms present. Other experiments have utilised the technique of laser induced infrared fluorescence to determine the total rate of removal of HCl (v' = 1) [1-4] and HCl (v' = 2) [1-4] in collisions with Br atoms. Leone et al. [1] and Arnoldi and Wolfrum [4] found that the rate constants increased by a factor of about 6 as the level of excitation was increased from v' = 1 to v' = 2. Smith [10] used a LEPS potential energy surface for a quasi-classical trajectory calculation of the effect of vibrational energy of HCl on the rate of this endoergic reaction. He covered the range v' = 1 to v' = 4 and T = 333.3K to 1000K. We are going to ignore Smith's work for two reasons. First we believe experimental values to be more accurate than classical trajectory values because the potential energy surface had to be guessed for this reaction. Second, Smith assumed that reaction and relaxation of HCl (v') in this reaction are equally important. This may or may not be true for this reaction. Furthermore, we also ignore his experimental values because his reaction mixture was contaminated with BrO, which also depletes HCl [22]. Results of all the other studies are summarized in Table 3.3.

Before we use the available rate constants for a surprisal analysis we must examine the consistency of these rate constants. There seems to exist a controversy as to whether the rates measured from v' = 1 are largely due to reaction or due to relaxation of HCl(v' = 1). Moore argued that relaxation of HCl(v' = 1) by Br is much faster than reaction of HCl(v' = 1) with Br. So he attributed the observed rate to relaxation [23]. However Moore assumed that his experimental procedure of extrapolation to [HCl] → 0 eliminates all but relaxation. All it really does is it eliminates V-V processes, but one still left with relaxation + reaction. On the other hand, Arnoldi's and Douglas' work showed that reaction is the dominant of the two [4, 6, 7]. Leone's work is consistent with both arguments because he measured the total rate for HCl(v' = 1) + Br (reaction + relaxation). We are going to distinguish between the two cases by examining the exothermic reaction (HBr(v) + Cl) along with microscopic reversibility. In order to calculate the endothermic rate for v' = 1 at 298 K [24] Pollak used the exothermic reaction rate constants measured by Maylotte et al [5] and microscopic reversibility in the form applicable to state-selected reactions:

$$k_{endo}(v') = k_{exo}(v)/(K_{eq}\ Y_{v'}{}^{eq}).$$

Here K_{eq} is the equilibrium constant for the thermal reaction Cl + HBr → HCl + Br, and $Y_{v'}{}^{eq}$ is the fraction of HCl molecules in the vibrational state v'. His work also shows that reaction is negligible compared to relaxation. Pollak's results are summarized in Table 3.3.

We have extended Pollak's work to the rate constant for v' = 0. Our value for v' = 0 agrees with Arnoldi's result. That is for k(v' = 0) a value around 1.66 x 10^{-23} cm^3 $molecule^{-1}$ sec^{-1} can be calculated. However one must note that our calculated value depends on Douglas' rate constant for k(v = 0 → v' = 0). This value was not measured in any experiment but rather obtained by a surprisal analysis, and the details for that analysis have never been published. Maylotte gave a range from 0 to 0.6 for this relative state-specific rate constant. Although we have included the calculation for comparison purposes in Table 3.3, but we have not actually used this value.

Kneba et al deduced the rates for v' = 0 at various temperatures [25]. They calculated the rates using the equilibrium constant and using the rate for the exothermic reaction. We shall attempt to reconstruct these rates more accurately. First we take Kneba's direct measurement for v' = 2 [25]. We plot the results for v' = 2 on a graph of ln k_2 vs 1/T and extrapolate a short interval to 4000 K. Then we employ microscopic reversibility (as in Pollak's work) in order to obtain the v' = 1 and v' = 0 rate constants at 298 K. As we stated earlier we are not going to attach any importance to the $v'=0$ rate constant because we are going to obtain a better estimate by means of a surprisal analysis. Once we have the $v'=0$ rate constant at 298 K then we use this rate constant and the activation energy of 69.08 kJ mole^{-1} for the reaction (HCl($v'=0$) +Br) to obtain the rate constants for this vibrational level at different temperatures. Thus we have rate constants for $v'=0$ and $v'=2$ at different temperatures. In the next step we obtain the rate constants for $v'=1$, 3 and 4. We use surprisal theory to obtain these values.

3.2 Surprisal Analysis

Basically there are two theoretical approaches, dynamical and statistical. Among the dynamical approaches the classical trajectory method has been successfully utilized for calculating specific rate constants for a diverse number of systems dating back to 1974 [26]. Later fully quantal calculations became available for reactive systems [27]. Although the reliability of these methods is high they are fairly costly and time consuming and always require a knowledge of the potential energy surface. The statistical approach is an attempt to avoid dynamical details. It calculates rate constants under certain statistical assumptions of energy partitioning [28]. The method is simple and quick, but experiment has shown that statistics alone do not suffice even for a qualitative description of the role of vibrational energy. Information theory (or surprisal analysis) takes up the slack.

We have carried out surprisal analyses of the vibrationally enhanced rate constants for the reaction (3.1) at temperatures covering the range 300-4000 K using the prescription described by Levine and Manz [29] for the prior (statistically expected) rate constant k^0_v. This is given by:

$$k_v^0 \propto \Delta^2 e^{\Delta}[\Delta K_1(\Delta) + (4+\Delta) K_2(\Delta)], \qquad (3.2)$$

Here $K_1(\Delta)$ and $K_2(\Delta)$ are the modified Bessel functions of order 1 and 2 respectively, and Δ is the dimensionless energy defect,

$$\Delta \equiv (E_{v'} - \Delta E_o)/2kT.$$

$E_{v'}$ is the vibrational energy of reagent level, v′, and ΔE_o is the heat of reaction. Both $k_{v'}(T)$ and $k^0_{v'}(T)$ increase strongly with $E_{v'}$ when $\Delta < 0$, but only moderately when $\Delta > 0$. The definition of a prior statistical rate is based on a statistical assumption. Since the dynamics are unknown one uses the least biased definition consistent with conservation laws. It has been noted [30] that there is no unique way of specifying what the statistical assumption must be. One can make different assumptions and still be consistent. Of these, one of two assumptions is generally used. The first is that at a given total energy all reagent states react with the same rate, or equivalently at a given total energy all product states are formed with the same rate. The second kind of assumption is that the prior cross section is the same for all reagent states at a given total energy. Stating this assumption differently , one can say that the rate is proportional to the final relative velocity of the outgoing molecules [29]. The quantity, $-\ln [k_{v'}(T) / k_{v'}{}^0]$, i.e. the surprisal, is a measure of how non-statistically the rate constants behave. Plotted versus Δ, the surprisal is often found to be linear with $|\text{slope}| \sim 1$ [31]. Since the surprisal of the systems being analysed is usually very large, the actual identification of the dynamical constraint is insensitive to which of the above two prior rates is used. We shall use the prior rate constant given by the assumption that at a given total energy all initial states react with the same rate [29, 32] in the absence of additional constraints, ie eq. (3.2).

Figs. 3.1- 3.5 show the dependence of ln $[k_{v'}(T) / k_{v'}{}^{0}]$ on Δ and T for reaction (3.1). At T=300K, v'=0, 2, 3, 4 are included; but at higher temperature v'=0 and v'=2 are shown, as described in section 3.1. The constant of proportionality in Eq. (3.2) has been neglected. This results in a constant shift of the ordinates without affecting the slope, which is what concerns us.

3.3 Procedure for the extraction of state-to-state rate constants from the linear surprisal analysis

The slope, $\bar{\lambda}$, of plots of the surprisal versus $(E_v - \Delta E_o)$ for reactions of the type A + BC(v) -AB + C are related to the slopes, λ, of surprisal plots for reaction of the type A + BC(v) - AB(v') + C. For the state-to-state reaction, ln $[k_{vv'} / k_{vv'}{}^{0}]$ often depends linearly on the absolute value of the energy defect $|E_v - E_{v'} - \Delta E_o|$ and λ is the corresponding slope. Thus,

$$\ln(k_{vv'} / k^{0}_{vv'}) = -\lambda_0 - \lambda|E_v - E_{v'} - \Delta E_0| / kT, \qquad (3.3)$$

Here the detailed prior rate constants, $k^{0}_{vv'}$, is given, according to Ref. [29] by

$$k^{0}_{v\,v'}(T) \propto \delta^2 e^{\delta} K_2(\delta), \qquad (3.4)$$

and where

$$\delta \equiv (E_v - E_{v'} - \Delta E_o)/2kT.$$

Eq. (3.3) is sometimes known as the exponential gap law [10]. The deviation of the observed rate constant from the prior rate constant depends on the absolute value of the energy defect. Plotted versus $(E_v - E_{v'} - \Delta E_0)/2kT$, the surprisal will thus necessarily show a cusp at $E_v - E_{v'} = \Delta E_0$, with slope $\mp\lambda$ on either side of the cusp. If we are not interested in the product vibrational states then we can sum $k_{vv'}$, in order to get k_v. This can be accomplished by substituting Eq. (3.2) into Eq. (3.3), summing over v', and dividing by $k^0_{v'}$. For the latter we can sum the priors of Eq. (3.4) discretely or use Eq. (3.2) directly. However, it must be pointed out that Eq. (3.2) is only an approximation wherein the summation had been replaced by an integral, the product AB was considered to be a simple harmonic oscillator, and v' was allowed to take any value up to ∞. We have followed the precise summation procedure. Thus

$$\frac{k_v}{k_v^0} \propto \frac{\sum_{v'} \delta^2 e^{\delta} K_2(\delta)\, e^{-2\lambda|\delta|}}{\sum_{v'} \delta^2 e^{\delta} K_2(\delta)} \qquad (3.5)$$

The constant of proportionality is exp $(-\lambda_0)$. In analogy to the procedure of Figs. 3.1 - 3.5 (which used experimental k_v) we have plotted in Fig. 3.6 the ln (k_v / k_v^0) obtained from Eq. (3.5) versus $(E_v - \Delta E_0)/kT$ for various choices of λ in the range -1 to +1. We have used the spectroscopic parameters for HBr [33] in order to calculate δ at various temperatures. (Note that we have switched the roles of v and v'). We note also three interesting properties of ln (k_v / k_v^0) : a) ln (k_v / k_v^0) is almost symmetrical (but not necessarily with respect to $(E - \Delta E_0)=0$); b) in the endothermic regime $(E_v < \Delta E_0)$ the slopes, $\bar{\lambda}$, are nearly equal to the slopes of the corresponding state-to-state surprisal plots, ie to λ; and c) in the exothermic regime $|\bar{\lambda}|$ bears little resemblance to $|\lambda|$, especially if $\lambda > 0$. More interestingly, $\bar{\lambda}$ is almost completely insensitive to λ in that latter regime. Consequently, if one wishes to deduce λ and hence state-to-state rate constants from a knowledge of k_v alone that would be nearly impossible if the available data were in the exothermic regime alone.

One simply has to superimpose experimental values of ln $(k_{v'} / k_{v'}^0)$ onto Fig. 3.6 and then shift the curves relative to each other until there is a match in slope, thus identifying λ. Once we have identified the λ approximately then we can re-plot Fig. 3.6 covering a narrower range of λ, as Fig 3.7, in order to identify λ more accurately. We have drawn graphs such as Fig. 3.6, one for each temperature and superimposed the results displayed in Figs. 3.1, 3.2, 3.3, 3.4 and 3.5 thereon. Note that in Figs. 3.2 , 3.3, 3.4 and 3.5 we have only two points. Two points are sufficient when trying to match the parameter λ in the endothermic region where the surprisals are linear. After an appropriate shift of the ln $(k_{v'} / k_{v'}^0)$ axis to make a perfect match we were able to deduce the parameters λ and the shift factors at each temperature. These results are summarized in Table 3.4 and Fig. 3.8. The parameters λ lie essentially on a perfect line. We then proceeded to use values of λ from this line. Some scatter in Fig. 3.8 exists, probably due to our finite ability to match experimental and theoretical curves perfectly. Then we proceeded to shift all theoretical curves appropriately. Our intention was to use the λ and shift factors to a) extrapolate $k_{v'}$ to larger values of v', and b)extrapolate k_v to larger values of v, and c) to deduce the state-to-state rate constants $k_{vv'}$ and $k_{v'v}$ using eq. (3.3).

3.4 Results

The calculation of prior rate constants, surprisals and $k_{v'v}$ were made using a computer FORTRAN program written by Teitelbaum. It is the same programme used to calculate the $k_{vv'}$

so successfully for the H + O_2 [36] reaction and used in chapter 2 of this study. This program has been included in Appendix C. It requires as input the spectroscopic constants for HCl and HBr as well as the heat of reaction and equilibrium constant for reaction 3.1. We have decided to extract state-to-state endothermic rate coefficients for $v=0$ to 9 and $v'=0$ to $v'=9$. The reason we decided to include only 10 vibrational levels is because the rate constants become very small after the ninth product vibrational level and the fractional population is very small for these levels. It was verified numerically that vibrational levels above $v=9$ and $v'=9$ do not play a significant role in the reaction. The rate constants, $k_{vv'}$, for the exothermic reaction, HBr (v) + Cl $\rightarrow$ HCl(v') + Br are calculated using microscopic reversibility. Thus,

$$k_{vv'} = (k_{v'v}/K_{eq})(Y_{v'}^{eq}/Y_{v}^{eq}),$$

where K_{eq} is the equilibrium constant for the thermal reaction, i.e.

$$K_{eq} = e^{-\Delta \overline{G_0}/RT},$$

and ΔG_0 is the standard molar free energy change, as obtained from JANAF tables [35]. Y_v^{eq} and $Y_{v'}^{eq}$ are the fractional vibrational level populations of HBr and of HCl respectively. Summation over v' gives k_v for the exothermic reaction and summation over v gives $k_{v'}$ for the endothermic reaction. The results are summarized in Tables 3.5-3.9.

3.4.1 Results for $k_{v'v}$ for HCl (v') + Br $\rightarrow$Cl + HBr(v).

The following trends were observed for $k_{v'}$ and $k_{v'v}$ in the Tables 3.5-3.9:

i) For a given v the rate coefficients $k_{v'v}$ increase first and then they decrease with increasing v'.

ii) For $v'=0$ to $v'=2$, the rate coefficients $k_{v'v}$ decrease with increasing v. For $v'=3$ to $v'=9$, the rate coefficients increase first and then they decrease with increasing v.

iii) $k_{v'}$ increases with increasing vibrational level v' and temperature.

The explanation of these trends is that $k_{v'v}$ depends on the energy gap. For example, when $v' = 0$ and v increases from 0 to 9, rate coefficients decrease because the energy gap increases. Another example to illustrate this phenomenon is that when $v = 0$ and v' increases from 0 to 9, the rate coefficients first increase because the energy gap is decreasing and then the rate coefficients start to decrease because the energy gap starts to increase. $k_{v'}$ increases with increasing vibrational level v' and temperature because as the HCl(v') molecules become more excited the increased energy helps to overcome the energy barrier. Once over the barrier extra energy is no longer useful, and instead, an increasing choice of final states becomes available for HBr.

Our calculated k_0 for the endothermic reaction at 300 K agrees with the value we calculated using Pollak's microscopic-reversibility relation and the relative rate constant ($v = 0$) as measured by Douglas [6] and by Maylotte [5]. Our value for k_o is 1.96 $\times 10^{-24}$ $cm^3 molecule^{-1} s^{-1}$ and the value calculated from micro-reversibility, k_o is 2.8 $\times$ 10^{-24} $cm^3 molecule^{-1} s^{-1}$. We had stated earlier that latter could not be trusted because Douglas' rate constant was obtained from a surprisal analysis lacking detailed information, and furthermore because Maylotte gave a wide range of values rather than a specific value. Now it appears as if the Douglas result was indeed obtained with great care. Our value of k_o also agrees with the one deduced by Arnoldi [7] but it is 8 times smaller than Wolfrum's [25]. Our entire surprisal analysis depends on the value for k_0. If this value is inaccurate then our entire surprisal analysis will be inaccurate. Therefore it is satisfying to see agreement with other approaches.

The cornerstone of our analysis rests on a calibration of k_1 and k_2 at 300K with the values obtained using Douglas' relative rate constants and Wolfrum's results [5, 6, 25]. In fact all of our k_2 rate constants at various temperatures are made to agree with Wolfrum's values. Our values for k_3 and k_4 at 300 K, on the other hand, derive from the surprisal analysis. They are slightly less than those calculated using a combination of the Douglas relative rate constants and Wolfrum's results but are within experimental error. One explanation for this discrepancy is that we obtained the k_3 and k_4 values from the surprisal plot in the region where it is non-linear ie in the exothermic region. However k_3 and k_4 are of the correct order of magnitude and are very large. Hence it does not make much of a difference from a practical point of view.

3.4.2 Results for $k_{vv'}$ for Cl + HBr(v) → HCl (v') + Br

This exothermic reaction exhibits similar trends to the endothermic reaction. But the state-to-state rate constants are much larger than those of the endothermic reaction; so there is considerably less variation. Some of the trends shown by this reaction are:

i) When v is kept constant $k_{vv'}$ first increases and then decreases with v'.

ii) In the range v' = 0 to 2 $k_{vv'}$ decreases with increasing v. In the range v' = 3 to 9, $k_{vv'}$ first increases and then decreases with increasing v.

iii) k_v are all of the same order of magnitude and they increase gently with increasing temperature.

The first two trends can once again be explained by the varying energy gap. k_v rate constants do not change much with increasing vibrational level v because the reaction is always exothermic, and the k_v are already very large. They depend, however, on the temperature.

Lim and Truhlar also attempted to extract state-to-state rate constants for the exothermic reaction [11, 12] at 300 K. We cannot make a direct comparison with their work because they have included the rotational levels, and they also did not specify the HBr vibrational levels from which the reaction is taking place. However, we can assume that at room temperature most of the reaction is taking place from $v=0$ for HBr. Thus all the rates given by Lim and Truhlar can be considered to be state specific: HBr ($v=0$) + Cl → HCl (v') + Br, where v' ranges from 0 to 3. To eliminate the rotational detail for HCl we simply add all the partial rotational data to give vibrational rate constants. All data are summarized in Table 3.10. Our rate constants are about a factor of 3 smaller than those of Lim and Truhlar. They made the assumption that the exothermic rate constants can be approximated, following Keren et al [34], by

$$k^{C,V,J} = K_1^{eq} P^{C,v} P^{C,v,j}$$

where $P^{C,v}$ and $P^{C,v,j}$ are the probabilities for the population of vib-rotational levels of HCl and where K_1^{eq} is the equilibrium constant for the thermal reaction. We, on other hand, did not make this assumption, but rather used the actual experimental values combined with surprisal analysis, and our results are therefore more realistic. Ours also covers a broad temperature range; whereas they considered 300 K alone.

3.5 Comparison with experimental results for the thermal reaction

A possible test of the results is a comparison with existing independent experimental measurements of the thermal rate coefficients. We can calculate k_f and k_r respectively by evaluating $\sum k_v Y_v^{eq}$ for the exoergic reaction and $\sum k_{v'} Y_{v'}^{eq}$ for the endoergic reaction. We have used the Persky and Rubin thermal rate coefficients for the exothermic reaction [18] and the equilibrium constant to deduce the experimental thermal rate coefficients for the endothermic reaction. We have summarized our comparison in Fig. 3.9. Clearly our calculated rates constants agree with the experimental values in the temperature range 500 to 1000 K. But there seems to be a large discrepancy at the higher temperatures and a more modest one at lower temperatures. Our results show non-Arrhenius behaviour at higher temperatures. Rubin and Persky's Arrhenius expression covers the temperature range 222 K to 504 K only. We have extrapolated their results to higher temperatures. Hence there might actually be non-Arrhenius behaviour at higher temperatures. The comparison for the exothermic reaction is shown in Fig. 3.10. Our results underestimate the rate coefficients at lower temperature and overestimate the results at higher temperatures. As we stated earlier we have extrapolated Rubin and Persky's results to higher temperatures. Hence it might not be wise to compare our results there.

The discrepancy at lower temperatures requires some elaboration. Our estimate of the endothermic thermal rate coefficient, especially at room temperature, depends on the value of k_0 for the endothermic reaction. Knowledge of this value is singularly lacking. We had the choice of extrapolating k_2 and k_1 obtained from state-selected chemiluminescence studies to k_0; or alternatively to fix the value of k_0 so as to reproduce thermal data as deduced from an application of the equilibrium constant to the exothermic rate coefficients. This study is designed to examine the validity of using equilibrium constants in such a way; and so we decided not to compromise our results, and instead to trust the state-selected data as published even if they are only relative rate constants. Under such circumstances, activation energies would be better gauges than absolute values. However, even the latter might come into agreement only once non-equilibrium populations are to be used (Chapter 4) to reconstruct thermal rate coefficients. The discrepancy between thermal and non-thermal approaches might be entirely due to such non-equilibrium phenomena. This notwithstanding, there remains the possibility that a slight underestimate of k_1 resulted in a magnifie underestimate of k_0 and hence in an underestimate of k_{endo} at room temperature.

3.6 Summary

In this chapter we have applied information theory to HBr (v) + Cl = HCl (v') + Br and obtained state-to-state rate constants. (These rate constants will be used in the next chapter to gauge non-equilibrium effects.) We used Wolfrum's rates for $v' = 2$ and Douglas' experimental relative rates to construct our surprisal plots for temperatures ranging from 300K to 4000K. We also made use of microscopic-reversibility to obtain the exothermic state-to-state rate constants. Our values for k_o for the endothermic reaction at 298 K agrees with Arnoldi's estimate, and with our estimated value using Douglas's exothermic rate and Pollack's microscopic-reversibility relation. Our entire surprisal analysis depends on the accuracy of this constant. We believe that we have estimated it making full use of all the information available to us.

Table 3.1 Part 1: Experimental rate constants for $HBr(0) + Cl \rightarrow HCl(v' \geq 0) + Br$.

HCl ($v'=0$)	0.6[a]	0 - 0.6[b]
HCl ($v'=1$)	1.0	1.0
HCl ($v'=2$)	0.4	0.4±0.06

[a] Relative rates obtained from ref [8]. [b] Relative rates obtained from ref. [5].

Table 3.1 Part 2: Classical trajectory rate constants for $HBr(v) + Cl \rightarrow HCl + Br$

HBr ($v=0$)	5.61×10^{-12} [a,b,c]	8.10×10^{-12} [c]	1.58×10^{-11} [c]
HBr ($v=1$)	2.04×10^{-11}	—	—

[a] All rates are given in units of cm^3 $molecule^{-1}$ s^{-1}. [b] Values are from ref. [15]. [c] First entry for T=220 K ; second entry for T= 300 K and third entry for T= 500 K.

Table 3.2 Comparison of results obtained from the kinetics of the Cl + HBr reaction.

Investigators	Range of T (K)	E/R[c]	k(298 K)[a]
Wodarcyzk & Moore [13]	295		7.6
Bergmann & Moore [14]	295		7.4
Mei & Moore [16]	218 - 402	460	8.5[b]
Nesbitt & Leone [17]	298		7.9
Rubin & Persky [18]	222 - 504	411	10.3[b]
Lamb et al. [19]	267 - 333	0	3.4
Dolson & Leone [20]	298		10.2
Broida & Persky [15]	220 - 500	410	8.1
Nicovich & Wine [21]	257- 404	400	4.9[b]

[a] In units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. [b] Calculated from Arrhenius parameters. [c] Units are in degrees K.

Table 3.3: Experimental and trajectory (calculated) rate constants for HCl(v') + Br.

Reaction	10^{-11} k_r [b]	k_r [d]	k_r [e]		k_r [j]
HC1 (v'=0)			2.63×10^{-13} [f, g] 1.66×10^{-15}	2.63×10^{-19} [f,i] 1.66×10^{-23}	3.67×10^{-13}
HC1 (v'=1)	0.10(±0.035)[c] —	0.1	—	—	7.70×10^{-7}
HC1 (v'=2)	1.5(±0.4) 0.15(±0.05)	0.19	1.98×10^{-10} [g, h] 8.32×10^{-11}	1.48×10^{-11} [h,i] 1.66×10^{-11}	0.19
HC1 (v'=3)	4.5(±0.7) 1.2(±0.3)	0.6	—	—	—
HC1 (v'=4)	5.6(±0.9) 2.1(±0.35)	1.0	—	—	—

[a] Absolute rate constants are in units of cm^3 $molecule^{-1}$ s^{-1}. [b] Results are from ref. [10]. [c] Upper entry for T=1000 K; lower entry for T= 333 K. [d] Relative rates are from refs. [6, 8] at 300 K. [e] Results are from ref. [3]. [f] Calculated values. [g] Upper entry for T= 2000 K; lower entry for T=1000K. [h] Extrapolated graphically. [i] Upper entry for T = 500 K; lower entry for T = 200 K. [j] Relative rate constants calculated by using microscopic reversibility and Douglas' data (after Pollak [24]).

Table 3.4 Shift factors and λ found by surprisal analysis for HBr (v) + Cl = HCl (v') + Br

Temperature (K)	λ	Shift
298	0.16	-28.23
500	0.33	-25.71
1000	0.683	-23.86
2000	1.314	-23.07
4000	2.81	-22.64

Table 3.5 State-to-State Rate costants at 298K.
λ = 0.16 T = 298 K shift = -28.23
K_{eq}(JANAF) = 4.938 x 10^{-12} q_{vib}(HBr) = 1.000004292 q_{vib}(HCl) = 1.000000954

$k_{v'v}$ for Br + HCl(v') - HBr(v) + Cl

v v'	0	1	2	3	4	5	6	7	8	9
0	.1956E-23	.1994E-29	.2897E-35	.6398E-41	.0000E+00	.0000E+00	.0000E+00	.0000E+00	.0000E+00	0000E+00
1	.7641E-17	.1125E-22	.1922E-28	.4654E-34	.1710E-39	.1401E-44	.0000E+00	.0000E+00	.0000E+00	.0000E+00
2	.1455E-11	.2394E-16	.6007E-22	.1718E-27	.6936E-33	.4241E-38	.4064E-43	.0000E+00	.0000E+00	.0000E+00
3	.1751E-11	.1642E-11	.7002E-16	.2996E-21	.1436E-26	.9661E-32	.9828E-37	.1564E-41	.0000E+00	.0000E+00
4	.5550E-12	.1739E-11	.1794E-11	.1926E-15	.1407E-20	.1129E-25	.1267E-30	.2144E-35	.5669E-40	.2803E-44
5	.1374E-12	.5783E-12	.1732E-11	.1916E-11	.5015E-15	.6263E-20	.8424E-25	.1575E-29	.4435E-34	.1949E-38
6	.3166E-13	.1526E-12	.6048E-12	.1730E-11	.2014E-11	.1244E-14	.2661E-19	.6001E-24	.1871E-28	.8763E-33
7	.7220E-14	.3765E-13	.1701E-12	.6344E-12	.1731E-11	.2093E-11	.2960E-14	.1087E-18	.4111E-23	.2137E-27
8	.1677E-14	.9203E-14	.4487E-13	.1899E-12	.6668E-12	.1736E-11	.2157E-11	.6789E-14	.4296E-18	.2727E-22
9	.4030E-15	.2292E-14	.1174E-13	.5355E-13	.2124E-12	.7019E-12	.1742E-11	.2209E-11	.1509E-13	.1654E-17

$k_{vv'}$ for Cl + HBr (v) - HCl(v') +Br

v v'	0	1	2	3	4	5	6	7	8	9
0	.3960E-12	.9357E-13	.2034E-13	.4346E-14	.9409E-15	.2099E-15	.4875E-16	.1187E-16	.3043E-17	.8241E-18
1	.1374E-11	.4688E-12	.1199E-12	.2807E-13	.6445E-14	.1498E-14	.3586E-15	.8934E-16	.2332E-16	.6409E-17
2	.3832E-12	.1460E-11	.5486E-12	.1518E-12	.3827E-13	.9445E-14	.2357E-14	.6053E-15	.1617E-15	.4527E-16
3	.1106E-17	.2404E-12	.1535E-11	.6350E-12	.1901E-12	.5163E-13	.1369E-13	.3667E-14	.1010E-14	.2895E-15
4	.1370E-23	.9942E-18	.1536E-12	.1595E-11	.7277E-12	.2358E-12	.6893E-13	.1964E-13	.5647E-14	.1669E-14
5	.2143E-29	.2089E-23	.9366E-18	.1002E-12	.1639E-11	.8259E-12	.2896E-12	.9117E-13	.2791E-13	.8613E-14
6	.5012E-35	.5599E-29	.3321E-23	.9184E-18	.6682E-13	.1666E-11	.9288E-12	.3526E-12	.1195E-12	.3931E-13
7	.1853E-40	.2238E-34	.1514E-28	.5459E-23	.9308E-18	.4542E-13	.1674E-11	.1035E-11	.4257E-12	.1554E-12
8	.0000E+00	.1406E-39	.1027E-33	.4202E-28	.9217E-23	.9682E-18	.3137E-13	.1662E-11	.1144E-11	.5097E-12
9	.0000E+00	.1401E-44	.1088E-38	.4799E-33	.1189E-27	.1586E-22	.1026E-17	.2191E-13	.1627E-11	.1252E-11

$\Delta E/kT$	$\ln(k_{v'}/k^c_{v'})$	$k^c_{v'}$	v'	$k_{v'}$	v	k_v
-.26373E+02	-.32450E+02	.24211E-09	0	.19556E-23	0	.21534E-11
-.12439E+02	-.30220E+02	.10178E-03	1	.76414E-17	1	.22633E-11
.99515E+00	-.28389E+02	.31064E+01	2	.14553E-11	2	.23769E-11
.13935E+02	-.29920E+02	.33476E+02	3	.33930E-11	3	.25140E-11
.26388E+02	-.30861E+02	.10336E+03	4	.40877E-11	4	.26693E-11
.38360E+02	-.31545E+02	.21867E+03	5	.43641E-11	5	.28360E-11
.49858E+02	-.32065E+02	.38226E+03	6	.45342E-11	6	.30096E-11
.60888E+02	-.32477E+02	.59498E+03	7	.46767E-11	7	.31871E-11
.71457E+02	-.32813E+02	.85629E+03	8	.48120E-11	8	.33511E-11
.81571E+02	-.33092E+02	.11646E+04	9	.49483E-11	9	.19670E-11

Table 3.6 State-to-State Rate costants at 500K.

λ = 0.33 T = 500 K shift = -25.71
K_{eq}(JANAF) = 1.928 x 10^{-7} q_{vib}(HBr) = 1.000635147 q_{vib}(HCl) = 1.000247359

$k_{v'v}$ for Br + HCl(v') - HBr(v) + Cl

v v'	0	1	2	3	4	5	6	7	8	9
0	.1997E-18	.1869E-22	.2147E-26	.3210E-30	.6429E-34	.1752E-37	.6559E-41	.2803E-44	.0000E+00	.0000E+00
1	.5014E-14	.6456E-18	.8599E-22	.1401E-25	.2967E-29	.8407E-33	.3240E-36	.1715E-39	.1261E-42	.0000E+00
2	.1480E-10	.1069E-13	.1982E-17	.3758E-21	.8683E-25	.2603E-28	.1044E-31	.5688E-35	.4256E-38	.4401E-41
3	.7046E-11	.1524E-10	.2175E-13	.5810E-17	.1568E-20	.5136E-24	.2181E-27	.1237E-30	.9529E-34	.1008E-36
4	.1336E-11	.6966E-11	.1549E-10	.4244E-13	.1634E-16	.6274E-20	.2915E-23	.1752E-26	.1405E-29	.1531E-32
5	.2094E-12	.1413E-11	.6922E-11	.1562E-10	.7984E-13	.4429E-16	.2420E-19	.1594E-22	.1356E-25	.1539E-28
6	.3144E-13	.2402E-12	.1502E-11	.6907E-11	.1564E-10	.1454E-12	.1163E-15	.9042E-19	.8443E-22	.1017E-24
7	.4775E-14	.3926E-13	.2768E-12	.1604E-11	.6917E-11	.1560E-10	.2573E-12	.2970E-15	.3287E-18	.4352E-21
8	.7533E-15	.6499E-14	.4919E-13	.3199E-12	.1718E-11	.6946E-11	.1550E-10	.4445E-12	.7413E-15	.1168E-17
9	.1251E-15	.1117E-14	.8862E-14	.6175E-13	.3705E-12	.1844E-11	.6990E-11	.1536E-10	.7522E-12	.1816E-14

$k_{vv'}$ for Cl + HBr (v) - HCl(v') + Br

v v'	0	1	2	3	4	5	6	7	8	9
0	.1036E-11	.1528E-12	.2131E-13	.2984E-14	.4312E-15	.6534E-16	.1048E-16	.1792E-17	.3279E-18	.6442E-19
1	.6435E-11	.1305E-11	.2112E-12	.3221E-13	.4921E-14	.7754E-15	.1281E-15	.2238E-16	.4168E-17	.8304E-18
2	.6327E-11	.7201E-11	.1622E-11	.2879E-12	.4799E-13	.8002E-14	.1375E-14	.2474E-15	.4711E-16	.9554E-17
3	.1348E-14	.4591E-11	.7959E-11	.1991E-11	.3876E-12	.7061E-13	.1285E-13	.2406E-14	.4718E-15	.9785E-16
4	.1528E-18	.1255E-14	.3391E-11	.8697E-11	.2416E-11	.5158E-12	.1027E-12	.2038E-13	.4161E-14	.8888E-15
5	.1907E-22	.2028E-18	.1206E-14	.2548E-11	.9400E-11	.2900E-11	.6790E-12	.1477E-12	.3198E-13	.7115E-14
6	.3026E-26	.3643E-22	.2767E-18	.1191E-14	.1946E-11	.1006E-10	.3447E-11	.8852E-12	.2103E-12	.4967E-13
7	.6417E-30	.8314E-26	.7118E-22	.3862E-18	.1201E-14	.1507E-11	.1065E-10	.4060E-11	.1144E-11	.2969E-12
8	.1861E-33	.2530E-29	.2326E-25	.1416E-21	.5485E-18	.1233E-14	.1179E-11	.1117E-10	.4741E-11	.1465E-11
9	.7451E-37	.1048E-32	.1010E-28	.6588E-25	.2852E-21	.7892E-18	.1282E-14	.9306E-12	.1160E-10	.5489E-11

$\Delta E/kT$	$\ln(k_{v'}/k^0_{v'})$	$k^0_{v'}$	v'	$k_{v'}$	v	k_v
-.15718E+02	-.30882E+02	.51585E-05	0	.19976E-18	0	0.13800E-10
-.74136E+01	-.28150E+02	.84301E-02	1	.50151E-14	1	0.13252E-10
.59311E+00	-.25910E+02	.26486E+01	2	.14807E-10	2	0.13206E-10
.83055E+01	-.27467E+02	.18930E+02	3	.22304E-10	3	0.13560E-10
.15727E+02	-.28450E+02	.54048E+02	4	.23838E-10	4	0.14203E-10
.22863E+02	-.29149E+02	.11056E+03	5	.24240E-10	5	0.15059E-10
.29716E+02	-.29679E+02	.18968E+03	6	.24468E-10	6	0.16075E-10
.36289E+02	-.30100E+02	.29173E+03	7	.24696E-10	7	0.17217E-10
.42588E+02	-.30444E+02	.41642E+03	8	.24986E-10	8	0.17727E-10
.48616E+02	-.30730E+02	.56294E+03	9	.25392E-10	9	0.73076E-11

Table 3.7 State-to-State Rate costants at 1000K.

λ= 0.683 T= 1000 K shift= -23.86
K_{eq}(JANAF)= 5.47 x 10^{-4} q_{vib}(HBr)= 1.0002594 q_{vib}(HCl)= 1.01602

$k_{v'v}$ for Br + HCl(v') - HBr(v) + Cl

v v'	0	1	2	3	4	5	6	7	8	9
0	.1165E-14	.3735E-17	.1327E-19	.5468E-22	.2674E-24	.1573E-26	.1122E-28	.9759E-31	.1040E-32	.1360E-34
1	.5946E-12	.2404E-14	.9626E-17	.4266E-19	.2190E-21	.1334E-23	.9767E-26	.8672E-28	.9389E-30	.1245E-31
2	.8182E-10	.9464E-12	.4802E-14	.2402E-16	.1327E-18	.8489E-21	.6437E-23	.5867E-25	.6483E-27	.8735E-29
3	.1976E-10	.7860E-10	.1464E-11	.9316E-14	.5818E-16	.4007E-18	.3193E-20	.3015E-22	.3420E-24	.4703E-26
4	.3011E-11	.1949E-10	.7554E-10	.2209E-11	.1761E-13	.1373E-15	.1178E-17	.1169E-19	.1374E-21	.1940E-23
5	.4088E-12	.3200E-11	.1934E-10	.7267E-10	.3260E-11	.3253E-13	.3164E-15	.3384E-17	.4180E-19	.6116E-21
6	.5466E-13	.4733E-12	.3422E-11	.1929E-10	.6998E-10	.4718E-11	.5889E-13	.7143E-15	.9518E-17	.1464E-18
7	.7503E-14	.6914E-13	.5506E-12	.3677E-11	.1932E-10	.6745E-10	.6715E-11	.1048E-12	.1585E-14	.2630E-16
8	.1080E-14	.1038E-13	.8776E-13	.6429E-12	.3965E-11	.1942E-10	.6507E-10	.9428E-11	.1838E-12	.3466E-14
9	.1648E-15	.1632E-14	.1438E-13	.1116E-12	.7524E-12	.4286E-11	.1957E-10	.6280E-10	.1309E-10	.3187E-12

$k_{vv'}$ for Cl HBr(v) - HCl (v') + Br

v v'	0	1	2	3	4	5	6	7	8	9
0	.2152E-11	.2737E-12	.3389E-13	.4273E-14	.5613E-15	.7785E-16	.1150E-16	.1817E-17	.3089E-18	.5659E-19
1	.1727E-10	.2771E-11	.3867E-12	.5243E-13	.7231E-14	.1038E-14	.1574E-15	.2540E-16	.4386E-17	.8143E-18
2	.4337E-10	.1991E-10	.3521E-11	.5388E-12	.7997E-13	.1206E-13	.1894E-14	.3137E-15	.5529E-16	.1043E-16
3	.2215E-12	.3497E-10	.2271E-10	.4420E-11	.7415E-12	.1204E-12	.1986E-13	.3408E-14	.6168E-15	.1188E-15
4	.8252E-15	.2120E-12	.2865E-10	.2563E-10	.5488E-11	.1009E-11	.1793E-12	.3232E-13	.6061E-14	.1198E-14
5	.3162E-17	.9828E-15	.2069E-12	.2379E-10	.2867E-10	.6746E-11	.1358E-11	.2640E-12	.5203E-13	.1066E-13
6	.1374E-19	.4724E-17	.1190E-14	.2053E-12	.2001E-10	.3180E-10	.8219E-11	.1812E-11	.3851E-12	.8294E-13
7	.7050E-22	.2579E-19	.7157E-17	.1462E-14	.2064E-12	.1699E-10	.3502E-10	.9932E-11	.2396E-11	.5568E-12
8	.4350E-24	.1659E-21	.4891E-19	.1096E-16	.1816E-14	.2097E-12	.1455E-10	.3831E-10	.1192E-10	.3146E-11
9	.3259E-26	.1281E-23	.3935E-21	.9347E-19	.1692E-16	.2273E-14	.2148E-12	.1253E-10	.4165E-10	.1420E-10

ΔE/kT	$\ln(k_{v'}/k^0_{v'})$	$k^0_{v'}$	v'	$k_{v'}$	v	k_v
-.78592E+01	-.29265E+02	.59915E-02	0	.11692E-14	0	.63006E-10
-.37068E+01	-.26439E+02	.18121E+00	1	.59705E-12	1	.58142E-10
.29655E+00	-.24147E+02	.25404E+01	2	.82767E-10	2	.55502E-10
.41527E+01	-.25384E+02	.10552E+02	3	.99829E-10	3	.54647E-10
.78637E+01	-.26272E+02	.25766E+02	4	.10027E-09	4	.55200E-10
.11431E+02	-.26928E+02	.48960E+02	5	.98906E-10	5	.56896E-10
.14858E+02	-.27434E+02	.80483E+02	6	.97991E-10	6	.59562E-10
.18145E+02	-.27838E+02	.12039E+03	7	.97897E-10	7	.62880E-10
.21294E+02	-.28165E+02	.16854E+03	8	.98809E-10	8	.56410E-10
.24308E+02	-.28431E+02	.22459E+03	9	.10094E-09	9	.17903E-10

Table 3.8 State-to-State Rate coefficients at 2000K.

λ = 1.392 T = 2000 K shift = -23.07
K_{eq}(JANAF) = 3.128 x 10^{-2} q_{vib}(HBr) = 1.191654 q_{vib}(HCl) = 1.145276

$k_{v'v}$ for Br + HCl(v') → HBr(v) + Cl

v v'	0	1	2	3	4	5	6	7	8	9
0	.5845E-13	.1035E-14	.1975E-16	.4169E-18	.9895E-20	.2667E-21	.8213E-23	.2903E-24	.1182E-25	.5554E-27
1	.4789E-11	.9726E-13	.2012E-14	.4483E-16	.1105E-17	.3064E-19	.9642E-21	.3467E-22	.1431E-23	.6802E-25
2	.1674E-09	.6676E-11	.1583E-12	.3824E-14	.9945E-16	.2863E-17	.9266E-19	.3405E-20	.1429E-21	.6887E-23
3	.2405E-10	.1545E-09	.9129E-11	.2524E-12	.7117E-14	.2161E-15	.7260E-17	.2743E-18	.1176E-19	.5765E-21
4	.2967E-11	.2366E-10	.1435E-09	.1227E-10	.3954E-12	.1300E-13	.4607E-15	.1807E-16	.7965E-18	.3987E-19
5	.3546E-12	.3169E-11	.2345E-10	.1340E-09	.1626E-10	.6097E-12	.2338E-13	.9660E-15	.4420E-16	.2274E-17
6	.4322E-13	.4138E-12	.3408E-11	.2338E-10	.1257E-09	.2126E-10	.9274E-12	.4143E-13	.1997E-14	.1066E-15
7	.5506E-14	.5520E-13	.4854E-12	.3683E-11	.2343E-10	.1184E-09	.2751E-10	.1395E-11	.7256E-13	.4076E-14
8	.7436E-15	.7701E-14	.7078E-13	.5717E-12	.3997E-11	.2357E-10	.1118E-09	.3529E-10	.2077E-11	.1258E-12
9	.1073E-15	.1139E-14	.1080E-13	.9100E-13	.6751E-12	.4349E-11	.2378E-10	.1058E-09	.4496E-10	.3071E-11

$k_{vv'}$ for Cl HBr(v) → HCl (v') + Br

v v'	0	1	2	3	4	5	6	7	8	9
0	.1944E-11	.2170E-12	.2443E-13	.2853E-14	.3510E-15	.4594E-16	.6437E-17	.9700E-18	.1577E-18	.2773E-19
1	.1998E-10	.2556E-11	.3122E-12	.3847E-13	.4916E-14	.6618E-15	.9476E-16	.1453E-16	.2395E-17	.4259E-18
2	.9436E-10	.2371E-10	.3318E-11	.4434E-12	.5977E-13	.8355E-14	.1230E-14	.1927E-15	.3231E-16	.5826E-17
3	.1971E-11	.7980E-10	.2783E-10	.4256E-11	.6220E-12	.9170E-13	.1402E-13	.2258E-14	.3868E-15	.7093E-16
4	.3802E-13	.1911E-11	.6841E-10	.3236E-10	.5404E-11	.8630E-12	.1391E-12	.2325E-13	.4095E-14	.7671E-15
5	.7635E-15	.4299E-13	.1878E-11	.5936E-10	.3732E-10	.6798E-11	.1186E-11	.2089E-12	.3817E-13	.7349E-14
6	.1678E-16	.1012E-14	.4920E-13	.1867E-11	.5203E-10	.4274E-10	.8482E-11	.1615E-11	.3109E-12	.6209E-13
7	.4132E-18	.2610E-16	.1355E-14	.5686E-13	.1875E-11	.4599E-10	.4863E-10	.1051E-10	.2184E-11	.4591E-12
8	.1155E-19	.7539E-18	.4090E-16	.1827E-14	.6621E-13	.1896E-11	.4092E-10	.5507E-10	.1295E-10	.2934E-11
9	.3694E-21	.2470E-19	.1383E-17	.6446E-16	.2478E-14	.7754E-13	.1928E-11	.3659E-10	.6210E-10	.1587E-10

$\Delta E/kT$	$\ln(k_{v'}/k^c_{v'})$	$k^c_{v'}$	v'	$k_{v'}$	v	k_v
-.39296E+01	-.28782E+02	.18815E+00	0	.59508E-13	0	.11829E-09
-.18534E+01	-.25928E+02	.89057E+00	1	.48882E-11	1	.10824E-09
.14828E+00	-.23623E+02	.31661E+01	2	.17426E-09	2	.10183E-09
.20764E+01	-.24464E+02	.79164E+01	3	.18797E-09	3	.98388E-10
.39319E+01	-.25167E+02	.15555E+02	4	.18282E-09	4	.97386E-10
.57157E+01	-.25719E+02	.26287E+02	5	.17786E-09	5	.98461E-10
.74289E+01	-.26159E+02	.40182E+02	6	.17517E-09	6	.10131E-09
.90724E+01	-.26513E+02	.57216E+02	7	.17500E-09	7	.10402E-09
.10647E+02	-.26799E+02	.77265E+02	8	.17750E-09	8	.77580E-10
.12154E+02	-.27029E+02	.10007E+03	9	.18276E-09	9	.19256E-10

Table 3.9 State-to-State Rate coefficients at 4000K.

λ= 2.81 T= 4000 K shift= -22.64

K_{eq}(JANAF)= 0.223 q_{vib}(HBr)= 1.567849 q_{vib}(HCl)= 1.689668

$k_{v'v}$ for Br + HCl(v') $\rightarrow$ HBr(v) + Cl

v v'	0	1	2	3	4	5	6	7	8	9
0	.3604E-12	.1413E-13	.5988E-15	.2775E-16	.1418E-17	.8036E-19	.5069E-20	.3570E-21	.2813E-22	.2485E-23
1	.1302E-10	.5436E-12	.2406E-13	.1151E-14	.6029E-16	.3482E-17	.2230E-18	.1590E-19	.1266E-20	.1128E-21
2	.2478E-09	.1714E-10	.8058E-12	.4024E-13	.2174E-14	.1286E-15	.8393E-17	.6075E-18	.4897E-19	.4407E-20
3	.2512E-10	.2239E-09	.2221E-10	.1176E-11	.6623E-13	.4039E-14	.2698E-15	.1989E-16	.1627E-17	.1482E-18
4	.2564E-11	.2468E-10	.2040E-09	.2841E-10	.1693E-11	.1075E-12	.7396E-14	.5579E-15	.4646E-16	.4293E-17
5	.2712E-12	.2751E-11	.2443E-10	.1872E-09	.3593E-10	.2407E-11	.1722E-12	.1337E-13	.1138E-14	.1071E-15
6	.3029E-13	.3189E-12	.2974E-11	.2435E-10	.1730E-09	.4497E-10	.3388E-11	.2731E-12	.2391E-13	.2297E-14
7	.3607E-14	.3903E-13	.3770E-12	.3232E-11	.2440E-10	.1606E-09	.5585E-10	.4728E-11	.4291E-12	.4235E-13
8	.4612E-15	.5096E-14	.5052E-13	.4477E-12	.3528E-11	.2456E-10	.1498E-09	.6889E-10	.6552E-11	.6693E-12
9	.6356E-16	.7140E-15	.7222E-14	.6560E-13	.5334E-12	.3864E-11	.2481E-10	.1401E-09	.8458E-10	.9031E-11

$k_{vv'}$ for Cl HBr(v) $\rightarrow$ HCl (v') + Br

v v'	0	1	2	3	4	5	6	7	8	9
0	.1499E-11	.1475E-12	.1519E-13	.1655E-14	.1926E-15	.2405E-16	.3236E-17	.4705E-18	.7409E-19	.1266E-19
1	.1918E-10	.2010E-11	.2161E-12	.2432E-13	.2899E-14	.3690E-15	.5041E-16	.7422E-17	.1181E-17	.2036E-18
2	.1341E-09	.2329E-10	.2660E-11	.3125E-12	.3843E-13	.5010E-14	.6973E-15	.1042E-15	.1679E-16	.2923E-17
3	.5187E-11	.1160E-09	.2797E-10	.3482E-11	.4465E-12	.6000E-13	.8550E-14	.1301E-14	.2128E-15	.3749E-16
4	.2093E-12	.5056E-11	.1015E-09	.3327E-10	.4513E-11	.6313E-12	.9268E-13	.1443E-13	.2402E-14	.4294E-15
5	.9075E-14	.2311E-12	.4985E-11	.8986E-10	.3925E-10	.5796E-11	.8846E-12	.1418E-12	.2413E-13	.4389E-14
6	.4303E-15	.1137E-13	.2576E-12	.4961E-11	.8025E-10	.4598E-10	.7389E-11	.1229E-11	.2151E-12	.3999E-13
7	.2253E-16	.6120E-15	.1436E-13	.2896E-12	.4977E-11	.7220E-10	.5354E-10	.9359E-11	.1697E-11	.3241E-12
8	.1311E-17	.3636E-16	.8758E-15	.1825E-13	.3275E-12	.5024E-11	.6535E-10	.6206E-10	.1179E-10	.2331E-11
9	.8505E-19	.2398E-17	.5893E-16	.1259E-14	.2330E-13	.3721E-12	.5095E-11	.5940E-10	.7167E-10	.1480E-10

$\Delta E/kT$	$\ln(k_{v'}/k^0_{v'})$	$k^0_{v'}$	v'	$k_{v'}$	v	k_v
-.19648E+01	-.28849E+02	.12686E+01	0	.37515E-12	0	.16022E-09
-.92670E+00	-.25983E+02	.26143E+01	1	.13592E-10	1	.14674E-09
.74139E-01	-.23639E+02	.49065E+01	2	.26577E-09	2	.13767E-09
.10382E+01	-.24144E+02	.83306E+01	3	.27244E-09	3	.13222E-09
.19659E+01	-.24627E+02	.12964E+02	4	.26143E-09	4	.12983E-09
.28579E+01	-.25032E+02	.18822E+02	5	.25321E-09	5	.13007E-09
.37144E+01	-.25365E+02	.25865E+02	6	.24931E-09	6	.13236E-09
.45362E+01	-.25637E+02	.34006E+02	7	.24973E-09	7	.13221E-09
.53236E+01	-.25855E+02	.43102E+02	8	.25451E-09	8	.85408E-10
.60770E+01	-.26029E+02	.52967E+02	9	.26299E-09	9	.17455E-10

Table 3.10 Comparison of the present state-to-state rate constants for HBr + Cl - HCl(v') + Br to Lim and Truhlar's results.

Investigators [a]	HCl(v'=0)	HCl(v'=1)	HCl(v'=2)	HCl(v'=3)
Lim & Truhlar [11]	1.365×10^{-12}	4.532×10^{-12}	1.788×10^{-12}	5.248×10^{-16}
This work	3.96×10^{-13}	1.37×10^{-12}	3.83×10^{-13}	1.11×10^{-18}

[a] All rates are given in units of cm^3 $molecule^{-1}$ s^{-1}.

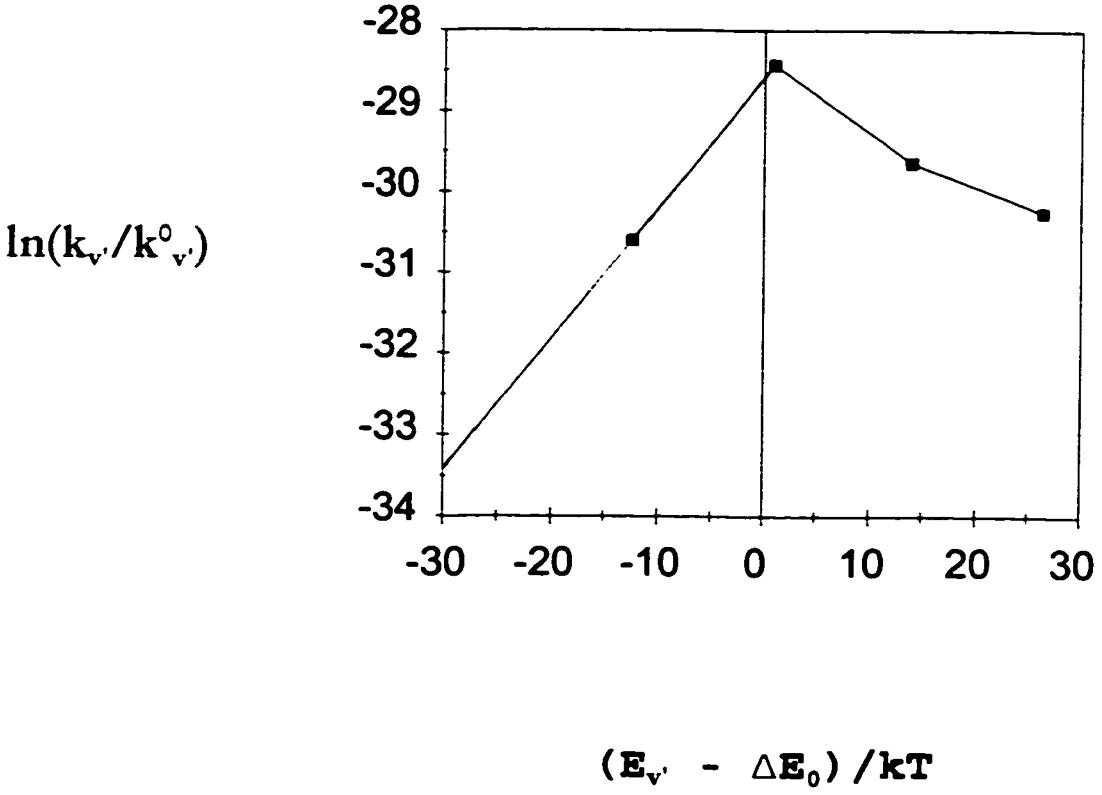

Fig. 3.1 Surprisal plot of the vibrationally enchanced rate constants for the reaction Br + HCl(v') - HBr(v) + Cl, as a function of $(E_{v'} - \Delta E_0)$ at 298 K.

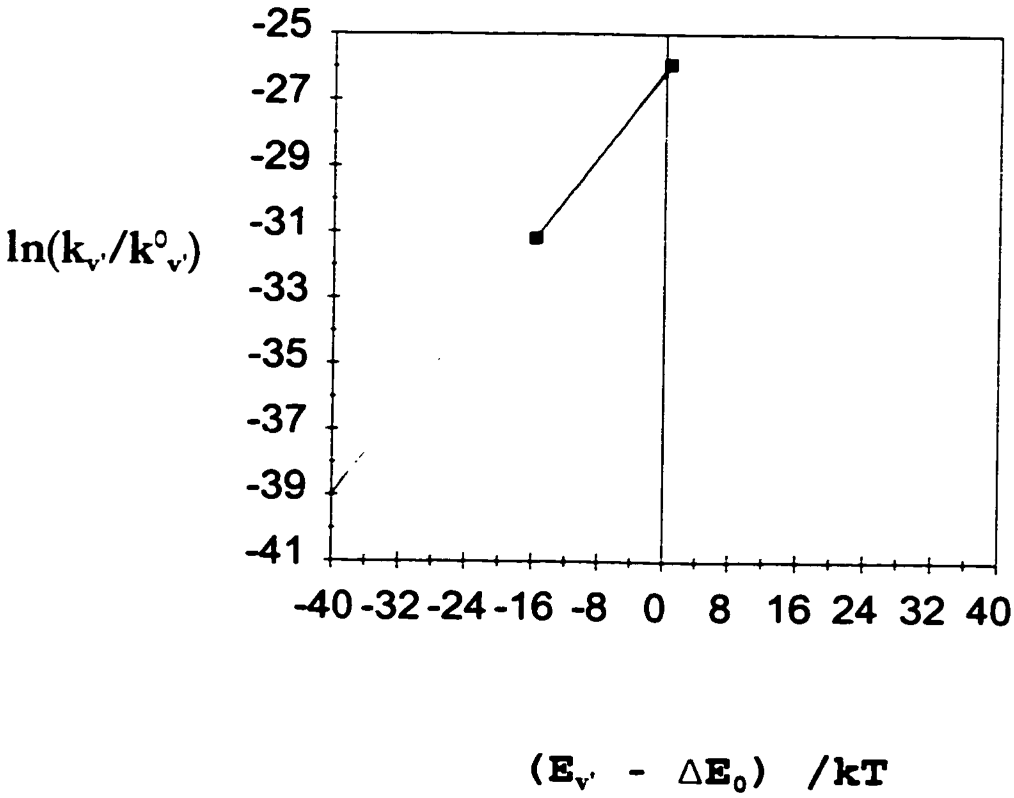

Fig. 3.2 Surprisal plot of the vibrationally enchanced rate constants for the reaction Br + HCl(v') - HBr(v) + Cl, as a function of $(E_{v'} - \Delta E_o)$ at 500 K.

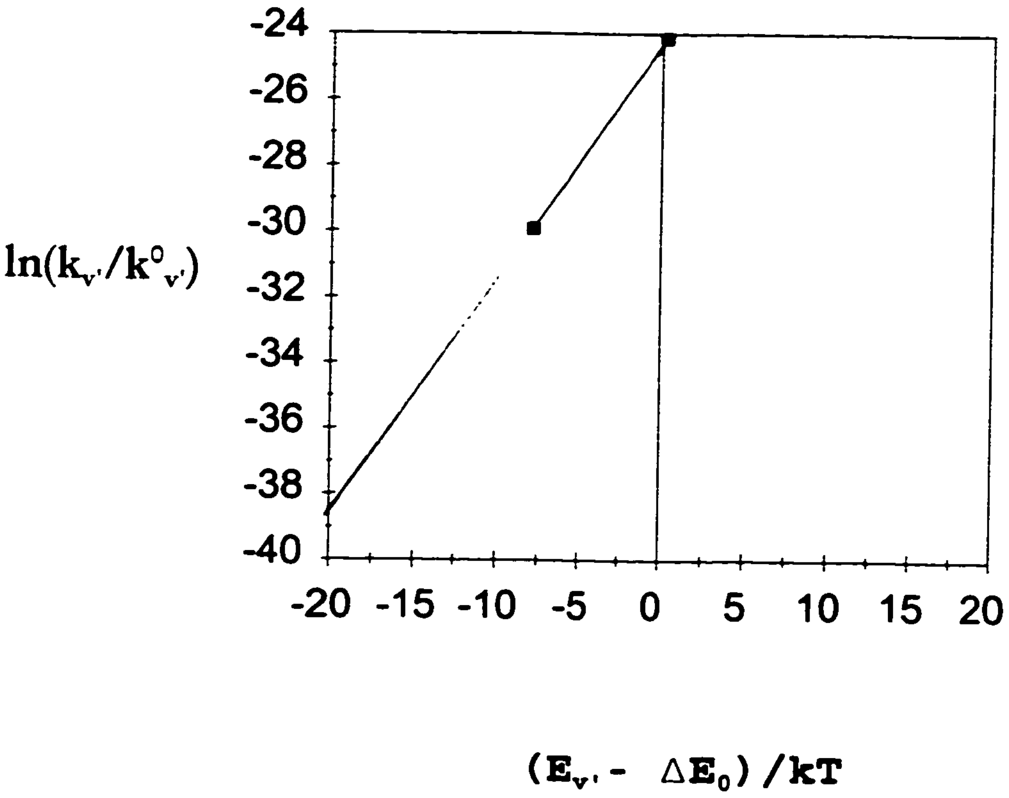

Fig. 3.3 Surprisal plot of the vibrationally enchanced rate constants for the reaction Br + HCl(v') → HBr(v) + Cl, as a function of ($E_{v'}$ - ΔE_o) at 1000 K.

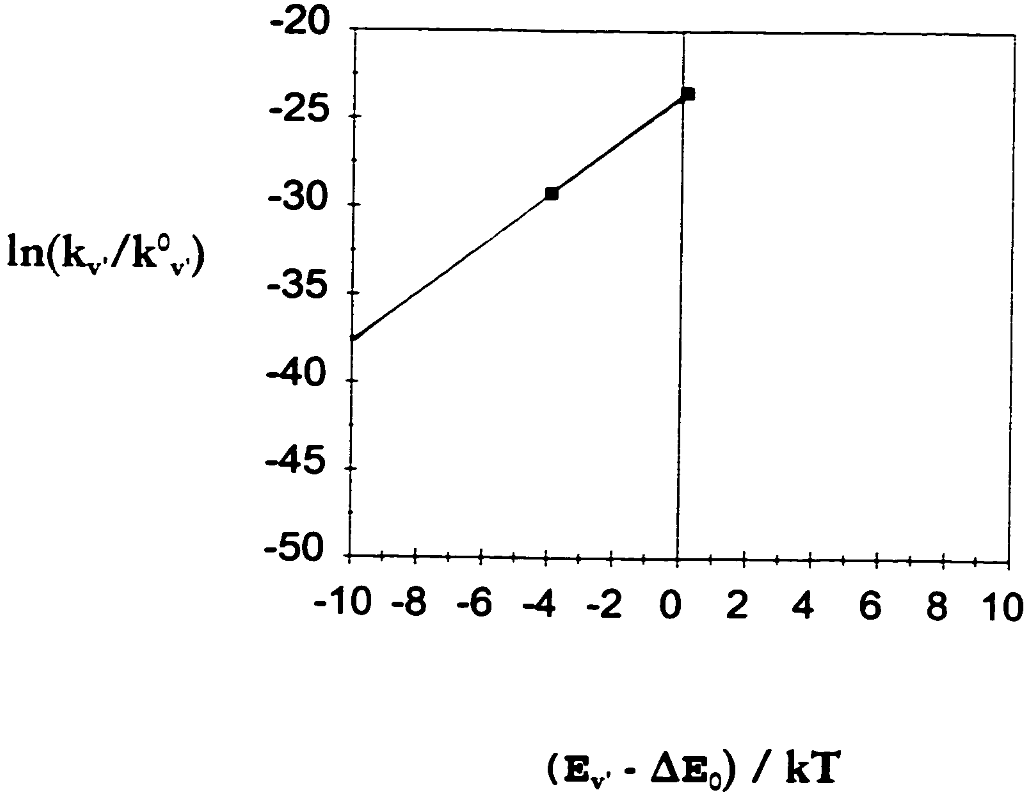

Fig. 3.4 Surprisal plot of the vibrationally enchanced rate constants for the reaction Br + HCl(v') - HBr(v) + Cl, as a function of $(E_{v'} - \Delta E_0)$ at 2000 K.

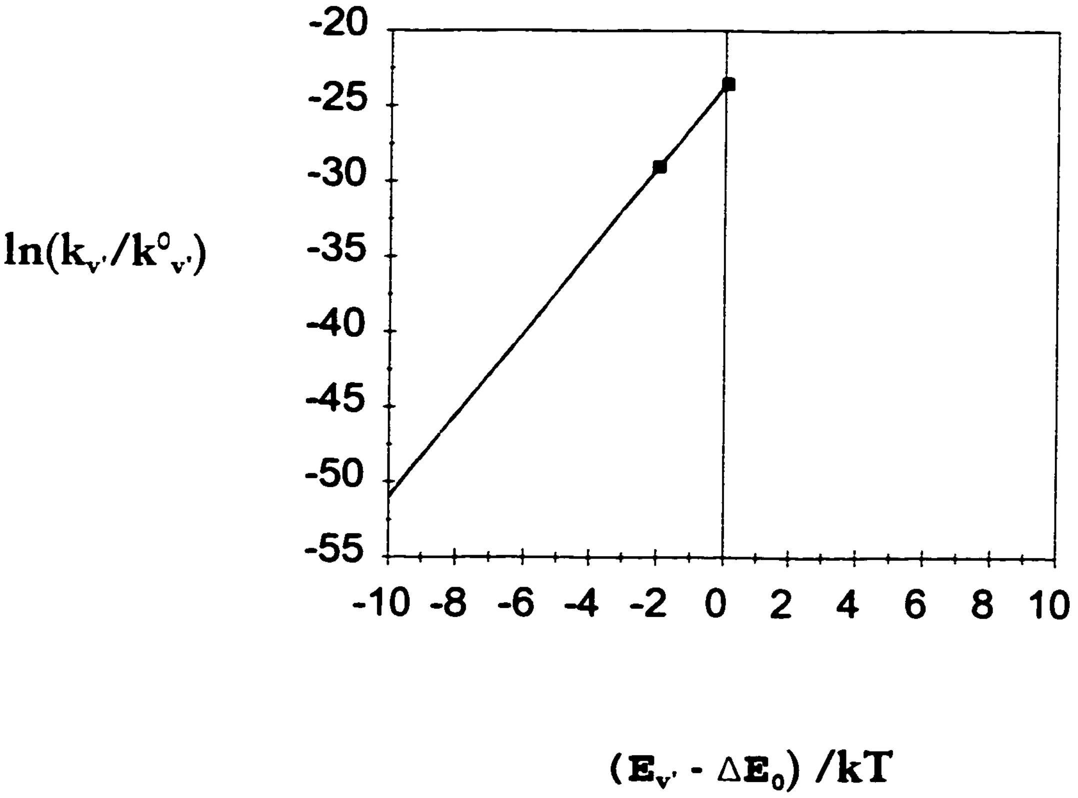

Fig. 3.5 Surprisal plot of the vibrationally enchanced rate constants for the reaction Br + HCl(v') → HBr(v) + Cl, as a function of $(E_{v'} - \Delta E_o)$ at 4000 K.

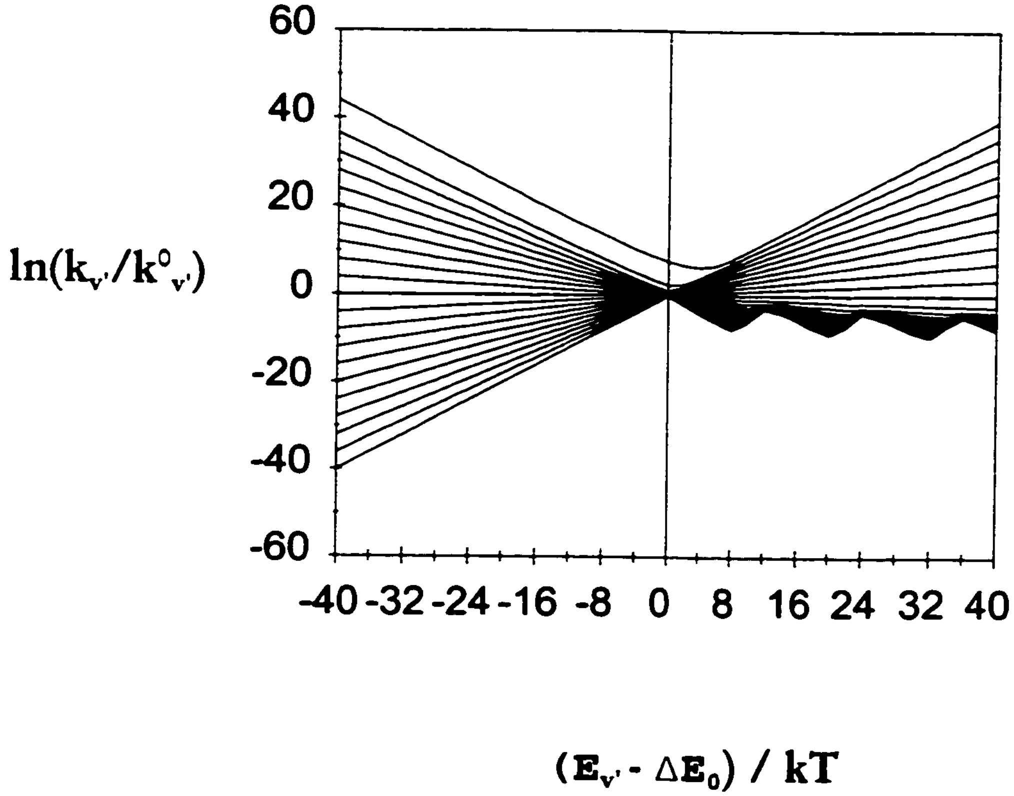

Fig. 3.6 Dependence of $\ln(k_{v'}/k^0_{v'})$ on the energy defect for the reaction, HCl (v') + Br → HBr(v) + Cl at 298K when the state-to-state rate constants obey an exponential gap law having a parameter λ. Curves are drawn for values of λ (from -1.0 to 1.0) seperated by increments of 0.1, and were obtained from Eq. (3.3).

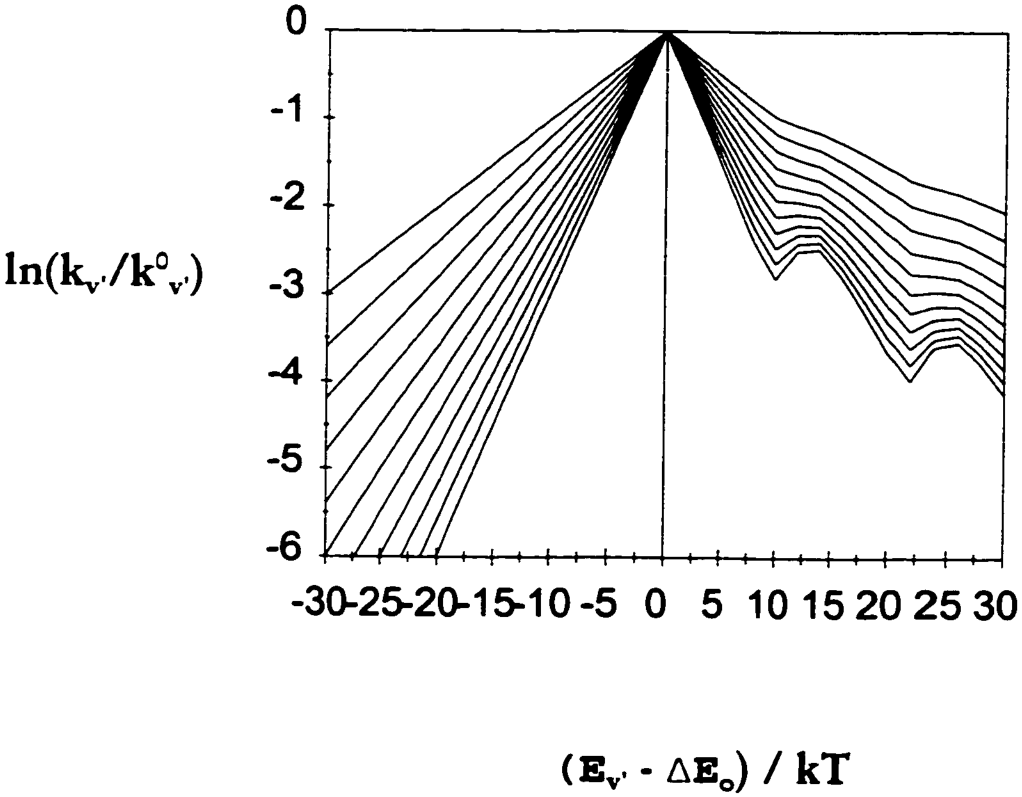

Fig. 3.7 Detail of fig. 3.6 on the dependence of ln $(k_{v'}/k^0_{v'})$ on the energy defect for the reaction, HCl (v') + Br → HBr(v) + Cl at 298K when the state-to-state rate constants obey an exponential gap law having parameter λ. Curves are drawn for values of λ (from 0.1 to 0.3) seperated by increments of 0.02, and were obtained from Eq. (3.3).

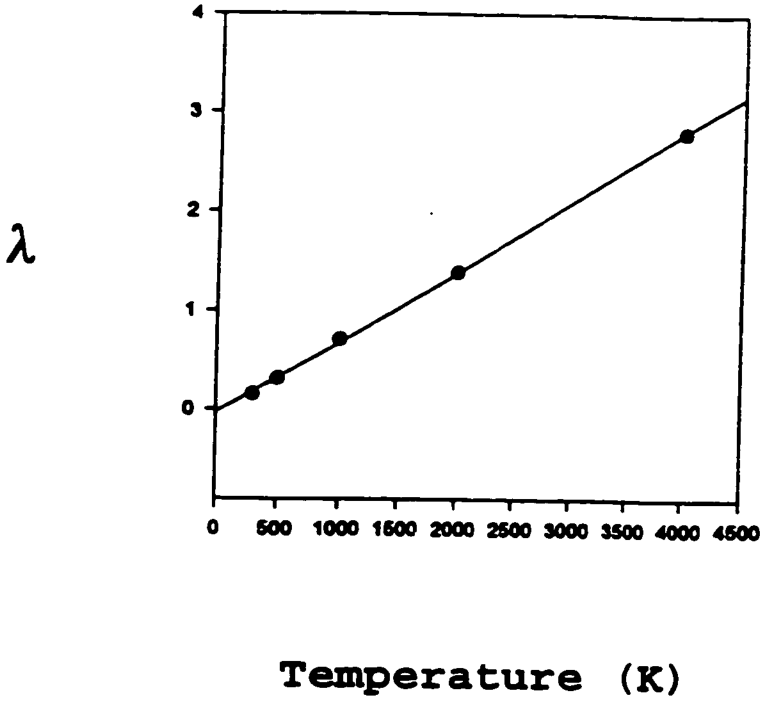

Fig. 3.8 Dependence of λ on temperature for the endothermic reaction: HCl (v') + Br → HBr(v) + Cl .

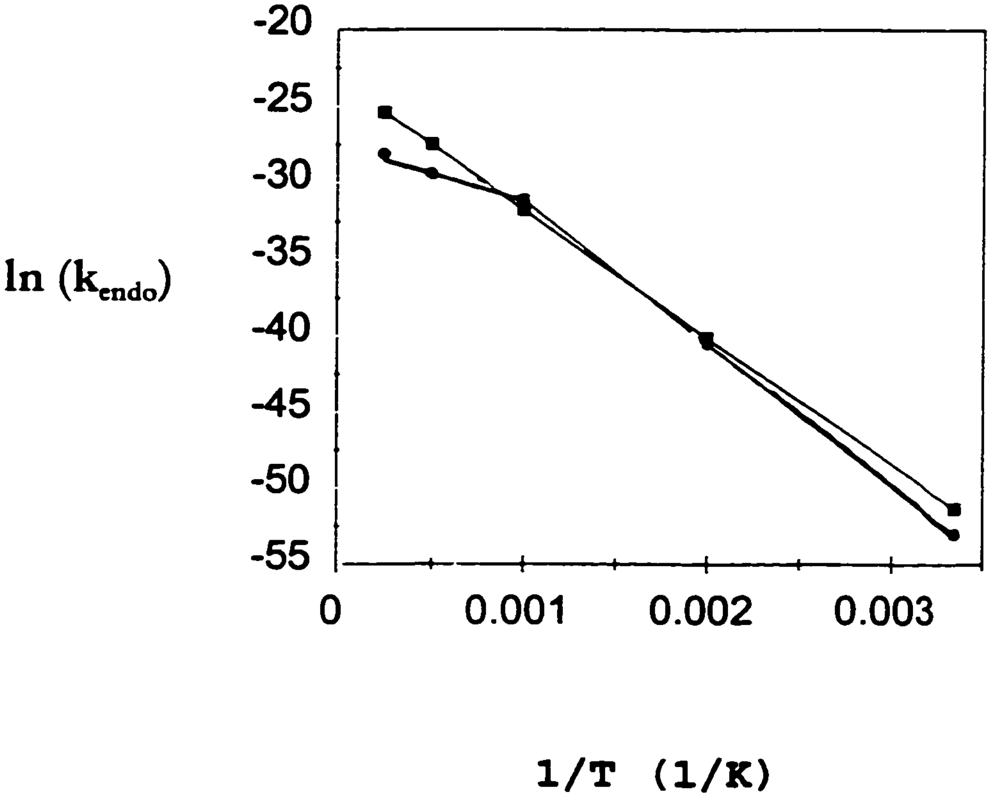

Fig. 3.9 ln(k_{endo}) vs 1/T for the endothermic reaction: HCl (v') + Br → HBr(v) + Cl. ● are the surprisal analysis results, and ■ are the experimental results adapted from Ref. [18].

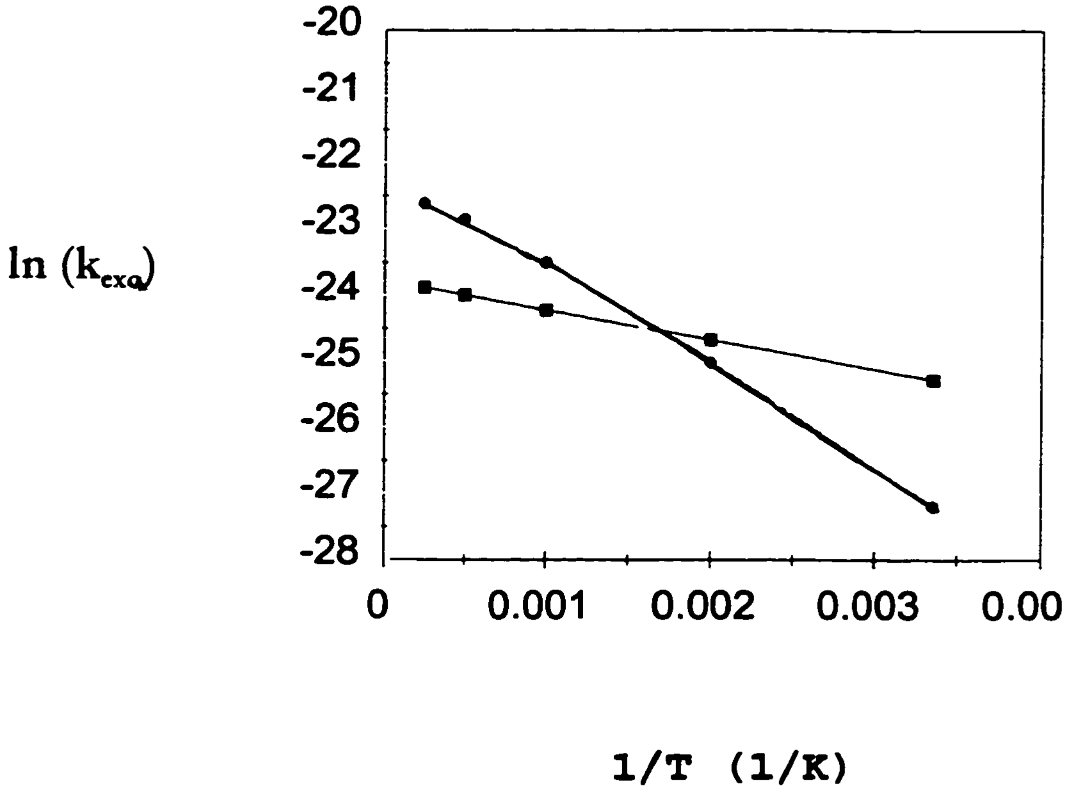

Fig. 3.10 $\ln(k_{ex\alpha})$ vs 1/T for the exothermic reaction: $HBr(v) + Cl \rightarrow HCl(v') + Br$. ● are the surprisal analysis results, and ■ are the experimental results adapted from Ref. [18].

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Chapter 4

Application of the Matrix Technique to Cl + HBr(v)⇌HCl (v')+Br

4.1 Introduction

In this chapter we shall apply our matrix technique to the reaction HCl (v') +Br ⇌ Cl + HBr(v). So far we have already used our matrix technique on the H + O_2 ⇌ OH + O reaction in chapter 2. First, we shall use the matrix technique to determine the non-equilibrium effect for this reaction. Finally we shall compare the two reactions to see which reaction shows the greater non-equilibrium effect.

4.2 HCl (v') +Br ⇌ Cl + HBr(v)

As input to our calculation we require values for the relaxation rate constants k^{HBr}_{10}, k^{Cl}_{10}, k^{HCl}_{10}, k^{Br}_{10} and k^{M}_{10} for both species of diatomic molecules, HCl and HBr as well as the state-to-state rate constants ($k^{f}_{m\rightarrow n}$ and $k^{r}_{n\rightarrow m}$). The reactive state-to-state rate constants are taken from the previous chapter over the temperature range 300-4000 K . These results were reconstructed from an application of information theory to those reactive rate constants already available from the literature.

k^{HCl}_{10} has been measured over a broad temperature range with M = Cl, HCl, and Ar as collision partners [1-7]. Over the years a number of groups have measured k^{HCl}_{10} for Br as a collision partner at 295 K [8-11]. But there is no information on the temperature dependence of this energy transfer rate constant in the literature. This rate constant is very large to begin with and we therefore assumed that $k^{HCl\text{-}Br}_{10}$ is independent of temperature. This is a reasonable assumption considering the nearness to the gas-kinetic collision frequency. Only sparse information is available for k^{HCl}_{10} with HBr as a collision partner. Chen and Moore measured the total rate of relaxation (V-V + V-T), and they concluded that the V-T contribution is less than 3 % [12]. From their experiments a rough value of ~ 3.0 x 10^{-14} $cm^3 molecule^{-1} s^{-1}$ could be deduced for this rate constant. Since the magnitude of this constant is approximately the same as that for relaxation of HCl by HCl ,then we shall assume that the dependence of the HCl-HBr rate constant on temperature is the same as that for the HCl-HCl relaxation. k^{HCl}_{10} for HCl as collision partner has been measured by many different groups [1-3]. Hopkins and Sharma measured the temperature dependence of this rate between 196 and 342 K [1]; Bird measured it between 700 and 1900 K [2]; while Bowman and Seery measured it between 1300 and 2200 K [3]. In order to obtain this rate constant at even higher temperatures we extrapolated a plot of ln k^{HCl}_{10} vs $T^{-1/3}$. $k^{HCl}_{10}$for Cl and Ar as collision partners has also been measured by many different groups over the years. For Cl, the energy transfer rate constant was measured as a function of temperature, first by Brown and Smith between 195 and 397 K [4], and later by Macdonald and Moore between 294 and 439 K [5]. For Ar the energy transfer rate constant was measured as a function of temperature, first by Bowman and Seery between 1000 and 2000 K [5], and then by Seery between 1166 and 1950 K [6], and later by Steele and Moore between 295 and 700 K [7]. Once again, in order to obtain the rates at higher temperatures we extrapolated a graph of ln k^{HCl}_{10} vs $T^{-1/3}$ for each energy transfer partner. There are other groups who also worked on the energy transfer rates for k^{HCl}_{10} with the above collision partners. We adopted the latest and probably most accurate results. Table 4.1 summarizes the rate constants, k^{HCl}_{10}.

The vibrational relaxation rate constants for HBr are considerably more problematical. Only sparse information is available for some collision partners. $k^{HBr}{}_{10}$ has been measured over a broad temperature range with HBr as a collision partner. The temperature dependence of $k^{HBr}{}_{10}$ for HBr as a partner was first measured by Kiefer and Bird between 800 and 1800 K [13] and later by Zittel and Moore between 169 and 505 K [14]. Once again, in order to obtain the rate constants at higher temperatures we extrapolated a graph of ln $k^{HCl}{}_{10}$ vs $T^{-1/3}$. Over the years a number of groups has measured $k^{HBr}{}_{10}$ for Br and HCl as collision partners at 295 K [9, 12, 15-17]. However there is no information on the temperature dependence for either colliding partner. Once again we shall assume that, since the $k^{HBr}{}_{10}$ rates at 295 K are very large, they are independent of temperature. For Cl as a collision partner there is no information at all available in the literature. We shall assume that the $k^{HBr}{}_{10}$ for Cl are smaller than those for Br and that they follow the same trend as $k^{HCl}{}_{10}$ for Br. The reasoning behind our logic is that Cl is a better relaxer of HCl, and Br is a better relaxer of HBr because of the probability of "sticky collisions" [18]. $k^{HBr}{}_{10}$ for Ar as a collision partner was first estimated to be $\leq 3.7 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 296 K by Chen [19]. More recently Schramm measured the temperature dependence of this rate constant between 150 K and 300 K [20]. He found it at 295 K to be 5.7×10^{-17} cm^3 molecule^{-1} s^{-1}. We cannot convincingly extrapolate these results to higher temperatures because the temperature range studied is too narrow. Nevertheless we shall include the extrapolated results for comparison purposes. Instead we plot the HCl-Ar rate constants and then on the same graph we plot the HI-Ar rate constants as measured by Green [21]. At a given temperature we plot $k^{HX\text{-}Ar}{}_{10}$ vs$(m_{HX}/(m_{HX} + m_{Ar}))^{13/6}(\nu_{HX})^{4/3}(1/(1-e^{-h\nu/kT}))$, a dependence predicted by theory [22]. We then estimated the $k^{HBr\text{-}Ar}{}_{10}$ rate constant by interpolation. Here X=Cl, Br, and I , and ν is the fundamental vibrational frequency of the diatomic molecule. Then in order to obtain the relaxation rate constants at higher temperature we plotted ln k vs $T^{-1/3}$. The results can be seen in Fig. 4.1. Our estimated value at 295 K is 5.71×10^{-18} cm^3 molecule^{-1} s^{-1}, in good agreement with the Schramm values [20]. k^{HBr}_{10} for all the collider species present in the mixture are summarized in Table 4.2.

4.3 Matrix Solution

We have used our computer programme, MRBIM, first described in Chapter 2, to analyse the reaction Br + HCl ⇌ HBr + Cl. HCl and HBr are truncated at M=9 and N=9; only V-T energy transfer processes are considered; Landau-Teller scaling of the energy transfer rate constants is employed. The reactive state-to-state rate constants were calculated using information theory as described in the previous chapter. The temperatures were chosen in the range 1000-4000 K. Ar was chosen as the inert collider species. Conditions for the reaction medium were chosen as in Table 4.3 and Table 4.4. Once again the smallest non-zero eigenvalue with physical meaning was chosen. This is the one corresponding to a positive unitary eigenvector, ie Y_m and Z_n. The magnitude of the eigenvalue corresponds to the overall rate. We shall use the same two definitions for each of k_f and k_r as described in section 2.5.

4.3.1 Case I: Close to Equilibrium

The reaction was set close to equilibrium by setting the relative concentrations of the species as in Table 4.3. The main trends observed in Table 4.5a and Table 4.5b are:

1) k_f is suppressed from its equilibrium value, while k_r shows little change from its equilibrium value.
2) The non-equilibrium factor $(k_f/k_r) / K_{eq}$ is less than but is very close to unity.
3) The maximum suppression of k_f occurs at 1000 K.
4) A decrease in the concentration of Ar suppresses k_f even more, but has no effect on k_r

The non-equilibrium factor is approximately 1 (with the possible exception of T = 1000 K). This is understandable because we set our conditions close to equilibrium. However, the individual rate coefficients k_f and k_r are suppressed. The maximum suppression of k_f occurs at 1000 K, because the critical vibrational level for this temperature (m = 2) is highly reactive (Fig. 4.2). Its loss is therefore more noticeable, and the reaction is choked even more. Furthermore, relative to reaction it happens that relaxation is poorest at 1000 K and is even less capable at replenishing the lost molecules than at other temperatures. The reverse reaction shows very little non-equilibrium effect. That k_r shows no change from its equilibrium value suggests that relaxation of HBr is fast enough to replace the molecules in the depleted higher vibrational levels. Even if energy transfer were effective it happens that the critical level from which the major contribution to the flux occurs is n = 0 (see fig 4.3) so that there is little to replinsh. Hence $k_r \approx k_r^{eq}$. Decreasing the concentration of argon has a little effect on the non-equilibrium factor, as it causes k_f to be slightly more suppressed. To some degree the kinetic mass action laws does hold for this reaction (with the exception of T = 1000 K), when close to equilibrium.

4.3.2 Case II: Far from Equilibrium

Conditions for the reaction media were chosen as in the Table 4.4. For reactions set far from equilibrium, the results are summarized in Table 4.6.1 and Table 4.6.2. Only representative results are shown to illustrate our main points. The main trends observed in Table 4.6.1 and Table 4.6.2 are:

1) The non-equilibrium factor is larger than unity when Q/K_{eq} is large and less than unity when Q/K_{eq} is small (with few exceptions at 4000 K). (Here $Q = [HBr][Cl] / [HCl][Br]$)
2) k_f is inflated when $Q/K_{eq} > 1$, and is suppressed when $Q/K_{eq} < 1$.
3) k_r 's behavior is opposite to that of k_f.
4) A decrease in the concentration of argon intensifies the deviation.

When reaction is occuring far from equilibrium the non-equilibrium factor is not unity because k_f and k_r are affected differently by the reaction. This is because the reaction disturbs the fractional level populations of the reactant and the products differently. The non-equilibrium factor is larger than unity when the value of Q/K_{eq} is large. The reverse reaction flux is then larger than that for the forward reaction. The forward reaction tends to deplete the HCl molecules in the higher vibrational levels, but the overwhelming reverse reaction produces HCl molecules in the most important vibrational levels. These two processes result in the fractional population of the important vibrational levels to increase, thus causing the reaction flux to increase from these levels, and hence k_f is inflated. This is supported by the fractional level population of HCl and HBr in Table 4.7a. The maximum inflation of k_f occurs at 1000 K. At this temperature not only is relaxation particularly poor, but also the important vibrational levels from where most of the reaction takes place is higher up the vibrational ladder, and they are more significant because of their extreme reactivity. Inflation of k_r values increases as Q/K_{eq} decreases. When Q/K_{eq} decreases the forward reaction flux increases. Thus the forward reaction leaves more and more HBr molecules in significant states. This causes flux from these levels to be larger than it should be; and hence k_r values are inflated even more.

The non-equilibrium factor is less than unity when Q/K_{eq} is small. Under these conditions the forward reaction flux is larger than that of the reverse reaction. Now, the k_f are suppressed and the k_r values are inflated. The k_f values are suppressed because the vibrational equilibration of HCl is not fast enough to replace the depleted excited vibrational levels. Although the reverse reaction is replacing HCl molecules in the important vibrational levels, nevertheless the forward reaction is depleting them faster because of its overriding importance when $Q < K_{eq}$. This is supported by the fractional level populations of HCl and HBr in Table 4.7b.

A decrease in the concentration of argon causes an intensification of the deviations. Essentially the reaction becomes relatively more reactive, and so all non-equilibrium phenomena become accentuated.

4.4 Comparison of the non-equilibrium effect for HCl + Br ⇌ HBr + Cl with the non- equilibrium effect for O_2 + H ⇌ OH + O .

For both reactions, the non-equilibrium effect is much more severe for reaction occuring far from equilibrium compared to reaction occuring close to equilibrium. The non-equilibrium factor is close to unity for reaction occuring close to equilibrium. The reaction $O_2 + H \rightleftharpoons OH + O$ shows the greatest non-equilibrium effect when temperature is 2000 K and the concentration of helium is small. The reaction $HCl + Br \rightleftharpoons HBr + Cl$ shows its greatest non-equilibrium effect when temperature is 1000 K and the concentration of argon is small. The reaction $HCl + Br \rightleftharpoons HCl + Cl$ shows much larger non-equilibrium effects compared to the reaction $O_2 + H \rightleftharpoons OH + O$ under similar conditions. This is because the relaxation rates for HBr and HCl are smaller than the relaxation rates for OH and O_2. Furthermore the reactivity of HCl is enhanced more by vibration than that of O_2. Thus the $O_2 + H \rightleftharpoons OH + O$ reaction shows a smaller non-equilibrium effect.

4.5 Summary

We have applied our matrix technique to the $HCl + Br \rightleftharpoons HCl + Br$ reaction using the previously calculated state-to-state rate constants.

As expected the non-equilibrium effect is much more severe for reaction occuring far from equilibrium compared with reaction occuring close to equilibrium where it is close to unity. The fractional population of higher vibrational levels is depleted for both extremes but it is more pronounced for reaction occuring far from equilibrium. When reaction is predominantly occuring from the right hand side k_f/k_r is greater than K_{eq}, and when reaction is predominantly occuring from the left side then k_f/k_r is less than K_{eq}. In other words, the kinetic mass action law breaks down, and the deviation of k_f/k_r from K_{eq} becomes more severe as the reaction gets further from equilibrium. The temperature dependence of the non-equilibrium factor is complex. The reaction

HCl + Br = HCl + Br shows greater non-equilibrium effects than the reaction O_2 + H = OH + O.

The two reactions which we have chosen are the only ones for which state-to-state reactive rate constants have either been published or could be relatively easily deduced. Both of them show a severe breakdown of the kinetic mass action law. Although our choices might have been coincidental it is more likely that it is a general result given the arbitray choice of reactions. Consequently, because of the pervasive use of the kinetic mass action law it would seem necessary to provide an alternative and more useful relationship. The lack of state-to-state data precludes making systematic evaluation of all reactions and therefore we resort to an approximate but analytical solution of the master equation, as elucidated in the next chapter.

Table 4.1 Rate constants ($cm^3 molecule^{-1} s^{-1}$) for vibrational de-excitation of HCl by M = HBr, Cl, HCl, Br, Ar ; HCl (v = 1) + M → HCl (v = 0) + M.

T/K	k^{HBr}_{10}[a, f]	k^{Cl}_{10}[b,f]	k^{Br}_{10}[c,f]	k^{HCl}_{10}[d,f]	k^{Ar}_{10}[e, f]
300	2.8×10^{-14}	7.4×10^{-12}	2.8×10^{-13}	2.8×10^{-14}	3.4×10^{-18}
500	5.7×10^{-14}	8.3×10^{-12}	3.1×10^{-13}	5.7×10^{-14}	3.7×10^{-17}
1000	1.0×10^{-13}	9.4×10^{-12}	3.5×10^{-13}	1.0×10^{-13}	3.3×10^{-15}
2000	1.1×10^{-12}	1.0×10^{-11}	3.8×10^{-13}	1.1×10^{-12}	2.1×10^{-14}
4000[g]	6.8×10^{-12}	1.1×10^{-11}	4.1×10^{-13}	6.8×10^{-12}	9.0×10^{-14}

[a] From ref. (13). [b] From ref. (4,5). [c] From ref. (8,11). [d] From ref. (1-3). [e] From ref (3,6,7). [f] See the text. [g] Data extrapolated from lower temperatures.

Table 4.2 Rate constants ($cm^3 molecule^{-1} s^{-1}$) for vibrational de-excitation of HBr by M = HCl, Cl, HBr, Br, Ar; HBr (v = 1) + M → HBr(v = 0) + M.

T/K	k^{HCl}_{10}[a, d]	k^{Br}_{10}[b, d]	k^{Cl}_{10}[c, d]	k^{HBr}_{10}[c, d]	k^{Ar}_{10}	
300	4.1×10^{-12}	4.6×10^{-12}	2.8×10^{-13}	1.8×10^{-14}	5.7×10^{-18}[d]	5.7×10^{-17}[e]
500	4.1×10^{-12}	4.6×10^{-12}	3.1×10^{-13}	3.2×10^{-14}	6.5×10^{-17}	7.8×10^{-16}
1000	4.1×10^{-12}	4.6×10^{-12}	3.5×10^{-13}	1.4×10^{-13}	4.5×10^{-15}	1.4×10^{-14}
2000	4.1×10^{-12}	4.6×10^{-12}	3.8×10^{-13}	7.7×10^{-13}	3.4×10^{-14}	1.5×10^{-13}
4000[f]	4.1×10^{-12}	4.6×10^{-12}	4.1×10^{-13}	3.0×10^{-12}	1.8×10^{-13}	9.3×10^{-13}

[a] From ref (12). [b] From ref (9, 15-17). [c] From ref (13, 14). [d] See the text. [e] From ref (20). [f] Data extrapolated from lower temperatures.

Table 4.3 Equilibrium concentrations for HCl (v') + Br ⇌ Cl + HBr(v).

T/K	$k^f_{eq}/k^r_{eq} = K_{eq}$[a]	[Br]/[HCl][b]	[Br]/[HBr][b]	[Br]/[Cl][b]
1000	5.470×10^{-4}	0.09356	13.0805	13.0805
2000	3.128×10^{-2}	0.06076	1.39378	1.39378
4000	0.2	0.02838	0.35666	0.35666

[a] Calculated using thermodynamic and data from the JANAF tables. [b] Calculated from a knowledge of K_{eq}.

Table 4.4 Concentrations set far from the equilibrium.

T/K	[Br]/[HBr]	[Br]/[Cl]	[Br]/[HCl]	Q/K_{eq}
1000[a]	0.01	0.01	1.0	2.2067×10^{7}
	1.0	1.0	1.0	2206.7
	1.0	1.0	0.1	220.67
	1.0	1.0	0.01	22. 067
	100	100	1.0	0.22067
	1000	100	1.0	0.022067
	100	1000	1.0	0.022067
	1000	1000	0.01	2.2067×10^{-5}
2000	0.01	0.01	0.01	3.19693×10^{5}
	1.0	1.0	1.0	31.9690
	1.0	1.0	0.1	3.19690
	1.0	1.0	0.01	0.31969
	100	100	1.0	0.0031969
	1000	100	1.0	3.1969×10^{-4}
	100	1000	1.0	3.1969×10^{-4}
	1000	1000	0.01	3.1969×10^{-7}
4000	0.01	0.01	0.01	50000
	1.0	1.0	1.0	5
	1.0	1.0	0.1	0.5
	1.0	1.0	0.01	0.05
	100	100	1.0	0.0005
	1000	100	1.0	5.0×10^{-5}
	100	1000	1.0	5.0×10^{-5}
	1000	1000	0.01	5.0×10^{-8}

Table 4.5a Rate coefficients (cm^{3}molecule^{-1}sec^{-1}) for $HCl\ (v') + Br \rightleftharpoons Cl + HBr(v)$ obtained by the matrix technique. Relative concentrations were set close to the equilibrium conditions of Table 4.3. All mixtures were diluted in an Ar bath ([Br]/[Ar] =0.001).

T/K	k_f	k_r	k_f^{eq}	k_r^{eq}	k_f/k_r	$(k_f/k_r)/K_{eq}$
1000	2.9089×10^{-14}	6.2890×10^{-11}	3.4520×10^{-14}	6.2889×10^{-11}	4.6254×10^{-4}	0.84256
2000	3.6516×10^{-12}	1.1648×10^{-10}	3.6534×10^{-12}	1.1648×10^{-10}	0.03135	0.99955
4000	3.7413×10^{-11}	1.5274×10^{-10}	3.9638×10^{-11}	1.5257×10^{-10}	0.24495	0.94287

Table 4.5b Rate coefficients (cm^{3}molecule^{-1}sec^{-1}) for $HCl\ (v') + Br \rightleftharpoons Cl + HBr(v)$ obtained by the matrix technique. Relative concentrations were set close to the equilibrium conditions of Table 4.3. All mixtures were diluted in an Ar bath ([Br]/[Ar] =0.01).

T/K	k_f	k_r	k_f^{eq}	k_r^{eq}	k_f/k_r	$(k_f/k_r)/K_{eq}$
1000	2.8499×10^{-14}	6.2890×10^{-14}	3.4520×10^{-14}	6.2889×10^{-11}	4.5315×10^{-4}	0.82547
2000	3.6455×10^{-12}	1.1648×10^{-10}	3.6534×10^{-12}	1.1648×10^{-10}	3.1297×10^{-2}	0.99784
4000	3.7065×10^{-11}	1.5257×10^{-10}	3.9638×10^{-11}	1.5257×10^{-10}	0.24257	0.93367

Table 4.6: Part 1 Rate coefficients ($cm^3 molecule^{-1} s^{-1}$) for HCl (v') +Br → Cl + HBr(v) obtained by the matrix technique. Relative concentrations were set far from equilibrium as in Table 4.4.

T/K	Q/K_{eq}	k_f [b]	k_r [b]	k_f/k_r [b]	k_f [c]	k_r [c]	k_f/k_r [c]
1000	2.2067×10^7	1.0030 (-10)[a]	2.3547 (-11)	4.25960	1.0031 (-10)	2.3190 (-11)	4.32550
	2206.7	2.5637 (-11)	6.2780 (-11)	0.40837	2.6956 (-11)	6.2753 (-11)	0.42955
	220.67	3.3827 (-12)	6.2850 (-11)	0.05382	3.5687 (-12)	6.2848 (-11)	0.05678
	22. 067	3.1688 (-13)	6.2889 (-11)	0.00504	3.3008 (-13)	6.2884 (-11)	0.00525
	0.22067	1.5140 (-14)	6.2895 (-11)	0.00024	1.1954 (-14)	6.2895 (-11)	1.90060 (-4)
	0.022067	1.1231 (-14)	6.2933 (-11)	1.7846 (-4)	7.4220 (-15)	6.2933 (-11)	1.17930 (-4)
	0.022067	1.1173 (-14)	6.2896 (-11)	1.7765 (-4)	7.1745 (-15)	6.2896 (-11)	1.14070 (-4)
	2.2067×10^{-5}	1.5340 (-14)	6.2954 (-11)	2.4367 (-4)	1.4173 (-14)	6.2956 (-11)	2.25120 (-4)
2000	3.19693×10^5	1.8125 (-10)	3.2659 (-11)	5.54980	1.8134 (-10)	3.0210 (-11)	6.00240
	31.9690	6.6264 (-11)	1.1569 (-10)	0.57220	7.6472 (-11)	1.1511 (-10)	0.66436
	3.19690	8.9131 (-12)	1.1617 (-10)	0.07672	9.5846 (-12)	1.1611 (-10)	0.08255
	0.31969	2.5970 (-11)	1.1665 (-10)	0.02227	2.5168 (-12)	1.1666 (-10)	0.02157
	0.0031969	8.7774 (-13)	1.1742 (-10)	0.00747	3.4869 (-13)	1.1767 (-10)	2.96322 (-3)
	3.1969×10^{-4}	8.6957 (-13)	1.1777 (-10)	0.00738	3.3862 (-13)	1.8600 (-10)	2.86960 (-3)
	3.1969×10^{-4}	8.6797 (-13)	1.1742 (-10)	0.0073	3.3467 (-13)	1.1768 (-10)	2.84400 (-3)
	3.1969×10^{-7}	2.0379 (-12)	1.1722 (-10)	0.01738	1.9099 (-12)	1.1727 (-10)	0.01628
4000	50000	2.5696 (-10)	5.2570 (-11)	4.93840	2.6021 (-10)	4.3920 (-11)	5.92420
	5	1.0235 (-10)	1.5151 (-10)	0.67557	1.2284 (-10)	1.4995 (-10)	0.81917
	0.5	3.9638 (-11)	1.5370 (-10)	0.16554	2.2364 (-11)	1.5440 (-10)	0.14484
	0.05	2.9938 (-11)	1.5406 (-10)	0.19433	2.9124 (-11)	1.5419 (-10)	0.188888
	0.0005	1.1556 (-11)	1.5683 (-10)	0.07368	3.6407 (-12)	1.5884 (-10)	0.02292
	5.0×10^{-5}	1.1542 (-11)	1.5723 (-10)	0.07341	3.6192 (-12)	1.5913 (-10)	0.02274
	5.0×10^{-5}	1.1539 (-11)	1.5683 (-10)	0.00735	3.6138 (-12)	1.5885 (-10)	0.02275
	5.0×10^{-8}	2.9376 (-11)	1.5434 (-10)	0.19033	2.8501 (-11)	1.5445 (-10)	0.18453

[a] 1.0030 (-10) means 1.0030×10^{-10}. [b] All mixtures were diluted in an Ar bath ([Br]/[Ar] = 0.001). [c] All mixtures were diluted in a n Ar bath([Br]/[Ar] = 0.01).

Table 4.6: Part 2 Non-equilibrium factor for HCl (v') +Br $\rightharpoonup$ Cl + HBr(v) obtained by the matrix technique. Relative concentrations were set far from equilibrium as in Table 4.4.

T/K	$(k_f/k_r)/K_{eq}$ [a]	Y_0/Y_0^{eq} [a]	Z_0/Z_0^{eq} [a]	$(k_f/k_r)/K_{eq}$ [b]	Y_0/Y_0^{eq} [b]	Z_0/Z_0^{eq} [b]
1000	7759.19	1.0716 (-8)	7.8200 (-9)	7829.280	9.9609 (-9)	7.3141 (-9)
	743.873	0.22664	0.97770	782.461	0.19887	0.97232
	98.0416	0.81161	0.99196	103.435	0.78871	0.99165
	9.17911	0.98446	0.99890	9.56144	0.98319	0.99889
	0.43848	1.00205	1.00116	0.34621	1.00547	1.00122
	0.32507	1.00249	1.00895	0.21487	1.00659	1.00910
	0.32360	1.00253	1.00142	0.20776	1.00696	1.00145
	0.44386	1.00119	1.01335	0.41007	1.00143	1.01139
2000	176.942	7.0028 (-9)	3.6565 (-9)	191.373	4.8528 (-9)	2.6038 (-8)
	18.2615	0.30046	0.92450	21.1817	0.20690	0.87117
	2.44630	0.92215	0.96951	2.63183	0.90553	0.96422
	0.71007	1.01456	1.01634	0.68781	1.01588	1.01771
	0.23833	1.04774	1.09435	0.09447	1.08971	1.12149
	0.23541	1.04789	1.13153	0.09148	1.09007	1.15806
	0.23569	1.04795	1.09481	0.09069	1.09067	1.12220
	0.55439	1.02255	1.07353	0.51924	1.02467	1.07951
4000	19.0089	1.1418 (-6)	5.2056 (-7)	22.0803	2.0515 (-9)	2.8915 (-9).
	2.60037	0.55924	0.92666	3.15315	0.41699	0.82530
	0.63719	1.10610	1.08121	0.55753	1.13292	1.13404
	0.74802	1.06988	1.10782	0.72705	1.07596	1.11818
	0.28363	1.22273	1.33449	0.08822	1.34840	1.53158
	0.28256	1.22287	1.37294	0.08745	1.34887	1.56338
	0.28321	1.22289	1.33479	0.08757	1.34904	1.53237
	0.77178	1.07404	1.13038	0.62748	1.08061	1.13885

[a] All mixtures were diluted in an Ar bath ([Br]/[Ar] =0.001). [b] All mixtures were diluted in an Ar bath ([Br]/[Ar]=0.01)

Table 4.7a Fractional level populations of reactants (HCl) and products (HBr) obtained by the matrix technique. Relative concentrations were set far from equilibrium conditions: [Br]/[HBr]= 1.0 [Br]/[Cl]= 1.0, [Br]/[HCl] = 0.01 and [Br]/[Ar]= 0.001 and T= 1000 K.

Vibrational levels	Y(m)	$Y^{eq}(m)$	Z(n)	$Z^{eq}(n)$
0	9.68922 (-1) [a]	9.84216 (-1)	9.73647 (-1)	9.74716 (-1)
1	2.74826 (-2)	1.54942 (-2)	2.55712 (-2)	2.45551 (-2)
2	3.49593 (-3)	2.83958 (-4)	7.55654 (-4)	7.04551 (-4)
3	9.71834 (-5)	6.05828 (-5)	2.52515 (-5)	2.30246 (-5)
4	2.63739 (-6)	1.50471 (-7)	9.56863 (-7)	8.57003 (-7)
5	7.89652 (-8)	4.35077 (-9)	4.11819 (-8)	3.63312 (-8)
6	2.68360 (-9)	1.46449 (-10)	2.01501 (-9)	1.75423 (-9)
7	1.04391 (-10)	5.73875 (-12)	1.12159 (-10)	9.64724 (-11)
8	4.66196 (-12)	2.61792 (-13)	7.10225 (-12)	6.04265 (-12)
9	2.39647 (-13)	1.39029 (-14)	5.11046 (-13)	4.31083 (-13)

[a] 9.68922(-1) means 9.68922 x 10^{-1}.

Table 4.7b Fractional level populations of reactants (HCl) and products (HBr) obtained by the matrix technique. Relative concentrations were set far from equilibrium conditions: [Br]/[HBr]=1000 [Br]/[Cl]=100, [Br]/[HCl] = 1.0 and [Br]/[Ar]= 0.01 and T=1000 K.

Vibrational levels	Y(m)	$Y^{eq}(m)$	Z(n)	$Z^{eq}(n)$
0	9.86674 (-1) [a]	9.84216 (-1)	9.83440 (-1)	9.74716 (-1)
1	1.33000 (-2)	1.54942 (-2)	1.62097 (-2)	2.45551 (-2)
2	2.56646 (-5)	2.83958 (-4)	3.41263 (-4)	7.04551 (-4)
3	1.28313 (-7)	6.05828 (-6)	8.84936 (-5)	2.30246 (-5)
4	1.65871 (-9)	1.50471 (-7)	2.74697 (-7)	8.57003 (-7)
5	3.39204 (-11)	4.35077 (-9)	1.00346 (-8)	3.63312 (-8)
6	8.90014 (-13)	1.46449 (-10)	4.27066 (-10)	1.75423 (-9)
7	2.82269 (-14)	5.73875 (-12)	2.10458 (-11)	9.64724 (-11)
8	1.05815 (-15)	2.61792 (-13)	1.19640 (-12)	6.04265 (-12)
9	4.65848 (-17)	1.39029 (-14)	7.86470 (-14)	4.31083 (-13)

[a] 9.86674(-1) means 9.86674 x 10^{-1}.

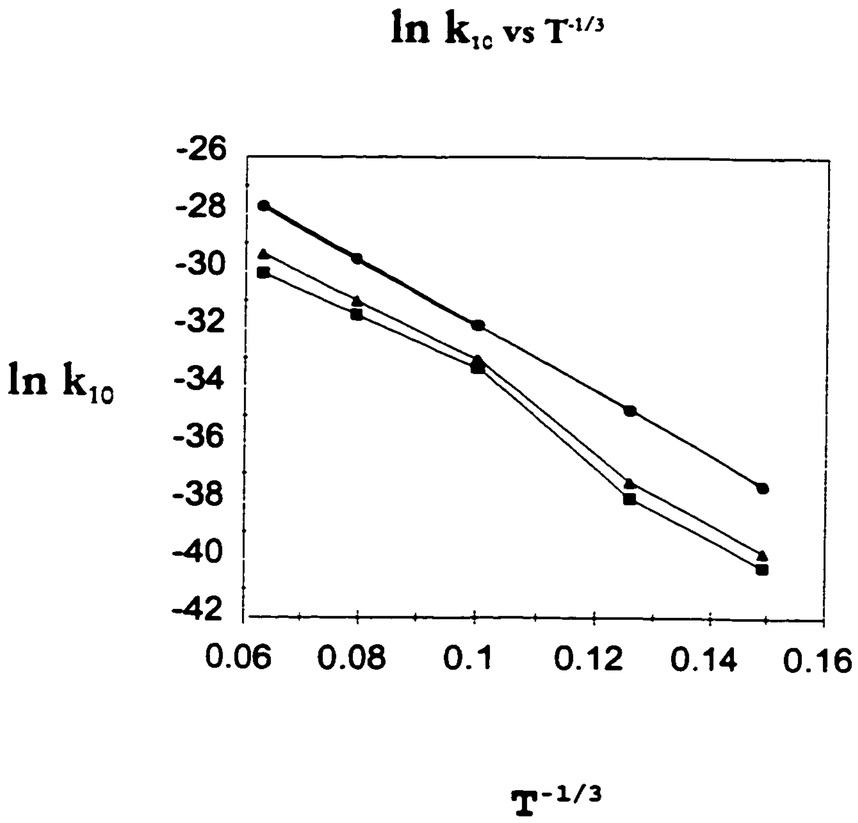

Fig 4.1 Graph of ln k_{10} vs $T^{-1/3}$. ■ is for the relaxation of $k_{10}^{HCl\text{-}Ar}$. ▲ is for the relaxation of $k_{10}^{HBr\text{-}Ar}$. ● is for the relaxation of $k_{10}^{HI\text{-}Ar}$.

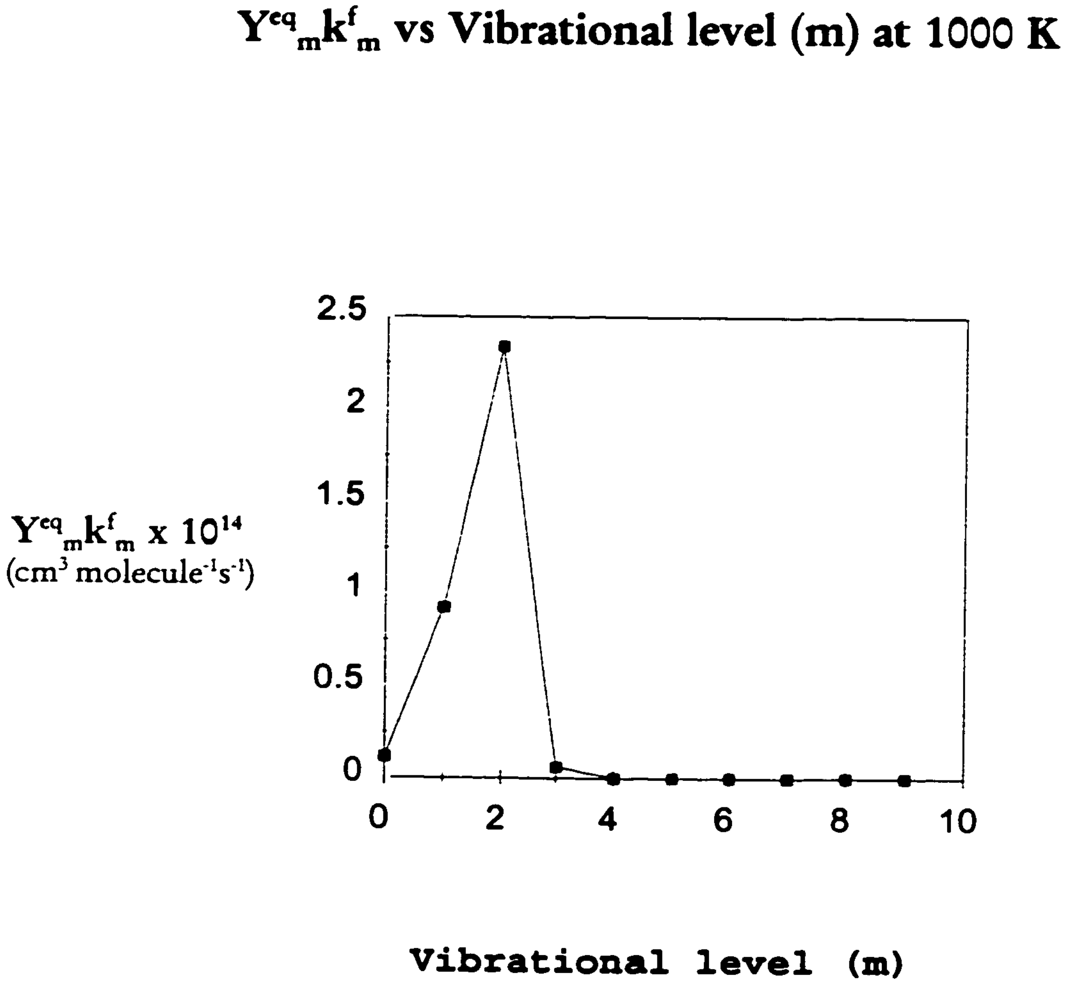

Fig. 4.2 $Y^{eq}_m k^f_m$ vs vibrational level (m) for the HCl (m) + Br → Cl + HBr reaction.

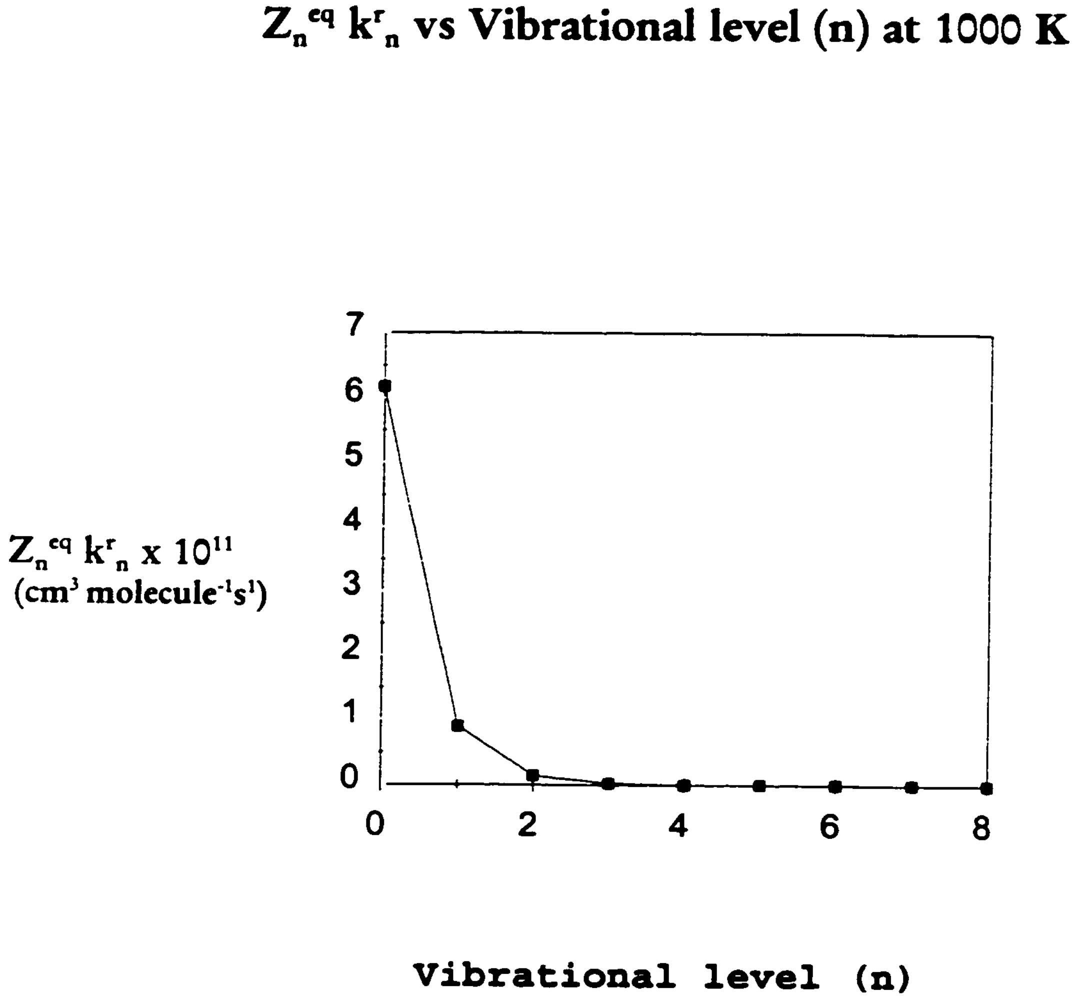

Fig. 4.3 Z_n^{eq} k^r_n vs vibrational level (n) for the Cl + HBr(n) →HCl +Br reaction.

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CHAPTER 5

Analytical Solutions of the Steady State Master Equation

5.1 Introduction

In chapter 2 we solved the steady state master equation exactly using a matrix technique. We allowed reaction to proceed from any vibrational level, m, of the reactants into any vibrational level, n, of the products. In this chapter we shall attempt to solve the set of vibrational-level-dependent rate equations by analytical means. This approach exploits all of Teitelbaum's findings [1-5]. We allow reaction to proceed from the single most important vibrational level m_* of the reactants to the single most important vibrational level n_* of the products and vice-versa. The reason we solve the problem analytically is because the approximate solution does not require us to know all of the state-to-state reactive rates (which are not available in the literature usually). If we can get a sufficiently good picture of the problem by solving the master equation approximately, there is no need to evaluate the exact solution (which requires us to know all of the state-to-state reactive rates). The analytical solution has the advantage of allowing us to see the relationship between the physical parameters. The matrix technique is more exact but it can be very inconvenient for practicing kineticists, in sense that they can not calculate the matrix eigenvalues by hand, and instead a program has to be written in order to solve the matrix numerically. Even if all state-to-state constants are available using them in a simulation of a modest kinetic reaction scheme becomes an unmanagable task. We shall check the validity of our analytical expression by comparing the results with those obtained using the matrix technique. If successful, we shall have an expression for k_f/k_r which, although not perfect, should be considerably better than the kinetic mass-action law currently used.

5.2 Analytical solution of the steady state master equation for A + BC ⇌ AB +C

The time evolution of the fractional or relative populations, Y_m and Z_n for vibrational levels m and n of molecules BC and AB respectively are given by the master equation:

$$\frac{dY_m}{dt}\frac{1}{N_M}=Y_m\left(k_f\frac{N_A}{N_M}-k_r\frac{N_C N_{AB}}{N_{BC}N_M}-k_m^f\frac{N_A}{N_M}-k^{BC}_{m,m-1}-k^{BC}_{m,m+1}\right)+Y_{m-1}k^{BC}_{m-1,m}+Y_{m+1}k^{BC}_{m+1,m}+\frac{N_{AB}N_C}{N_{BC}N_M}\sum_n k^r_{n-m}Z_n \qquad (5.1a)$$

$$\frac{dZ_n}{dt}\frac{1}{N_M}=Z_n\left(k_r\frac{N_C}{N_M}-k_f\frac{N_A N_{BC}}{N_{AB}N_M}-k_n^r\frac{N_C}{N_M}-k^{AB}_{n,n-1}-k^{AB}_{n,n+1}\right)+Z_{n-1}k^{AB}_{n-1,n}+Z_{n+1}k^{AB}_{n+1,n}+\frac{N_{BC}N_A}{N_{AB}N_M}\sum_m k^f_{m-n}Y_m \qquad (5.1b)$$

where $k^f_m \equiv \Sigma_n k^f_{m-n}$, and $k^r_n \equiv \Sigma_m k^r_{n-m}$. We have solved this set of equations in the steady-state limit (approximation 2)($dY_m/dt = 0$, $dZ_n/dt = 0$), using Landau-Teller scaling to relate k_{ij} to k_{10}^{AB} and k_{10}^{BC} ie $k_{m,m-1} = mk_{10}$, (approx. 3) (k_{10}^{AB} and k_{10}^{BC} being usually the only rate constants available in the literature) and using microscopic reversibility, $k_{01}^{AB}/k_{10}^{AB} = e^{-v}$ and $k_{01}^{BC}/k_{10}^{BC} = e^{-u}$, where $u = h\nu^{BC}/k_BT$ and $v = h\nu^{AB}/k_BT$. Also using the dimensionless parameters,

$$\gamma=\frac{k_f}{k_{10}^{BC}}\frac{N_A}{N_M},\quad \beta=\frac{k_r}{k_{10}^{BC}}\frac{N_C}{N_M},\quad \chi=\frac{k_{10}^{AB}}{k_{10}^{BC}}$$

we have

$$Y_m(\Upsilon-\beta\frac{N_{AB}}{N_{BC}}-\frac{N_A}{N_M}\frac{k_m^r}{k_{10}^{BC}}-m-(m+1)e^{-u})+Y_{m-1}me^{-u}+(m+1)Y_{m+1}+\frac{N_{AB}N_C}{K_{10}^{BC}N_{BC}N_M}\sum_n k_{n-m}^r Z_n=0 \qquad (5.2a)$$

$$Z_n(\beta-\Upsilon\frac{N_{BC}}{N_{AB}}-\frac{N_C}{N_M}\frac{k_n^r}{k_{10}^{BC}}-\chi n-\chi(n+1)e^{-v})+Z_{n-1}\chi ne^{-v}+\chi(n+1)Z_{n+1}+\frac{N_{BC}N_A}{k_{10}^{BC}N_{AB}N_M}\sum_m k_{m-n}^r Y_m=0 \qquad (5.2b)$$

At this point it was decided to approximate the summation in eq. (5.2a) by considering only the largest term to contribute most to the summation, whatever it happens to be, even if it is changing with time (approximation 4). Methods for choosing these associated critical levels, m_* and n_*, are discussed in more detail in the application section (Section 5.7). This assumption implies that the identity of m_* and n_* does not change in the time period between steady-state and equilibrium (approximation 5). A similar procedure was carried out to identify the maximum term in the summation in eq.(5.2b). An additional approximation (approximation 6) was made that reaction essentially takes place from the vibrational level m_* into the vibrational level n_* and vice-versa . This approximation implies that for all vibrational levels, m, there is only one product vibrational level n_* and for all vibrational levels n there is only one reactant vibrational level m_*. Hence, the steady-state distribution is given by the set of equations,

$$Y_m[\Upsilon-\beta\frac{N_{AB}}{N_{BC}}-m-(m+1)e^{-u}]+mY_{m-1}e^{-u}+(m+1)Y_{m+1}=0 \qquad (5.3a)$$

$$Z_n[\beta - \gamma\frac{N_{BC}}{N_{AB}} - Xn - X(n+1)e^{-v}] + nXZ_{n-1}e^{-v} + X(n+1)Z_{n+1} = 0 \qquad (5.3b)$$

for all m and n except m = 0, n = 0, m = $m_\bullet$, and n = $n_\bullet$. For m = 0 and n = 0 downward transitions do not take place. Thus

$$Y_0[\gamma - \beta\frac{N_{AB}}{N_{BC}} - e^{-u}] + Y_1 = 0 \qquad (5.4a)$$

$$Z_0[\beta - \gamma\frac{N_{BC}}{N_{AB}} - Xe^{-v}] + XZ_1 = 0 \qquad (5.4b)$$

For m = $m_\bullet$ and n = $n_\bullet$ we assume that upward transitions do not take place, but that reaction does. Thus

$$Y_{m_\bullet}[\gamma - \beta\frac{N_{AB}}{N_{BC}} - \frac{N_A}{N_M}\frac{k^f_{m_\bullet}}{k^{BC}_{10}} - m_\bullet] + Y_{m_\bullet - 1}m_\bullet e^{-u} + \frac{N_{AB}N_C}{k^{BC}_{10}N_{BC}N_M}k^r_{n_\bullet - m_\bullet}Z_{n_\bullet} = 0 \qquad (5.5a)$$

$$Z_{n_\bullet}[\beta - \gamma\frac{N_{BC}}{N_{AB}} - \frac{N_C}{N_M}\frac{k^r_{n_\bullet}}{k^{BC}_{10}} - Xn_\bullet] + Z_{n_\bullet - 1}n_\bullet Xe^{-v} + \frac{N_{BC}N_A}{k^{AB}_{10}N_{AB}N_M}k^f_{m_\bullet - n_\bullet}Y_{m_\bullet} = 0 \qquad (5.5b)$$

At this stage, we have 4 equations and 6 variables to solve for. We shall build 2 constraints to eliminate two of the variables. Summation of eq. (2.1a) for all m, and use of eq.(2.3a) leads to

$$\frac{dN_{BC}}{dt} = -\sum_m \sum_n k^f_{m-n} N^{BC}_m N_A + \sum_m \sum_n k^r_{n-m} N^{AB}_n N_C$$

$$= -N_{BC} N_A \sum_m k^f_m Y_m + N_{AB} N_C \sum_m \sum_n k^r_{n-m} Z_n \qquad (5.6a)$$

Similarly, summation of eq. (2.1b) for all n and use of eq. (2.3b) leads to

$$\frac{dN_{AB}}{dt} = -\sum_n \sum_m k^r_{n-m} N^{AB}_n N_C + \sum_n \sum_m k^f_{m-n} N^{BC}_m N_A$$
$$= -N_{AB} N_C \sum_n k^r_n Z_n + N_{BC} N_A \sum_n \sum_m k^f_{m-n} Y_m \qquad (5.6b)$$

Comparing eq. (5.6a) and eq. (5.6b) with the phenomenological rate laws $dN_{BC}/dt = -dN_{AB}/dt = -k_f N_A N_{BC} + k_r N_{AB} N_C$ we see that (approximation 7),

$$k_f = \sum_m k^f_m Y_m \quad \text{and} \quad k_r = \sum_n k^r_n Z_n$$

This one-to-one identification is only one of many possible ones. Since Z_n and Y_m are functions of all concentrations then other identifications may be possible. Nevertheless, we decided to designate k_f and k_r in this fashion. Consequences of this designation will become clear later on. Furthermore, recalling the approximation that reaction only takes place from vibrational level m. into vibrational level n. and vice-versa, then we can say that:

$$k_f \approx k^f_{m^*} . Y_{m^*} , \quad (5.7a)$$

$$k_r \approx k^r_{n^*} . Z_{n^*} . \quad (5.7b)$$

Eqs.(5.7) are already the solutions to our problem, except that we do not know, at this point, the value of the fractional populations of the uppermost levels, Y_{m^*} and Z_{n^*} under non-equilibrium conditions. The equations (5.3) are made non-linear by virtue of the dependence of k_f on Y_{m^*} and k_r on Z_{n^*}.

5.3 Solution of the Master Equation

We solve equations (5.3-5.5) by recursion, and begin with $m=0$ (eq. (5.4a)) and $n=0$ (eq. (5.4b)), which leads to

$$\frac{Y_1}{Y_0} = e^{-u} - (\gamma - \beta \frac{N_{AB}}{N_{BC}}) \quad (5.8a)$$

$$\frac{Z_1}{Z_0} = e^{-v} - \frac{(\beta - \gamma \frac{N_{BC}}{N_{AB}})}{X} \quad (5.8b)$$

Eqs. (5.8) shows that even though reaction occurs directly only from m. and n., the disruption it causes is felt even at the lowest vibrational level. Now, we divide eq. (5.3a) by Y_m and eq. (5.3b) by Z_n, thus obtaining a recursion formula for all other $m \neq m_*$ and $n \neq n_*$, expressing the relative fractional population of two neighbouring levels in terms of the pair just lower down the vibrational ladder, i.e.

$$\frac{Y_{m+1}}{Y_m} = e^{-u} + \frac{m}{m+1}\left(1 - \frac{e^{-u}}{Y_m/Y_{m-1}}\right) - \frac{\left(\gamma - \frac{N_{AB}}{N_{BC}}\beta\right)}{m+1} \qquad (5.9a)$$

$$\frac{Z_{n+1}}{Z_n} = Xe^{-v} + \frac{Xn}{n+1}\left(1 - \frac{e^{-v}}{Z_n/Z_{n-1}}\right) - \frac{\left(\beta - \frac{N_{BC}}{N_{AB}}\gamma\right)}{n+1}\ . \qquad (5.9b)$$

Starting with the expression for Y_1/Y_0 we apply eq.(5.9a) successively $(m_* - 1)$ times, and starting with Z_1/Z_0 we apply eq. (5.9b) successively $(n_* - 1)$ times, arriving exactly at

$$\frac{Y_{m_*}}{Y_{m_*-1}} = e^{-u}\left(1 + \frac{(\beta N_{AB}/N_{BC} - \gamma)}{m_*} e^{u} F_{m_*-1}\right) \qquad (5.10a)$$

$$\frac{Z_{n_*}}{Z_{n_*-1}} = e^{-v}\left(1 + \frac{(\gamma N_{BC}/N_{AB} - \beta)}{Xn_*} e^{v} G_{n_*-1}\right) \qquad (5.10b)$$

where F_{m_*-1} and G_{n_*-1} satisfy the following continued fractions,

$$F_{m-1} = 1 + \frac{e^{u} F_{m-2}}{1 + \frac{[\beta N_{AB}/N_{BC} - \gamma]}{(m-1)} e^{u} F_{m-2}} \qquad (5.11a)$$

$$G_{n-1} = 1 + \frac{e^{v} G_{n-2}}{1 + \frac{(\gamma N_{BC}/N_{AB} - \beta)}{x(n-1)} e^{v} G_{n-2}} \qquad (5.11b)$$

with $F_0 = 1$ and $G_0 = 1$. $\gamma = k^{f}_{m^*} Y_{m^*} N_A / k^{BC}_{10} N_M$ and $\beta = k^{r}_{n^*} Z_{n^*} N_C / k^{BC}_{10} N_M$ are the desired quantities. Combining the two expressions for Y_{m^*}/Y_{m^*-1} and also combining the two expressions for Z_{n^*}/Z_{n^*-1}, we obtain

$$Y_{m_*}[\gamma - \beta \frac{N_{AB}}{N_{BC}} - \frac{N_A}{N_M} \frac{k^{f}_{m_*}}{k^{BC}_{10}} - m_* + (\frac{m_*^2}{m_* + (\beta N_{AB}/N_{BC} - \gamma) e^{u} F_{m_*-1}}] + \frac{N_{AB} N_C}{k^{BC}_{10} N_{BC} N_M} k^{r}_{n_*-m_*} Z_{n_*} = 0 \qquad (5.12a)$$

$$Z_{n_*}[\beta - \gamma \frac{N_{BC}}{N_{AB}} - \frac{N_C}{N_M} \frac{k^{r}_{n_*}}{k^{BC}_{10}} - X n_* + \frac{X^2 n_*^2}{X n_* + (\beta N_{AB}/N_{BC} - \gamma) e^{v} G_{n_*-1}}] + \frac{N_{BC} N_A}{k^{BC}_{10} N_M N_{AB}} k^{f}_{m_*-n_*} Y_{m_*} = 0 \qquad (5.12b)$$

These two equations represent a condensation of all the steady-state equations. Solutions are determined by evaluating F_{m^*-1} and G_{n^*-1} with the aid of eq. (5.11a) and eq. (5.11b), respectively.

Special cases:

Two special cases can be identified in eq. (5.11a) and eq. (5.11b):

(I) $(\gamma - \beta N_{AB}/N_{BC}) << 1$; and

(II) $(\gamma - \beta N_{AB}/N_{BC}) >> 1$.

The equivalent approximations for eq 5.12 are $(\beta - \gamma N_{BC}/N_{AB})/X << 1$ and $(\beta - \gamma N_{BC}/N_{AB})/X >> 1$. One can show that the interior of the parentheses is proportinal to $(k_f/k_r - Q)$ where $Q = N_{AB}N_C/N_{BC}N_A$), and is thus a measure of extent from equilbrium. The inequality in this form refers to a comparison of relaxation rate to reaction rate. Consequently case I is an approximation valid for reactions occuring close to equilibrium; case II is an approximation valid for reactions occuring not only far from equilibrium but at rates which are much faster than energy transfer rates.

5.3.1 Case (I) The unperturbed ground-level approximation (A8').

With the approximation $|\gamma - \beta N_{AB}/N_{BC}| << 1$ eqs. (5.11) can be solved by recursion and inductive reasoning. We obtain

$$\frac{1}{F_m} \approx \frac{e^{-mu}}{S_m}\left(1 + \left(\beta\frac{N_{AB}}{N_{BC}} - \gamma\right)\sum_{i=1}^{m} \frac{e^{iu}}{i} S_{i-1}\right) \qquad (5.13a)$$

$$\frac{1}{G_n} \approx \frac{e^{-nv}}{\sigma_n}\left(1 + \frac{1}{X}\left(\gamma\frac{N_{BC}}{N_{AB}} - \beta\right)\sum_{k=1}^{n} \frac{e^{kv}}{k}\sigma_{k-1}\right) \quad (5.13b)$$

where

$$S_{i-1} = \sum_{j=0}^{i-1} e^{-ju}, \qquad \sigma_{k-1} = \sum_{j=0}^{k-1} e^{-jv}$$

We shall see in the discussion of the population distribution function that $|\gamma - \beta N_{AB}/N_{BC}| << 1$ really means $Y_0 \approx Y_0^{eq}$ and $Z_0 \approx Z_0^{eq}$. Here we shall concentrate on an expression for $A = Y_{m*}/Y_{m*}^{eq}$ and $B = Z_{n*}/Z_{n*}^{eq}$. Setting $m = m_*-1$ in eq. (5.13a) and $n = n_*-1$ in eq. (5.13b), and then substituting the results into eq. (5.12a) and eq. (5.12b), respectively, we obtain

$$A^3(k')^2(Y_{m*}^{eq})^2\delta - A^2k'(1+k'Y_{m*}^{eq}\delta) - 2A^2Bk''k'Z_{n*}^{eq}Y_{m*}^{eq}\frac{N_{AB}}{N_{BC}}\delta + ABk''\frac{Z_{n*}^{eq}}{Y_{m*}^{eq}}\frac{N_{AB}}{N_{BC}}(1+2k'Y_{m*}^{eq}\delta) + Ak'$$

$$+AB^2(k'')^2(Z_{n*}^{eq})^2\left(\frac{N_{AB}}{N_{BC}}\right)^2\delta - Bk''\frac{Z_{n*}^{eq}}{Y_{m*}^{eq}}\frac{N_{AB}}{N_{BC}} - B^2(k'')^2\frac{(Z_{n*}^{eq})^2}{Y_{m*}^{eq}}\left(\frac{N_{AB}}{N_{BC}}\right)^2\delta = 0 \quad (5.14a)$$

$$B^3(k'')^2(Z_{n*}^{eq})^2\Psi - B^2k''(1+k''Z_{n*}^{eq}\Psi) - 2B^2Ak''k'Y_{m*}^{eq}Z_{n*}^{eq}\frac{N_{BC}}{N_{AB}}\psi + ABk'\frac{Y_{m*}^{eq}}{Z_{n*}^{eq}}\frac{N_{BC}}{N_{AB}}(1+2k''Z_{n*}^{eq}\psi) + Bk''$$

$$+A^2B(k')^2(Y_{m\bullet}^{eq})^2(\frac{N_{BC}}{N_{AB}})^2\psi-Ak'\frac{Y_{m\bullet}^{eq}}{Z_{n\bullet}^{eq}}\frac{N_{BC}}{N_{AB}}-A^2(k')^2\frac{(Y_{m\bullet}^{eq})^2}{Z_{n\bullet}^{eq}}(\frac{N_{BC}}{N_{AB}})^2\psi=0 \qquad (5.14b)$$

where

$$k'=\frac{k_{m\bullet}^{f}}{k_{10}^{BC}}\frac{N_A}{N_M}, \qquad k''=\frac{k_{n\bullet}^{r}}{k_{10}^{BC}}\frac{N_C}{N_M}$$

and

$$\delta=(\sum_{i=1}^{m\bullet}\frac{e^{iu}}{i}S_{i-1}+\frac{e^{m\bullet u}S_{m\bullet-1}}{m_\bullet}), \qquad \psi=\frac{1}{X}(\sum_{k=1}^{n\bullet}\frac{e^{kv}}{k}\sigma_{k-1}+\frac{e^{n\bullet v}\sigma_{n\bullet-1}}{n_\bullet})$$

Noting that at equilibrium

$$k_{m\bullet}^{f}Y_{m\bullet}^{eq}N_{BC}^{eq}N_A^{eq}=k_{n\bullet}^{r}Z_{n\bullet}^{eq}N_{AB}^{eq}N_C^{eq}$$

$$k_{m\bullet}^{f}Y_{m\bullet}^{eq}=K_{eq}k_{n\bullet}^{r}Z_{n\bullet}^{eq} \qquad (5.15)$$

and setting

$$\varepsilon=k'Y_{m\bullet}^{eq}\delta, \quad \Phi=k''Z_{n\bullet}^{eq}\psi, \quad \kappa_T=\frac{1}{K_{eq}}(\frac{N_{AB}N_C}{N_AN_{BC}}) \qquad (5.16)$$

we finally arrive at

$$A^{2}(1+\varepsilon)-A^{3}Y_{m\cdot}^{eq}\varepsilon-AB\kappa_{T}(1+2\varepsilon)+B\kappa_{T}-A+B^{2}(\kappa_{T})^{2}\varepsilon-AB^{2}Y_{m\cdot}^{eq}\varepsilon+2A^{2}BY_{m\cdot}^{eq}(\kappa_{T})\varepsilon=0 \quad (5.17a)$$

$$B^{2}(1+\Phi)-B^{3}Z_{n\cdot}^{eq}\Phi-\frac{AB}{\kappa_{T}}(1+2\Phi)+\frac{A}{\kappa_{T}}-B+\left(\frac{A}{\kappa_{T}}\right)^{2}\Phi+2\frac{AB^{2}}{\kappa_{T}}Z_{n\cdot}^{eq}\Phi-\frac{A^{2}B}{\kappa_{T}}Z_{n\cdot}^{eq}\Phi=0 \quad (5.18b)$$

Factoring out the common factor and rewriting the equations, we have

$$A-1+\varepsilon[A-\kappa_{T}B][1-AY_{m\cdot}^{eq}]=0 \quad (5.18a)$$

$$B-1+\Phi[B-\frac{1}{\kappa_{T}}A][1-BZ_{n\cdot}^{eq}]=0 \quad (5.18b)$$

We shall seek more approximate solutions to these equations by making the following approximations (A9')

$$AY_{m\cdot}^{eq}\ll 1, \qquad BZ_{n\cdot}^{eq}\ll 1$$

Using the definitions of A and B, then these approximations really mean

$$Y_{m\cdot}\ll 1, \qquad Z_{n\cdot}\ll 1$$

which are clearly reasonable since no fractional population of any level will approach 1.

Consequently

$$A(1+\epsilon)-\kappa_T B=1 \qquad (5.19a)$$

$$B(1+\Phi)-\frac{1}{\kappa_T}A=1 \qquad (5.19b)$$

Therefore to a good approximation at all temperatures

$$A=\frac{(1+\Phi+\kappa_T\varepsilon)}{(1+\Phi+\varepsilon)}, \qquad B=\frac{(1+\epsilon+\Phi/\kappa_T)}{(1+\Phi+\varepsilon)} \qquad (5.20)$$

Here A and B are the non-equilibrium correction factors to the rate law. These two solutions will be used later on to write the improved rate expression.

5.3.2 Case (II) Extreme perturbation(A8").

With the approximation $|\gamma - \beta N_{AB}/N_{BC}| >> 1$ eq.(5.11a) and eq. (5.11b) can be solved by recursion and inductive reasoning. We obtain

$$\frac{1}{F_m}\approx\frac{(\gamma-\beta\frac{N_{AB}}{N_{BC}})\sum_{i=1}^{m}\frac{e^{iu}}{i}S_{i-1}+e^{mu}S_m-1}{(\gamma-\beta\frac{N_{AB}}{N_{BC}})\sum_{i=1}^{m}\frac{e^{iu}}{i}S_{i-1}} \qquad (5.21a)$$

$$\frac{1}{G_n} \approx \frac{\frac{1}{X}(\beta - \gamma\frac{N_{BC}}{N_{AB}})\sum_{k=1}^{n} \frac{e^{kv}}{k}\sigma_{k-1} + e^{nv}\sigma_n - 1}{\frac{1}{X}(\beta - \gamma\frac{N_{BC}}{N_{AB}})\sum_{k=1}^{n} \frac{e^{kv}}{k}\sigma_{k-1}} \qquad (5.21b)$$

where S_{i-1} and σ_{k-1} have the same definitions as in the previous case (I).

Setting $m=m_{\bullet}-1$ in eq. (5.21a) and $n=n_{\bullet}-1$ in eq. (5.21b), and then substituting the results into eq. (5.12a) and eq. (5.12b), respectively, we obtain

$$k'm_{\bullet}.Y_{m_{\bullet}}^{2}.e^{u}\sum_{i=1}^{m_{\bullet}} - k''m_{\bullet}.Z_{n_{\bullet}}.e^{u}\frac{N_{AB}}{N_{BC}}\sum_{i=1}^{m_{\bullet}} + (1-Y_{m_{\bullet}})\,[m_{\bullet}-m_{\bullet}e^{-u}e^{m_{\bullet}u}S_{m_{\bullet}-1} + (k')^{2}Y_{m_{\bullet}}^{2}.e^{u}\sum_{i=1}^{m_{\bullet}}$$

$$-k'Y_{m_{\bullet}}.m_{\bullet}.\sum_{i=1}^{m_{\bullet}} - 2k''k'Z_{n_{\bullet}}.Y_{m_{\bullet}}.\frac{N_{AB}}{N_{BC}}e^{u}\sum_{i=1}^{m_{\bullet}} + k''Z_{n_{\bullet}}.m_{\bullet}.\frac{N_{AB}}{N_{BC}}\sum_{i=1}^{m_{\bullet}} + (k'')^{2}Z_{n_{\bullet}}^{2}.(\frac{N_{AB}}{N_{BC}})^{2}e^{u}\sum_{i=1}^{m_{\bullet}}\,] = 0 \quad (5.22a)$$

$$k''Xn_{\bullet}.Z_{n_{\bullet}}^{2}.e^{v}\sum_{k=1}^{n_{\bullet}} - k'Xn_{\bullet}.Y_{m_{\bullet}}.Z_{n_{\bullet}}.\frac{N_{BC}}{N_{AB}}e^{v}\sum_{k=1}^{n_{\bullet}} + (1-Z_{n_{\bullet}})\,[Xn_{\bullet}-e^{-v}e^{n_{\bullet}v}\sigma_{n_{\bullet}-1} + (k'')^{2}Z_{n_{\bullet}}^{2}.e^{v}\sum_{k=1}^{n_{\bullet}}$$

$$-k''Xn_{\bullet}.Z_{n_{\bullet}}.\sum_{k=1}^{n_{\bullet}} - 2k''k'Z_{n_{\bullet}}.Y_{m_{\bullet}}.e^{v}\frac{N_{BC}}{N_{AB}}\sum_{k=1}^{n_{\bullet}} + k'Xn_{\bullet}.Y_{m_{\bullet}}.\frac{N_{BC}}{N_{AB}}\sum_{k=1}^{n_{\bullet}} + (k')^{2}Y_{m_{\bullet}}^{2}.e^{v}(\frac{N_{BC}}{N_{AB}})^{2}\sum_{k=1}^{n_{\bullet}}\,] = 0 \quad (5.22b)$$

where k' and k'' have the same definitions as in case (I), and where

$$\sum_{i=1}^{m_\bullet} = \sum_{i=1}^{m_\bullet} \frac{e^{iu}}{i} S_{i-1}, \qquad \sum_{k=1}^{n_\bullet} = \sum_{k=1}^{n_\bullet} \frac{e^{kv}}{k} \sigma_{k-1}$$

Once again we shall write equations (5.22) in terms of A and B. Furthermore, we shall seek more approximate solutions to these equations similar to those used in case (I) (approximation 9''):

$$Y_{m_\bullet} \ll 1, \qquad Z_{n_\bullet} \ll 1$$

Also making use of microscopic reversibility (eq. (5.15)), we have

$$A^2 Y_{m_\bullet}^{eq} e^{u}\left(1+\frac{k'}{m_\bullet}\right) - ABY_{m_\bullet}^{eq}\kappa_T e^{u}\left(1+\frac{2k'}{m_\bullet}\right) - A + B\kappa_T + B^2\frac{k'}{m_\bullet} Y_{m_\bullet}^{eq}\kappa_T^2 e^{u} + \frac{(1-e^{-u}e^{m_\bullet u}S_{m_\bullet -1})}{k' Y_{m_\bullet}^{eq}\sum_{i=1}^{m_\bullet}} = 0 \quad (5.23a)$$

$$B^2 Z_{n_\bullet}^{eq}\kappa_T e^{v}\left(1+\frac{k''}{Xn_\bullet}\right) - ABZ_{n_\bullet}^{eq} e^{v}\left(1+\frac{2k''}{Xn_\bullet}\right) - B\kappa_T + A + A^2\frac{k''}{\kappa_T Xn_\bullet} Z_{n_\bullet}^{eq} e^{v} + \frac{K_T(1-e^{-v}e^{n_\bullet v}\sigma_{n_\bullet -1})}{k'' Z_{n_\bullet}^{eq} X\sum_{k=1}^{n_\bullet}} = 0 \quad (5.23b)$$

Close inspection of these equations reveals that the terms

$$\frac{(1 - e^{-u} e^{m_{\bullet} u} S_{m_{\bullet}-1})}{k' Y_{m_{\bullet}}^{eq} \sum_{i=1}^{m_{\bullet}}} << |A - \mathrm{K}_T B| \quad and \quad \frac{\mathrm{K}_T (1 - e^{-v} e^{n_{\bullet} v} \sigma_{n_{\bullet}-1})}{k'' Z_{n_{\bullet}}^{eq} X \sum_{k=1}^{n_{\bullet}}} << |A - \mathrm{K}_T B|$$

can be ignored (approximation 10). The approximations made here will be discussed in greater detail later on. We finally arrive at

$$A^2 Y_{m_{\bullet}}^{eq} e^{u} (1 + \frac{k'}{m_{\bullet}}) - ABY_{m_{\bullet}}^{eq} \mathrm{K}_T e^{u} (1 + \frac{2k'}{m_{\bullet}}) - A + B\mathrm{K}_T + B^2 \frac{k'}{m_{\bullet}} Y_{m_{\bullet}}^{eq} \mathrm{K}_T^2 e^{u} = 0 \quad (5.24a)$$

$$B^2 Z_{n_{\bullet}}^{eq} \mathrm{K}_T e^{v} (1 + \frac{k''}{Xn_{\bullet}}) - ABZ_{n_{\bullet}}^{eq} e^{v} (1 + \frac{2k''}{Xn_{\bullet}}) - B\mathrm{K}_T + A + A^2 \frac{k''}{Xn_{\bullet} \mathrm{K}_T} Z_{n_{\bullet}}^{eq} e^{v} = 0 \quad (5.24b)$$

Factoring out the common factor and rewriting the equations, we have

$$(A - \mathrm{K}_T B)[cA - d\mathrm{K}_T B - 1] = 0 \qquad (5.25a)$$

$$(\mathrm{K}_T B - A)[fB - \frac{gA}{\mathrm{K}_T} - 1] = 0 \qquad (5.25b)$$

where

$$c = Y_{m\bullet}^{eq} e^{u} \left(1 + \frac{k'}{m_{\bullet}}\right), \quad d = \frac{k'}{m_{\bullet}} Y_{m\bullet}^{eq} e^{u}$$

and

$$f = Z_{n\bullet}^{eq} e^{v} \left(1 + \frac{k''}{Xn_{\bullet}}\right), \quad g = Z_{n\bullet}^{eq} e^{v} \frac{k''}{Xn_{\bullet}}.$$

Therefore to a good approximation at all temperature eq.(5.24a) and eq.(5.24b) reduce to

$$A = \frac{dK_T + f}{fc - dg}, \quad B = \frac{c + 1/K_T g}{fc - dg} \qquad (5.26)$$

Once again these solutions to the master equation will be used below to write the improved rate expression.

5.4 Generalization of the Rate Law and of the Non-Equilibrium Kinetic Mass Action law.

5.4.1 Case (I):

The reaction rate is given by: rate = $k_f[A][BC] - k_r[AB][C]$ which, at our level of approximation (eq. 5.7), is $k^f_{m\bullet} \cdot Y_{m\bullet} \cdot [A][BC] - k^r_{n\bullet} \cdot Z_{n\bullet} \cdot [AB][C]$. A and B describe departures from the equilibrium population distributions. Therefore

$$rate = k^f_{eq}[A][BC]A - k^r_{eq}[AB][C]B. \qquad (5.27)$$

Using our newly found solutions (A and B) the rate law becomes,

$$rate = \frac{k^f_{eq}(1+\Phi+K_T\varepsilon)[A][BC] - k^r_{eq}(1+\varepsilon+1/K_T\Phi)[AB][C]}{(1+\Phi+\varepsilon)} \qquad (5.28)$$

When we simplify this further, we finally obtain

$$rate = \frac{k^f_{eq}[A][BC] - k^r_{eq}[AB][C]}{(1+\Phi+\varepsilon)}. \qquad (5.29)$$

The denominator $((1+\Phi+\epsilon))$, may be termed the non-equilibrium correction factor for the overall rate, where

$$\varepsilon = \frac{k^f_m . N_A}{m . k^{BC}_{10} N_M}(1 - Y^{eq}_{m\bullet} + m . Y^{eq}_{m\bullet} \sum_{i=1}^{m\bullet-1} \frac{e^{iu}}{i} S_{i-1})$$

and

$$\Phi = \frac{k^r_n . N_C}{n . k^{AB}_{10} N_M}(1 - Z^{eq}_{n\bullet} + n . Z^{eq}_{n\bullet} \sum_{k=1}^{n\bullet-1} \frac{e^{kv}}{k} \sigma_{k-1}).$$

The rate expression(eq.(5.29)) is valid for those reactions occurring “close to equilibrium” even though the forward and reverse components might deviate individually considerably from their equilibrium rates by the large factor $(1+\epsilon+\Phi)$. It is now, worth examining the approximation:

$$\| \gamma - \frac{N_{AB}}{N_{BC}} \beta \| \ll 1$$

Noting the definitions of γ and β , we see that this means

$$\| k_f N_A N_{BC} - k_r N_C N'_{AB} \| \ll k_{10}^{BC} N_{BC} N_M.$$

Apparently the forward rate and reverse rate have to be of the same magnitude, so that their difference would be smaller than the magnitude of the energy transfer rate. It is also important to point out that individual rates can still be very large in magnitude even though their difference has to be smaller than the magnitude of the energy transfer rate. Hence, the necessary condition for a significant uni-directional non-equilibrium effect, (ie. that reaction has to be faster than energy transfer) can still be satisfied.

When evaluating the ratio of forward and reverse rate coefficients using eq. (5.29), the non-equilibrium factor cancels out. This corresponds to the experimental kineticist's usage of phenomenological rate coefficients k_f and k_r, as variation of the overall rate with respect to reagent concentrations or product concentrations respectively keeping other variables constant. However, when writing the equilibrium expression using eq. (5.28),

$$K = \frac{k_f}{k_r} = \frac{k_{eq}^{f}}{k_{eq}^{r}} \frac{A}{B} = K_{eq} \frac{(1 + \Phi + K_T \epsilon)}{(1 + \epsilon + 1/K_T \Phi)} \qquad \textbf{(5.30)}$$

the non-equilibrium factors do not cancel out. This scenario arises from an experimental dynamicist's designation of k_f and k_r as population weighted averages of state selected rate constants. It is obvious now that some of the terms in $\Sigma_m k^f_m Y_m$ may be contributing to the phenomenological k_r and some of the terms in $\Sigma_n k^r_n Z_n$ may be contributing to the phenomenological k_f. It is important to point out that our designations are not contradictory but rather they are simply convenient but arbitrary ones for the experimenter to make. Since concentrations are involved in the non-equilibrium factor, there may be many different ways of defining k_f and k_r.

5.4.2 case (II):

Starting with the expression for the rate (eq.(5.27)) and using the solutions found for A and B, we obtain

$$Rate = \frac{k^f_{eq}[BC][A]Z^{eq}_{n\bullet}e^{v} - k^r_{eq}[AB][C]Y^{eq}_{m\bullet}e^{u}}{Z^{eq}_{n\bullet}Y^{eq}_{m\bullet}e^{u+v}\left(1 + \frac{k'}{m_\bullet} + \frac{k''}{Xn_\bullet}\right)} \quad (5.31)$$

This rate expression is valid for those reactions occurring far from equilibrium. It is now worth examining the approximation:

$$\| \gamma - \frac{N_{AB}}{N_{BC}} \beta \| \gg 1$$

Noting the definitions of γ and β , we see that

$$\| k_f N_A N_{BC} - k_r N_C N_{AB} \| \gg k_{10}^{BC} N_{BC} N_M$$

This approximation applies, not only to individual rates being larger but also their difference being larger than the energy transfer rate. This does not mean that one of the rates has to be much smaller than other. The non-equilibrium condition can still be satisfied even close to equilibrium if the individual reaction rates are sufficiently large or the relaxation rate spectacularly small.

When evaluating the ratio of forward to reverse rate coefficients using eq. (5.31), we find

$$\frac{k_f}{k_r} = K_{eq} \frac{Z_{n*}^{eq} e^{v}}{Y_{m*}^{eq} e^{u}} \qquad \textbf{(5.32)}$$

The non-equilibrium factors do not cancel out. Furthermore, according to eq. (5.32) equilibrium will never be achieved. This is because we assumed from the start that reaction is taking place far from equilibrium. However, when writing the equilibrium expression using eq. (5.27) we find

$$\frac{k_f}{k_r} = \frac{k_{eq}^{f} A}{k_{eq}^{r} B} = K_{eq}\left(\frac{\kappa_T d + f}{1/\kappa_T g + c}\right) \quad (5.33)$$

Once again this scenario is attributed to our designation of k_f and k_r as population-weighted averages of state selected rate constants.

Additional approximations (eqs. (5.23)) had been made to solve the master equations. It is now worth examining these approximations. In eq. (5.23a), the terms $e^{m^* u} S_{m^*-1}$ and $\Sigma_{i=1}^{m^*}$ have approximately the same magnitude; and furthermore, $k' Y_{m^*}^{eq}$ is of the order of γ ($>>1$). The last term in equation 5.32a reduces to $1/e^{u}\gamma$ which is indeed $1<<1$. Hence, the terms we neglected are indeed approximately zero.

5.5 Non-equilibrium population distributions

Once $Y_{m^*} / Y_{m^*}^{eq}$ and $Z_{n^*} / Z_{n^*}^{eq}$ are determined then so are γ, β, F_{m^*-1} and G_{n^*-1}. Repetitive application of eq. (5.9) leads to the values of Y_m ($m < m_*-1$) and Z_n ($n < n_*-1$).

Case (I):

We apply the identity

$$\frac{Y_{m-1}}{Y_{m-1}^{eq}} = \frac{Y_{m-1}}{Y_m} \frac{Y_m}{Y_m^{eq}} \frac{Y_m^{eq}}{Y_{m-1}^{eq}} \quad (5.34)$$

to $m = m_*$ and use the analytical expressions for $Y_{m^*}/Y_{m^*}^{eq}$ (eq. (5.20)) as well as eq. (5.10a) relating Y_{m^*-1} to Y_{m^*}, and the equilibrium ratio, $Y_m^{eq}/Y_{m-1}^{eq} = e^{-u}$ in order to obtain an expression for $Y_{m^*-1}/Y_{m^*-1}^{eq}$. We re-apply eq. (5.34) to successively smaller values of m, and use the recursion relation eq. (5.9a), to finally obtain, by inductive reasoning, the following relation:

$$\frac{Y_m}{Y_m^{eq}} = \frac{Y_{m^*}}{Y_{m^*}^{eq}} + \frac{(1-K_T)\alpha \sum_{i=m+1}^{m^*} \frac{m^*}{i} \frac{e^{iu}-1}{e^{m^*u}-1}}{(1+\Phi+\varepsilon)} \qquad (5.35a)$$

where

$$\alpha = k'(1 - Y_{m^*}^{eq})/m.$$

It is gratifying to note that for k' = 0, and k'' = 0, Y_m/Y_m^{eq} becomes exactly unity. If there is no reaction, then the equilibrium populations are not disturbed. A similar procedure leads to the expression for the population distribution of the products,

$$\frac{Z_n}{Z_n^{eq}} = \frac{Z_{n^*}}{Z_{n^*}^{eq}} + \frac{(1-\frac{1}{K_T})\lambda \sum_{i=n+1}^{n^*} \frac{n^*}{i} \frac{e^{iv}-1}{e^{n^*v}-1}}{1+\Phi+\varepsilon} \qquad (5.35b)$$

where

$$\lambda = k''(1 - Z_{n^*}^{eq})/n.X.$$

One can easily show that for $m=0$, Y_0/Y_0^{eq} becomes exactly unity and for $n=0$, Z_0/Z_0^{eq} becomes unity even under conditions of disequilibrium, which is why we have called the approximation leading to eqs. (5.19) and $|\gamma - \beta N_{AB}/N_{BC}| << 1$ the "unperturbed ground-level" approximation.

Case (II):

We apply the identities in case (I) and use the analytical expression for $Y_{m^*}/Y_{m^*}^{eq}$ and $Z_{n^*}/Z_{n^*}^{eq}$ (eq.(5.26))to successively smaller values of m and n, and use recursion relations in eqs. (5.10a). We finally obtain, by inductive reasoning, the following relation:

$$\frac{Y_n}{Y_n^{eq}} = \left\{ \begin{array}{ll} A & n = m^* \\ \\ \dfrac{A}{\prod_{i=0}^{m^*-(n+1)} [1 + \dfrac{(\beta N_{AB}/N_{BC} - \gamma))]e\,^{u}F_{m^*-1}}{m^* - i}]} & n \neq m^* \quad (5.36a) \end{array} \right\}$$

$$\frac{Z_k}{Z_k^{eq}} = \left\{ \begin{array}{ll} B & k = n* \\ \\ \dfrac{B}{\prod\limits_{i=0}^{n*-(k+1)} [1 + \dfrac{(\gamma N_{BC}/N_{AB} - \beta) e^{\,v} G_{n*-1}}{X(n*-i)}]} & k \neq n* \end{array} \right\} \qquad (5.36b)$$

It is not clear what the ground level populations would be in this extreme case; but they are less than the values of A and B, which could be either less than unity or greater than unity.

5.6 Application 1: $H + O_2 \rightleftharpoons OH + O$

As input to our calculation we require values for the relaxation rate constants k^H_{10}, k^O_{10}, k^{OH}_{10}, k^{O2}_{10} and k^M_{10} for both species of diatomic molecules, OH and O_2, as well as ($k^f_{m\rightarrow n}$ and $k^r_{n\rightarrow m}$) state-to-state rate constants. We used the same data base of microscopic rate constants as in Table 2.1 and Table 2.2 originating from the calculations of Teitelbaum over the temperature range 300-8000 K [1]. These results were reconstructed from an application of information theory to reactive rate constants available in the literature and are summarized in Appendix B. Mixture compositions were chosen as in chapter 2 (Table 2.4 and Table 2.7).

The main question which remains to be answered is how to choose the critical levels (m_* and n_*) for the purpose of applying our analytical expression. We note that Y_m and Z_n are strongly decreasing functions of m and n (even if there is a disturbance to the distribution caused by reaction). $k^f{}_m$ and $k^r{}_n$ are usually monotonic functions of m and n, respectively [see e.g. ref. 2]. For chemical reactions where vibrational enhancement is weak or negative, the product $Y_m k^f{}_m$ (or $Z_n k^r{}_n$) clearly also decreases strongly with m (or n). The more interesting case occurs when there is a strong vibrational enhancement of the rate. In this class of reactions $Y_m k^f{}_m$ is the product of a decreasing and an increasing function of m. The result is strongly peaked because of the sharp decrease of Y_m with m. The maximum will generally occur at some non-integral value of m. The vibrational level closest to that value will thus contribute most to the sum Σ $Y_m k^f{}_m$. We denote the quantum number of this single critical level as m_*. This leads to eqn(5.7). This simple expression (eqn(5.7)) also applies to the case of vibrational non-enhancement, for which $m_*=0$. Fig. 5.1 shows an example for the reaction $H + O_2 \rightleftharpoons OH + O$ at 4000 K. Clearly the levels $m_*=0$ and $n_*=0$ account for 50% of the equilibrium flux. We note that if an appropriate temperature is chosen just right it is possible that the maximum of $Y_m k^f{}_m$ or $Z_n k^r{}_n$ is exactly between two levels. Then each level contributes equally to the sum. Thus, use of eqn (5.7) would underestimate the k_f or k_r by a factor of 2 for this unusual situation but less than 2 otherwise. Furthermore, we emphasize that it is not the intention to use eqn (5.7) in order to calculate k_f and k_r but rather to calculate the non-equilibrium factor k_f/k_f^{eq} and k_r/k_r^{eq}. The errors in the numerators and denominators are very similar. Thus the ratios would not suffer as much. This assumption also implies that the identity of m_* and n_* do not change between steady-state and equilibrium . The procedure is adequate for identifying m_* and n_*. We note that nothing actually prevents the practitioner from using the proper steady-state values of Y_m and Z_n in eqn (5.6): The techniques for calculating analytically the non-equilibrium population distributions are available, as seen in section 5.5. The present procedure is considerably simpler, however.

Fig. 5.1 shows that the equilibrium flux maximizes at $m_* = 0$ and $n_* = 0$ at 4000 K, but $m_* = 1$ and $n_* = 1$ levels also contribute nearly equally to the equilibrium flux. Setting $m_* = 0$ and $n_* = 0$, is the equivalent of saying that energy-transfer processes do not play a role in this reaction. This makes our analytical expression not usable. We shall therefore set the critical levels to be $m_* = 1$ and $n_* = 1$ (these levels do contribute ~45% to the equilibrium flux). We are introducing an error of a factor of 2 into our calculations for k_f and k_r, but this causes us to overestimate the value of the non-equilibrium factors only sightly and permits us to use the analytical expressions at least. Table 5.1 shows the vibrational levels m_* and n_* contributing most to k_f^{eq} and k_r^{eq} at 2000, 4000 and 8000 K, as well as the values of the ratio of rate constants (k_f^{eq} / k_r^{eq}).

5.6.1 Special Case I (Close to Equilibrium)

In Table 5.2 and Table 5.3 we have summarized our results. In Table 5.2, relative concentrations were chosen to satisfy the condition that reaction occurs close to equilibrium. These concentrations were calculated from a knowledge of the K_{eq} value. The main trends that are observed in Table 5.3 are:

1) The values of ϵ and Φ decrease with increasing temperature.

2) The non-equilibrium correction factor (A/B) is ~ 1 for all temperatures.

3) Decreasing the concentration of the solvent He has a minor effect on the non-equilibrium factor even though the suppression of k_f and k_r intensifies.

ϵ represents a competition between the forward reaction and the relaxation of the BC (O_2) molecule. As the temperature increases, the relaxation rate of BC increases. Hence the value of ϵ decreases. On the other hand, Φ represents a competition between the reverse reaction and the relaxation rate of the AB (OH) molecule. As the temperature increases, competition increases between the reverse reaction and the energy transfer of AB. The relaxation rate becomes larger than the reaction rate. Hence the value of Φ decreases. The non- equilibrium factor (A/B) is nearly unity for all temperatures. This is reasonable because we set our reaction to be close to equilibrium where the kinetic mass action law ($k_f / k_r = K_{eq}$) is expected to be satisfied exactly. The term κ_T is approximately unity; hence the non-equilibrium correction factor as determined by eq (5.30) also nearly cancels out. The two different equilibrium expressions obtained for this case give the same results. Our one-to-one designation of phenomenological k_r and k_f agrees with the working definition apparently, in this limit.

The maximum depression of k_f and k_r occurs at 4000 K. Each rate coefficient is suppressed by $(1+\epsilon+\Phi)$. As the temperature is increased the correction factor to the rate coefficient decreases. Overall reaction occurs close to equilibrium but each individual rate is faster than the rate of the vibrational relaxation process. Hence the 2 directions each exhibit a strong non-equilibrium effect. However, each is equally affected or nearly equally affected. Therefore, close to equilibrium $k_f/k_r \approx k_f^{eq}/k_r^{eq} = K_{eq}$. As mentioned, above a decrease in the concentration of He relative to that of H has no effect on the equilibrium factor, but the suppression of k_f and k_r becomes more profound. This is because the mixture has become relatively more reactive.

5.6.2 Special Case II (Far from Equilibrium)

The results are summarized in Table 5.4 and Table 5.5. The relative concentrations were chosen to satisfy the criterion that reaction occurs far from equilibrium. Once again, knowledge of the value of K_{eq} allowed us to choose these appropriate relative concentrations. The main trends that are observed in Table 5.4 and Table 5.5 are:

1) The non-equilibrium factor $(k_f/k_f^{eq}) / (k_r/k_r^{eq})$ calculated using eqn (5.32) is independent of concentrations for a given temperature, and increases with increasing temperature.

2) Individual rate coefficients, k_f and k_r, are inflated rather than depressed.

3) The non-equilibrium factors calculated using eqn (5.33) exhibit a different concentration and temperature dependence compared to those calculated using eqn (5.32).

   a) As the concentrations of C and AB are increased with respect to that of A, the non-equilibrium factor increases.

   b) As the concentration of BC is increased with respect to that of A, the non- equilibrium factor decreases.

   c) The non-equilibrium factor is temperature dependent.

4) The ground level populations for reactant (Y_0/Y_0^{eq}) and for product (Z_0/Z_0^{eq}) are larger than unity.

The deviation of k_f/k_r from K_{eq} , as predicted by eqn (5.32), is independent of concentration for a single temperature, which is not surprising. However suppression of the individual rate coefficients does depend on the chemical environment. As can be seen from Table 5.4 the rate coefficients are larger than their equilibrium values. Apparently the higher vibrational levels are getting depleted and the more important lower levels are becoming relatively more populated; hence the flux increases from these low levels. Thus the rate coefficients are actually larger than their equilibrium values.

The non-equilibrium factor obtained using eqn (5.33) does not agree with the non-equilibrium factor (A/B) obtained using the eqn (5.32). This is again due to our different designations of k_r and k_f. It is not a matter for concern because of the arbitrariness of the definitions of k_r and k_f The non-equilibrium factor is greater than unity because the rate coefficients k_f and k_r are not inflated by the same magnitude. As the concentrations of AB and C are increased the non-equilibrium factor increases. This occurs because the forward reaction starts to exhibit a more pronounced non-equilibrium effect. The reaction is leaving molecules in more important lower levels, hence the flux increases from these low levels. The non-equilibrium factor decreases with an increase of concentration of BC because the reverse reaction starts to exhibit a more pronounced non-equilibrium effect.

We are now at the stage where we can evaluate the ground level population of the products and reactants when reaction is occurring far from the equilibrium. Since we could not determine by inspection of the population distribution expression (eqn(5.36)) what the ground level population of products and reactants would be, we have summarized the results in Table 5.5. It is clear that the ground level population (Y_0/Y_0^{eq} or Z_0/Z_0^{eq}) are far from unity. The reactant and product relative populations are always greater than unity. This explains why our rate coefficients can be larger than their equilibrium values when $m_* \approx 0$ and $n_* \approx 0$. A change in the concentration of helium has little effect on the non-equilibrium factor. However, one should note that helium is not always the most important solvent but rather sometimes O_2 or O or OH are, depending on the initial concentrations.

5.6.3 Comparison between the Analytical and the Matrix Techniques

We have solved the master equation by analytical means and also by an alternative numerical method (the matrix technique). The numerical technique is exact ; however, the approximate analytical solution has the advantage of allowing us to see the relationship between the physical parameters. Since we want to able to use the analytical expressions to study non-equilibrium systems, we must establish that its basic assumptions are not serious. We are now in a position to compare the results of the matrix technique with those obtained from the analytical solution of the master equation. The comparison is summarized in Tables 5.6 - 5.9. Detailed comparison of the population distributions cannot be made since we obtained the analytical expression under the assumption of domination by a single vibrational level, whereas the matrix techniques uses all vibrational levels. Nevertheless, we can compare how much the rate coefficients deviate from their equilibrium values, ie. k^f/k^f_{eq} and k^r/k^r_{eq}. First we shall compare the results for reaction occuring close to equilibrium. Then in the second part of this section we shall compare the results for reaction occuring far from equilibrium. The reader is reminded that when we say the reaction is occuring close to equilibrium we are saying that the forward and reverse fluxes are nearly the same in magnitude so that their difference is much smaller than the rate of the energy transfer processes even though individually they may be larger. When reaction is occuring far from equilibrium the difference of the two rates is much larger than the magnitude of the rate of the energy transfer process, so that one of the rates is much larger than the other.

Close to equilibrium

When reaction is occurring close to equilibrium, the agreement between the approximate formula (eqn (5.29))and the exact solution (eqn(2.9)) is good to excellent. See (Table 5.6 & 5.7). Both approaches predict an insignificant suppression or inflation of the individual rate coefficients (k_f and k_r). Furthermore we learn that the non-equilibrium factor ((k_f /k_r)/K_{eq}) is approximately unity when reaction occurs close to equilibrium.

Far from equilibrium

When reaction is occurring far from equilibrium, the agreement between the approximate formula (eqn (5.31))and the exact formula (eqn(2.9)) is not good. A comparison of the results is summarized in Table 5.8 and Table 5.9. Both approaches show that k_f and k_r can be suppressed or can be inflated from their equilibrium values. But the magnitude of the suppression and inflation given by the approximate solution is not the same as given by the exact solution. In fact, when the approximate solution predicts the inflation of k_f and k_r the matrix technique sometimes shows suppression, and when it predicts suppression of k_f and k_r the matrix technique sometimes shows inflation.

The matrix and approximate solutions might not show good agreement between themselves, but two different definitions of k_f and k_r within each technique show some agreement. When a large amount of [OH] or [O] is present, ie when the reverse reaction dominates, the k_r values from the two definitions agree with each other, while, the k_f values for the two definitions do not agree with each other. When a large amount of [O_2] is present, ie when the forward reaction dominates, the situation is reversed: the k_f values for the two definitions agree with each other while the k_r values show disagreement.

The non-equilibrium factor for the approximate solution increases with increasing temperature, while for the matrix solution it decreases with increasing temperature. Furthermore, the two definitions within each solution do not show any agreement between themselves. The reader should realize that it is not necessary that the dynamic and kinetic definitions for k_f and k_r be in agreement. There are actually an infinite number of ways of partitioning the interlocking components of the master equation into two terms. None of these definitions necessarily agree with each other. This is particularly so whenever a phenomenological quantity is involved which is not a true constant. For example $\partial Rate/\partial[O_2]$ cannot be evaluated unambiguously unless k_f and k_r are really constants in concentrations, and this is manifestly not the case here. Therefore we expect differences, and we merely chose 2 definitions in common use. Indeed if we must analyse the discrepancies we should do so focussing on the differences between the analytical and numerical approaches rather than on the definitions.

5.7 Aplication 2: HCl + Br $\rightleftharpoons$ HBr + Cl

As input to our calculation we require values for the relaxation rate constants $k^{HBr}{}_{10}$, $k^{Cl}{}_{10}$, $k^{HCl}{}_{10}$, $k^{Br}{}_{10}$ and $k^{M}{}_{10}$ for both species of diatomic molecules, HCl and HBr as well as the state-to-state rate constants ($k^{f}{}_{m\rightarrow n}$ and $k^{r}{}_{n\rightarrow m}$). The reactive state-to-state rate constants were taken from the previous chapter over the temperature range 300-4000 K . These results were reconstructed from an application of information theory to those reactive rate constants already available from the literature. Mixture compositions were chosen as in Chapter 4 (Table 4.3 and Table 4.4) We used the same data base of microscopic rate constants as in Table 4.1 and Table 4.2 .

We shall use our analytical expressions derived in section 5.4 to determine the non-equilibrium effect on the HCl (v') +Br $\rightleftharpoons$ Cl + HBr(v) reaction, when the reaction is occuring close to equilibrium, and when the reaction is occuring far from equilibrium. The reader is once again reminded that when we speak of reaction occuring close to equilibrium we mean that the forward rate and reverse rate have to be of nearly the same magnitude so that their difference would be smaller than the magnitude of the energy transfer rate. When we speak of reaction occuring far from equilibrium we mean that the difference between the forward rate and reverse rate is larger than the magnitude of the energy transfer rate.

Once again we need to identify the m. and n. for the purpose of using our analytical expression.

We shall follow the procedure described in section 5.7. We plot $Y^{eq}_m k^f_m$ vs vibrational level m and $Z^{eq}_n k^r_n$ vs vibrational levels n, for each temperature. From the maxima of the two graphs we identify the m_* and n_*. Fig.5.3 and Fig. 5.4 show that the equilibrium flux maximizes at $m_* = 2$ and $n_* = 0$ for 1000 K. Setting $n_* = 0$ makes our analytical expression not usable. We shall therefore set the critical levels for the reverse reaction to be $n_* = 1$ (this level does contribute ~ 45% to the equilibrium flux). We have the same scenario as in the $H + O_2 = OH + O$ reaction where we had to assume $n_* = 1$ (and additionally $m_* = 1$). We introduced an error of a factor of 2 into our calculation of the correction factors for k_f and k_r. However, for our new reaction the error should be smaller because we did not have to make the assumption that $m_* = 1$. Table 5.10 shows the vibrational levels m_* and n_* contributing most to k_f^{eq} and k_r^{eq} at 1000, 2000 and 4000 K, as well as the values of the ratio of rate constants (k_f^{eq} / k_r^{eq}). Note that m_* for 4000 K also had to be set to 1. So we suspect that at this temperature we shall have a larger error in our calculation.

5.7.1 Case I: Close to Equilibrium

Table 5.11 shows the relative concentrations chosen to satisfy the condition that reaction occur close to equilibrium. These concentrations were calculated from a knowledge of K_{eq}. From past experience we know that reactions do not exhibit non-equilibrium effects at 300 K, and therefore we have decided to investigate the reaction in the temperature range 1000 K to 4000 K. We have summarized our results (calculated using eqs. 5.29 and 5.30) in Table 5.12 and Table 5.13. The main trends that are observed in Table 5.12 are:

1) The values of ϵ and Φ decrease with increasing temperature.

2) The non-equilibrium correction factor (A/B) is ~ 1 for all temperatures.

3) A change in the concentration of solvent has a minor effect on the non-equilibrium factor.

ϵ represents a competition between the forward reaction and the relaxation of the HCl molecule. As the temperature increases, the relaxation rate of HCl increases. Hence the value of ϵ decreases. On the other hand, Φ represents a competition between the reverse reaction and the relaxation rate of the HBr. As the temperature increases, the relaxation rate of HBr increases. Hence the value of Φ decreases. The non-equilibrium factor (A/B) is nearly one for all temperatures. This is reasonable because we set our reaction to be close to equilibrium where the kinetic mass action law ($k_f/k_r = K_{eq}$) is expected to be satisfied exactly. The two different expressions for k_f / k_r obtained for this case do not give the same results.

The maximum depression of k_f and k_r occurs at 1000 K. Each rate coefficient is suppressed by $(1+\epsilon+\Phi)$. As the temperature is increased the correction factor to the rate coefficient decreases. Overall reaction occurs close to equilibrium, but each individual rate is faster than the vibrational relaxation process. Hence the 2 directions each exhibit a strong non-equilibrium effect. However, each is equally affected or nearly equally affected. Therefore, close to equilibrium $k_f/k_r \approx k_f^{eq} / k_r^{eq} = K_{eq}$. Decreasing [Ar], at the expense of [Br], has no effect on the non-equilibrium factor, but it does cause k_f and k_r each to be suppressed more because the mixture becomes more reactive.

5.7.2 Case II: Far from Equilibrium

The relative concentrations were chosen to satisfy the requirement that reaction occurs far from equilibrium. Once again, knowledge of K_{eq} allowed us to choose these appropriate relative concentrations. Relative concentrations were chosen in such a manner that we can observe non-equilibrium effects by approaching equilibrium from both sides of the reaction and see what effect changes in [HCl], [HBr] and [Cl] have on the non-equilibrium factor. The appropriate gauge is Q defined as [Cl] [HBr]/[Br] [HCl]. We used Eq. 5.31, Eq. 5.32 and Eq. 5.33, and the results are summarized in Table 5.14 and Table 5.15 for the temperature range 1000 to 4000 K. The main trends observed are:

1) The non-equilibrium factor is not 1. It is sometimes dramatically very far from unity.

2) When the reverse reaction dominates and the concentration of HCl is increased the inflation of k_f increases while the k_r values are less suppressed.

3) k_r is sometimes suppressed and sometimes inflated. Suppression occurs when the value of Q/K_{eq} is large, and inflation occurs when Q/K_{eq} is small.

4) Maximum inflation of k_f occurs at 1000 K.

5) The ground level population for the HCl molecules is larger than that given by the Boltzmann distribution.

6) A decrease in concentration of Ar affects the reaction in a complex way.

The non-equilibrium factor is not 1 for this reaction. Thus the kinetic mass action laws breaks down. It does so because k_f and k_r are affected differently, and the fractional level populations of the reactant and products are disturbed seriously by the reaction as compared to reaction occuring close to equilibrium. The maximum inflation of k_f occurs at 1000 K. There are two reason why k_f values are inflated from their equilibrium values. First, the reverse reaction is selectively dumping molecules into the important low lying vibrational levels of HCl (m = 0, 1 and 2); so the flux of the forward reaction from these levels increases. This is supported by the fact that the ground level population is larger than the ground level population given by the Boltzmann distribution. Second, higher vibrational levels of HCl are depleted while relaxation of HCl is not fast enough to replace these molecules at 1000 K. Hence the lower levels increase in population relatively. This is supported by the observation that inflation of k_f increases with increasing amount of the HCl. k_r values are sometimes suppressed and sometimes inflated. According to the dynamic definition, k_r in Table 5.15.2 is suppressed when the value of Q/K_{eq} is large and inflation occurs when the value of Q/K_{eq} is small. k_r values are suppressed because most of the reaction flux is from $n_* = 1$ (supposedly), and relaxation of HBr is not fast enough to replenish excited molecules. According to the kinetic definition, k_r in Table 5.15.1 is always suppressed for all temperatures except for 4000 K where k_r values are always inflated. The inflation of k_r occurs when the dominant forward reaction leaves the HBr molecules in excited vibrational levels. The flux of the reaction is thus increased from these vibrational levels.

The two expressions for k_f/k_r do not agree with each other. One expression, eq. 5.32, shows the non-equilibrium factor depending only on the temperature, whereas the expression, eq. 5.33, shows the non-equilibrium factor depending not only on the temperature but also on the concentrations of the species present. A change in concentration of Ar affects the non-equilibrium factor in a complex way. The maximum non-equilibrium effect occurs at 1000 K. The reason for the maximum at this temperature is that the most important vibrational level ($m_* = 2$) is extremely reactive. Hence its suppression by inefficient energy transfer is felt most keenly.

5.7.3 Comparison between the Analytical and Matrix Techniques

We are now in a position to compare the results of the matrix technique with those obtained from the analytical solution of the master equation for Br + HCl = HBr + Cl. The comparison is summarized in Tables 5.16-5.19. We cannot expect perfect agreement in absolute values of k_f and k_r because we solve the analytical expression for a single reactive vibrational level, whereas the matrix technique uses ten reactive vibrational levels. However, we can compare how much the rate coefficients deviate from their equilibrium values, ie. k^f/k^f_{eq} and k^r/k^r_{eq}. First we shall compare the results for reaction occuring close to equilibrium. Then in the second part of this section we shall compare the results for reaction occuring far from equilibrium. The reader is reminded that when we say the reaction is occuring close to equilibrium we are saying that the forward and reverse fluxes are nearly equal in magnitude so that their difference is much smaller than the rate of the energy transfer processes even though individually they may be larger. When reaction is occuring far from equilibrium the difference of the two rates is much larger than the magnitude of the rate of the energy transfer process, and that one of the rates is much larger than the other. We are going to use the two definitions for each of k_f and k_r as defined in section 5.6.

Close to Equilibrium

When reaction is occuring close to equilibrium, the agreement between the approximate formula (eq. (5.29) and the exact solution (eq. (2.9) is not good. The results are compared in Table 5.16 and Table 5.17. Both techniques predict a suppression or inflation of the individual rate coefficients (k_f and k_r) when appropriate. However, the magnitude of the suppression or inflation is different for the two techniques.

The two definitions of k_f and k_r(kinetic and dynamic) show little agreement between themselves. We do not expect the two definitions to show agreement however, because they are merely two arbitrary ways of defining the rate coefficients. k_f and k_r can be defined in many different ways. All assume that they are true constants. The insufficiency of this approximation leads inevitably to ambiguity. The experimental definitions of k_f and k_r for both techniques at least show that both rate coefficients are suppressed by the same factor. Hence the non-equilibrium factor is approximately unity for both techniques with few exceptions.

The analytical expression for the population distribution predicts that the ground level population is the same as the ground level population of a Boltzmann distribution. However, our matrix technique shows that the ground level population increases due to the reaction. We have already seen that we need to improve our analytical expression. We would get better results if we did not have to set $n_* = 0$ as the critical level. In this sense this reaction also is not an ideal one.

Far from Equilibrium

When reaction is occuring far from equilibrium, the agreement between the approximate formula (eqn (5.31)) and the exact formula (eqn (2.9)) is also not good. The results are compared in Table 5.18 and Table 5.19 for sets of relative concentrations which satisfy some of our approximations and conditions we made to solve the master equation analytically. Note that some of the rate constants (k_r) are not available in Table 5.18 and Table 5.19 because the reaction was too endothermic for an accurate determination. The first and the third sets of concentrations of HBr, Cl and HCl make sure that the reaction is very far from equilibrium. The second set of concentrations of HBr, Cl and HCl is far from the equilibrium, but not at either extreme of Q/K_{eq} as in the other two cases. The disagreement between the analytical expression and the matrix technique is very large when the concentrations are set at the either extreme. But both techniques predict that the kinetic mass action law breaks down. When reaction is predominantly occuring from the right hand side k_f/k_r is greater than K_{eq}, and when reaction is predominantly occuring from the left side then k_f/k_r is less than K_{eq}. However, our analytical expression has to be modified. Before we do so we should examine the main approximations we made in the analytical approach.

5.8 Examination of the Approximations

5.8.1 $O_2 + H \rightleftharpoons OH + O$

In order to determine the source of the discrepancy noted above we must look at our main approximations in more detail. Upon close examination we first notice that the population of the vibrational level, m_* and n_*, contributing most to the reaction rate, is sometimes so suppressed that by virtue of the reaction itself, it no longer contributes most. In other words, the identity of m_* should be determined from the maximum of $Y_m k^f_m$ instead of from $Y_m^{eq} k^f_m$. Similarly, the identity of n_* should be determined from the maximum of $Z_n k^r{}_n$ instead of from $Z_n^{eq} k^r{}_n$. We also made the approximation that $m_*=1$ and $n_*=1$ instead of the more correct $m_*=0$ and $n_*=0$, in order to use the analytical expression. Thus k_f and k_r predicted by the analytical solution show larger suppressions from their equilibrium values than those that actually occur. We might get better results if we were to study a different reaction which does not have $m_*=0$ and $n_*=0$ as the critical levels. The second approximation is

$$\| \gamma - \frac{N_{AB}}{N_{BC}} \beta \| >> 1$$

This approximation states that our analytical solution of the steady-state master equation is valid for those reactions for which one of the rates is much larger than the other. We shall substitute for the γ, β and N_{AB}/N_{BC} in the above expression using the newly determined values of k_f and k_r, in order to see if this condition is satisfied; and the results are summarized in Table 5.20. We see from the above expression that the ratio N_{AB}/N_{BC} has to be very large. For our concentrations the condition is never satisfied. In other words when we thought that we were far away from equilibrium, we were not actually far enough from equilibrium for the above criterion actually to be satisfied. Let us test our analytical and matrix technique under conditions when this criterion is satisfied. The results are summarized in Table 5.21.

The matrix technique now shows a much larger non-equilibrium effect for this reaction. In this environment, $[O_2]$ is very small compared to the concentration of the other species present in the mixture. Now the k_r values of the two definition show very good agreement between themselves; but disagreement between the k_f values is still large. It looks as if the forward reaction is not playing any role and this amplifies the problem and is the reason why the two techniques do not agree with each other. The analytical results are better but still not in very good agreement with the exact results. Note that even though we satisfied the above approximation, we still did not simultaneously satisfy the complementary approximation ($|\beta - N_{BC}/ N_{AB} \gamma |/X >> 1$).

According to this approximation the difference between the two rates has to be larger than the rate of relaxation of OH. There are apparently no sets of concentrations which can satisfy both approximations simultaneously. Along with the problem in identifying a satisfactory value for m_* and n_* this leads us to conclude that our reaction is not an ideal choice to test our analytical expression.

Let us now look at our next major approximation made to solve the master equation:

$$\frac{(1-e^{-u}e^{m_* u}S_{m_*-1})}{k' Y_{m_*}^{eq} \sum_{i=1}^{m_*}} << |A-\kappa_T B| \quad and \quad \frac{\kappa_T(1-e^{-v}e^{n_* v}\sigma_{n_*-1})}{k'' Z_{n_*}^{eq} X \sum_{k=1}^{n_*}} << |A-\kappa_T B|$$

These approximations reduce to $1/\gamma e^{u} << |A - \kappa_T B|$ and $\kappa_T/X\beta e^{v} << |A - \kappa_T B|$. γ is a very small term; so unless κ_T is a very large term our approximations are not always valid here. These terms have to be included in the master equation for a better approximation. We shall not attempt to solve the master equation analytically with these terms included since the resulting expression is far too complicated to be of value. Hence, $H + O_2 \rightleftharpoons OH + O$ is not an ideal choice of reaction to test our analytical expression. $H + O_2 \rightleftharpoons OH + O$ was chosen for our calculation because this is the only reaction for which the microscopic state-to-state rate constants were available in the literature over a wide temperature range before we commenced this study.

5.8.2 HCl + Br $\rightleftharpoons$ HBr + Cl

Let us look at the main approximations for HCl + Br $\rightleftharpoons$ HBr + Cl reaction in greater detail. The first set of approximations are:

$$\|\gamma - \frac{N_{AB}}{N_{BC}}\beta\| >> 1 \qquad and \qquad \frac{1}{x}\|\beta - \frac{N_{BC}}{N_{AB}}\gamma\| >> 1$$

These approximations state that our analytical solution of the steady-state master equation is valid for those reactions for which one of the rates is much larger than the other. We substitute for the γ, β, X and N_{AB}/N_{BC} in the above expressions using the newly determined values of k_f and k_r, in order to see if these conditions are met. We see that our first set of concentrations for HBr, Cl and HCl satisfies the first approximation but not the second approximation. Our third set of concentrations for HBr, Cl and HCl satisfies the second approximation but not the first approximation. In other words, both sets of conditions can never be satisfied simultaneously for this reaction. Note that when first condition is satisfied the non-equilibrium factor is large and Q/K_{eq} is large, i.e. the reverse reaction dominates. When Q/K_{eq} is less than unity the non-equilibrium factor is small and the forward reaction then dominates the reaction. When the reverse reaction is dominant, the two different definitions of k_r (kinetic and dynamic) agree with each other while the two definitions of k_f do not agree with each other. When the forward reaction is dominant the two different definitions of k_f agree with each other while the two definitions of k_r do not agree with each other. This suggests that we should treat each reaction separately and ignore the opposite process in each case. Nevertheless, the opposite process does disturb the fractional populations of the reactant and the product. This leads us to conclude that this reaction is also not an ideal one to test our analytical expression. The analytical results for the second set of concentrations of HBr, Cl and HCl are not too bad compared to those of the matrix technique.

Let us look at our next major set of approximations made to solve the master equation analytically:

$$\frac{(1-e^{-u}e^{m_* u}S_{m_*-1})}{k' Y_{m_*}^{eq}\sum\limits_{i=1}^{m_*}} << |A-K_T B| \quad and \quad \frac{\kappa_T(1-e^{-v}e^{n_* v}\sigma_{n_*-1})}{k'' Z_{n_*}^{eq} X\sum\limits_{k=1}^{n_*}} << |A-K_T B|$$

When m_* and n_* are equal to 1 these terms exactly equal to zero. We cannot evaluate these terms when $m_* = 0$ and $n_* = 0$ because the summations are then undefined. When m_* is equal to 2 in the case of 1000 K, these terms cannot be ignored because they are very large compared to the A and B terms except when K_T is large. We shall have to include these terms for the temperatures that do not have critical levels equal to one. As we stated earlier, including these terms makes solution of the master equation too intractable analytically. For $H + O_2 \rightleftharpoons OH + O$ the critical levels had to be set to equal to 1, but they were really closer to zero. Hence for this reason these approximations could not be made. For $HCl + Br \rightleftharpoons HBr + Cl$ the critical levels were equal to one for most of the cases. Thus these terms can be ignored.

5.9 SUMMARY

We have solved the steady-state master equations for the reversible reaction, by analytical means. We have described how non-equilibrium population distributions lead to a depression of the rate coefficients for the disappearance of reagents in great excess. The main results of the chapter are generalized expressions for the thermal rates of bimolecular exchange reactions occuring under strongly non-equilibrium conditions:

$$rate = \frac{k_{eq}^{f}[BC][A] - k_{eq}^{r}[AB][C]}{(1 + \Phi + \varepsilon)} \qquad (case\ I)$$

$$rate = \frac{k_{eq}^{f}[BC][A]Z_{n_\bullet}^{eq}e^{v} - k_{eq}^{r}[AB][C]Y_{m_\bullet}^{eq}e^{u}}{Z_{n_\bullet}^{eq}Y_{m_\bullet}^{eq}e^{u+v}(1 + \frac{k'}{m_\bullet} + \frac{k''}{Xn_\bullet})} \qquad (case\ II)$$

The second problem we have investigated was the uncritical use of the mass-action law: $K_{eq} = k_f/k_r$. For the first case, the forward and reverse non-equilibrium effects cancel out; but for case II the forward and reverse non-equilibrium effects do not cancel out. In case II the magnitude of the non-equilibrium correction factor will vary from reaction to reaction and will depend on the chemical environment since k' and k'' depend on N_A, N_C and N_M. We have applied our analytical expressions to the $H + O_2 \rightleftharpoons OH + O$ reaction and to the $HCl + Br \rightleftharpoons HBr + Cl$. We have come to the conclusion that when reaction occurs close to equilibrium the non-equilibrium factor tends to unity even though the individual rate coefficients are sometimes suppressed from their equilibrium values and sometimes larger than their equilibrium values. When reaction occurs far from equilibrium, not only are the individual rate coefficients inflated but also the non-equilibrium factor is not unity.

The results from the analytical expression do not compare well with those of the matrix technique, when reaction occurs far from equilibrium, and we attribute this to the pathological nature of our chosen reactions ($m_* = 0$ and/ or $n_* = 0$). Physically the significance of $n_* = 0$ is that essentially only one product vibrational level is involved. It is the ground and the most populated one. This means that the reverse reaction need not be decomposed into its vibrational components. It is as if all the reagent levels always lead to an indistinct product. When far from equilibrium this is simply a unidirectional reaction. It is a problem which has already been addressed and solved by Teitelbaum. (In the present study we wanted to generalize the problem to include multiple product vibrational levels.) The solution to the simpler problem ($n_* = 0$, far from equilibrium) is simply $k_f / k_f^{eq} = 1/(1+\epsilon)$. The expression has been tested successfully for several reactions [1-5] and found to be in quite good agreement with numerical treatments. Therefore the analytical approach works. It is simply unfortunate that our two choices of reaction in the present study, as demonstrably non-equilibrium as they are, are pathological in the sense that $n_* = 0$, and that our more general expression cannot be tested. In retrospect, it is not surprising because our choices were made on the basis of importance and availability of reactive rate constants rather than on the basis of $n_* \neq 0$. Consequently, we shall devote the next chapter to a model study designed to identify those reactions which could be tested, at least in principle, once the state-to-state rate constants become available. We shall vary the fundamental vibration frequencies and k_{m-n} in such way as to vary m_* and n_* as well as vary the equilibrium constant, K_{eq}, the reagent and product concentrations and the energy transfer rate constants

Table 5.1 Reactivity data for $H + O_2 = OH + O$.

T/K	m*	n*	u	v	k^f_{m*} [a] $cm^3mol^{-1}s^{-1}$	k^r_{n*} [a] $cm^3mol^{-1}s^{-1}$	$k^f_{eq}/k^r_{eq}=K_{eq}$ [b]
2000	1	1	0.5669	1.3300	3.325(11)[c]	4.493(12)	0.2294
4000	1	1	0.2835	0.6650	4.867(12)	3.859(12)	1.5386
8000	1	1	0.1417	0.3325	1.322(13)	3.330(12)	2.8289

a) From ref. (1) and fig. 5.1 & 5.2 (see text). b) Obtained using thermodynamic and data from the JANAF tables c) 4.317(12) means 4.317 x 10^{12}.

Table 5.2 Relaxation data and concentrations used for $H + O_2 = OH + O$ in a bath of He

				[H]/[He]=0.001		[H]/[He]=0.1	
T/K	$[H]/[O_2]$ [a]	$[H]/[O]$ [a]	$[H]/[OH]$ [a]	$k^{BC}_{10}N_M/N_H$ [b,c]	X [d,e]	$k^{BC}_{10}N_M/N_H$ [b,c]	X [d,c]
2000	0.02794	0.34905	0.34905	4.4255(14)	2.0903	5.3480(13)	4.9499
4000	0.00695	0.06720	0.06720	4.2148(15)	0.7582	9.4777(14)	1.6796
8000	0.00403	0.03776	0.03776	3.4634(16)	0.4329	9.4878(15)	0.9540

[a] Calculated from a knowledge of K_{eq} in Table 5.1. [b] units of $cm^3mol^{-1}s^{-1}$. [c] Calculated using the data in Table 2.1 and eqn (2.10). [d] $X = k^{AB}_{10}/k^{BC}_{10}$. [e] Calculated using Table 2.1 and Table 2.2.

Table 5.3a Non-equilibrium factor for the $H + O_2 = OH + O$ reaction occurring close to equilibrium in a bath of He ([H]/[He]=0.001).

T/K	ϵ^a	Φ^a	$(1+\epsilon+\Phi)$	A^b	B^b	A/B
2000	0.001008	0.018365	1.019374	0.999998	1.000026	0.999972
4000	0.000974	0.027604	1.027604	0.999996	1.000116	0.999880
8000	0.000183	0.005343	1.005341	0.999998	1.000047	0.999952

[a] calculated using eqn (5.16). [b] calculated using eqn (5.20).

Table 5.3b Non-equilibrium factor for the $H + O_2 = OH + O$ reaction occurring close to equilibrium in a bath of He ([H]/[He]=0.1).

T/K	ϵ^a	Φ^a	$(1+\epsilon+\Phi)$	A^b	B^b	A/B
2000	0.008346	0.089129	1.097476	0.999988	1.000119	0.999869
4000	0.004334	0.055415	1.059749	0.999982	1.000226	0.999756
8000	0.000668	0.008850	1.009518	0.999994	1.000077	0.999917

[a] calculated using eqn (5.16). [b] calculated using eqn (5.20).

Table 5.4 Part 1: Non-equilibrium factor for the reaction H + O_2 = OH + O ocuring far from equilibrium in a He bath.

T/K	[H]/[OH]	[H]/[O]	[H]/[O_2]	k_f / k^{eq}_f [b]	k_r / k^{eq}_r [b]	Q / K_{eq}
2000[a]	1.0	1.0	1.0	1.47969	1.07636	1.37471
	0.1	1.0	1.0	1.48201	1.07805	1.37471
	0.01	1.0	1.0	1.48757	1.08210	1.37471
	1.0	0.1	1.0	1.40745	1.02381	1.37471
	1.0	0.01	1.0	1.11132	0.80841	1.37471
	1.0	1.0	0.1	1.48018	1.07673	1.37471
	1.0	1.0	0.01	1.48324	1.07890	1.37471
4000	1.0	1.0	1.0	2.36096	1.39120	1.69706
	0.1	1.0	1.0	2.36191	1.39177	1.69706
	0.01	1.0	1.0	2.36588	1.39411	1.69706
	1.0	0.1	1.0	2.36135	1.39144	1.69706
	1.0	0.01	1.0	2.02243	1.19172	1.69706
	1.0	1.0	0.1	2.36117	1.39133	1.69706
	1.0	1.0	0.01	2.36270	1.39223	1.69706
8000	1.0	1.0	1.0	4.16464	2.19836	1.89442
	0.1	1.0	1.0	4.16500	2.19856	1.89442
	0.01	1.0	1.0	4.16715	2.19969	1.89442
	1.0	0.1	1.0	4.12958	2.17986	1.89442
	1.0	0.01	1.0	3.85291	2.03381	1.89442
	1.0	1.0	0.1	4.16474	2.19842	1.89442
	1.0	1.0	0.01	4.16571	2.19893	1.89442

[a] All mixtures were diluted in a He bath ([H]/[He] = 0.001). [b] Calculated using eqn (5.31).

Table 5.4 Part 2: Non-equilibrium factor for the reaction $H + O_2 = OH + O$ occuring far from equilibrium in a He bath.

T/K	[H]/[OH]	[H]/[O]	$[H]/[O_2]$	A[b]	B[b]	A/B	Y_0/Y_0^{eq}	Z_0/Z_0^{eq}
2000[a]	1.0	1.0	1.0	1.4927	1.0793	1.3830	1.4915	1.0841
	0.1	1.0	1.0	1.5214	1.0789	1.4101	1.5064	1.0836
	0.01	1.0	1.0	1.6193	1.0824	1.4960	1.5706	1.0838
	1.0	0.1	1.0	1.5198	1.0264	1.4807	1.5016	1.0831
	1.0	0.01	1.0	1.5866	0.8095	1.9600	1.4779	1.1791
	1.0	1.0	0.1	1.4893	1.0977	1.3568	1.4899	1.0898
	1.0	1.0	0.01	1.4889	1.2106	1.2299	1.4898	1.1223
4000[a]								
	1.0	1.0	1.0	2.3677	1.4016	1.6892	2.3673	1.4004
	0.1	1.0	1.0	2.3789	1.3944	1.7060	2.3638	1.3961
	0.01	1.0	1.0	2.4424	1.3953	1.7505	2.3729	1.3961
	1.0	0.1	1.0	2.3788	1.3941	1.7063	2.3784	1.3960
	1.0	0.01	1.0	2.4319	1.1980	2.0299	2.2965	1.3622
	1.0	1.0	0.1	2.3666	1.4744	1.6051	2.3678	1.4414
	1.0	1.0	0.01	2.3665	1.9821	1.1939	2.3679	1.6847
8000[a]								
	1.0	1.0	1.0	4.1690	2.2108	1.8858	4.1683	2.2088
	0.1	1.0	1.0	4.1726	2.2001	1.8960	4.1614	2.2013
	0.01	1.0	1.0	4.1987	2.2006	1.9080	4.1349	2.2010
	1.0	0.1	1.0	4.1726	2.1920	1.9303	4.1606	2.1986
	1.0	0.01	1.0	4.1966	2.0435	2.0536	4.0907	2.1201
	1.0	1.0	0.1	4.1687	2.3098	1.8048	4.1691	2.2815
	1.0	1.0	0.01	4.1688	3.0625	1.3612	4.1692	2.7846

[a] All mixtures were diluted in a He bath ([H]/[He]=0.001. [b] Calculated using eqn (5.26)

Table 5.5 Part 1: Non-equilibrium factor for the reaction H + O_2 = OH + O ocuring far from equilibrium in a He bath.

T/K	[H]/[OH]	[H]/[O]	[H]/[O_2]	k_f / k^{eq}_f [b]	k_r / k^{eq}_r [b]	Q / K_{eq}
2000[a]	1.0	1.0	1.0	1.35383	0.98481	1.37471
	0.1	1.0	1.0	1.46075	1.06259	1.37471
	0.01	1.0	1.0	1.48680	1.08154	1.37471
	1.0	0.1	1.0	1.04492	0.76010	1.37471
	1.0	0.01	1.0	0.88219	0.64172	1.37471
	1.0	1.0	0.1	1.40187	1.01976	1.37471
	1.0	1.0	0.01	1.45829	1.06080	1.37471
4000	1.0	1.0	1.0	2.12466	1.25196	1.69706
	0.1	1.0	1.0	2.30773	1.35984	1.69706
	0.01	1.0	1.0	2.36238	1.39205	1.69706
	1.0	0.1	1.0	1.74876	1.03047	1.69706
	1.0	0.01	1.0	1.48817	0.87690	1.69706
	1.0	1.0	0.1	2.19997	1.29634	1.69706
	1.0	1.0	0.01	2.29936	1.35491	1.69706
8000	1.0	1.0	1.0	3.93259	2.07587	1.89442
	0.1	1.0	1.0	4.09652	2.16241	1.89442
	0.01	1.0	1.0	4.16107	2.19648	1.89442
	1.0	0.1	1.0	3.38155	1.78499	1.89442
	1.0	0.01	1.0	2.80909	1.48282	1.89442
	1.0	1.0	0.1	4.02240	2.12330	1.89442
	1.0	1.0	0.01	4.13421	2.18230	1.89442

[a] All mixtures were diluted in a He bath ([H]/[He] = 0.1). [b] Calculated using eqn (5.31).

Table 5.5 Part 2: Non-equilibrium factor for the reaction $H + O_2 \rightleftharpoons OH + O$ occuring far from equilibrium in a He bath.

T/K	[H]/[OH]	[H]/[O]	$[H]/[O_2]$	A[b]	B[b]	A/B	Y_0/Y_0^{eq}	Z_0/Z_0^{eq}
2000[a]	1.0	1.0	1.0	1.53443	1.02624	1.4951	1.5216	1.0925
	0.1	1.0	1.0	1.64766	1.06688	1.5444	1.5941	1.0831
	0.01	1.0	1.0	1.68047	1.08198	1.5531	1.6168	1.0838
	1.0	0.1	1.0	1.60281	0.77289	2.0737	1.4717	1.2482
	1.0	0.01	1.0	1.60306	0.64337	2.4916	1.3954	1.7574
	1.0	1.0	0.1	1.47591	1.18962	1.2407	1.4892	1.1239
	1.0	1.0	0.01	1.47193	1.37365	1.0716	1.4847	1.1612
4000[a]	1.0	1.0	1.0	2.30376	1.52753	1.5081	2.3008	1.4905
	0.1	1.0	1.0	2.46653	1.38427	1.7818	2.3814	1.3945
	0.01	1.0	1.0	2.53164	1.39465	1.8152	2.4221	1.3959
	1.0	0.1	1.0	2.44312	1.13730	2.1482	2.1974	1.4329
	1.0	0.01	1.0	2.47177	0.89204	2.7709	2.0528	1.5287
	1.0	1.0	0.1	2.27175	2.40075	0.9463	2.3145	1.8230
	1.0	1.0	0.01	2.31093	3.13541	0.7370	2.3362	2.0378
8000[a]	1.0	1.0	1.0	4.08927	2.51912	1.6233	4.0690	2.4409
	0.1	1.0	1.0	4.20535	2.19319	1.9174	4.1061	2.1990
	0.01	1.0	1.0	4.27055	2.19958	1.9415	4.1443	2.2005
	1.0	0.1	1.0	4.19930	2.01633	2.0826	3.9306	2.1704
	1.0	0.01	1.0	4.23813	1.52324	2.7823	3.6774	1.9354
	1.0	1.0	0.1	4.09300	4.11937	0.9936	4.1101	3.3570
	1.0	1.0	0.01	4.14588	5.48503	0.7558	4.1518	3.9648

[a] All mixtures were diluted in a He bath ([H]/[He]=0.1. [b] Calculated using eqn (5.26).

Table 5.6 Part 1: Comparison of the relative rate coefficients obtained from the analytical expression to those obtained by the matrix technique. Relative concentrations are set close to equilibrium as in Table 5.2. All mixtures were diluted in a He bath ([H]/[He] = 0.001).

	Analytical Expression				Matrix Technique			
	Forward		Reverse		Forward		Reverse	
T/K	k^f/k^f_{eq} [a]	k^f/k^f_{eq} [b]	k^r/k^r_{eq} [a]	k^r/k^r_{eq} [b]	k^f/k^f_{eq} [c]	k^f/k^f_{eq} [d]	k^r/k^r_{eq} [e]	k^r/k^r_{eq} [f]
2000	0.981	1.000	0.981	1.000	0.908	1.003	0.989	1.004
4000	0.972	1.000	0.972	1.000	0.981	1.002	0.981	1.000
8000	0.994	1.000	0.994	1.000	1.001	1.001	1.010	0.999

[a] Calculated using eq. (5.29). [b] Calculated using eq (5.20). [c] calculated using $\partial(\lambda k^{BC}_{1d}[H]/[OH])/\partial[OH]$ while keeping the concentration of [H], $[O_2]$ and [O] constant and where $\lambda = (k_f[H]/k^{BC}_{1d}[M] - k_r[O][OH]/k^{BC}_{1d}[M][O_2])$. [d] Calculated using $\sum_m k^f_m Y_m / \sum_m k^f_m Y^{eq}_m$ [e] Calculated using $([H]/[OH])^2 ([O_2]/[H])/([O]/[H])\partial(\lambda k^{BC}_{1d})/\partial[OH]$ while keeping the concentration of [H], $[O_2]$ and [O] constant. [f] Calculated using $\sum_n k^r_n Z_n / \sum_n k^r_n Z^{eq}_n$.

Table 5.6 Part 2: Comparison of the kinetic mass action law obtained from the analytical expression to that obtained by the matrix technique. Relative concentrations are set close to equilibrium as in Table 5.2. All mixtures were diluted in a He bath ([H]/[He] = 0.001).

	Analytical expression		Matrix Technique	
T/K	$(k_f/k_r)/K_{eq}$ [a]	$(k_f/k_r)/K_{eq}$	$(k_f/k_r)/K_{eq}$	$(k_f/k_r)/K_{eq}$
2000	1.0	1.0	0.918	1.002
4000	1.0	1.0	1.000	1.001
8000	1.0	1.0	0.991	1.002

[a] $K_{eq} = k^f_{eq} / k^r_{eq}$.

Table 5.7 Part 1: Comparison of the rate relative coefficients obtained from the analytical expression to those obtained by the matrix technique. Relative concentrations are set close to equilibrium as in Table 5.2 All mixtures were diluted in a He bath ([H]/[He] = 0.1).

	Analytical Expression				Matrix Technique			
	Forward		Reverse		Forward		Reverse	
T/K	k^f/k^f_{eq} [a]	k^f/k^f_{eq} [b]	k^r/k^r_{eq} [a]	k^r/k^r_{eq} [b]	k^f/k^f_{eq} [c]	k^f/k^f_{eq} [d]	k^r/k^r_{eq} [e]	k^r/k^r_{eq} [f]
2000	0.911	1.000	0.911	1.000	0.922	0.999	0.923	1.000
4000	0.943	1.000	0.943	1.000	0.876	0.999	0.878	1.000
8000	0.990	1.000	0.990	1.000	0.974	0.999	0.872	0.999

[a] Calculated using eq. (5.29). [b] Calculated using eq (5.20). [c] calculated using $\partial(\lambda k^{BC}_{10}[H]/[OH])/\partial[OH]$ while keeping the concentration of [H], $[O_2]$ and [O] constant and where $\lambda = (k_f[H]/k^{BC}_{10}[M] - k_r[O][OH]/k^{BC}_{10}[M][O_2])$. [d] Calculated using $\sum_m k^f_m Y_m / \sum_m k^f_m Y^{eq}_m$ [e] Calculated using $([H]/[OH])^2 ([O_2]/[H])/([O]/[H]) \partial(\lambda k^{BC}_{10})/\partial[OH]$ while keeping the concentration of [H], $[O_2]$ and [O] constant. [f] Calculated using $\sum_n k^r_n Z_n / \sum_n k^r_n Z^{eq}_n$.

Table 5.7 Part 2: Comparison of the kinetic mass action law obtained from the analytical expression to that obtained by the matrix technique. Relative concentrations are set close to equilibrium as in Table 5.2. All mixtures were diluted in a He bath ([A]/[He] = 0.1).

	Analytical expression		Matrix Technique	
T/K	$(k_f/k_r)/K_{eq}$ [a]	$(k_f/k_r)/K_{eq}$	$(k_f/k_r)/K_{eq}$	$(k_f/k_r)/K_{eq}$
2000	1.0	1.0	0.999	0.999
4000	1.0	1.0	0.998	0.999
8000	1.0	1.0	1.118	1.006

[a] $K_{eq} = k^f_{eq} / k^r_{eq}$.

Table 5.8 Part 1: Comparison of the relative rate coefficients obtained from the analytical expression to those obtained by the matrix technique. Relative concentrations are far from equilibrium: [H]/[O] = 1.0, 0.01 and 1.0; [H]/[O_2] = 1.0, 1.0 and 0.01; and [H]/ [OH] = 0.01, 1.0 and 1.0. All mixtures were diluted in a He bath ([H]/[He] = 0.001).

	Analytical Expression				Matrix Technique			
	Forward		Reverse		Forward		Reverse	
T/K	k^f/k^f_{eq} [a]	k^f/k^f_{eq} [b]	k^r/k^r_{eq} [a]	k^r/k^r_{eq} [b]	k^f/k^f_{eq} [c]	k^f/k^f_{eq} [d]	k^r/k^r_{eq} [e]	k^r/k^r_{eq} [f]
2000	1.487	1.619	1.082	1.082	1.972	2.146	1.000	1.000
	1.111	1.586	0.808	0.809	1.562	2.028	0.978	0.978
	1.483	1.488	1.078	1.210	0.985	0.987	0.980	1.007
4000	2.365	2.442	1.394	1.395	1.287	1.440	1.413	1.000
	2.022	2.431	1.191	1.198	1.083	1.375	0.963	0.967
	2.362	2.366	1.392	1.982	0.982	0.982	0.975	1.023
8000	4.167	4.198	2.199	2.200	0.820	1.170	0.990	0.999
	3.983	4.197	2.102	2.108	0.874	1.183	0.925	0.993
	4.167	4.168	2.199	2.619	0.989	0.989	0.961	1.021

[a] Calculated using eq. (5.31). [b] Calculated using eq (5.26). [c] Calculated using $\partial(\lambda k^{BC}_{1c}[H]/[OH])/\partial[OH]$ while keeping the concentration of [H], [O_2] and [H] constant and where $\lambda = (k_f[H]/k^{BC}_{1c}[M] - k_r[O][OH]/k^{BC}_{1c}[M][O_2])$. [d] Calculated using $\sum_m k^f_m Y_m / \sum_m k^f_m Y^{eq}_m$. [e] Calculated using $([H]/[OH])^2 ([O_2]/[H])/([O]/[H])\partial(\lambda k^{BC}_{1c})/\partial[OH]$ while keeping the concentration of [H], [O_2] and [O] constant. [f] Calculated using $\sum_n k^r_n Z_n / \sum_n k^r_n Z^{eq}_n$.

Table 5.8 Part 2 : Comparison of the kinetic mass action law obtained from the analytical expression to that obtained by the matrix technique. Relative concentrations are far from equilibrium: [H]/[O] = 1.0, 0.01 and 1.0; [H]/[O$_2$] = 1.0, 1.0 and 0.01; and [H]/ [OH] =0.01 1.0 and 1.0. All mixtures were diluted in a He bath ([H]/[He] = 0.001).

	Analytical expression		Matrix Technique	
T/K	$(k_f/k_r)/K_{eq}$ [a]	$(k_f/k_r)/K_{eq}$	$(k_f/k_r)/K_{eq}$	$(k_f/k_r)/K_{eq}$
2000	1.374	1.496	1.971	2.146
	1.374	1.960	1.597	2.073
	1.374	1.229	1.005	0.980
4000	1.697	1.750	0.910	1.440
	1.697	2.029	1.124	1.422
	1.697	1.193	1.007	0.960
8000	1.894	1.907	0.828	1.171
	1.894	1.990	0.944	1.191
	1.894	1.591	1.029	0.969

[a] $K_{eq} = k^f_{eq} / k^r_{eq}$.

Table 5.9 Part 1: Comparison of the relative rate coefficients obtained from the analytical expression to those obtained by the matrix technique. Relative concentrations are far from equilibrium: [H]/[O] = 1.0, 0.01 and 1.0; [H]/[O_2] = 1.0, 1.0 and 0.01; and [H]/ [OH] = 0.01, 1.0 and 1.0. All mixtures were diluted in a He bath ([H]/[He] = 0.1).

	Analytical Expression				Matrix Technique			
	Forward		Reverse		Forward		Reverse	
T/K	k^f/k^f_{eq} [a]	k^f/k^f_{eq} [b]	k^r/k^r_{eq} [a]	k^r/k^r_{eq} [b]	k^f/k^f_{eq} [c]	k^f/k^f_{eq} [d]	k^r/k^r_{eq} [e]	k^r/k^r_{eq} [f]
2000	1.486	1.680	1.081	1.081	2.387	2.323	1.001	0.999
	0.882	1.603	0.641	0.643	1.730	2.137	0.969	0.968
	1.458	1.471	1.060	1.373	0.848	0.883	0.414	1.005
4000	2.362	2.531	1.392	1.394	1.615	1.632	1.000	0.999
	1.481	2.471	0.876	0.892	1.582	3.497	0.749	0.778
	2.299	2.310	1.354	3.135	0.812	0.825	0.979	1.011
8000	4.153	4.270	2.192	2.195	1.350	1.306	1.003	0.998
	3.267	4.249	1.724	1.752	0.112	1.414	0.323	0.359
	4.141	4.145	2.186	3.331	0.913	0.918	0.512	1.028

[a] Calculated using eq. (5.31). [b] Calculated using eq (5.26). [c] Calculated using $\partial(\lambda k^{BC}_{1d}[H]/[OH])/\partial[OH]$ while keeping the concentration of [H], [O_2] and [H] constant and where $\lambda = (k_f[H]/k^{BC}_{1d}[M] - k_r[O][OH]/k^{BC}_{1d}[M][O_2])$. [d] Calculated using $\sum_m k^f{}_m Y_m / \sum_m k^f{}_m Y^{eq}{}_m$. [e] Calculated using $([H]/[OH])^2 ([O_2]/[H])/([O]/[H])\partial(\lambda k^{BC}{}_{1d})/\partial[OH]$ while keeping the concentration of [H], [O_2] and [O] constant. [f] Calculated using $\sum_n k^r{}_n Z_n / \sum_n k^r{}_n Z^{eq}{}_n$.

Table 5.9 Part 2 : Comparison of the kinetic mass action law obtained from the analytical expression to that obtained by the matrix technique. Relative concentrations are far from equilibrium: [H]/[O] = 1.0, 0.01 and 1.0; [H]/[O_2] = 1.0, 1.0 and 0.01; and [H]/ [OH] = 0.01, 1.0 and 1.0. All mixtures were diluted in a He bath ([H]/[He] = 0.1).

	Analytical expression		Matrix Technique	
T/K	$(k_f/k_r)/K_{eq}$ [a]	$(k_f/k_r)/K_{eq}$	$(k_f/k_r)/K_{eq}$	$(k_f/k_r)/K_{eq}$
2000	1.374	1.553	2.384	2.324
	1.374	2.491	1.786	2.206
	1.374	1.071	2.048	0.878
4000	1.697	1.815	1.614	1.633
	1.697	2.770	2.110	4.492
	1.697	0.737	0.979	0.816
8000	1.894	1.945	1.345	1.308
	1.894	2.424	0.346	3.932
	1.894	1.244	1.781	0.893

[a] $K_{eq} = k^f_{eq} / k^r_{eq}$.

Table 5.10 Reactivity data for $HCl(v') + Br \rightleftharpoons Cl + HBr(v)$.

T/K	m_* [a]	n_* [a]	u	v	k^f_{m*} $cm^3 molecule^{-1} s^{-1}$	k^r_{n*} $cm^3 molecule^{-1} s^{-1}$	$k^f_{eq}/k^r_{eq} = K_{eq}$ [b]
300	1	1	12.700	14.339	1.125×10^{-23}	4.688×10^{-13}	4.938×10^{-12}
500	1	1	7.620	8.604	6.456×10^{-19}	1.305×10^{-12}	1.928×10^{-7}
1000	2	1	3.810	4.302	9.464×10^{-13}	1.991×10^{-11}	5.470×10^{-4}
2000	1	1	1.900	2.151	9.726×10^{-14}	2.556×10^{-12}	3.128×10^{-2}
4000	1	1	0.952	1.075	5.436×10^{-13}	2.010×10^{-12}	0.2

[a] Fig. 5.3 and Fig. 5.4 (see text). [b] Calculated using data from ref (21).

Table 5.11 Relaxation data and concentrations used for $HCl(v') + Br \rightleftharpoons Cl + HBr(v)$ in a bath of Ar.

				[Br]/[He]=0.001		[Br]/[He]=0.01	
T/K	[Br]/[HCl] [a]	[Br]/[HBr] [a]	[Br]/[Cl] [a]	$k^{HCl}_{10}N_M/N_{Br}$ [b,c]	X [d,e]	$k^{HCl}_{10}N_M/N_{Br}$ [b,c]	X [d,e]
1000	0.09356	13.0805	13.0805	5.7843×10^{-12}	11.56	2.8143×10^{-11}	22.321
2000	0.06076	1.39378	1.39378	4.7448×10^{-11}	2.2531	2.8548×10^{-11}	2.6728
4000	0.02838	0.35666	0.35666	3.7792×10^{-10}	0.8913	2.9892×10^{-10}	0.5969

[a] Calculated from a knowledge of K_{eq} in Table 5.10. [b] units of $cm^3 molecule^{-1} s^{-1}$. [c] Calculated using the data in Table 4.1 and eqn (2.10). [d] $X = k^{HBr}_{10}/k^{HCl}_{10}$. [e] Calculated using Table 4.1 and Table 4.2.

Table 5.12 Non-equilibrium factor for the HCl (v') +Br ⇌ Cl + HBr(v) reaction occuring close to equilibrium in a bath of Ar ([Br]/[Ar]=0.001). Relative concentrations were set close to equilibrium as in Table 5.11.

T/K	ϵ^a	Φ^a	$(1+\epsilon+\Phi)$	A^b	B^b	A/B
1000	0.09890	0.08255	1.18146	0.99998	1.00001	0.99997
2000	0.00300	0.03927	1.04227	1.00000	1.00000	1.00000
4000	0.00168	0.02313	1.02481	1.00000	1.00000	1.00000

[a] calculated using eqn (5.16). [b] calculated using eqn (5.20).

Table 5.13 Non-equilibrium factor for the HCl (v') +Br ⇌ Cl + HBr(v) reaction occuring close to equilibrium in a bath of Ar ([Br/[Ar]=0.01). Relative concentrations were set close to equilibrium as in Table 5.11.

T/K	ϵ^a	Φ^a	$(1+\epsilon+\Phi)$	A^b	B^b	A/B
1000	0.20328	0.08792	1.29120	0.99997	1.00001	0.99995
2000	0.00499	0.05501	1.06000	1.00000	1.00000	1.00000
4000	0.00213	0.04367	1.04579	1.00000	1.00000	1.00000

[a] calculated using eqn (5.16). [b] calculated using eqn (5.20).

Table 5.14 Part 1: Non-equilibrium factor for the reaction HCl (v') +Br → Cl + HBr(v) occuring far from equilibrium in an Ar bath.

T/K	[Br]/[HBr]	[Br]/[Cl]	[Br]/[HCl]	Q/K_{eq}	k_f / k_f^{eq} [b]	k_r / k_r^{eq} [b]	$(k_f/k_r)/K_{eq}$
1000[a]	0.01	0.01	1.0	2.2067×10^{7}	2.36286	0.01671	141.436
	1.0	1.0	1.0	2206.7	31.3239	0.22147	141.436
	1.0	1.0	0.1	220.67	54.6595	0.38646	141.436
	1.0	1.0	0.01	22.067	73.0400	0.51642	141.436
	100	100	1.0	0.22067	76.9359	0.54396	141.436
	1000	100	1.0	0.022067	68.5296	0.48452	141.436
	100	1000	1.0	0.022067	69.1890	0.48453	141.436
	1000	1000	0.01	2.2067×10^{-5}	75.0425	0.53057	141.436
2000	0.01	0.01	1.0	3.19693×10^{5}	0.52097	0.33337	1.56274
	1.0	1.0	1.0	31.9690	1.28667	0.82334	1.56274
	1.0	1.0	0.1	3.19690	1.32064	0.84508	1.56274
	1.0	1.0	0.01	0.31969	1.35676	0.86819	1.56274
	100	100	1.0	0.0031969	1.35874	0.86946	1.56274
	1000	100	1.0	3.1969×10^{-4}	1.35874	0.86946	1.56274
	100	1000	1.0	3.1969×10^{-4}	1.35944	0.86991	1.56274
	1000	1000	0.01	3.1969×10^{-7}	1.36434	0.87304	1.56274
4000	0.01	0.01	1.0	50000	1.36452	1.15486	1.18154
	1.0	1.0	1.0	5	1.68368	1.42498	1.18154
	1.0	1.0	0.1	0.5	1.68922	1.42967	1.18154
	1.0	1.0	0.01	0.05	1.70236	1.44079	1.18154
	100	100	1.0	0.0005	1.69959	1.43845	1.18154
	1000	100	1.0	5.0×10^{-5}	1.69958	1.43844	1.18154
	100	1000	1.0	5.0×10^{-5}	1.69974	1.43857	1.18154
	1000	1000	0.01	5.0×10^{-8}	1.70805	1.44561	1.1815

[a] All mixtures were diluted in an Ar bath ([Br]/[Ar] = 0.001). [b] Calculated using eqn (5.31).

Table 5.14 Part 2: Non-equilibrium factor for the reaction HCl (v') + Br ⇌ Cl + HBr(v) occurring far from equilibrium in an Ar bath.

T/K	[Br]/[HBr]	[Br]/[Cl]	[Br]/[HCl]	A[b]	B[b]	A/B	Y_0/Y_c^{eq}	Z_c/Z_c^{eq}
1000[a]	0.01	0.01	1.0	229.528	0.01672	13728.89	3.7352×10^{-5}	7.2575×10^{-7}
	1.0	1.0	1.0	91.3397	0.25429	359.182	84.196	0.2209
	1.0	1.0	0.1	78.5336	0.51705	151.887	78.528	0.5117
	1.0	1.0	0.01	76.6988	0.71655	107.038	76.698	0.7164
	100	100	1.0	77.0532	1.18518	65.0134	77.053	1.1851
	1000	100	1.0	69.5640	57.0692	1.21894	69.564	54.808
	100	1000	1.0	69.2933	6.19365	11.1878	69.293	6.1909
	1000	1000	0.01	75.3991	19501.85	0.00387	75.399	0.0156
2000[a]	0.01	0.01	0.01	10.5182	0.33340	31.5481	0.0723	0.3899
	1.0	1.0	1.0	1.43791	0.82807	1.73645	1.3697	0.8852
	1.0	1.0	0.1	1.36849	0.86005	1.59117	1.3668	0.8820
	1.0	1.0	0.01	1.36466	0.89291	1.52834	1.3652	0.8807
	100	100	1.0	1.35956	1.12755	1.20577	1.3638	0.9290
	1000	100	1.0	1.35955	3.41700	0.39787	1.3638	1.0871
	100	1000	1.0	1.35953	1.28159	1.20508	1.3638	0.9290
	1000	1000	0.01	1.36439	150.6481	0.00906	1.3651	1.1890
4000[a]	0.01	0.01	0.01	11.6859	1.15509	10.1168	0.7111	1.3992
	1.0	1.0	1.0	1.73151	1.43565	1.20607	1.7252	1.4433
	1.0	1.0	0.1	1.70603	1.46715	1.16282	1.7081	1.4531
	1.0	1.0	0.01	1.70813	1.56939	1.08841	1.7087	1.4836
	100	100	1.0	1.69978	1.85011	0.91874	1.7053	1.5540
	1000	100	1.0	1.69977	5.48345	0.30998	1.7053	1.8871
	100	1000	1.0	1.69976	1.85030	0.91864	1.7053	1.5541
	1000	1000	0.01	1.70806	130.204	0.01311	1.7087	2.1176

[a] All mixtures were diluted in an Ar bath ([Br]/[Ar] = 0.001). [b] Calculated using eqn (5.26)

Table 5.15Part 1: Non-equilibrium factor for the reaction $HCl(v') + Br \rightarrow Cl + HBr(v)$ occuring far from equilibrium in an Ar bath.

T/K	[Br]/[HBr]	[Br]/[Cl]	[Br]/[HCl]	Q/K_{eq}	k_f / k_f^{eq} [b]	k_r / k_r^{eq} [b]	$(k_f/k_r)/K_{eq}$
1000[a]	0.01	0.01	1.0	2.2067×10^7	2.213379	0.01565	141.4363
	1.0	1.0	1.0	2206.7	25.06880	0.17724	141.4363
	1.0	1.0	0.1	220.67	53.05579	0.37512	141.4363
	1.0	1.0	0.01	22.067	72.80345	0.51474	141.4363
	100	100	1.0	0.22067	49.91774	0.35293	141.4363
	1000	100	1.0	0.022067	73.84080	0.52207	141.4363
	100	1000	1.0	0.022067	48.72309	0.34448	141.4363
	1000	1000	0.01	2.2067×10^5	74.68880	0.52807	141.4363
2000	0.01	0.01	0.01	3.19693×10^5	0.45347	0.29017	1.56274
	1.0	1.0	1.0	31.9690	1.13828	0.72838	1.56274
	1.0	1.0	0.1	3.19690	1.29431	0.82823	1.56274
	1.0	1.0	0.01	0.31969	1.35606	0.86775	1.56274
	100	100	1.0	0.0031969	1.32762	0.86954	1.56274
	1000	100	1.0	3.1969×10^{-4}	1.32752	0.84948	1.56274
	100	1000	1.0	3.1969×10^{-4}	1.32922	0.85057	1.56274
	1000	1000	0.01	3.1969×10^{-7}	1.36416	0.87293	1.56274
4000	0.01	0.01	0.01	50000	1.10493	0.935155	1.18154
	1.0	1.0	1.0	5	1.57865	1.33609	1.18154
	1.0	1.0	0.1	0.5	1.65033	1.39676	1.18154
	1.0	1.0	0.01	0.05	1.70011	1.43889	1.18154
	100	100	1.0	0.0005	1.65317	1.39916	1.18154
	1000	100	1.0	5.0×10^{-5}	1.65298	1.39001	1.18154
	100	1000	1.0	5.0×10^{-5}	1.65394	1.39981	1.18154
	1000	1000	0.01	5.0×10^{-8}	1.70790	1.44548	1.18154

[a] All mixtures were diluted in an Ar bath ([Br]/[Ar] = 0.01). [b] Calculated using eqn (5.31).

Table 5.15 Part 2: Non-equilibrium factor for the reaction HCl (v') +Br → Cl + HBr(v) occuring far from equilibrium in an Ar bath.

T/K	[Br]/[HBr]	[Br]/[Cl]	[Br]/[HCl]	A[b]	B[b]	A/B	Y_0/Y_0^{eq}	Z_C/Z_0^{eq}
1000[a]	0.01	0.01	1.0	220.385	0.01566	14072.0	3.1296 (-5)	2.8907 (-07)
	1.0	1.0	1.0	91.7603	0.21370	429.339	78.3132	0.16195
	1.0	1.0	0.1	78.6558	0.51515	152.684	78.6558	0.50892
	1.0	1.0	0.01	76.5123	0.71761	106.619	76.5123	0.71752
	100	100	1.0	51.0382	6.48192	7.87392	51.0382	6.47779
	1000	100	1.0	74.0019	9.33579	7.92668	74.0019	9.32743
	100	1000	1.0	48.8329	6.34869	7.69180	48.8329	6.34286
	1000	1000	0.01	74.6924	196.540	0.38003	74.69237	130.3082
2000[a]	0.01	0.01	0.01	9.46753	0.29020	32.623	0.0526	0.2230
	1.0	1.0	1.0	1.51214	0.74008	2.04320	1.29582	0.94143
	1.0	1.0	0.1	1.37076	0.85214	1.60859	1.36851	0.88772
	1.0	1.0	0.01	1.36455	0.89429	1.52583	1.36526	0.88120
	100	100	1.0	1.33049	1.74832	0.76101	1.35665	0.99707
	1000	100	1.0	1.33033	9.64034	0.13799	1.35653	1.12611
	100	1000	1.0	1.32951	1.75136	0.75912	1.35633	0.99738
	1000	1000	0.01	1.36422	187.602	0.00727	1.36508	1.18934
4000[a]	0.01	0.01	0.01	14.4001	0.93545	15.3938	0.41842	1.50361
	1.0	1.0	1.0	1.77979	1.38094	1.28882	1.72551	1.42984
	1.0	1.0	0.1	1.70341	1.51512	1.12427	1.70599	1.46682
	1.0	1.0	0.01	1.70341	1.61477	1.05773	1.70872	1.49613
	100	100	1.0	1.65444	4.21770	0.39226	1.68718	1.79865
	1000	100	1.0	1.65422	29.1872	0.05667	1.68709	2.01773
	100	1000	1.0	1.65406	4.21996	0.39196	1.67800	1.79992
	1000	1000	0.01	1.70791	78.4066	0.00957	1.70870	2.12049

[a] All mixtures were diluted in anAr bath ([Br]/[Ar]=0.01. [b] Calculated using eqn (5.26).

Table 5.16 Part 1: Comparison of the rate coefficients (cm^{3}molecule^{-1}s^{-1}) obtained from the analytical expression to those obtained by the matrix technique. Relative concentrations are set close to equilibrium as in Table 5.11. All mixtures were diluted in an Ar bath ([Br]/[Ar] = 0.001).

	Analytical Expression				Matrix Technique			
	Forward		Reverse		Forward		Reverse	
T/K	k^f/k^f_{eq} [a]	k^f/k^f_{eq} [b]	k^r/k^r_{eq} [a]	k^r/k^r_{eq} [b]	k^f/k^f_{eq} [c]	k^f/k^f_{eq} [d]	k^r/k^r_{eq} [e]	k^r/k^r_{eq} [f]
1000	0.846	0.999	0.846	1.000	0.342	0.842	0.340	1.000
2000	0.959	1.000	0.955	1.000	0.348	0.999	0.347	1.000
4000	0.975	1.000	0.975	1.000	0.588	0.950	0.587	1.001

[a] Calculated using eq. (5.29). [b] Calculated using eq (5.20). [c] calculated using $\partial(\lambda k^{HCl}_{1d}[Br]/[HBr])/\partial[HBr]$ while keeping the concentration of [Br], [HCl] and [Cl] constant and where $\lambda = (k_f[Br]/k^{HCl}_{1d}[M] - k_r[Cl][HBr]/k^{HCl}_{1d}[M][Br][HCl])$. [d] Calculated using $\sum_m k^f_m Y_m \,/\, \sum_m k^f_m Y^{eq}_m$ [e] Calculated using $([Br]/[HBr])^2\,([HCl]/[Br])/([Cl]/[Br])\partial(\lambda k^{HCl}_{1c})/\partial[HBr]$ while keeping the concentration of [Br], [HCl] and [Cl] constant. [f] Calculated using $\sum_n k^r_n Z_n/\sum_n k^r_n Z^{eq}_n$.

Table 5.16 Part 2: Comparison of k_f/k_r obtained from the analytical expression to that obtained by the matrix technique. Relative concentrations are set close to equilibrium as in Table 5.11. All mixtures were diluted in an Ar bath ([Br]/[Ar] = 0.001).

	Analytical expression		Matrix Technique	
T/K	$(k_f/k_r)/K_{eq}$ [a]	$(k_f/k_r)/K_{eq}$	$(k_f/k_r)/K_{eq}$	$(k_f/k_r)/K_{eq}$
1000	1.000	1.000	1.006	0.843
2000	1.000	1.000	1.003	1.000
4000	1.000	1.000	1.001	0.943

[a] $K_{eq} = k^f_{eq} / k^r_{eq}$.

Table 5.17 Part 1: Comparison of the rate coefficients (cm^{3}molecule^{-1}s^{-1}) obtained from the analytical expression to those obtained by the matrix technique. Relative concentrations are set close to equilibrium as in Table 5.11 All mixtures were diluted in an Ar bath ([Br]/[Ar] = 0.01).

	Analytical Expression				Matrix Technique			
	Forward		Reverse		Forward		Reverse	
T/K	k^f/k^f_{eq} [a]	k^f/k^f_{eq} [b]	k^r/k^r_{eq} [a]	k^r/k^r_{eq} [b]	k^f/k^f_{eq} [c]	k^f/k^f_{eq} [d]	k^r/k^r_{eq} [e]	k^r/k^r_{eq} [f]
1000	0.774	0.999	0.774	1.000	0.275	0.825	0.276	1.000
2000	0.943	1.000	0.943	1.000	0.266	0.997	0.267	1.000
4000	0.956	1.000	0.956	1.000	0.528	0.935	0.528	1.000

[a] Calculated using eq. (5.29). [b] Calculated using eq (5.20). [c] calculated using $\partial(\lambda k^{HCl}_{1d}[Br]/[HBr])/\partial[HBr]$ while keeping the concentration of [Br], [HCl] and [Cl] constant and where $\lambda = (k_f[Br]/k^{HCl}_{1d}[M] - k_r[Cl][HBr]/k^{HCl}_{1d}[M][Br][HCl])$. [d] Calculated using $\sum_m k^f_m Y_m / \sum_m k^f_m Y^{eq}_m$ [e] Calculated using $([Br]/[HBr])^2([HCl]/[Br])/([Cl]/[Br])\partial(\lambda k^{HCl}_{1d})/\partial[HBr]$ while keeping the concentration of [Br], [HCl] and [Cl] constant. [f] Calculated using $\sum_n k^r_n Z_n/\sum_n k^r_n Z^{eq}_n$.

Table 5.17 Part 2: Comparison of k_f/k_r obtained from the analytical expression to that obtained by the matrix technique. Relative concentrations are set close to equilibrium as in Table 5.11. All mixtures were diluted in an Ar bath ([Br]/[Ar] = 0.01).

	Analytical expression		Matrix Technique	
T/K	$(k_f/k_r)/K_{eq}$ [a]	$(k_f/k_r)/K_{eq}$	$(k_f/k_r)/K_{eq}$	$(k_f/k_r)/K_{eq}$
1000	1.00	0.99	0.99	0.82
2000	1.00	1.00	0.99	0.99
4000	1.00	1.00	0.99	0.93

[a] $K_{eq} = k_f^{eq} / k_r^{eq}$

Table 5.18 Part 1: Comparison of k_f/k_r obtained from the analytical expression to those obtained by the matrix technique. Relative concentrations are far from equilibrium: [Br]/[Cl] = 0.01, 1.0 and 1000; [Br]/[HCl] = 1.0, 0.01 and 0.01; and [Br]/ [HBr] = 0.01, 1.0 and 1000. All mixtures were diluted in an Ar bath ([Br]/[Ar] = 0.001).

		Analytical Expression				Matrix Technique			
		Forward		Reverse		Forward		Reverse	
T/K	Q/K_{eq}	k^f/k^f_{eq} [a]	k^f/k^f_{eq} [b]	k^r/k^r_{eq} [a]	k^r/k^r_{eq} [b]	k^f/k^f_{eq} [c]	k^f/k^f_{eq} [d]	k^r/k^r_{eq} [e]	k^r/k^r_{eq} [f]
1000	2.2067×10^7	2.362	229.5	0.016	0.016	357722	2905.56	0.394	0.374
	22.067	73.04	76.69	0.516	0.716	0.564	9.179	0.389	1.000
	2.2067×10^{-5}	75.04	75.39	0.530	19501.8	0.444	0.444	0.527	1.000
2000	3.1969×10^5	0.520	10.51	0.333	0.333	16681.1	49.61	0.332	0.280
	0.31969	1.356	1.364	0.868	0.893	0.573	7.108	0.570	1.001
	3.1969×10^{-7}	1.364	1.364	0.873	150.64	0.557	0.557	(N.A) [g]	1.006
4000	5.0×10^4	1.364	11.68	1.154	1.155	3757.70	6.482	0.442	0.344
	0.05	1.702	1.708	1.440	1.850	0.743	0.755	0.712	1.009
	5×10^{-8}	1.708	1.708	1.44	130.20	0.741	0.741	(N.A) [g]	1.011

[a] Calculated using eq. (5.31). [b] Calculated using eq (5.26). [c] Calculated using $\partial(\lambda k^{HCl}_{1c}[Br]/[HBr])/\partial[HBr]$ while keeping the concentrations of [Br], [HCl] and [Cl] constant and where $\lambda = (k_f[Br]/k^{HCl}_{1c}[M] - k_r[Cl][HBr]/k^{HCl}_{1c}[M][Br][HCl]$. [d] Calculated using $\sum_m k^f{}_m Y_m / \sum_m k^f{}_m Y^{eq}{}_m$. [e] Calculated using $([Br]/[HBr])^2 ([HCl]/[Br])/([Cl]/[Br])\partial(\lambda k^{HCl}{}_{1c})/\partial[HBr]$ while keeping the concentrations of [Br], [HCl] and [Cl] constant. [f] Calculated using $\sum_n k^r{}_n Z_n / \sum_n k^r{}_n Z^{eq}{}_n$. [g] Not available

Table 5.18 Part 2: Comparison of k_f/k_r obtained from the analytical expression to those obtained by the matrix technique. Relative concentrations are far from equilibrium: [Br]/[Cl] =0.01, 1.0 and 1000; [Br]/[HCl] = 1.0, 0.01 and 0.01; and [Br]/ [HBr] =0.01, 1.0 and 1000. All mixtures were diluted in an Ar bath ([Br]/[Ar] = 0.001).

		Analytical expression		Matrix Technique	
T/K	Q/K_{eq}[a]	$(k_f/k_r)/K_{eq}$	$(k_f/k_r)/K_{eq}$	$(k_f/k_r)/K_{eq}$	$(k_f/k_r)/K_{eq}$
1000	2.2067×10^{7}	141.43	13728.8	907247.6	7829.2
	22.067	141.43	107.03	1.069	9.179
	2.2067×10^{-5}	141.43	0.003	1.140	0.443
2000	3.1969×10^{5}	1.562	31.54	50110.9	176.94
	0.31969	1.562	1.528	1.005639	0.7100
	3.1969×10^{-7}	1.562	0.009	(N.A)[b]	0.554
4000	5.0×10^{4}	1.181	10.11	8492.7	19.00
	0.05	1.181	1.081	1.043	0.748
	5×10^{-8}	1.181	0.013	(N.A)[b]	0.771

[a] $K_{eq} = k^{f}_{eq} / k^{r}_{eq}$. [b] Not available

Table 5.19 Part 1: Comparison of k_f/k_r obtained from the analytical expression to those obtained by the matrix technique. Relative concentrations are far from equilibrium: [Br]/[Cl] = 0.01, 1.0 and 1000; [Br]/[HCl] = 1.0, 0.01 and 0.01; and [Br]/ [HBr] = 0.01, 1.0 and 1000. All mixtures were diluted in an Ar bath ([Br]/[Ar] = 0.01).

		Analytical Expression				Matrix Technique			
		Forward		Reverse		Forward		Reverse	
T/K	Q/K_{eq}	k^f/k^f_{eq} [a]	k^f/k^f_{eq} [b]	k^r/k^r_{eq} [a]	k^r/k^r_{eq} [b]	k^f/k^f_{eq} [c]	k^f/k^f_{eq} [d]	k^r/k^r_{eq} [e]	k^r/k^r_{eq} [f]
1000	2.2067×10^7	2.213	220.3	0.015	0.015	358227	2905.8	0.388	0.368
	22.067	72.80	76.51	0.514	0.717	0.544	9.582	0.505	0.999
	2.2067×10^{-5}	74.68	74.69	0.528	196.5	0.410	0.410	0.329	1.001
2000	3.1969×10^5	0.453	9.467	0.290	0.290	17101.1	49.63	0.313	0.259
	0.31969	1.356	1.364	0.867	0.894	0.540	0.688	0.538	1.001
	3.1969×10^{-7}	1.364	1.364	0.872	187.6	0.522	0.522	(N.A.) [g]	1.006
4000	5.0×10^4	1.104	14.40	0.93	0.935	4367.7	16.56	0.401	0.287
	0.05	1.700	1.703	1.43	1.614	0.722	0.734	0.684	1.010
	5×10^{-8}	1.707	1.707	1.44	78.40	0.719	0.719	(N.A.) [g]	1.012

[a] Calculated using eq. (5.31). [b] Calculated using eq (5.26). [c] Calculated using $\partial(\lambda k^{HCl}_{1c}[Br]/[HBr])/\partial[HBr]$ while keeping the concentrations of [Br], [HCl] and [Cl] constant and where $\lambda = (k_f[Br]/k^{HCl}_{1c}[M] - k_r[Cl][HBr]/k^{HCl}_{1c}[M][Br][HCl]$. [d] Calculated using $\sum_m k^f{}_m Y_m / \sum_m k^f{}_m Y^{eq}{}_m$. [e] Calculated using $([Br]/[HBr])^2 ([HCl]/[Br])/([Cl]/[Br])\partial(\lambda k^{HCl}{}_{1c})/\partial[HBr]$ while keeping the concentrations of [Br], [HCl] and [Cl] constant. [f] Calculated using $\sum_n k^r{}_n Z_n / \sum_n k^r{}_n Z^{eq}{}_n$. [g] Not available

Table 5.19 Part 2: Comparison of k_f/k_r obtained from the analytical expression to those obtained by the matrix technique. Relative concentrations are far from equilibrium: [Br]/[Cl] =0.01, 1.0 and 1000; [Br]/[HCl] = 1.0, 0.01 and 0.01; and [Br]/ [HBr] =0.01, 1.0 and 1000. All mixtures were diluted in an Ar bath ([Br]/[Ar] = 0.01).

		Analytical expression		Matrix Technique	
T/K	Q/K_{eq} [a]	$(k_f/k_r)/K_{eq}$	$(k_f/k_r)/K_{eq}$	$(k_f/k_r)/K_{eq}$	$(k_f/k_r)/K_{eq}$
1000	2.2067×10^7	141.43	14072	921747.9	7829.2
	22.067	141.43	106.61	1.077	9.561
	2.2067×10^{-5}	141.43	0.3800	1.244	0.410
2000	3.1969×10^5	1.562	32.623	54608	191.3
	0.31969	1.562	1.5258	1.005	0.687
	3.1969×10^{-7}	1.562	0.0072	(N.a.) [b]	0.519
4000	5.0×10^4	1.181	15.39	10875.7	22.08
	0.05	1.181	1.057	1.055	0.727
	5×10^{-8}	1.181	0.009	(N.a.) [b]	0.627

[a] $K_{eq} = k^f_{eq} / k^r_{eq}$. [b] Not available

Table 5.20 Evaluation of $(\gamma\text{-}\beta N_{AB}/N_{BC})$ for the reaction $O_2 + H = OH + O$ far from equilibrium.

T/K	[A]/[AB]	[A]/[C]	[A]/[BC]	γ^a	β^b	$(\gamma\text{-}N_{AB}N_C/N_{BC}N_A\beta)$
2000	1.0	1.0	1.0	0.0033	0.01423	-0.01094
	0.1	1.0	1.0	0.0008	0.0033	-0.03240
	0.01	1.0	1.0	8.865(-05)	0.0004	-0.03817
	1.0	0.1	1.0	0.0008	0.0033	-0.03240
	1.0	0.01	1.0	8.865(-05)	0.0004	-0.03817
	1.0	1.0	0.1	0.0032	0.1402	0.00185
	1.0	1.0	0.01	0.0028	0.0122	0.00269
4000	1.0	1.0	1.0	0.0121	0.0079	0.00423
	0.1	1.0	1.0	0.0036	0.0023	-0.01968
	0.01	1.0	1.0	0.0004	0.0003	-0.02839
	1.0	0.1	1.0	0.0036	0.0023	-0.01968
	1.0	0.01	1.0	0.0004	0.0003	-0.02839
	1.0	1.0	0.1	0.0112	0.0073	0.01044
	1.0	1.0	0.01	0.0062	0.0040	0.00616
8000	1.0	1.0	1.0	0.0046	0.0015	0.00308
	0.1	1.0	1.0	0.0017	0.0006	-0.00409
	0.01	1.0	1.0	0.0002	8.171(-5)	-0.00792
	1.0	0.1	1.0	0.0018	0.0006	-0.00409
	1.0	0.01	1.0	0.0002	8.171(-5)	-0.00792
	1.0	1.0	0.1	0.0036	0.0012	0.00345
	1.0	1.0	0.01	0.0011	0.0004	0.0010

[a] $\gamma = k^f_{m*} Y_{m*}/k^{BC}_{10}$. [b] $\beta = k^r_{n*} Z_{n*}/k^{BC}_{10}$.

Table 5.21 Part1: Comparison of the relative rate coefficients obtained from the analytical expression with those obtained by the matrix technique. The relative concentrations are set very far from equilibrium. [H]/[OH] = 1.0, [H]/[O] = 1.0, [H]/[He] = 0.1 and [H]/[O_2] = 1000.

	Analytical Expression				Matrix Technique			
	Forward		Reverse		Forward		Reverse	
T/K	k^f/k^f_{eq}[a]	k^f/k^f_{eq}[b]	k^r/k^r_{eq}[a]	k^r/k^r_{eq}[b]	k^f/k^f_{eq}[c]	k^f/k^f_{eq}[d]	k^r/k^r_{eq}[e]	k^r/k^r_{eq}[f]
2000	1.343	65.81	0.977	0.992	19.17	3.075	0.993	0.991
4000	2.239	45.91	1.319	1.386	11.36	2.009	0.989	0.982
8000	3.918	23.32	2.068	2.123	5.317	1.619	0.947	0.952
8000[g]	3.918	196.6	2.068	2.122	40.00[i]	1.628[i]	0.963[i]	0.952[i]

[a] Calculated using eq. (5.31). [b] Calculated using eq (5.20). [c] Calculated using $\partial(\lambda k^{BC}_{1d}[H]/[OH])/\partial[OH]$ while keeping the concentration of [H], [O_2] and [O] constant and where $\lambda = (k_f[H]/k^{O2}_{1d}[M] - k_r[O][OH]/k^{O2}_{1d}[M][O_2])$. [d] Calculated using $\sum_m k^f_m Y_m / \sum_m k^f_m Y^{eq}_m$. [e] Calculated using $([H]/[OH])^2 ([O_2]/[H])/([O]/[H])\partial(\lambda k^{BC}_{1d})/\partial[OH]$ while keeping the concentration of [H], [O_2] and [O] constant. [f] Calculated using $\sum_n k^r_n Z_n / \sum_n k^r_n Z^{eq}_n$. [g] The relative concentrations were: [H]/[OH] = 1.0, [H]/[O] = 1.0, [H]/[He] = 0.1 and [H]/[O_2] = 10000. [i] Partial derivatives were calculated using better precision.

Table 5.21 Part 2: Comparison of the kinetic mass action law obtained from the analytical expression to that obtained by the matrix technique. The relative concentrations are set very far from equilibrium. [H]/[OH] = 1.0, [H]/[O] = 1.0, [H]/[He] = 0.1 and [H]/[O_2] = 1000.

	Analytical expression		Matrix Technique	
T/K	$(k_f/k_r)/K_{eq}$[a]	$(k_f/k_r)/K_{eq}$	$(k_f/k_r)/K_{eq}$	$(k_f/k_r)/K_{eq}$
2000	1.374	66.32	19.29	3.102
4000	1.697	33.11	11.48	2.045
8000	1.894	10.98	5.613	1.704
8000[b]	1.894	92.61	41.52	1.709

[a] $K_{eq} = k_f^{eq}/k_r^{eq}$ [b] The relative concentrations are: [H]/[OH] = 1.0, [H]/[OH] = 1.0, [H]/[He] = 0.1 [H]/[O_2] = 10000.

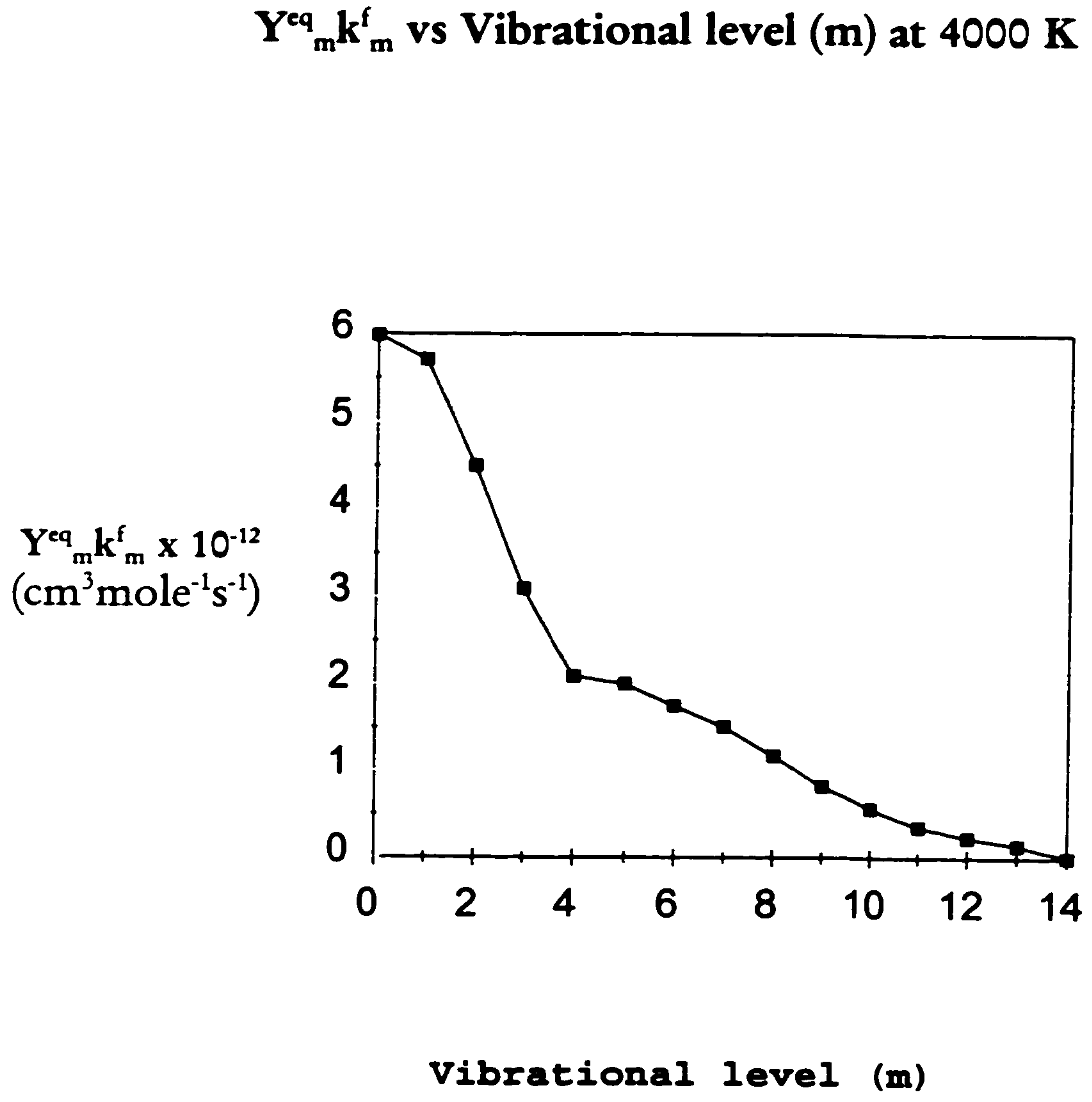
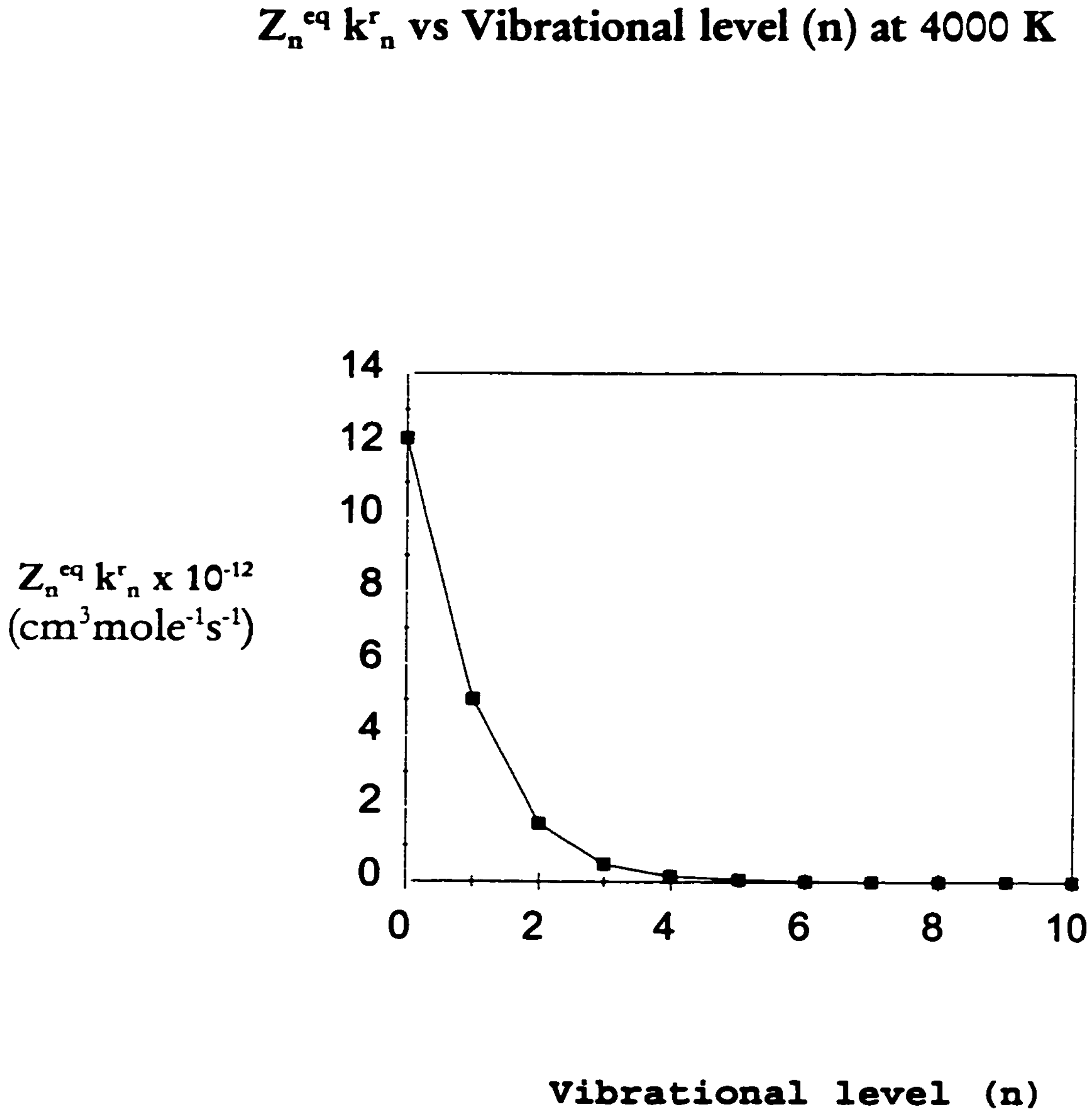


Fig. 5.1 Plot of $Y_m^{eq} k^f_m$ vs vibrational levels (m) for $O_2 (m) + H \rightarrow OH + O$.



$Z_n^{eq}\,k^r_n$ vs Vibrational level (n) at 4000 K

Fig. 5.2 Plot of $Z_n^{eq} k^r_n$ vs vibrational levels (n) for $OH(n) + O \rightarrow O_2 + H$.

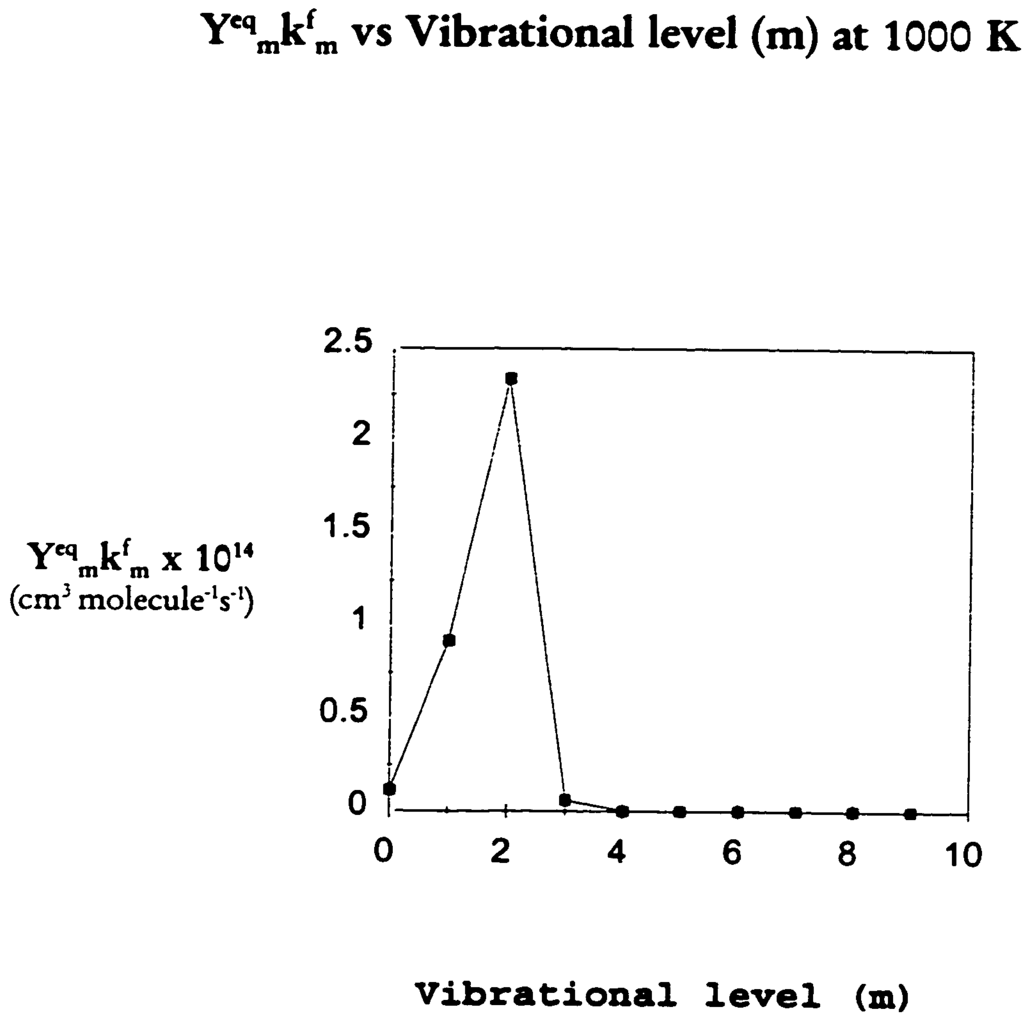


Fig. 5.3 $Y^{eq}_m k^f_m$ vs vibrational level (m) for the HCl (m) + Br → Cl + HBr reaction.

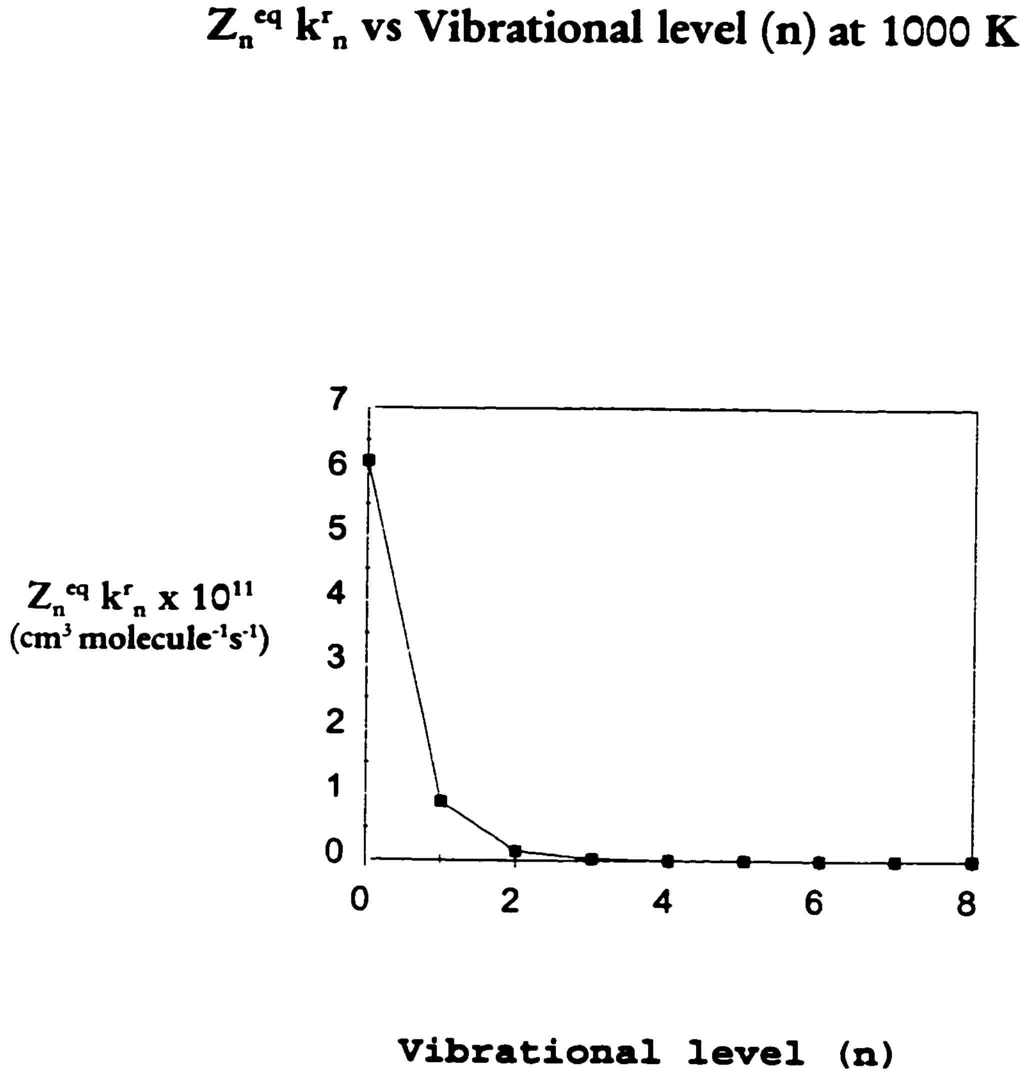


Fig. 5.4 Z_n^{eq} k^r_n vs vibrational level (n) for the Cl + HBr(n) → HCl + Br reaction.

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Chapter 6
Model Studies

6.1 Introduction

In this chapter shall search for the ideal type of reaction for which the necessary approximations are satisfied permitting us to test for agreement between our analytical expression and the numerical technique. One must be cautious that there might never be a perfect agreement between the two methods because in the numerical technique the reaction is allowed to take place from any vibrational level of the reagent to any vibrational level of the product; whereas in the analytical expression reaction is allowed from the most important level of the reagent to the most important level of the products. Nevertheless, kineticists would be satisfied with a useable expression giving an error of say 20% compared with the current potential for 1000%. Our job here is to first build a 15-parameters model and then later identify the parameters of the model reaction which makes the two techniques agree. Then from the best parameters we can identify the types of real reactions in nature for which we can use the improved rate law.

6.2 Model Reaction

$$k_{v'v} = A(v')^2 e^{-b/v} e^{-c'v} \qquad (6.1)$$

The first step is to construct a set of reactive rate constants $k_{vv'}$ of the form

Here A is a constant which can be set equal to 1 because it is only ratios of rate constants which are important. b and c are parameters we are going to vary. Eq. (6.1) is of sufficiently general form to allow $k_{vv'}$ to increase or decrease with respect to v and v' (depending on the sign of b and c), and it contains the minimum number of parameters needed to mimic the combined prior statistical and exponential gap behaviours expected in real systems. Normally b>0 and c >0 , but we are going to vary b and c from -8 to 8. The reason we are varying b and c over such a large range is that so we can cover all possible reactions. The second step is to construct model molecules BC and AB, ie choose the fundamental frequency ω_e for each. This determines the steepness of the Boltzmann distributions for the reagent, y_v^{eq} , and for the product, $z_{v'}^{eq}$ ignoring anharmonicity. The Boltzmann distribution for the reagent y_v^{eq} is proportional to e^{-u} and the Boltzmann distribution for the product $z_{v'}^{eq}$ is proportional to e^{-v}, where $u = h\nu^{BC}/k_BT$ and $v = h\nu^{AB}/k_BT$. We are going to vary u and v from 10 to 0.5. In this way we do not need to know the exact values of the temperature and frequencies. We discover that when u = 0.5, 1 and 2, the critical level m. can be non-zero. So our standard reaction is going to have these parameters. We then used microscopic reversibility to find $k_{v'v}$, ie $z_{v'}^{eq} k_{v'v} = C\, y_v^{eq} k_{vv'}$ where C is $1/K_{eq}$. We now have two more parameters (C and $v = h\nu^{AB}/k_BT$)to vary. The values of C chosen are 0.01, 1, and 100 representing exothermic, thermoneutral and endothermic reactions respectively; and values of v are 0.5, 1 and 2 (same as for u). Note that $\sum_v Z_{v'}^{eq} k_{v'v} = Z_{v'}^{eq} \sum_v k_{v'v}$. This is simply $Z_{v'}^{eq} k_{v'}$, ie the reverse reactive flux from level v'. Microscopic reversibility shows that this is also $\sum_v CY_v^{eq} e^{-b/v'} v'^2 e^{-cv'} \propto v'^2 e^{-cv'}$. The maximum contribution to the flux is thus determined uniquely at level n. = 2/c, whereas m. is determined by both b and u. Thus a minimum of 5 parameters: b, c, C, u and v are needed to fix the reactivity.

The next step was to construct non-reactive rate constants, ie k_{10}^{BC} and k_{10}^{AB} for various collision partners. We have to make energy transfer processes less probable than reactive processes for a non-equilibrium condition to be satisfied. We varied the $k_{10}^{BC\text{-}BC}$ to equal $0.01k_0$, $0.1k_0$, $1k_0$ and $100k_0$, where k_0 is the rate coefficient for forward reaction taking place from v=0. In this way we have made sure that sometimes the reaction is the dominant processes and sometimes energy transfer is the dominant process. The relative collision efficiencies of A, AB, C and He were also varied to be 0.01, 1, and 100 times that of BC. The next step was to construct $k_{10}^{AB\text{-}BC}$. We varied $k_{10}^{AB\text{-}BC}$ to equal 0.1 $k_{10}^{BC\text{-}BC}$, 1 $k_{10}^{BC\text{-}BC}$ and $100k_{10}^{BC\text{-}BC}$. In this way, sometimes BC relaxes more quickly and sometimes AB does. These 6 additional parameters fix the relaxation behaviour. Finally the concentration ratios [A]/[AB], [A]/[BC], [A]/[C] and [A]/[He] could be varied. Together with the $k_{vv'}$ they determine the reaction rate. While together with the k_{10} they determine the relaxation rates. An interesting combination, QC= [AB][C]/([A][AB]K_{eq}), expresses the extent from equilibrium. The concentration ratios were also varied to be 0.01, 1 and 100.

Our standard reaction has the following parameters: b=8, c=1, u=0.5, v=0.5, C=1.01, $k_{10}^{BC\text{-}BC}$ = $0.01k_0$, relative collision efficiencies of unity, and $k_{10}^{AB} = 1k_{10}^{BC}$ as well as [A]=[AB]=[BC]=[He] = [C]. The conditions are such that QC = 1.01 which means that initially the reaction was close to equilibrium with the reverse reaction slightly dominating. Then we varied each parameter as stated above.

6.3 The matrix technique applied to the model reaction

Once we constructed all the $k_{vv'}$ and $k_{v'v}$ for our standard reaction and for other cases we applied our matrix technique. Results are summarized in Figs. 6.1 to 6.15. From Fig. 6.1 one can see that, a non-equilibrium effect exists only when $b > 0$ ie when vibrational energy enhances reactivity . The effects are small in the forward direction because one is close to equilibrium. They are even smaller for the reverse reaction because $c=1$, ie reactivity enhancement of AB < reactivity enhancement of BC non zero.

From Fig. 6.2 one can see that, c determines how vibration enhances or inhibits reactivity for the reverse reaction. $n_* = 2/c$. Clearly as c decreases higher and higher vibrational levels of AB become more important. The reverse reaction becomes suppressed, and k_f/k_r becomes much larger than expected. This time the reactivity enhancement of AB by vibration is greater than that of BC. Therefore the reverse reaction is affected more than the forward reaction is.

When u is increased the k_r/k_r^{eq} remain unchanged for standard c, but values of k_f/k_f^{eq} and the non-equilibrium factor increase (Fig. 6.3). When u is increased the Boltzmann distribution is made steeper. Thus most of the equilibrium population of BC is in the ground level. Less is excited. For this reaction at our reference conditions $Q/Keq > 1$, which means that the reverse reaction is dominating. The reverse reaction is leaving BC molecules in excited vibrational levels. Thus the Boltzmann distribution is skewed. This leads to slight inflation of k_f values. However k_f^{eq} becomes smaller; hence K/K_{eq} becomes larger. When v is increased the trends for k_r/k_r^{eq}, k_f/k_f^{eq} and the non-equilibrium factor are switched with those trends when u is increased (Fig. 6.4). Then the product's Boltzmann distribution is made steeper and most of the reactants are in the ground level at equilibrium, leaving less in excited states. Thus k_r^{eq} decreases. k_r/k_r^{eq} increases; and hence K/K_{eq} decreases.

When the parameter C ($1/K_{eq}$) is increased dramatic effects are observed. k_f/k_f^{eq} and the non-equilibrium factor increase, while k_r/k_r^{eq} decreases (Fig 6.5). This is understandable because the extent from equilibrium increases and the reverse reaction flux increases, thus causing k_f to inflate and causing k_r to be suppressed. This is further supported by the variations discussed below. Interesting results occur when C=1 exactly. Both k_f/k_f^{eq} and k_r/k_r^{eq} are unity. This situation is essentially a thermoneutral reaction. Here forward and reverse process are in perfect equilibrium since Q=1.

Deviation from equilibrium can also be achieved by adjusting concentrations. When [AB] or [C] is decreased, $k_r/k_r^{eq\ q}$ values increase while k_f/k_f^{eq} and the non-equilibrium factor decrease. When [AB] or [C] is large, the reverse reaction dominates. Thus k_f are inflated from their equilibrium values while k_r is suppressed. When [AB] or [C] is small k_f value is suppressed and k_r is inflated because then the forward reaction dominates. This is further supported by Fig 6.9 where we see that when [BC] is decreased the effect is the same as when [AB] is increased. Decreasing [He] has little effect on the reverse reaction but it does cause k_f values to be less inflated and also decreases the non-equilibrium factor, K/K_{eq}. The role of He is as an energy transfer agent. Reducing its amount causes the forward reaction rate to increase, thus reducing the overpopulation of BC (under conditions where the reverse reaction dominates).

In general when k_{10}^{BC} is increased either by increasing $k_{10}^{BC\text{-}BC}$ or by increasing the energy transfer rate constants of other collisions partners ($k_{10}^{BC\text{-}A}$ or $k_{10}^{BC\text{-}C}$ or $k_{10}^{BC\text{-}He}$ or $k_{10}^{BC\text{-}AB}$), k_r/k_r^{eq} remains unchanged while k_f/k_f^{eq} and the non-equilibrium factor decrease slightly. That k_r/k_r^{eq} remains unchanged is understandable since we are increasing the energy transfer rates for BC molecules only, which should not affect the reverse reaction. The non-equilibrium factor decreases because k_f/k_f^{eq} decreases: When the energy transfer rate is increased, the distorted molecular populations of higher vibrational levels are replenished more quickly. Hence the non-equilibrium effect is moderated. However when k_{10}^{AB} is increased, k_r/k_r^{eq} still remains unchanged, while k_f/k_f^{eq} and the non-equilibrium factor increase: When k_{10}^{AB} is increased AB molecules depleted in higher vibrational levels would normally be replenished. However it happens that for our set of standard parameters, $k_r/k_r^{eq} \approx 1$ already. Improving energy transfer rates will therefore not have much of an effect. The reverse reaction at the same time is leaving BC molecules in important vibrational levels, thus causing k_f values to inflate from their equilibrium value. Because b=8 and c=1 only, the effect on the forward rate coefficient is more dramatic than on the reverse reaction's.

The behaviour observed in Figs. 6.6 to 6.9 indicates to us that a more universal parameter might be Q=[C][AB]/[BC][A]. Therefore in Fig. 6.16 we plotted k_f/k_f^{eq} , k_r/k_r^{eq} and $(k_f/k_f^{eq}/\ k_r/k_r^{eq})$ vs Q/K_{eq}. Q/K_{eq} measures how far we are from equilibrium in either direction. We see that when $Q/K_{eq} > 1$, ie when the reverse reaction dominates the non-equilibrium factor is large, k_r is suppressed and k_f is inflated from their equilibrium values. When $Q/K_{eq} < 1$, ie when the forward reaction dominates the non-equilibrium factor is small, k_f is suppressed and k_r is inflated form their equilibrium values. Apparently, it is always the population of those highly excited molecules associated with the dominant reaction which are depleted while those of its counterpart are always inflated. As the departure from equilibrium increases in favour of the reverse reaction (k_f/k_r) becomes increasingly larger than K_{eq}. As the departure from equilibrium increases in favour of the forward reaction (k_f / k_r) becomes increasingly smaller than K_{eq}. How severe this general principle is depends on the values of the reactive and energy transfer parameters - the most sensitive being b, c, and C.

6.4 Comparison between the numerical solution and the analytical expression for the model reaction

In this section we compare the matrix technique with the analytical expression to see for which set of parameters the analytical expression is valid. Over 60 calculations were carried out. However, only representative results are shown in order to illustrate our main points. Analytical results are considered good, if they differ from those obtained by the matrix technique by less than 5%. The results are summarized in Table 6.1. One can see that agreement between the analytical expression and matrix technique is good when all our conditions are obeyed. Our first set of conditions was that m. and n. have to be greater than 0. (When n. is zero one may apply the simpler Teitelbaum expression [1]). Our next set of conditions are $|\gamma\text{-}N_{AB}/N_{BC}\,\beta| >>1$ and $|\beta - N_{BC}/N_{AB}\,\gamma| >> X$. These two conditions have to be satisfied simultaneously. Those model reactions which gave good results satisfied these two restrictions. According to Table 6.1 these approximations seem to mean that only reactions with $C\approx 1$ are the one's which give good agreement between the two techniques. When C is equal to one the reaction is essentially thermonetural (see below). Our chosen reactions:

$H + O_2 \rightleftharpoons OH + H$ and $HCl + Br \rightleftharpoons HBr + Cl$ did not satisfy the requirement that n. > 0, and also the value of C was not approximately equal to one except at high enough temperatures where $K_{eq} \rightarrow 1$. Now, however, we are in a position to identify real reactions which will be described by our analytical expression. Physically they corresponds to reactions for which $|\Delta G^0| << RT$. For bimolecular exchange reactions $\Delta S^0 \approx 0$. Therefore, this means that $|\Delta H^0| << RT$, ie the reaction should be thermoneutral. That m* and n* >0 requires vibrational enhancement of forward and reverse reactions, ie b>>1 and 0<c<2. Information theory teaches us that such dramatic enhancement occurs only when $|\delta| >> 0$, ie when $\Delta E_0 >> RT$. In other words, there must be a high barrier to reaction.

6.5 Summary

We have shown that our analytical expression is valid when all our major approximations are satisfied. The $H + O_2$ and $Br + HCl$ reactions did not satisfy the approximations necessary to test our expression. However, there is hope that when sufficient data become available for identifiable reactions our predictions can be tested in the lab. Most importantly we have shown that the kinetic mass action law is not valid in general under reactive conditions far from equilibrium even for those reactions for which our analytical expression cannot be used. This is a result which has far-reaching consequences for chemical kinetics.

Table 6.1 Part Comparison of Matrix Technique with Analytical expression

								Matrix Technique			Analytical Expression		
b	c	u	v	C	m.	n.	Q	K/K_{eq}	k_f/k_f^{eq}	k_r/k_r^{eq}	K/K_{eq}	k_f/k_f^{eq}	k_r/k_r^{eq}
2	1	0.5	0.5	1	2	2	1	0.9998	1.0001	1.0003	0.9981	0.9984	1.0003
8	2	0.5	0.5	1	4	1	1	3.8514	1.1521	0.2991	3.6588	1.1520	0.3148
8	1	2.0	0.5	1	2	2	1	1.0972	1.0974	1.0002	1.1301	1.1315	1.0012
8	1	0.5	2.0	1	4	2	1	0.9766	0.9791	1.0026	1.0254	0.9789	0.9546
8	1	0.5	0.5	0.01	4	2	1	0.0099	0.0099	1.0006	1.0263	11.156	10.870
8	1	0.5	0.5	100	4	2	1	17.452	3.9787	0.2279	177.52	3.4561	0.0194

Table 6.1 Part 2 Comparison of Matrix Technique with Analytical expression

$(\gamma - N_{AB}/N_{BC}\,\beta) >> 1$	$(\beta - N_{BC}/N_{AB}\,\gamma) >> X$
2913432.031	- 2913432.031
-9.406347826	9.406347826
-3580504.998	3580504.998
328520.7809	-328520.7809
17.2341	0.00124
0.00124	-17.2341

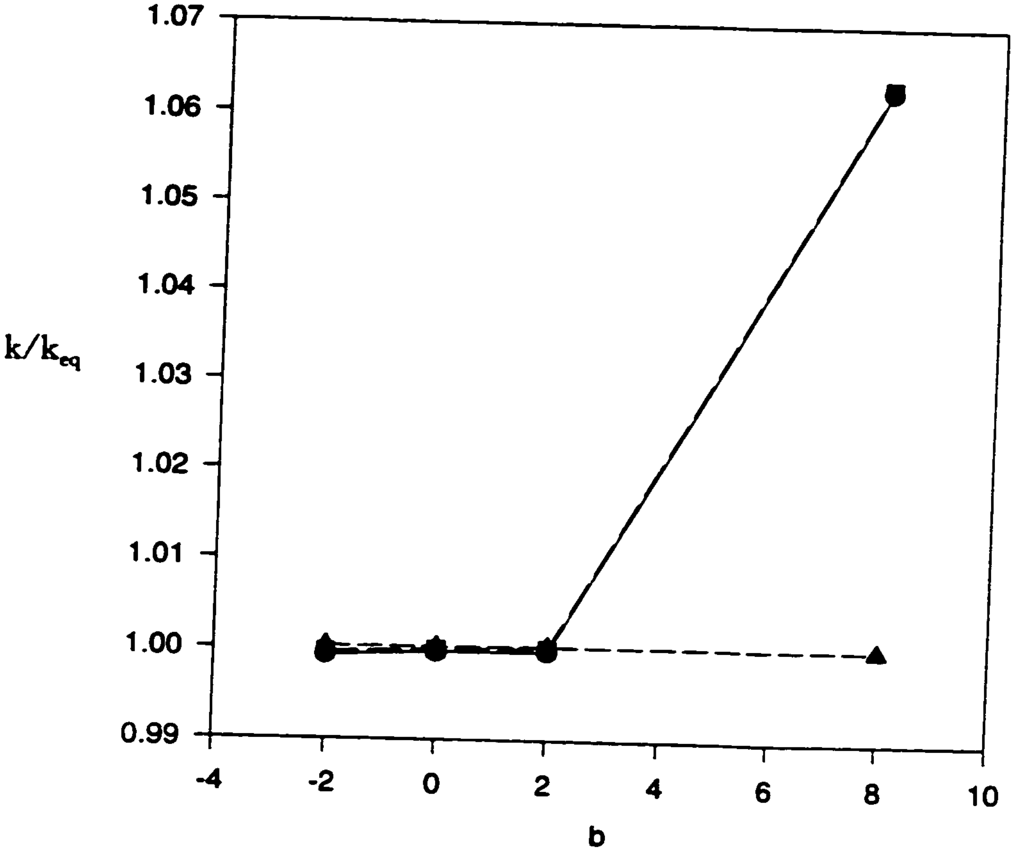

Figure 6.1: The ratio of k/k_{eq} vs. b, while keeping other parameters constant. ■ is for K/K_{eq}. ● is for k_f/k_f^{eq}. ▲ is for k_r/k_r^{eq}.

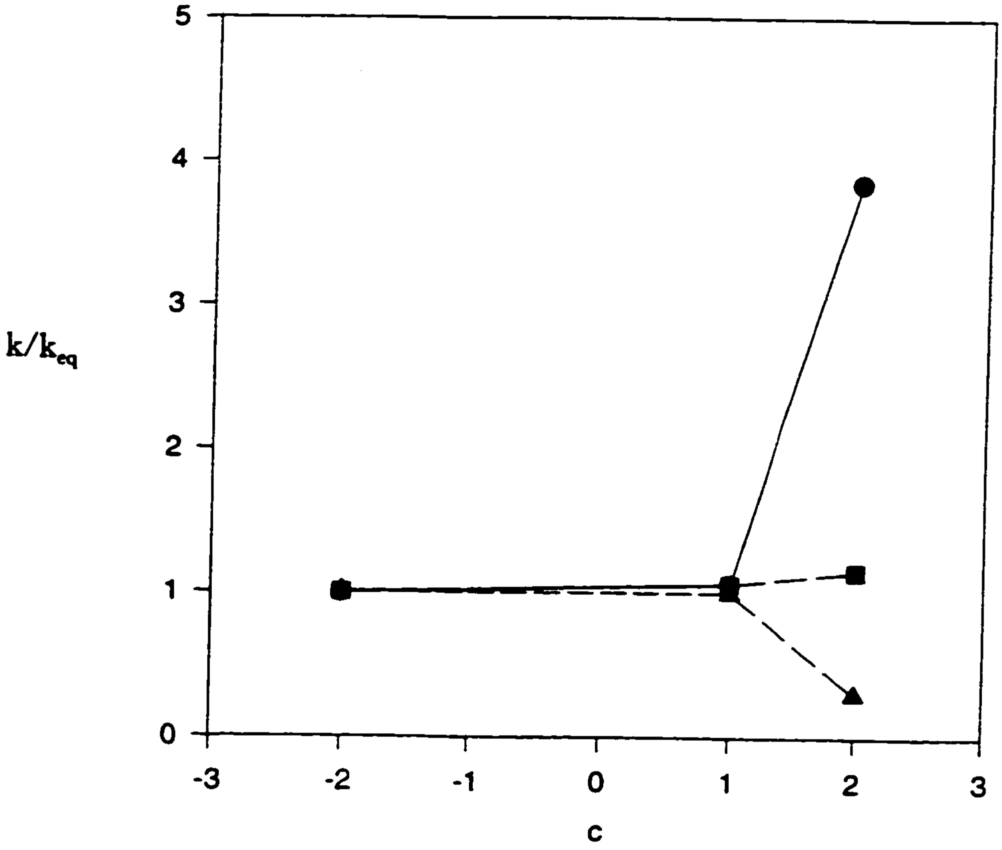

Figure 6.2: The ratio of k/k_{eq} vs. C, while keeping other parameters constant. ■ is for K/K_{eq}. ● is for k_f/k_f^{eq}. ▲ is for k_r/k_r^{eq}.

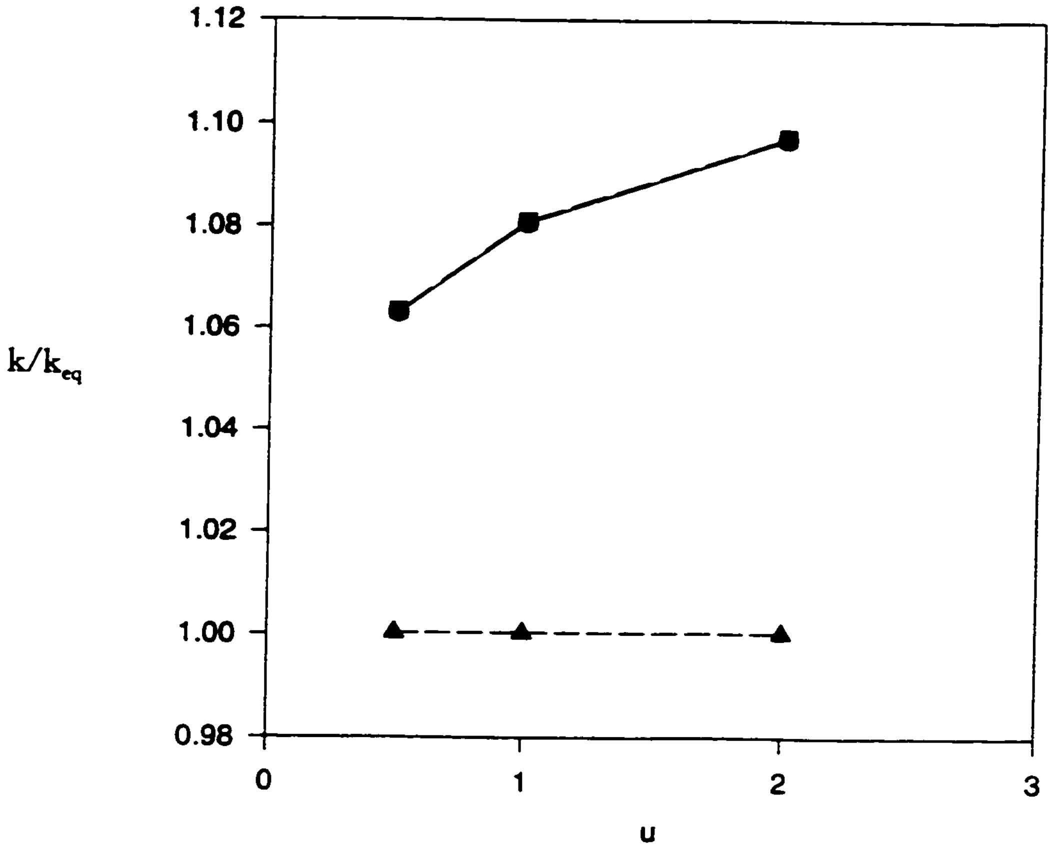

Figure 6.3: The ratio of k/k_{eq} vs. u, while keeping other parameters constant. ■ is for K/K_{eq}. ● is for k_f/k_f^{eq}. ▲ is for k_r/k_r^{eq}.

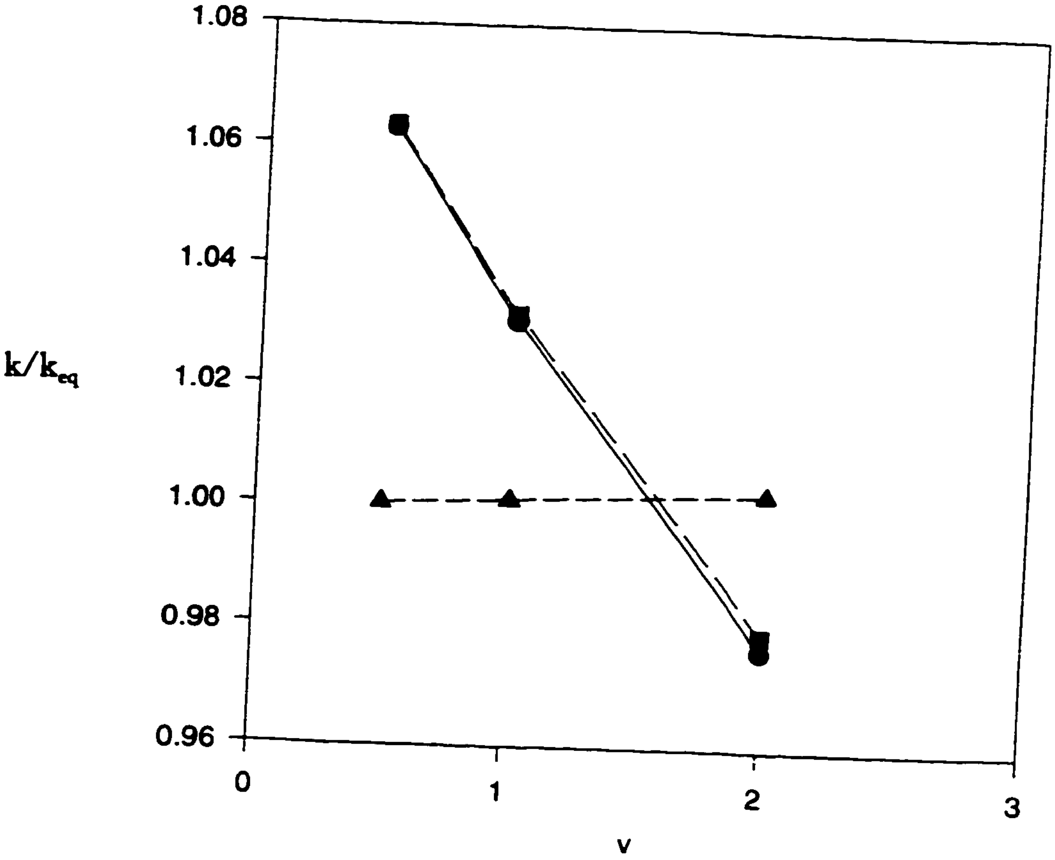

Figure 6.4: The ratio of k/k_{eq} vs. u, while keeping other parameters constant. ■ is for K/K_{eq}. ● is for k_f/k_f^{eq}. ▲ is for k_r/k_r^{eq}.

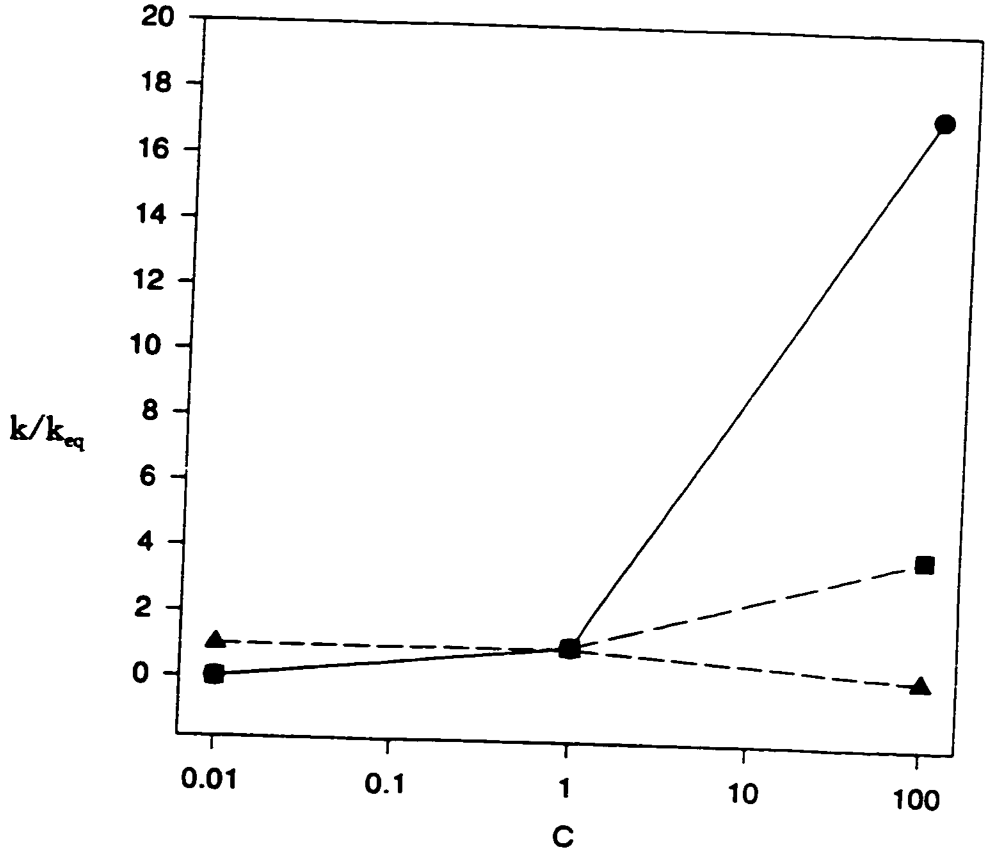

Figure 6.5: The ratio of k/k_{eq} vs. C, while keeping other parameters constant. ■ is for K/K_{eq}. ● is for k_f/k_f^{eq} .▲ is for k_r/k_r^{eq}.

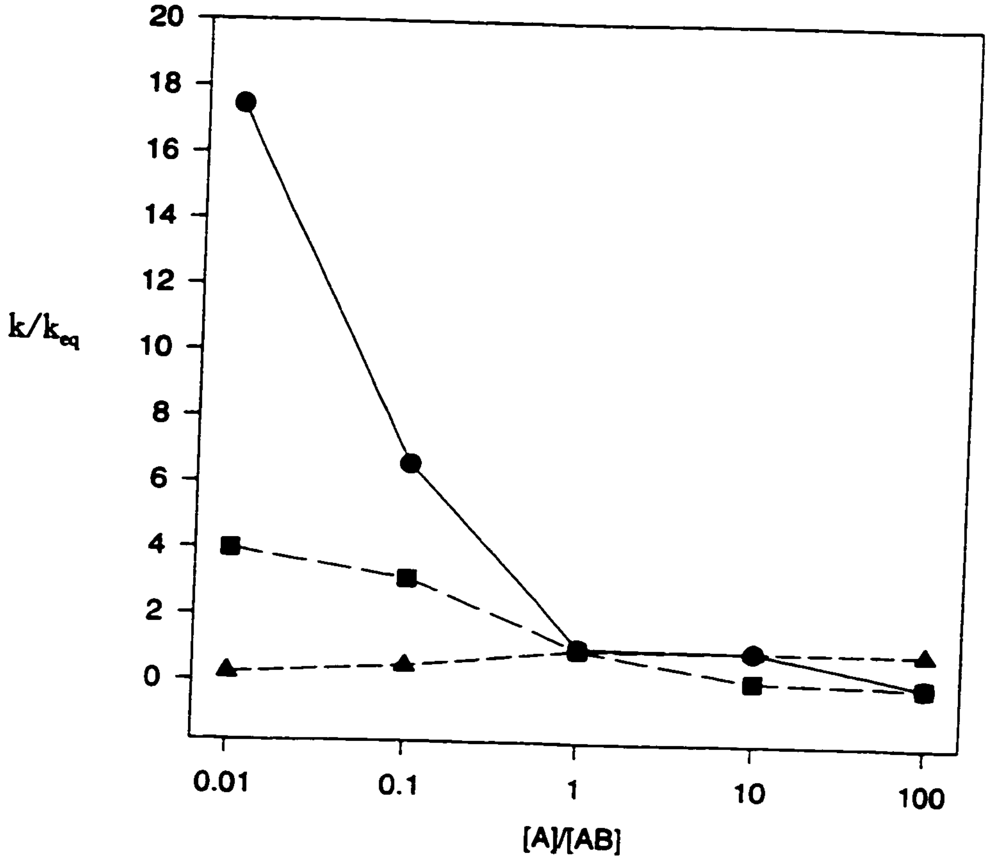

Figure 6.6: The ratio of k/k_{eq} vs. [A]/[AB],while keeping other parameters constant. ■ is for K/K_{eq}. ● is for k_f/k_f^{eq}. ▲ is for k_r/k_r^{eq}.

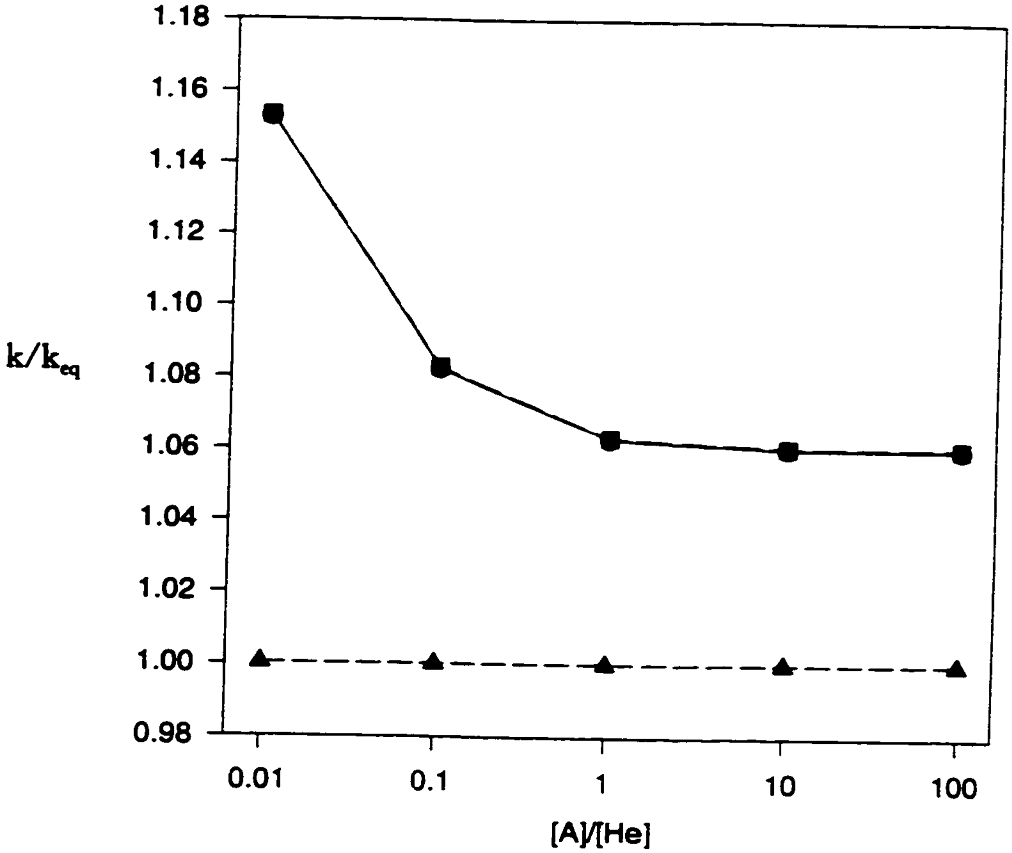

Figure 6.7: The ratio of k/k_{eq} vs. [A]/[He], while keeping other parameters constant. ■ is for K/K_{eq}. ● is for k_f/k_f^{eq}. ▲ is for k_r/k_r^{eq}.

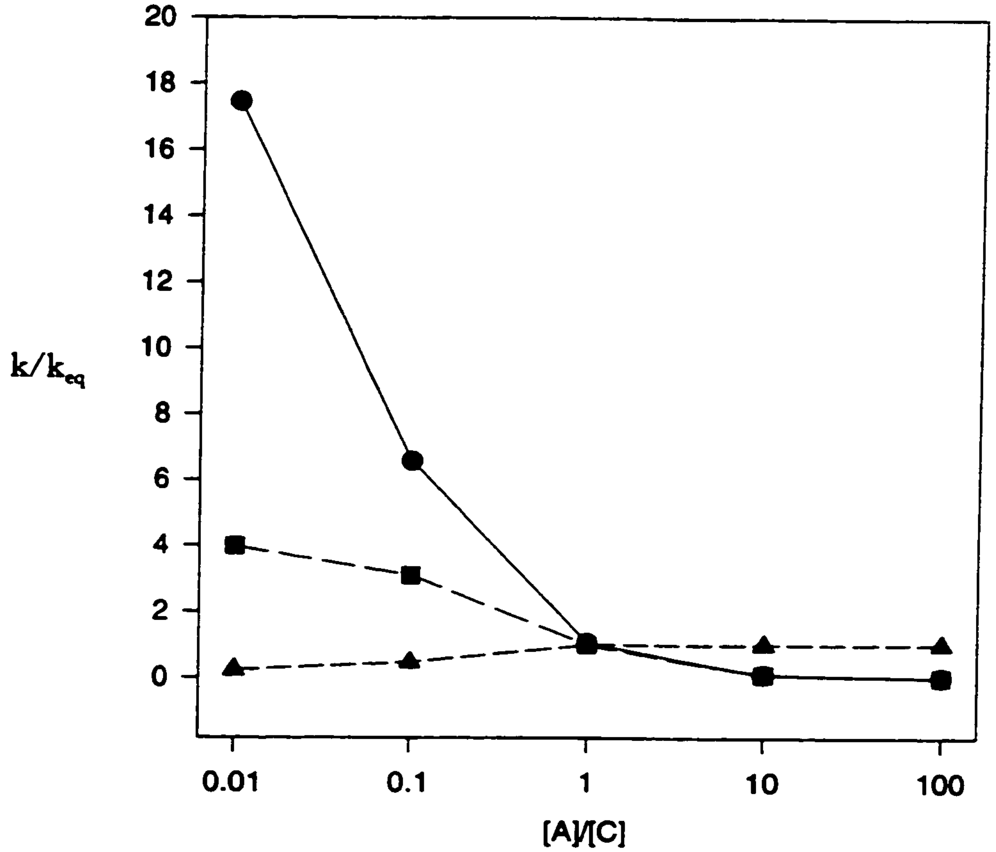

Figure 6.8: The ratio of k/k_{eq} vs. [A]/[C], while keeping other parameters constant. ■ is for K/K_{eq}. ● is for k_f/k_f^{eq}. ▲ is for k_r/k_r^{eq}.

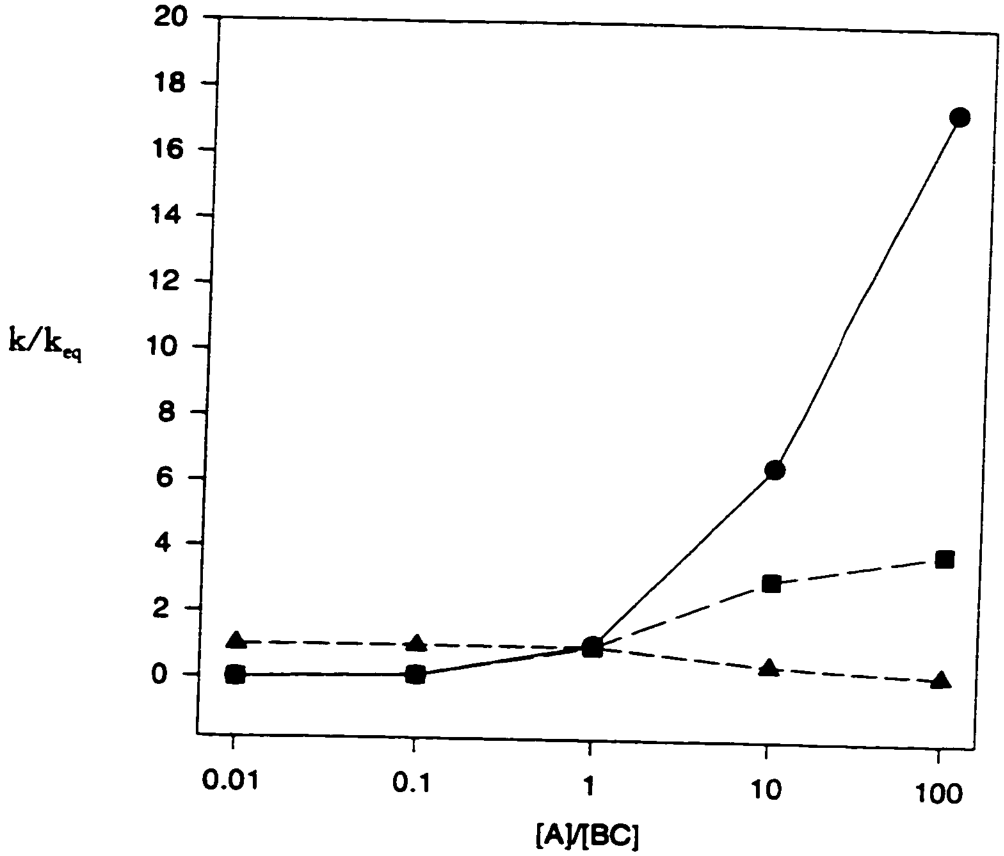

Figure 6.9: The ratio of k/k$_{eq}$ vs. [A]/[BC], while keeping other parameters constant. ■ is for K/K$_{eq}$. ● is for k_f/k_f^{eq}. ▲ is for k_r/k_r^{eq}.

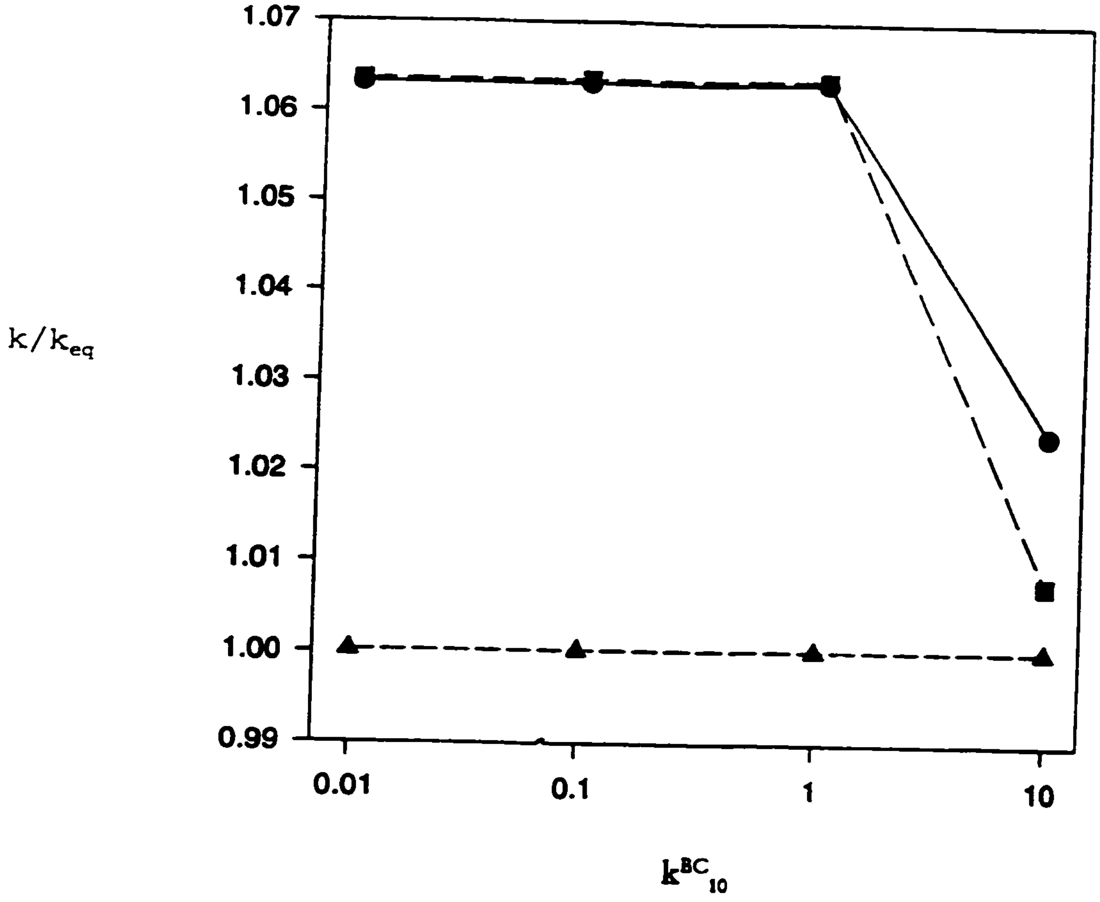

Figure 6.10: The ratio of k/k_{eq} vs. k^{BC}_{10},($k^{BC\text{-}A}_{10}$ is increased). while keeping other parameters constant. ■ is for K/K_{eq}. ● is for k_f/k_f^{eq}. ▲ is for k_r/k_r^{eq}.

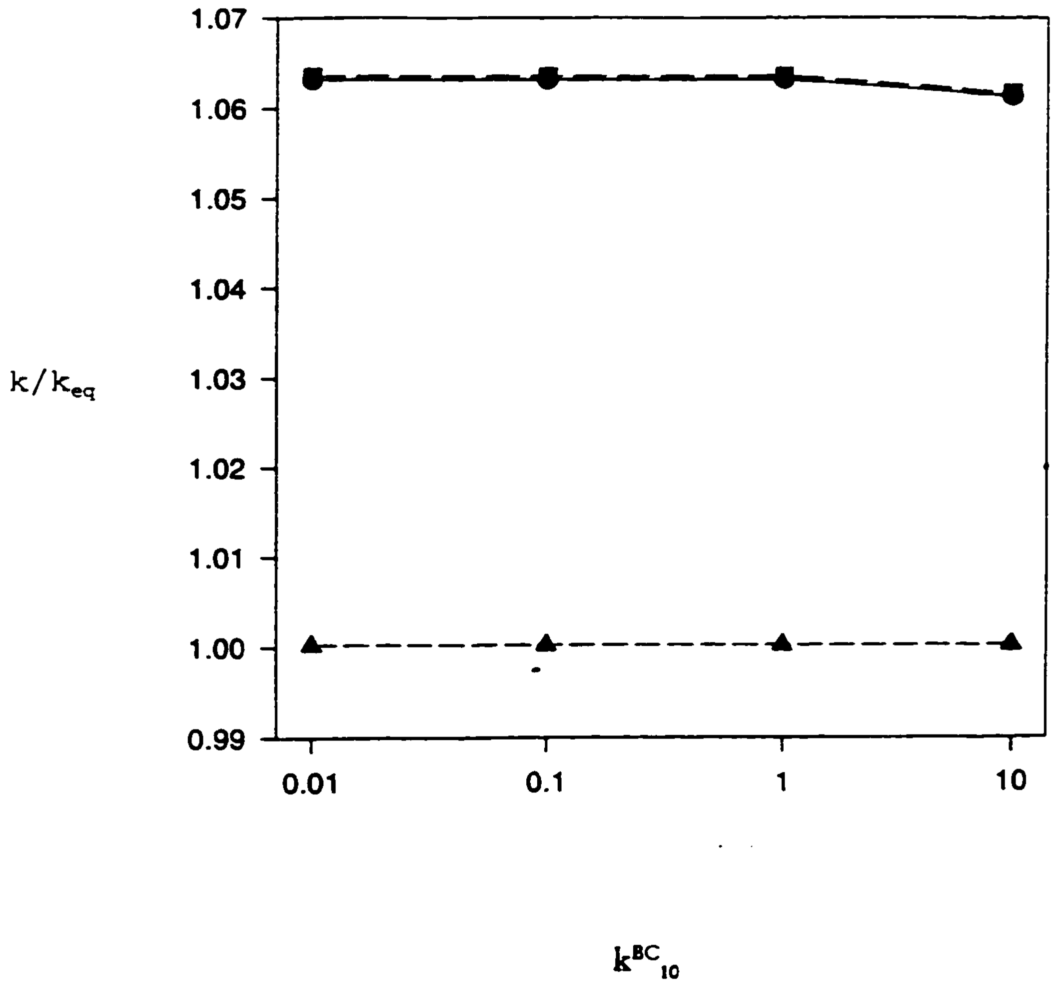

Figure 6.11: The ratio of k/k_{eq} vs. $k^{BC}{}_{10}$, ($k^{BC\text{-}BC}{}_{10}$ is increasd) while keeping other parameters constant. ■ is for K/K_{eq}. ● is for k_f/k_f^{eq}. ▲ is for k_r/k_r^{eq}.

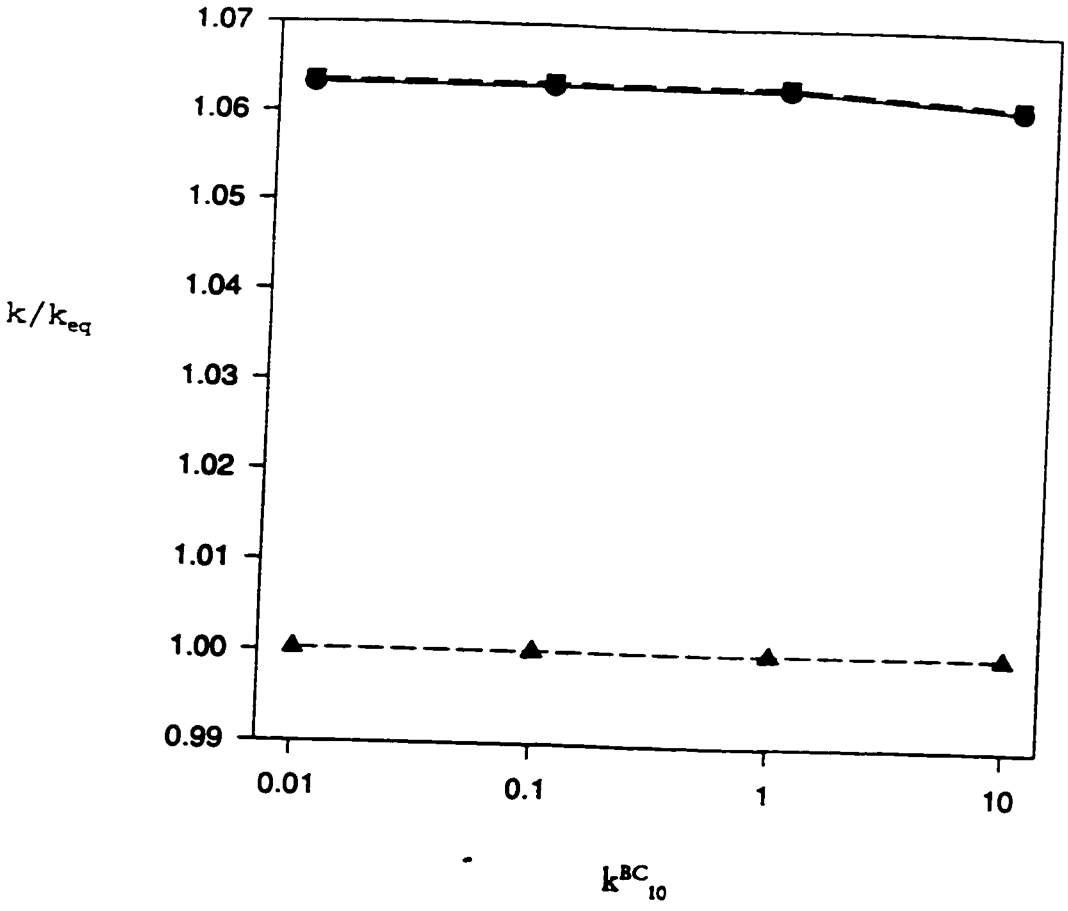

Figure 6.12: The ratio of k/k_{eq} vs. k^{BC}_{10}, (k^{BC-C}_{10} is increased) while keeping other parameters constant. ■ is for K/K_{eq}. ● is for k_f/k_f^{eq}. ▲ is for κ_r/k_r^{eq}.

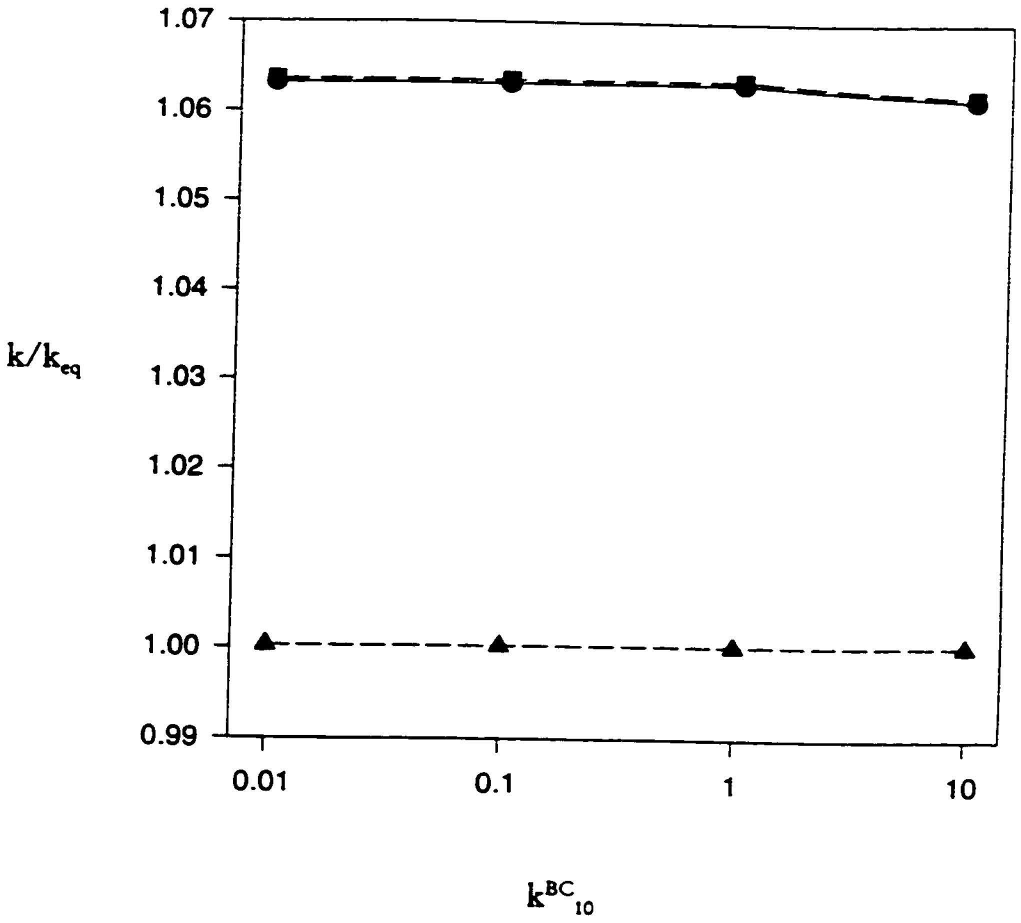

Figure 6.13: The ratio of k/k_{eq} vs. k^{BC}_{10},($k^{BC\text{-}AB}_{10}$ is increased) while keeping other parameters constant. ■ is for K/K_{eq}. ● is for k_f/k_f^{eq}. ▲ is for k_r/k_r^{eq}.

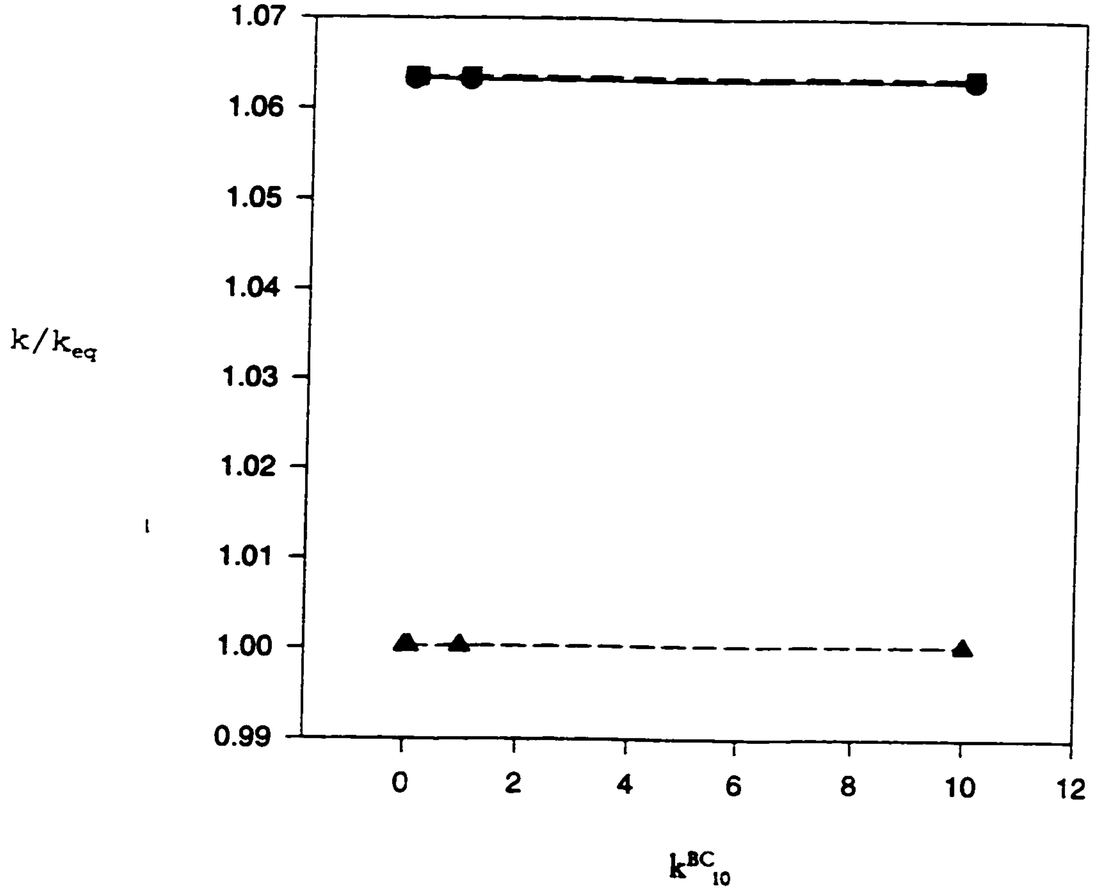

Figure 6.14: The ratio of k/k_{eq} vs. k^{BC}_{10},($k^{BC\text{-}He}_{10}$ is increased) while keeping other parameters constant. ■ is for K/K_{eq}. ● is for k_f/k_f^{eq}. ▲ is for k_r/k_r^{eq}.

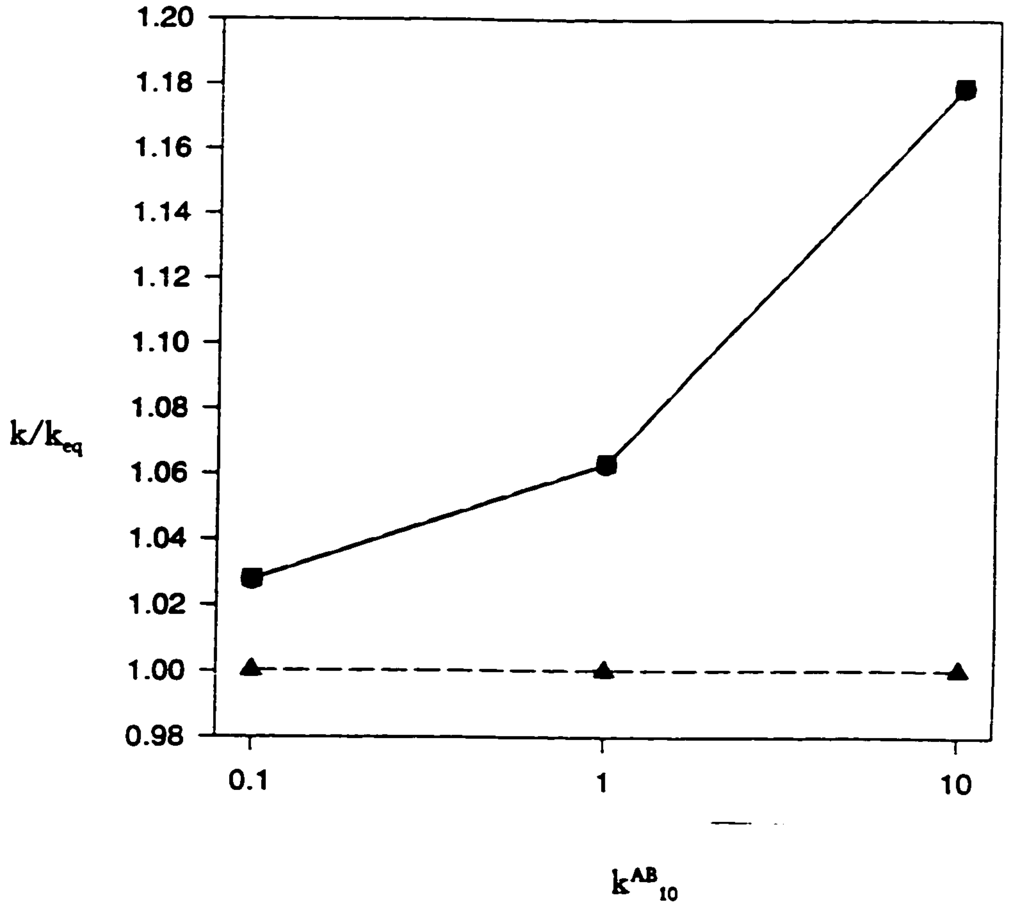

Figure 6.15: The ratio of k/k_{eq} vs. k^{AB}_{10}, while keeping other parameters constant. ■ is for K/K_{eq}. ● is for k_f/k_f^{eq} .▲ Is for k_r/k_r^{eq} .

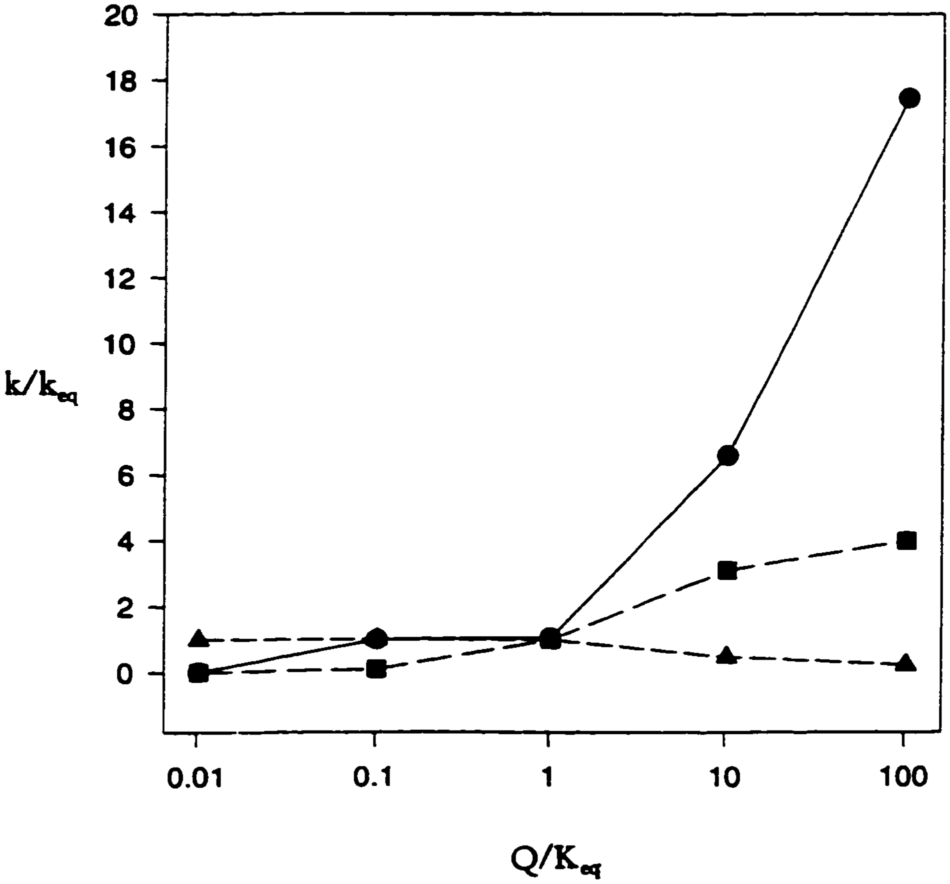

Figure 6.16: The ratio of k/k_{eq} vs. Q/K_{eq}, while keeping other parameters constant. ■ is for K/K_{eq}. ● is for k_f/k_f^{eq}. ▲ is for k_r/k_r^{eq}.

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[1] H. Teitelbaum, J. Phys. Chem. **94** (1990) 3328.

Chapter 7

Conclusion and Suggestions for Future Studies

7.1 Conclusion

We have already applied our analytical expression and matrix technique to the H + O_2 ⇌ OH + H reaction and to the Br + HCl ⇌ HBr + Cl reaction. We concluded that non-equilibrium effects are very important and that the kinetic mass action law breaks down over a very wide range of conditions. Our analytical expressions predict the same behaviour when the reactions are far from equilibrium. Unfortunately our 2 reactions are pathological in the sense that our analytical expressions could not be tested on them. A series of tests on a model reaction, however does confirm the validity of our expressions when reactivity is vibrationally enhanced, when relaxation is slow, and when reaction is far from equilibrium. In our case this latter condition apparently refers to cases where $K_{eq} \approx 1$ ie when forward and reverse reactions can contribute with equal potential. Our model calculations are therefore useful in predicting not only that the magnitude of the effect can be enormous, but also in predicting for what kind of reactions our analytical expressions can be useful replacements of the classic kinetic mass action law.

In order to make progress in this field further model studies will not help. We must study real systems. The two reactions studies in this work are the only ones for which sufficient reactivity data is available. In order to evaluate the generality of our conclusions a massive effort by the world's chemical dynamicists is needed in the direction of determining values of b and c. This is a mega man-year project. Another area where additional work is feasible is discussed below. However, again here, a case-by-case study is needed, and again complete data bases are required.

7.2 Suggestions for Further Study

The one remaining major assumption of the present study is the steady-state assumption. The $HCl + Br = Cl + HBr$ reaction is known to occur with a steady-state Population distribution [3]. We shall therefore briefly examine the steady-state approximation for the $H + O_2 = OH + O$ reaction. We need to solve the time-dependent master equations (eq. 2.1a and eq. 2.1b) exactly. These equations are "stiff" non-linear ordinary differential equations. The method chosen to solve them is Gear's method [2]. A FORTRAN program has been written by Atik [4] to solve these differential equations. We have chosen the same concentrations as in Table 6.1 for the initial conditions. A representative calculation is shown for 8000 K in Fig 7.1-7.3. We have plotted the ratio of k_f/k_f^{eq}, k_r/k_r^{eq} and $(k_f/k_r) / K_{eq}$ vs log ξ on the same graph, where ξ is the extent of the reaction. $\xi = ([A]_t - [A]_0) / ([A]_{eq} - [A]_0)$ where the subscript t corresponds to time, t. Under these conditions our steady state treatment would predict a negligible non-equilibrium effect. We see that for over 90% of the reaction ($\xi < 0.9$) the individual rate coefficients are impressively depressed and correspond to initial (room temperature) vibrational level distributions. Essentially reaction is occuring long before the high temperature distribution can be established under these conditions. More work is required to map out the behaviour for other conditions. However it should be noted that the $H + O_2$ reaction is an extremely unusual reaction - perhaps the only one (see Chapter 1) where transient effects have been postulated.

Where the real work lies ahead is in time-dependent studies of <u>complex</u> reactions. For example, the skeletal mechanism of the H_2/O_2 reaction consists not only of $H + O_2 \rightarrow OH + O$, but also $H_2 + OH \rightarrow H_2O + H$, $H_2 + O \rightarrow OH + H$, and (at low pressures) $OH \rightarrow$ Wall. It would be very valuable to simulate the H_2/O_2 first limit explosion at the vibrational level of detail. Certainly many surprises await us -not because of transient effects uniquely- but because of the synergy and feedback effects expected when one elementary reactions produces or uses excited molecules that are used by or produced by previous or subsequent steps in the mechanism. Work in this area is progressing in our lab.

7.3 Claims to original Research

1. A FORTRAN program, MRBIM, has been written to examine the non-equilibrium kinetics of bimolecular exchange reactions in the steady-state limit.
2. MRBIM's essential feature is its ability to extend the calculation of Teitelbaum by including the reverse reaction.
3. MRBIM has been validated, and it has been used to test the analytical expression for the generalized rate law and the kinetic mass action law.
4. It was found that non-equilibrium effects can be impressive for the $H + O_2$ reaction. The magnitude depends on the temperature, [H], $[O_2]$, [OH] , [O] and [He].
5. Near equilibrium the kinetic mass action law holds to some degree, but it breaks down when the $H + O_2$ reaction is occuring far from equilibrium. The individual rate coefficients are sometimes suppressed and sometimes inflated from their equilibrium values depending on whether forward or reverse reaction dominates.

6. We find that higher vibrational levels of the diatomic molecule involved as reagents in the dominant direction are depleted, whereas the product diatomic is generally more excited than at equilibrium.

7. We have applied information theory to the HBr (v) + Cl = HCl (v') + Br reaction and obtained state-to-state rate constants. We used Wolfrum's rate constants for $v'=2$ and Douglas' experimental relative rates to construct our surprisal plots for temperatures ranging from 300 K to 4000 K [5,6]. We also made use of microscopic-reversibility to obtain the exothermic state-to-state rate constants. Our values for k_o for the endothermic reaction at 298 K agrees with Arnoldi's estimate and with our calculated value using Douglas' exothermic rate and Pollak's microscopic-reversibility relation.

8. It was found that non-equilibrium effects can be impressive for the HCl + Br reaction. The magnitude depends on the temperature, [Br], [HCl], [HBr] , [Cl] and [He].

9. Near equilibrium the kinetic mass action law holds to some degree, but it breaks down when the HCl + Br reaction is occuring far from equilibrium. The individual rate coefficients are sometimes suppressed and sometimes inflated from their equilibrium values depending on whether forward or reverse reaction dominates.

10. We find that higher vibrational levels of the diatomic molecule involved as reagents in the dominant direction are depleted, whereas the product diatomic is generally more excited than at equilibrium.

11. The steady-state master equation has been solved by analytical means for the special case where reaction from excited reagent and product are improtant.

12. Close to equilibrium the rate law is given by

$$rate = \frac{k^{f}_{eq}[BC][A] - k^{r}_{eq}[AB][C]}{(1 + \Phi + \varepsilon)}$$

and $k_f/k_r = k_f^{eq}/k_r^{eq} = K_{eq}$

13. Far from equilibrium the rate law is given by

$$rate = \frac{k^{f}_{eq}[BC][A]Z^{eq}_{n*}e^{v} - k^{r}_{eq}[AB][C]Y^{eq}_{m*}e^{u}}{Z^{eq}_{n*}Y^{eq}_{m*}e^{u+v}(1 + \frac{k'}{m_*} + \frac{k''}{Xn_*})}$$

and $k_f/k_r = K_{eq} Z_{n*}^{eq} e^{v} / Y_{m*}e^{u} \neq K_{eq}$

This is a result which has evaded kineticists for 100 years.

14. The analytical expression for reaction occuring close to equilibrium gives good results compared to those from the matrix technique; but the analytical expression for reaction occuring far away from equilibrium does not agree quantitatively with those results calculated using MRBIM for the H $+ O_2$ reaction and the Br + HCl reaction.

15. Model studies of the steady state bimolecular exchange reaction were approached numerically. The analytical expressions are found to be valid when the approximations are satisfied - namely high vibrational enhancement of reactivity, poor energy transfer, and reaction far from equilibrium. Our analytical expressions are most useful for reaction where the equilibrium constants is of the order of unity.

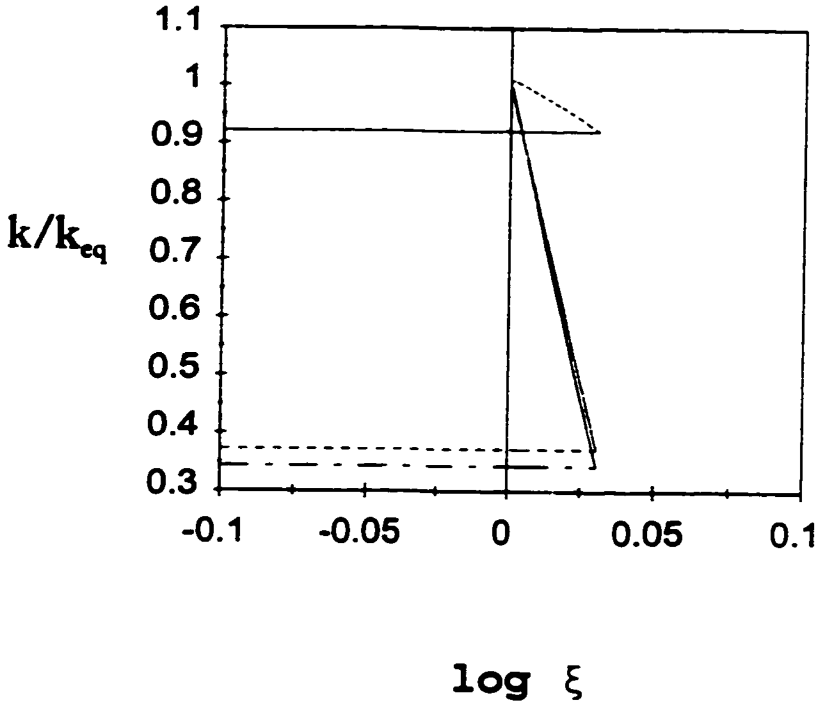

Fig 7.1 : The ratio k/k_{eq} vs. log ξ for [H]/[He] = 0.0001, [H]/[O] = 1.0, [H]/[O_2] = 1.0 and [H]/[OH] = 0.01 and T = 8000 K. – . . – is for k^f/k^f_{eq}. - - - is for $(k^f/k^r)/K_{eq}$. —— is for k^r/k^r_{eq}.

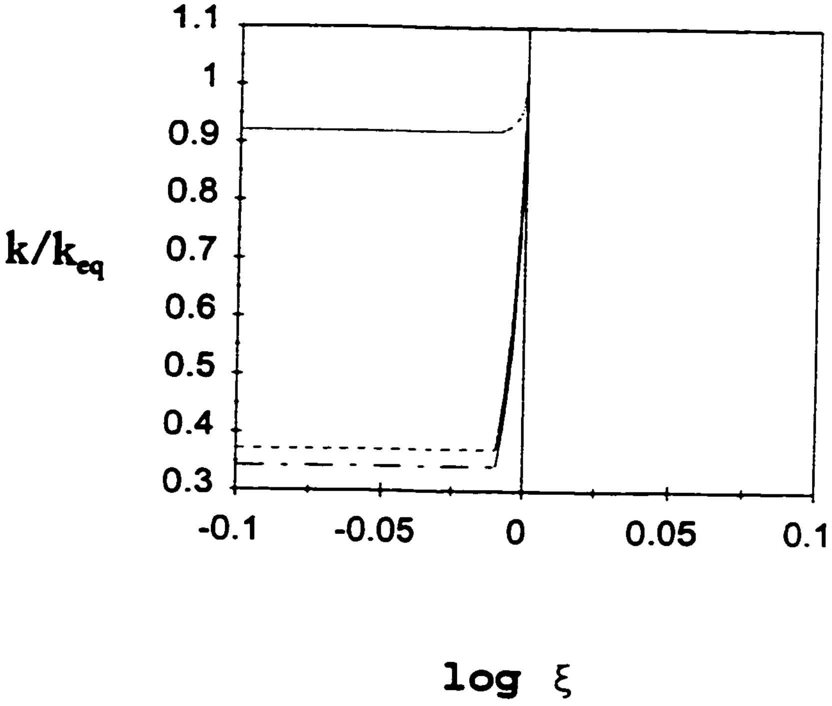

Fig.7.2 : The ratio k/k_{eq} vs. log ξ for [H]/[He] =0.001, [H]/[O] =0.01 [H]/[O_2] = 1.0 and [H]/[OH] = 1.0 and T = 8000 K. – . – is for k^f/k^f_{eq}. - - - is for (k^f/k^r) / K_{eq}. —— is for k^r/k^r_{eq}.

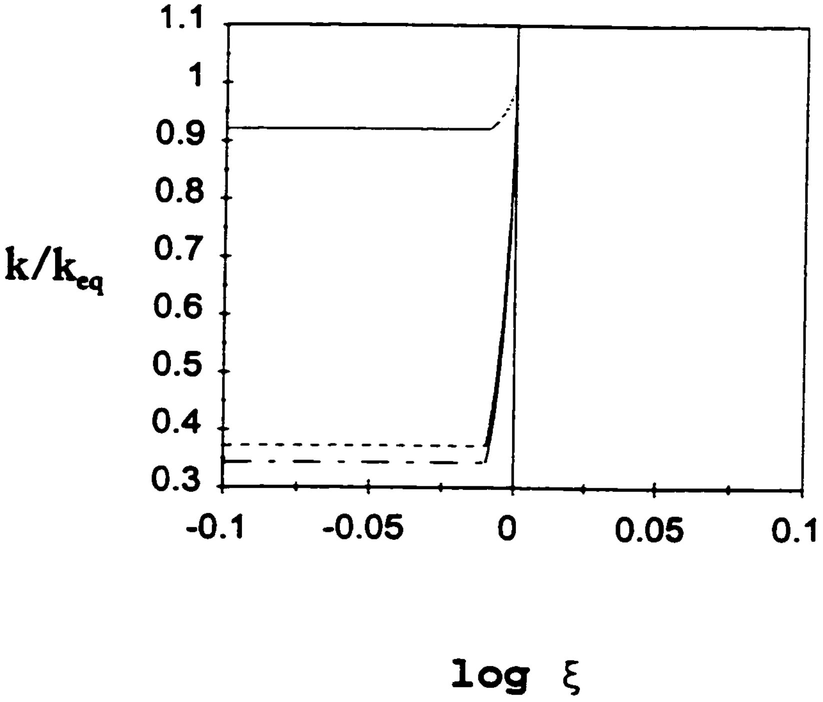

Fig . 7.3 : The ratio k/k_{eq} vs. log ξ for [H]/[He] = 0.001, [H]/[O] = 0.01 [H]/[O_2] = 1.0 and [H]/[OH] = 1.0 and T = 8000 K. – . – is for k^f/k^f_{eq}. - - - is for (k^f/k^r) / K_{eq}. ___ is for k^r/k^r_{eq}.

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[1] H. Teitelbaum, J. Phys. Chem. **94** (1990) 3328.

[2] C. Gear, Numerical Initial Value problem in Ordinary Differential Equations. Prentice-Hall, Englewood Cliff, N. J., (1971).

[3] C. Carruthers, Msc. Thesis, University of Ottawa, (1992).

[4] J. Atik, Msc. Thesis, University of Ottawa, (in progress).

[5] D. Arnoldi and J. Wolfrum, Ber. Bunsenges. Phys. Chem. **80** (1976) 892.

[6] D. J. Douglas, J. C. Polanyi and J. J. Sloan, Chem. Phys. **59** (973) 6679.

Appendix A. Description Of MRBIM

The important features of MRBIM will be outlined in this appendix.

A. 1 Program Flow

MRBIM is a conventional program in the sense that it begins by obtaining input parameters to indicate the reaction system, and the temperatures, etc. Then it proceeds to calculate what is required (in this case the non-equilibrium rate coefficients and the non- Boltzmann distribution for both products and reactants - the name of the routine here is **DEVCRG**) and writes the results, as they become available, to the output files. MRBIM is designed to be easily modified by those who use it (and not just by the author). There are extensive comments throughout the program. MRBIM is also designed to handle a very wide range of initial conditions. The source code for the program is also included in this appendix.

A.2 Flexible input

MRBIM has two ways of obtaining input parameters: the user can be prompted for input from the keyboard , or input can be from a file. In addition, when the input expected by MRBIM is a physical quantity that has units associated with it, the user mu st supply the units. That is the reader has to make sure that the energy transfer rate constants and reactive rate constants have the same units. An example of input file is included in this appendix.

A.3 Example of output file

The output file contains the results of calculations performed by the program at each step and carries the comments along with the calculations. The main results of the program are summarized at the end of the file with their appropriate units. An example of an output file is included in this appendix.

A1

MRBIM

```
     program test
     double complex eval(20), evec(20,20)
     implicit real*8 (a-h,o-z)

     dimension rkfsum(20), rkrsum(20), rkf(20,20), rkr(20,20)
     dimension y(20), yeq(20), z(20), zeq(20), reval(20)


c    These are energy transfer matrice for BC and AB diatomic
c    molecules.
     dimension AetBC(20,20), BCetBC(20,20), CetBC(20,20), ABetBC(20,20)

     dimension RetBC(20,20), AetAB(20,20), BCetAB(20,20), CetAB(20,20)
     dimension ABetAB(20,20), RetAB(20,20)
     dimension etBC(20,20), etAB(20,20),a(20,20)
     dimension enAB(20,20), enBC(20,20), SumetAB(20), SumetBC(20)

     read (5,*) T, mm, nn, weBC, wexeBC, weAB, wexeAB
     read (5,*) A2AB,A2M, A2C, A2BC
     AB2BC = A2BC/A2AB

     write (6,*) ' '

c    Read unnormalized reactive rate constants for forward and reverse
c    reaction.

     do 1 n=1, nn+1
   1 read (5,*) (rkf(n,i),i=1, mm+1)

     do 2 n=1, mm+1
   2 read (5,*) (rkr(n,i),i=1, nn+1)

c    Summing up the reactive rates for each vibrational level

     do 3 i=1, mm+1
     do 3 n=1, nn+1
       rkfsum(i)= rkfsum(i)+rkf(n,i)
   3 continue
c


     do 4 n=1, nn+1
     do 4 i=1, mm+1
   4 rkrsum(n) = rkrsum(n)+rkr(i,n)


c    Read downward energy transfer rate constants. Make sure that
c    all elments are unnormalized  and that the diagonal
c    elements are all zero. Repeat for A, BC, AB, C and M.
```

```
      do 10 m = 1, mm+1
   10 read (5,*) (AetBC(m,i), i = 1,m)

      do  13 m = 1, mm+1
   13 read (5,*) (BCetBC(m,i), i = 1,m)

      do 14 m = 1, mm+1
   14 read (5,*) (CetBC(m,i), i = 1,m)

      do 16 m = 1, mm+1
   16 read (5,*)  (ABetBC(m,i), i = 1,m)

      do 17 m = 1, mm+1
   17 read (5,*) (RetBC(m,i), i = 1,m)

c     Energy transfer rates for product 'AB'

      do 35 n = 1, nn+1
   35 read (5,*) (AetAB(n,i), i = 1,n)
      do 120 n = 1,nn+1
  120 read (5,*) (ABetAB(n,i), i = 1,n)
      do 121 n = 1,nn+1
  121 read (5,*) (BCetAB(n,i), i = 1,n)
      do 122 n = 1,nn+1
  122 read (5,*) (CetAB(n,i), i = 1,n)
      do 123 n = 1,nn+1
  123 read (5,*) (RetAB(n,i), i = 1,n)

c     calculate the energy difference between m and i in wavenumbers
      do 18 m = 1, mm+1
      do 18 i = 1, mm+1
   18 enBC(m,i) = (weBC-WexeBC)*(i-m)-wexeBC *((i-1)**2-(m-1)**2)
      write (6,*) ' '
      write (6,*) 'matrix of energy difference between m and i '
      write (6,11)
      write (6,*) 'm'
      do 22 m = 1, mm+1
      write (6,23) m-1, (enBC(m,i), i = 1,mm+1)
   23 format(i3,16f8.1)
   22 continue
c     calculate the energy difference between n and i in wavenumbers
      do 19 n = 1, nn+1
      do 19 i = 1, nn+1
   19 enAB(n,i) = (WeAB-WexeAB)*(i-n)-wexeAB*((i-1)**2-(n-1)**2)
      write (6,*) ' '
      write (6,*) 'matrix of energy difference between n and i'
      write (6,*) ' '
      write (6,11)
      write (6,*) 'n'
      do 24 n = 1, nn+1
      write (6,25) n-1, (enAB(n,i), i = 1, nn+1)
```

```
 25  format (i3, 16f8.1)
 24  continue

c     calculate the upwards energy-transfer rate constants for reactants
      do 27 m=1, mm+1
      do 27 i=m+1, mm+1
      AetBC(m,i) = AetBC(i,m)*exp(-enBC(m,i)*1.4388/T)
      BCetBC(m,i) = BCetBC(i,m)*exp(-enBC(m,i)*1.4388/T)
      ABetBC(m,i) = ABetBC(i,m)*exp(-enBC(m,i)*1.4388/T)
      CetBC(m,i) = CetBC(i,m)*exp(-enBC(m,i)*1.4388/T)
 27   RetBC(m,i) = RetBC(i,m)*exp(-enBC(m,i)*1.4338/T)

      write (6,*) ' '

      write (6,*)
100   format(/,'matrix of rate constant for energy transfer by A')
      write (6,*)
      write (6,11)
      write (6,*) 'm'
      write (6,*) ' '
      do 32 m=1, mm+1
      write (6,33) m-1, (AetBC (m,i), i= 1, mm+1)
 33   format (i3, 1p16e8.1)
 32   continue


      write (6,*)
      write (6,*) 'matrix of rate constants for energy transfer by BC'
      write (6,*)
      write (6,11)

      write (6,*) 'm'
      write (6,*) ' '
      do 34 m=1, mm+1
      write (6,33) m-1, (BCetBC (m,i), i= 1, mm+1)
 34   continue
      write (6,*) ' '
      write (6,*) 'matrix of rate constants for energy transfer by C'
      write (6,*)
      write (6,11)
      write (6,*) 'm'
      write (6,*) ' '
      do 36 m=1, mm+1
      write (6,33) m-1, (CetBC (m,i), i=1, mm+1)
 36   continue
      write (6,*) ' '
      write (6,*)'matrix of rate constants for energy transfer by AB'
      write (6,*)
      write (6,*) ' '
      write (6,11)
      write (6,*) 'm'
```

```
      write (6,*) ' '
      do 37 m=1, mm+1
      write (6,33) m-1, (ABetBC (m,i), i=1, mm+1)
 37   continue
      write (6,*) ' '
      write (6,*) 'matrix of rate cosntants for energy transfer by M'
      write (6,*)
      write (6,*) 'm'
      write (6,11)
      write (6,*) ' '
      do 38 m=1, mm+1
      write (6,33) m-1, (RetBC (m,i), i=1, mm+1)
 38   continue

c     calculate the upwards energy transfer rate cosntants for products

      do 41 n=1, nn+1
      do 41 i=n+1, nn+1
      AetAB(n,i) =AetAB(i,n)*exp(-enAB(n,i)*1.4388/T)
      BCetAB(n,i) = BCetAB(i,n)*exp(-enAB(n,i)*1.4388/T)
      ABetAB(n,i) = ABetAB(i,n)*exp(-enAB(n,i)*1.4388/T)
      CetAB(n,i) = CetAB(i,n)*exp(-enAB(n,i)*1.4388/T)
      RetAB(n,i)= RetAB(i,n)*exp(-enAB(n,i)*1.4338/T)
 41   continue

      write (6,*)
      write (6,*) ' '
      write (6,*) 'matrix of rate constants for energy transfer by A'
      write (6,*) ' '
      write (6,11)
      write (6,*) 'n'

      do 42 n=1,nn+1
 42   write (6,43) n-1, (AetAB(n,i), i=1, nn+1)

 43   format (i3,1p16e8.1)
      write (6,*) ' '
      write (6,*) ' '
      write (6,*) 'matrix of rate constants for energy transfer by BC'
      write (6,*) ' '
      write (6,11)
      write (6,*) 'n'
      do 44 n=1, nn+1
      write (6,43) n-1, (BCetAB(n,i), i=1, nn+1)
 44   continue
      write (6,*) ' '
      write (6,*) ' '
      write (6,*) 'matrix of rate costansts for energy transfer by AB'
      write (6,*) ' '
      write (6,11)
```

```
      write (6,*) ' '
      write (6,*) 'n'
      do 46 n=1, nn+1
      write (6,43) n-1, (ABetAB(n,i), i=1, nn+1)
   46 continue
      write (6,*) ' '
      write (6,*) 'matrix of rate constants for energy transfer by C'
      write (6,*) ' '
      write (6,11)
      write (6,*) ' '
      write (6,*) 'n'
      do 47 n=1, nn+1
      write (6,43) n-1, (CetAB(n,i), i=1, nn+1)
   47 continue
      write (6,*) ' '
      write (6,*) 'matrix of rate constants for energy transfer by M'
      write (6,*) ' '
      write (6,11)
      write (6,*) 'n'
      do 48 n=1, nn+1
      write (6,43) n-1, (RetAB(n,i), i=1, nn+1)
   48 continue

c     calculate the effective energy transfer rate constant
c     matrix and normalizes it with respect to k10

      do 51 m=1, mm+1
      do 51 i=1, mm+1
   51 etBC(m,i) = AetBC(m,i)+(BCetBC(m,i)/A2BC)+(RetBC(m,i)/A2M)
     &               +(CetBC(m,i)/A2C)+(ABetBC(m,i)/A2AB)
      con = etBC(2,1)
      do 52 m=1,mm+1
      do 52 i=1,mm+1
   52 etBC(m,i)=etBC(m,i)/con

      write (6,*) ' '
      write (6,*) 'matrix of normalized energy transfer rate constants'
      write (6,*) ' '
      write (6,*) ' '
      write (6,*) 'm'

      do 53 m=1, mm+1
      write (6,33) m-1,(etBC(m,i), i=1,nn+1)
   53 continue

      do 54 m=1, nn+1
      do 54 i=1, nn+1
   54 etAB(m,i) =(AetAB(m,i)+(BCetAB(m,i)/A2BC)+(ABetAB(m,i)/A2AB)
     &               +(CetAB(m,i)/A2C)+(RetAB(m,i)/A2M))/con

      X=etAB(2,1)
```

```
      do 56 m=1, nn+1
      do 56 i=1, nn+1
  56  etAB(m,i) =(etAB(m,i)*AB2BC)
      write (6,*) ' '
      write (6,*) 'matrix of normalized energy transfer rate constants'
      write (6,*) ' '
      write (6,*) 'n'
      do 57 m=1, mm+1
      write (6,33)      n-1, (etAB(m,i), i=1,nn+1)
  57  continue

c     Add up the energy transfer rates.
      do 58 m=1, mm+1
      sumetBC(m) =0.0
      do 58 i=1,mm+1
  58  sumetBC(m) = sumetBC(m)+etBC(m,i)
      do 59 n=1,nn+1
      sumetAB(n)=0.0

      do 59 i=1, nn+1
  59  sumetAB(n) = sumetAB(n)+etAB(n,i)
c     Normalized the reactive rates.
      do 9 i=1,mm+1
      rkfsum(i)= rkfsum(i)/con
   9  continue

      do 77 i=1,nn+1
      rkrsum(i) =(rkrsum(i)*AB2BC)/(A2C*con)
  77  continue

c     Write up the entire Matrix.

      do 62 m=1,mm+1
      do 62 i=1,mm+1
      if (i.lt.m) go to 64
      if (i.eq.m) go to 66
      if (i.gt.m) go to 68
      go to 62
  64  a(m,i)=-etBC(i,m)
      go to 62
  66  a(m,i)=sumetBC(m)+rkfsum(m)
      go to 62
  68  a(m,i)=-etBC(i,m)
  62  continue

      do 81 m=1,mm+1
      j=1
      do 81 i=mm+2,mm+nn+2
         a(m,i)=(-rkr(m,j)*AB2BC)/(A2C*con)
         j=j+1
  81  continue
```

```
      j=0
      do 82 m= mm+2,mm+nn+2
      j=j+1
      do 82 i=1,mm+1
      a(m,i) = rkf(j,i)/con
   82 continue
      j=0

      do 83 m=mm+2, mm+nn+2
      j=j+1
      k=0
      do 83 i=mm+2, mm+nn+2
      if(i.lt.m) go to 85
      if(i.eq.m) go to 86
      if(i.gt.m) go to 87
      go to 83
   85 k=k+1
      a(m,i) = etAB(k,j)
      go to 83
   86 k=k+1
      a(m,i) = -sumetAB(j)-rkrsum(j)
      go to 83
   87 k=k+1
      a(m,i)= etAB(k,j)
      go to 83
   83 continue

      write (6,*) ' '
      write (6,*) ' '
      write (6,99)
   99 format (1x,/ 'matrix of rates of reaction and energy
     & transfer whose eigenvalues and eigenvectors are determine')
      write (6,*) ' '
      write (6,*) 'm'
      write (6,*) ' '
      write (6,*) ' '
      do 92 m=1,nn+mm+2
      write (6,33) m-1,(a(m,i),i=1,nn+mm+2)
   92 continue
      call devcrg(nn+mm+2, a, 20, eval, evec, 20)
      write (6,*) ' '
      write (6,*) ' '
      write (6,*) 'eigenvalues'
      write (6,*) ' '
      do 93 i=1,mm+nn+2
      reval(i) = real(eval(i))
      reval(i)= abs(reval(i))
   93 write (6,*)      reval(i)

c     This subroutine determines the lowest eigenvalue with
c     physical meaning.
```

```
      rk = reval(1)
      do 144 m = 1,nn+mm+2
      r= reval(m)
      if (r .lt. rk) go to 146
      go to 144
 146  rk = r
      ik=m
      go to 144
 144  continue
      ik=ik-1
      ck=ik
      do 350 n=1,ck
      do 300 m=1, mm+nn+2
      ak=real(evec(m,ik))
      if (ak .lt. 0.0) go to 400
 300  continue
      go to 450
 400  ik=ik-1
 350  continue
 450  n=ck
      write (6,*) ' '
      write (6,*) 'min is at i=',ik,'and its value is',reval (ik)


      do 94 m=1, mm+1
 94   y(m) =real(evec(m,ik))

      do 195 m=mm+2, mm+nn+2
      i=m-mm-1
 195  z(i) =real (evec(m,ik))

      do 96 i= 1, mm+1
 96   yeq(i) = exp(-((weBC-wexeBC)*(i-1)-wexeBC*(i-1)**2)*1.4388/T)

      do 97 i=1, nn+1
 97   zeq(i) =exp(-((weAB-wexeAB)*(i-1)-wexeAB*(i-1)**2)*1.4388/T)

      sumy=0.0
      sumz=0.0
      sum1y=0.0
      sum1z=0.0
      akeqf=0.0
      akeqr=0.0
      akf=0.0
      akr=0.0

      do 98 i=1,mm+1
      sumy=sumy+y(i)
 98   sum1y=sum1y+yeq(i)
```

```
     do 105 i=1, nn+1
     sumz=sumz+z(i)
105  sum1z=sum1z+zeq(i)

     do 106 i=1, mm+1
     yeq(i) = yeq(i)/sum1y
106  y(i) = y(i)/sumy

     do 107 i=1, nn+1
     zeq(i) = zeq(i)/sum1z
107  z(i) =z(i)/sumz

     do 108 i=1,mm+1
     do 108 j=1,nn+1
     akf=akf+y(i)*rkf(j,i)
108  akeqf=akeqf+yeq(i)*rkf(j,i)

     do 109 j=1, nn+1
     do 109 i=1, mm+1
     akr=akr+z(j)*rkr(i,j)
109  akeqr= akeqr+zeq(j)*rkr(i,j)
     write (6,*) ' '
     write (6,6) T, mm, nn, akf, akeqf, akr, akeqr
 6   format (1x,/ 'T=',f6.0,/ 'mm=', i3, /'nn=',i3,/ ' akf=', e12.5,
    & ' cm3/mol.s',/ 'akeqf=', e12.5, ' cm3/mol.s',/ 'akr=', e12.5,
    & ' cm3/mol.s',/'akeqr=', e12.5, ' cm3/mol.s')
     write (6,7) A2BC, A2C, A2AB, AB2BC
 7   format(1x,/'[A]/[BC]=', e8.1,/ '[A]/[C]=',
    & e8.1,/ '[A]/[AB]=',e8.1,/ '[AB]/[BC]=',
    & e8.1)

 12  format (i3,16f8.5)
 11  format (1x,/ ' i 0    1    2    3    4',
    &'    5    6    7    8    9    10    11',
    &'    12    13    14    15')
     write (6,*)
     write (6,110)
110  format (/'  m       y(m)       yeq(m)')
     write(6,*) ' '
     write(6,112) ((i-1), y(i),yeq(i), i=1,mm+1)
112  format (1x, I3,1p2e15.5)

     write (6,*) ' '
     write (6,114)
114  format ('  n       z(n)       zeq(n)')
     write (6,*) ' '
     write (6,116)((j-1), z(j),zeq(j), j=1,nn+1)
116  format (1x, I3,1p2e15.5)
     akdiff = (akf-akr*(AB2BC/A2C))/con

     equilibriumn = akf/akr
```

```
    equilibrium = akeqf/akeqr
    write (6,199) equilibriumn, equilibrium, akdiff,con,X
199  format(1x,/ 'k = ',e12.5,/ 'keq = ',e12.5,/ 'kdiff = ',
   & e12.5,/ 'con = ', e12.5,/ 'X = ',e12.5)


   stop

   end
```

A11

Sample of the Data Input for MRBIM

```
2000  5 5 1580.3 12.07 3737.7 84.881
0.00095 1.0 0.001 1.0
1.651e+12 3.798e+12 6.012e+12 6.502e+12 6.026e+12 2.156e+13
6.497e+10 3.325e+11 1.188e+12 2.982e+12 5.286e+12 6.599e+12
5.672e+08 6.035e+09 4.477e+10 2.343e+11 8.738e+11 2.341e+12
1.430e+06 3.015e+07 4.408e+08 4.530e+09 3.311e+10 1.742e+11
1.302e+3  5.223e+04 1.443e+06 2.786e+07 3.806e+09 3.726e+09
0.5204e+0 3.832e+01 1.929e+03 6.736e+04 1.654e+06 2.894e+07
5.241e+12 3.936e+12 2.068e+12 7.552e+11 2.402e+11 2.998e+11
2.690e+12 4.449e+12 5.327e+12 4.517e+12 2.748e+12 1.197e+12
2.720e+11 9.444e+11 2.326e+12 4.110e+12 5.261e+12 4.918e+12
7.012e+09 4.866e+10 2.362e+11 8.193e+11 2.056e+12 3.773e+12
5.922e+07 7.754e+08 7.114e+09 4.635e+10 2.174e+11 7.425e+11
1.948e+5  4.681e+06 7.823e+07 9.222e+08 7.772e+09 4.745e+10
0
1.95e+12 0
0 3.90e+12 0
0 0 5.85e+12 0
0 0 0 7.8e+12 0
0 0 0 0 9.75e+12 0
0
3.78e+10 0
0 7.56e+10 0
0 0 11.53e+10 0
0 0 0 1.5e+11 0
0 0 0 0 1.9e+11 0
0
8.07e+12 0
0 16.14e+12 0
0 0 24.21e+12 0
0 0 0 3.2e+13 0
0 0 0 0 4.0e+13 0
0
8.07e+12 0
0 16.1e+12 0
0 0 24.2e+12 0
0 0 0 3.2e+13 0
0 0 0 0 4.0e+13 0
0
3.93e+11 0
0 7.86+11 0
0 0 1.18e+12 0
0 0 0 1.57e+12 0
0 0 0 0 1.97e+12 0
0
1.08e+13 0
0 2.16e+13 0
```

```
0 0 3.24e+13 0
0 0 0 4.32e+13 0
0 0 0 0 5.40e+13 0
0
2.4e+13 0
0 4.8e+13 0
0 0 7.2e+14 0
0 0 0 9.6e+14 0
0 0 0 0 1.2e+14 0
0
4.5e+12 0
0 9.0e+12 0
0 0 1.35e+13 0
0 0 0 1.8e+13 0
0 0 0 0 2.25e+13 0
0
6.0e+12 0
0 1.2e+13 0
0 0 1.8e+13 0
0 0 0 2.4e+13 0
0 0 0 0 3.0e+13 0
0
6.67e+11 0
0 1.33e+12 0
0 0 2.00e+12 0
0 0 0 2.67e+12 0
0 0 0 0 3.33e+12 0
```

Sample of the Data Output from MRBIM

```
matrix of energy difference between m and i

i 0    1     2     3    4    5    6    7    8    9    10    11    12    13    14    15
m
0     .0  1556.2  3088.2  4596.1  6079.8  7539.4
1 -1556.2     .0  1532.0  3039.9  4523.6  5983.2
2 -3088.2 -1532.0     .0  1507.9  2991.6  4451.2
3 -4596.1 -3039.9 -1507.9     .0  1483.7  2943.3
4 -6079.8 -4523.6 -2991.6 -1483.7     .0  1459.6
5 -7539.4 -5983.2 -4451.2 -2943.3 -1459.6     .0

matrix of energy difference between n and i


i 0    1     2     3    4    5    6    7    8    9    10    11    12    13    14    15
n
0     .0  3567.9  6966.1 10194.5 13253.2 16142.1
1 -3567.9     .0  3398.2  6626.6  9685.2 12574.1
2 -6966.1 -3398.2     .0  3228.4  6287.1  9176.0
3-10194.5 -6626.6 -3228.4     .0  3058.7  5947.5
4-13253.2 -9685.2 -6287.1 -3058.7     .0  2888.9
5-16142.1-12574.1 -9176.0 -5947.5 -2888.9     .0


i 0    1     2     3    4    5    6    7    8    9    10    11    12    13    14    15
m

0 0.0E+00 6.4E+11 0.0E+00 0.0E+00 0.0E+00 0.0E+00
1 2.0E+12 0.0E+00 1.3E+12 0.0E+00 0.0E+00 0.0E+00
2 0.0E+00 3.9E+12 0.0E+00 2.0E+12 0.0E+00 0.0E+00
3 0.0E+00 0.0E+00 5.8E+12 0.0E+00 2.7E+12 0.0E+00
4 0.0E+00 0.0E+00 0.0E+00 7.8E+12 0.0E+00 3.4E+12
5 0.0E+00 0.0E+00 0.0E+00 0.0E+00 9.8E+12 0.0E+00

matrix of rate constants for energy transfer by BC

I 0    1     2     3    4    5    6    7    8    9    10    11    12    13    14    15
m

0 0.0E+00 1.2E+10 0.0E+00 0.0E+00 0.0E+00 0.0E+00
1 3.8E+10 0.0E+00 2.5E+10 0.0E+00 0.0E+00 0.0E+00
2 0.0E+00 7.6E+10 0.0E+00 3.9E+10 0.0E+00 0.0E+00
3 0.0E+00 0.0E+00 1.2E+11 0.0E+00 5.2E+10 0.0E+00
4 0.0E+00 0.0E+00 0.0E+00 1.5E+11 0.0E+00 6.6E+10
5 C.0E+00 0.0E+00 0.0E+00 0.0E+00 1.9E+11 0.0E+00
```

matrix of rate constants for energy transfer by C

```
 i 0   1    2    3    4    5    6    7    8    9    10    11    12    13    14    15
m

 0 0.0E+00 2.6E+12 0.0E+00 0.0E+00 0.0E+00 0.0E+00
 1 8.1E+12 0.0E+00 5.4E+12 0.0E+00 0.0E+00 0.0E+00
 2 0.0E+00 1.6E+13 0.0E+00 8.2E+12 0.0E+00 0.0E+00
 3 0.0E+00 0.0E+00 2.4E+13 0.0E+00 1.1E+13 0.0E+00
 4 0.0E+00 0.0E+00 0.0E+00 3.2E+13 0.0E+00 1.4E+13
 5 0.0E+00 0.0E+00 0.0E+00 0.0E+00 4.0E+13 0.0E+00
```

matrix of rate constants for energy transfer by AB

```
 i 0   1    2    3    4    5    6    7    8    9    10    11    12    13    14    15
m

G  0 0.0E+00 2.6E+12 0.0E+00 0.0E+00 0.0E+00 0.0E+00
 1 8.1E+12 0.0E+00 5.3E+12 0.0E+00 0.0E+00 0.0E+00
 2 0.0E+00 1.6E+13 0.0E+00 8.2E+12 0.0E+00 0.0E+00
 3 0.0E+00 0.0E+00 2.4E+13 0.0E+00 1.1E+13 0.0E+00
 4 0.0E+00 0.0E+00 0.0E+00 3.2E+13 0.0E+00 1.4E+13
 5 0.0E+00 0.0E+00 0.0E+00 0.0E+00 4.0E+13 0.0E+00
```

matrix of rate cosntants for energy transfer by M

```
 i 0   1    2    3    4    5    6    7    8    9    10    11    12    13    14    15
m

 0 0.0E+00 2.3E+09 0.0E+00 0.0E+00 0.0E+00 0.0E+00
 1 7.1E+09 0.0E+00 4.7E+09 0.0E+00 0.0E+00 0.0E+00
 2 0.0E+00 1.4E+10 0.0E+00 7.2E+09 0.0E+00 0.0E+00
 3 0.0E+00 0.0E+00 2.1E+10 0.0E+00 9.7E+09 0.0E+00
 4 0.0E+00 0.0E+00 0.0E+00 2.8E+10 0.0E+00 1.2E+10
 5 0.0E+00 0.0E+00 0.0E+00 0.0E+00 3.5E+10 0.0E+00
```

matrix of rate constants for energy transfer by A

```
 I 0   1    2    3    4    5    6    7    8    9    10    11    12    13    14    15
n
0 0.0E+00 8.3E+11 0.0E+00 0.0E+00 0.0E+00 0.0E+00
1 1.1E+13 0.0E+00 1.9E+12 0.0E+00 0.0E+00 0.0E+00
2 0.0E+00 2.2E+13 0.0E+00 3.2E+12 0.0E+00 0.0E+00
3 0.0E+00 0.0E+00 3.2E+13 0.0E+00 4.8E+12 0.0E+00
4 0.0E+00 0.0E+00 0.0E+00 4.3E+13 0.0E+00 6.8E+12
5 0.0E+00 0.0E+00 0.0E+00 0.0E+00 5.4E+13 0.0E+00
```

matrix of rate constants for energy transfer by BC

```
i 0   1   2   3   4   5   6   7   8   9   10   11   12   13   14   15
n
0 0.0E+00 5.1E+07 0.0E+00 0.0E+00 0.0E+00 0.0E+00
1 6.7E+08 0.0E+00 1.2E+08 0.0E+00 0.0E+00 0.0E+00
2 0.0E+00 1.3E+09 0.0E+00 2.0E+08 0.0E+00 0.0E+00
3 0.0E+00 0.0E+00 2.0E+09 0.0E+00 3.0E+08 0.0E+00
4 0.0E+00 0.0E+00 0.0E+00 2.7E+09 0.0E+00 4.1E+08
5 0.0E+00 0.0E+00 0.0E+00 0.0E+00 3.3E+09 0.0E+00
```

matrix of rate costansts for energy transfer by AB

```
i 0   1   2   3   4   5   6   7   8   9   10   11   12   13   14   15

n
0 0.0E+00 4.6E+11 0.0E+00 0.0E+00 0.0E+00 0.0E+00
1 6.0E+12 0.0E+00 1.0E+12 0.0E+00 0.0E+00 0.0E+00
2 0.0E+00 1.2E+13 0.0E+00 1.8E+12 0.0E+00 0.0E+00
3 0.0E+00 0.0E+00 1.8E+13 0.0E+00 2.7E+12 0.0E+00
4 0.0E+00 0.0E+00 0.0E+00 2.4E+13 0.0E+00 3.8E+12
5 0.0E+00 0.0E+00 0.0E+00 0.0E+00 3.0E+13 0.0E+00
```

matrix of rate constants for energy transfer by C

```
i 0   1   2   3   4   5   6   7   8   9   10   11   12   13   14   15

n
0 0.0E+00 4.6E+11 0.0E+00 0.0E+00 0.0E+00 0.0E+00
1 6.0E+12 0.0E+00 1.0E+12 0.0E+00 0.0E+00 0.0E+00
2 0.0E+00 1.2E+13 0.0E+00 1.8E+12 0.0E+00 0.0E+00
3 0.0E+00 0.0E+00 1.8E+13 0.0E+00 2.7E+12 0.0E+00
4 0.0E+00 0.0E+00 0.0E+00 2.4E+13 0.0E+00 3.8E+12
5 0.0E+00 0.0E+00 0.0E+00 0.0E+00 3.0E+13 0.0E+00
```

matrix of rate constants for energy transfer by M

```
i 0   1   2   3   4   5   6   7   8   9   10   11   12   13   14   15
n
0 0.0E+00 2.3E+08 0.0E+00 0.0E+00 0.0E+00 0.0E+00
1 2.9E+09 0.0E+00 5.1E+08 0.0E+00 0.0E+00 0.0E+00
2 0.0E+00 5.9E+09 0.0E+00 8.7E+08 0.0E+00 0.0E+00
3 0.0E+00 0.0E+00 8.8E+09 0.0E+00 1.3E+09 0.0E+00
4 0.0E+00 0.0E+00 0.0E+00 1.2E+10 0.0E+00 1.9E+09
5 0.0E+00 0.0E+00 0.0E+00 0.0E+00 1.5E+10 0.0E+00
```

```
matrix of normalized energy transfer rate constants

m
 0 0.0E+00 3.3E-01 0.0E+00 0.0E+00 0.0E+00 0.0E+00
 1 1.0E+00 0.0E+00 6.6E-01 0.0E+00 0.0E+00 0.0E+00
 2 0.0E+00 2.0E+00 0.0E+00 1.0E+00 0.0E+00 0.0E+00
 3 0.0E+00 0.0E+00 3.0E+00 0.0E+00 1.4E+00 0.0E+00
 4 0.0E+00 0.0E+00 0.0E+00 4.0E+00 0.0E+00 1.7E+00
 5 0.0E+00 0.0E+00 0.0E+00 0.0E+00 5.0E+00 0.0E+00

matrix of normalized energy transfer rate constants

n
 6 0.0E+00 5.8E-03 0.0E+00 0.0E+00 0.0E+00 0.0E+00
 6 7.6E-02 0.0E+00 1.3E-02 0.0E+00 0.0E+00 0.0E+00
 6 0.0E+00 1.5E-01 0.0E+00 2.2E-02 0.0E+00 0.0E+00
 6 0.0E+00 0.0E+00 2.3E-01 0.0E+00 3.4E-02 0.0E+00
 6 0.0E+00 0.0E+00 0.0E+00 3.0E-01 0.0E+00 4.7E-02
 6 0.0E+00 0.0E+00 0.0E+00 0.0E+00 3.8E-01 0.0E+00


matrix of rates of reaction and energy transfer whose eigenvalues and eigenvectors are determine

m

0   3.5E-01-1.0E+00 0.0E+00 0.0E+00 0.0E+00 0.0E+00-2.7E-02-2.0E-02-1.1E-02-3.9E-03-1.2E-03-1.6E-03
1  -3.3E-01 1.7E+00-2.0E+00 0.0E+00 0.0E+00 0.0E+00-1.4E-02-2.3E-02-2.8E-02-2.3E-02-1.4E-02-6.2E-03
2   0.0E+00-6.6E-01 3.1E+00-3.0E+00 0.0E+00 0.0E+00-1.4E-03-4.9E-03-1.2E-02-2.1E-02-2.7E-02-2.6E-02
3   0.0E+00 0.0E+00-1.0E+00 4.5E+00-4.0E+00 0.0E+00-3.6E-05-2.5E-04-1.2E-03-4.2E-03-1.1E-02-2.0E-02
4   0.0E+00 0.0E+00 0.0E+00-1.4E+00 5.9E+00-5.0E+00-3.1E-07-4.0E-06-3.7E-05-2.4E-04-1.1E-03-3.9E-03
5   0.0E+00 0.0E+00 0.0E+00 0.0E+00-1.7E+00 5.4E+00-1.0E-09-2.4E-08-4.1E-07-4.8E-06-4.0E-05-2.5E-04

6   2.3E-02 5.3E-02 8.4E-02 9.1E-02 8.4E-02 3.0E-01-4.8E-02 7.6E-02 0.0E+00 0.0E+00  0.0E+00 0.0E+00
7   9.1E-04 4.7E-03 1.7E-02 4.2E-02 7.4E-02 9.2E-02 5.8E-03-1.4E-01 1.5E-01 0.0E+00 0.0E+00 0.0E+00
8   7.9E-06 8.4E-05 6.3E-04 3.3E-03 1.2E-02 3.3E-02 0.0E+00 1.3E-02-2.3E-01 2.3E-01 0.0E+00 0.0E+00
9   2.0E-08 4.2E-07 6.2E-06 6.3E-05 4.6E-04 2.4E-03 0.0E+00 0.0E+00 2.2E-02-3.1E-01 3.0E-01 0.0E+00

10   1.8E-11 7.3E-10 2.0E-08 3.9E-07 5.3E-05 5.2E-05 0.0E+00 0.0E+00 0.0E+00  3.4E-02-4.0E-01 3.8E-01
11   7.3E-15 5.4E-13 2.7E-11 9.4E-10 2.3E-08 4.1E-07 0.0E+00 0.0E+00 0.0E+00 0.0E+00 4.7E-02-4.4E-01
eigenvalues

9.31807449787803321
5.68253204371342679
3.32534310189059967
1.78304088552212803
0.798080881986466428
0.574365403418784060
```

```
 0.380928898421636852
 0.263537748289276119
 0.185227345305967656
 0.117063721633654264
 0.241924722424046411E-02
 0.211428097252053249E-13

 min is at i=  11 and its value is 0.241924722424046411E-02


T=  2000.
mm=  5
nn=  5
 akf=  .29080E+13 cm^3/mol/s
akeqf=  .30219E+13 cm^3/mol/s
akr=  .83144E+13 cm^3/mol/s
akeqr=  .83050E+13 cm^3/mol/s

[A]/[BC]=  .2E-01
[A]/[C]=  .2E+00
[A]/[AB]=  .2E+00
[AB]/[BC]=  .9E-01


  m      y(m)       yeq(m)

  0   6.87477E-01   6.71801E-01
  1   2.16071E-01   2.19305E-01
  2   6.67250E-02   7.28444E-02
  3   2.09135E-02   2.46200E-02
  4   6.66709E-03   8.46682E-03
  5   2.14611E-03   2.96275E-03


  n      z(n)       zeq(n)

  0   9.14459E-01   9.22357E-01
  1   7.84763E-02   7.08212E-02
  2   6.46203E-03   6.14421E-03
  3   5.45142E-04   6.02293E-04
  4   5.19686E-05   6.67097E-05
  5   5.68672E-06   8.34851E-06

k=  .34975E+00
keq=  .36386E+00
kdiff=  -.24192E-02
con=  .71435E+14
X=  .75646E-01
```

```
lamda1= -0.3000000     lamda2= -6.1950004E-03          B1
T=    300.0000     shift=    25.77000      f=  0.5197370
Keq(JANAF)=  9.8879004E-12 qvibOH=    1.000000     qvibO2=    1.000570

factor, f, is used to make QCT agree with experiment

                          kvvp for H + O2(v) = OH(vp) + O

   vp  0           1           2           3           4           5           6           7           8
  v
   0 0.1046E+03 0.5064E-06 0.1662E-15 0.6486E-26 0.4788E-37 0.0000E+00 0.0000E+00 0.0000E+00 0.0000E+00
   1 0.1248E+06 0.3458E-02 0.5504E-11 0.9402E-21 0.2793E-31 0.0000E+00 0.0000E+00 0.0000E+00 0.0000E+00
   2 0.5822E+08 0.1000E+02 0.7726E-07 0.5705E-16 0.6710E-26 0.1927E-36 0.0000E+00 0.0000E+00 0.0000E+00
   3 0.9170E+10 0.1237E+05 0.4718E-03 0.1493E-11 0.6853E-21 0.7097E-31 0.0000E+00 0.0000E+00 0.0000E+00
   4 0.3068E+12 0.6468E+07 0.1281E+01 0.1734E-07 0.3067E-16 0.1128E-25 0.1279E-35 0.0000E+00 0.0000E+00
   5 0.8746E+13 0.1327E+10 0.1566E+04 0.9165E-04 0.6193E-12 0.7978E-21 0.2942E-30 0.0000E+00 0.0000E+00
   6 0.5635E+14 0.7483E+11 0.8612E+06 0.2252E+00 0.5793E-08 0.2584E-16 0.3056E-25 0.1376E-34 0.0000E+00
   7 0.1538E+15 0.2279E+13 0.2048E+09 0.2612E+03 0.2573E-04 0.3939E-12 0.1475E-20 0.1962E-29 0.0000E+00
   8 0.2088E+15 0.2405E+14 0.1780E+11 0.1437E+06 0.5543E-01 0.2900E-08 0.3402E-16 0.1319E-24 0.2356E-33
   9 0.1526E+15 0.9594E+14 0.4548E+12 0.3670E+08 0.5885E+02 0.1055E-04 0.3844E-12 0.4294E-20 0.2070E-28
  10 0.6312E+14 0.1878E+15 0.8973E+13 0.3971E+10 0.3103E+05 0.1938E-01 0.2182E-06 0.6951E-16 0.8932E-24
  11 0.1536E+14 0.1997E+15 0.5147E+14 0.1162E+12 0.8046E+07 0.1825E+02 0.6360E-05 0.5732E-12 0.1943E-19
  12 0.2271E+13 0.1222E+15 0.1397E+15 0.3002E+13 0.9711E+09 0.8900E+04 0.9710E-02 0.2465E-08 0.2183E-15
  13 0.2098E+12 0.4487E+14 0.2064E+15 0.2489E+14 0.4352E+11 0.2240E+07 0.7893E+01 0.5643E-05 0.1296E-11
  14 0.1243E+11 0.1021E+14 0.1778E+15 0.9067E+14 0.9070E+12 0.2808E+09 0.3452E+04 0.7010E-02 0.4159E-08

  deltaE/kT    ln(kv/kv0)       kv0          kv        v

 -0.28322E+02 0.29297E+02 0.19760E-10 0.10458E+03  0
 -0.20858E+02 0.29332E+02 0.22763E-07 0.12475E+06  1
 -0.13507E+02 0.28692E+02 0.20154E-04 0.58221E+08  2
 -0.62677E+01 0.27407E+02 0.11474E-01 0.91704E+10  3
  0.86111E+00 0.26024E+02 0.15307E+01 0.30681E+12  4
  0.78812E+01 0.27750E+02 0.77694E+01 0.87476E+13  5
  0.14794E+02 0.28839E+02 0.16862E+02 0.56427E+14  6
  0.21601E+02 0.29227E+02 0.31620E+02 0.15603E+15  7
  0.28305E+02 0.29147E+02 0.51158E+02 0.23286E+15  8
  0.34906E+02 0.28821E+02 0.75725E+02 0.24897E+15  9
  0.41406E+02 0.28520E+02 0.10685E+03 0.25994E+15 10
  0.47806E+02 0.28256E+02 0.14279E+03 0.26669E+15 11
  0.54109E+02 0.27994E+02 0.18592E+03 0.26724E+15 12
  0.60316E+02 0.27795E+02 0.23458E+03 0.27641E+15 13
  0.66428E+02 0.27595E+02 0.28973E+03 0.27961E+15 14

 ln(kv/kv0) fits experimental data
 sum(kvv0) = kv0 is the prior which normalizes data
 sum(kvv) is used to extrapolate kv

                          kvpv for OH(vp) + O = O2(v) + H

   vp  0           1           2           3           4           5           6           7           8
  v
   0 0.1057E+14 0.1395E+13 0.5656E+10 0.1256E+07 0.2469E+02 0.6567E-04 0.3467E-10 0.5148E-17 0.2951E-24
   1 0.7226E+13 0.5459E+13 0.1073E+12 0.1044E+09 0.8255E+04 0.8186E-01 0.1500E-06 0.7212E-13 0.1253E-19
   2 0.2165E+13 0.1013E+14 0.9673E+12 0.4066E+10 0.1273E+07 0.4626E+02 0.2891E-03 0.4428E-09 0.2294E-15
   3 0.2448E+12 0.9000E+13 0.4241E+13 0.7640E+11 0.9334E+08 0.1223E+05 0.2564E+00 0.1231E-05 0.1872E-11
   4 0.6566E+10 0.3772E+13 0.9229E+13 0.7113E+12 0.3349E+10 0.1558E+07 0.1079E+03 0.1598E-02 0.7027E-08
   5 0.1673E+09 0.6917E+12 0.1009E+14 0.3359E+13 0.6043E+11 0.9850E+08 0.2217E+05 0.9980E+00 0.1250E-04



   6 0.1072E+07 0.3860E+11 0.5518E+13 0.8211E+13 0.5624E+12 0.3176E+10 0.2292E+07 0.3088E+03 0.1066E-01
   7 0.3235E+04 0.1306E+10 0.1451E+13 0.1053E+14 0.2762E+13 0.5349E+11 0.1223E+09 0.4867E+05 0.4741E+02
   8 0.5389E+01 0.1692E+08 0.1547E+12 0.7105E+13 0.7299E+13 0.4831E+12 0.3460E+10 0.4014E+07 0.1068E+04
   9 0.5353E-02 0.9171E+05 0.5373E+10 0.2467E+13 0.1053E+14 0.2389E+13 0.5314E+11 0.1776E+09 0.1275E+06
  10 0.3329E-05 0.2700E+03 0.1593E+09 0.4013E+12 0.8350E+13 0.6596E+13 0.4534E+12 0.4323E+10 0.8275E+07
  11 0.1345E-08 0.4767E+00 0.1518E+07 0.1950E+11 0.3595E+13 0.1031E+14 0.2194E+13 0.5919E+11 0.2989E+09
  12 0.3641E-12 0.5341E-03 0.7543E+04 0.9224E+09 0.7944E+12 0.9210E+13 0.6135E+13 0.4659E+12 0.6148E+10
  13 0.6780E-16 0.3951E-06 0.2246E+02 0.1541E+08 0.7176E+11 0.4671E+13 0.1005E+14 0.2150E+13 0.7359E+11
  14 0.0000E+00 0.1991E-09 0.4287E-01 0.1244E+06 0.3314E+10 0.1298E+13 0.9739E+13 0.5919E+13 0.5231E+12

  vp     kvp

  0 0.20214E+14
  1 0.30492E+14
  2 0.31766E+14
  3 0.32887E+14
  4 0.34035E+14
  5 0.35018E+14
  6 0.28629E+14
  7 0.85990E+13
  8 0.60315E+12
```

```
   lamda1= -0.4000000     lamda2= -1.3062500E-02            B2
   T=   500.0000      shift=   26.35600     f=  0.8080000
   Keq(JANAF)=  8.3572002E-07 qvibOH=    1.000000      qvibO2=   1.011500

   factor, f, is used to make QCT agree with experiment

                               kvvp for H + O2(v) = OH(vp) + O

      vp  0           1           2           3           4           5           6           7           8           9
    v
    0 0.7409E+07 0.7745E+02 0.8820E-04 0.1709E-10 0.8100E-18 0.1289E-25 0.9161E-34 0.0000E+00 0.0000E+00 0.0000E+
    1 0.4142E+09 0.1666E+05 0.6367E-01 0.3812E-07 0.5222E-14 0.2265E-21 0.4149E-29 0.4161E-37 0.0000E+00 0.0000E+
    2 0.1142E+11 0.1890E+07 0.2433E+02 0.4463E-04 0.1748E-10 0.2039E-17 0.9507E-25 0.2302E-32 0.0000E+00 0.0000E+
    3 0.1396E+12 0.1136E+09 0.5012E+04 0.2805E-01 0.3108E-07 0.9643E-14 0.1130E-20 0.6531E-28 0.2362E-35 0.0000E+
    4 0.7049E+12 0.3575E+10 0.5650E+06 0.9662E+01 0.3004E-04 0.2452E-10 0.7143E-17 0.9732E-24 0.7696E-31 0.4740E-
    5 0.9792E+13 0.5566E+11 0.3514E+08 0.1857E+04 0.1612E-01 0.3428E-07 0.2455E-13 0.7799E-20 0.1404E-26 0.1783E-
    6 0.4812E+14 0.3436E+12 0.1201E+10 0.2020E+06 0.4898E+01 0.2693E-04 0.4693E-10 0.3440E-16 0.1359E-22 0.3615E-
    7 0.1214E+15 0.3259E+13 0.2184E+11 0.1257E+08 0.8573E+03 0.1212E-01 0.5097E-07 0.8532E-13 0.7524E-19 0.4036E-
    8 0.1777E+15 0.2299E+14 0.1883E+12 0.4479E+09 0.8775E+05 0.3188E+01 0.3209E-04 0.1216E-09 0.2245E-15 0.2541E-
    9 0.1607E+15 0.7757E+14 0.9382E+12 0.8972E+10 0.5309E+07 0.4978E+03 0.1194E-01 0.1015E-06 0.3996E-12 0.9178E-
   10 0.9342E+14 0.1502E+15 0.1000E+14 0.9444E+11 0.1906E+09 0.4684E+05 0.2671E+01 0.5062E-04 0.4214E-09 0.1955E-
   11 0.3605E+14 0.1807E+15 0.4442E+14 0.4047E+12 0.4018E+10 0.2685E+07 0.3653E+03 0.1536E-01 0.2682E-06 0.2487E-
   12 0.9472E+13 0.1416E+15 0.1105E+15 0.4068E+13 0.4773E+11 0.9432E+08 0.3097E+05 0.2881E+01 0.1049E-03 0.1450E-
   13 0.1733E+13 0.7461E+14 0.1708E+15 0.2367E+14 0.2764E+12 0.2020E+10 0.1645E+07 0.3396E+03 0.2567E-01 0.9301E-
   14 0.2253E+12 0.2717E+14 0.1735E+15 0.7366E+14 0.1579E+13 0.2564E+11 0.5513E+08 0.2547E+05 0.3987E+01 0.2691E-

   deltaE/kT     ln(kv/kv0)       kv0          kv          v

  -0.16993E+02 0.29381E+02 0.12874E-05 0.74094E+07  0
  -0.12515E+02 0.29316E+02 0.76812E-04 0.41421E+09  1
  -0.81041E+01 0.28740E+02 0.37681E-02 0.11420E+11  2
  -0.37606E+01 0.27676E+02 0.13353E+00 0.13970E+12  3
   0.51666E+00 0.26564E+02 0.20596E+01 0.70844E+12  4
   0.47287E+01 0.27957E+02 0.71116E+01 0.98474E+13  5
   0.88765E+01 0.28834E+02 0.14558E+02 0.48460E+14  6
   0.12961E+02 0.29190E+02 0.26231E+02 0.12470E+15  7
   0.16983E+02 0.29215E+02 0.41202E+02 0.20091E+15  8
   0.20943E+02 0.29009E+02 0.60308E+02 0.23916E+15  9
   0.24843E+02 0.28739E+02 0.83804E+02 0.25374E+15 10
   0.28684E+02 0.28487E+02 0.11118E+03 0.26162E+15 11
   0.32466E+02 0.28246E+02 0.14361E+03 0.26561E+15 12
   0.36190E+02 0.28040E+02 0.18005E+03 0.27109E+15 13
   0.39857E+02 0.27852E+02 0.22152E+03 0.27618E+15 14

     ln(kv/kv0) fits experimental data
     sum(kvv0) = kv0 is the prior which normalizes data
     sum(kvv) is used to extrapolate kv

                             kvpv for OH(vp) + O = O2(v) + H

     vp  0           1           2           3           4           5           6           7           8           9
   v
   0 0.8765E+13 0.2650E+13 0.5430E+11 0.1189E+09 0.4037E+05 0.2946E+01 0.6198E-04 0.4907E-09 0.1662E-14 [illegible]
   1 0.5560E+13 0.6469E+13 0.4448E+12 0.3010E+10 0.2954E+07 0.5873E+03 0.3185E-01 0.2166E-06 0.5436E-11 [illegible]
   2 0.1862E+13 0.8913E+13 0.2065E+13 0.4281E+11 0.1201E+09 0.6424E+05 0.8867E+01 0.4145E-03 0.8391E-08 0.1069E-
   3 0.2957E+12 0.6961E+13 0.5526E+13 0.3496E+12 0.2774E+10 0.3946E+07 0.1370E+04 0.1527E+00 0.7017E-05 0.1062E-
   4 0.2073E+11 0.3041E+13 0.8647E+13 0.1671E+13 0.3722E+11 0.1393E+09 0.1201E+06 0.3159E+02 0.3256E-02 0.1649E-
   5 0.4266E+10 0.7014E+12 0.7967E+13 0.4757E+13 0.2960E+12 0.2885E+10 0.6118E+07 0.3751E+04 0.8577E+00 0.9192E-




   6 0.3312E+09 0.6841E+11 0.4302E+13 0.8179E+13 0.1421E+13 0.3581E+11 0.1846E+09 0.2614E+06 0.1312E+03 0.5344E-
   7 0.1407E+08 0.1092E+11 0.1317E+13 0.8569E+13 0.4186E+13 0.2714E+12 0.3378E+10 0.1091E+08 0.1190E+05 0.5536E+
   8 0.3690E+06 0.1380E+10 0.2034E+12 0.5469E+13 0.7676E+13 0.1278E+13 0.3811E+11 0.2786E+09 0.6536E+06 0.6241E+
   9 0.6355E+04 0.8874E+08 0.1931E+11 0.2087E+13 0.8848E+13 0.3603E+13 0.2701E+12 0.4432E+10 0.2217E+08 0.4305E+
  10 0.7480E+02 0.3479E+07 0.4168E+10 0.4447E+12 0.6429E+13 0.7244E+13 0.1223E+13 0.4474E+11 0.4731E+09 0.1852E+
  11 0.6201E+00 0.8992E+05 0.3977E+09 0.4095E+11 0.2913E+13 0.8923E+13 0.3594E+13 0.2916E+12 0.6470E+10 0.5062E+
  12 0.3712E-02 0.1604E+04 0.2253E+08 0.9378E+10 0.7882E+12 0.7140E+13 0.6941E+13 0.1247E+13 0.5766E+11 0.8949E+
  13 0.1639E-04 0.2041E+02 0.8408E+06 0.1317E+10 0.1102E+12 0.3690E+13 0.8900E+13 0.3546E+13 0.3404E+12 0.1041E+
  14 0.5443E-07 0.1899E+00 0.2182E+05 0.1047E+09 0.1608E+11 0.1197E+13 0.7618E+13 0.6794E+13 0.1351E+13 0.6092E+

   vp     kvp

   0 0.16509E+14
   1 0.28815E+14
   2 0.30550E+14
   3 0.31625E+14
   4 0.32723E+14
   5 0.33586E+14
   6 0.28589E+14
   7 0.11928E+14
   8 0.17560E+13
   9 0.92280E+11
  10 0.19945E+10
```

B3

one.for; 4
kvp.dat; 5
a1000.dat; 8

```
T=   1000.000    shift=   27.15000    f=    1.097610
Keq(JANAF)=  3.9047999E-03 qvibOH=    1.005920      qvibO2=    1.119870

factor, f, is used to make QCT agree with experiment

                       kvvp for H + O2(v) = OH(vp) + O

    vp   0            1            2            3            4            5            6            7            8            9            10
 v
  0 0.2703E+11 0.6627E+06 0.2335E+05 0.1696E+01 0.3617E-04 0.2478E-09 0.8165E-15 0.1509E-20 0.1893E-26 0.1915E-32 0.0000E+0
  1 0.1698E+12 0.1229E+10 0.1151E+07 0.2080E+03 0.9884E-02 0.1610E-06 0.1139E-11 0.4331E-17 0.1073E-22 0.2059E-28 0.3583E-3
  2 0.6246E+12 0.1389E+11 0.3468E+08 0.1550E+05 0.1720E+01 0.6230E-04 0.9371E-09 0.7258E-14 0.3515E-19 0.1269E-24 0.3994E-3
  3 0.1287E+13 0.7630E+11 0.6680E+09 0.7132E+06 0.1834E+03 0.1464E-01 0.4636E-06 0.7244E-11 0.6797E-16 0.4569E-21 0.2581E-2
  4 0.1814E+13 0.4080E+12 0.7600E+10 0.2061E+08 0.1221E+05 0.2128E+01 0.1406E-03 0.4391E-08 0.7909E-13 0.9819E-18 0.9867E-2
  5 0.1230E+14 0.1030E+13 0.5640E+11 0.3795E+09 0.5154E+06 0.1949E+03 0.2662E-01 0.1647E-05 0.5644E-10 0.1283E-14 0.2275E-1
  6 0.4373E+14 0.1434E+13 0.2649E+12 0.4506E+10 0.1402E+08 0.1142E+05 0.3202E+01 0.2892E-03 0.2516E-07 0.1036E-11 0.3222E-1
  7 0.9430E+14 0.5335E+13 0.7770E+12 0.3481E+11 0.2494E+09 0.4860E+06 0.2489E+03 0.5895E-01 0.7131E-05 0.5302E-09 0.2858E-1
  8 0.1324E+15 0.2410E+14 0.1359E+13 0.1755E+12 0.2932E+10 0.1098E+08 0.1270E+05 0.5819E+01 0.1307E-02 0.1737E-06 0.1614E-1
  9 0.1263E+15 0.6476E+14 0.2198E+13 0.5737E+12 0.2302E+11 0.1852E+09 0.4320E+06 0.3804E+03 0.1575E+00 0.3712E-04 0.5902E-0
 10 0.8441E+14 0.1133E+15 0.1251E+14 0.1181E+13 0.1212E+12 0.2115E+10 0.9932E+07 0.1672E+05 0.1267E+02 0.5261E-02 0.1421E-0
 11 0.4050E+14 0.1358E+15 0.4098E+14 0.1413E+13 0.4266E+12 0.1651E+11 0.1563E+09 0.5009E+06 0.6911E+03 0.5021E+00 0.2289E-0
 12 0.1426E+14 0.1153E+15 0.8704E+14 0.6293E+13 0.7869E+12 0.8858E+11 0.1703E+10 0.1037E+08 0.2591E+05 0.3276E+02 0.2503E-0
 13 0.3733E+13 0.7108E+14 0.1273E+15 0.2467E+14 0.1424E+13 0.3266E+12 0.1297E+11 0.1502E+09 0.6769E+06 0.1480E+04 0.1885E+0
 14 0.7422E+12 0.3249E+14 0.1330E+15 0.6205E+14 0.3156E+13 0.8181E+12 0.6940E+11 0.1537E+10 0.1248E+08 0.4696E+05 0.9920E+02

   deltaE/kT     ln(kv/kv0)        kv0          kv        v

 -0.84967E+01  0.29626E+02 0.36864E-02 0.27101E+11   0
 -0.62574E+01  0.29565E+02 0.24729E-01 0.17098E+12   1
 -0.40521E+01  0.29101E+02 0.14683E+00 0.63850E+12   2
 -0.18803E+01  0.28278E+02 0.72496E+00 0.13841E+13   3
  0.25833E+00  0.27491E+02 0.25643E+01 0.22294E+13   4
  0.23644E+01  0.28467E+02 0.58033E+01 0.13390E+14   5
  0.44382E+01  0.29086E+02 0.10603E+02 0.45435E+14   6
  0.64804E+01  0.29388E+02 0.17341E+02 0.10045E+15   7
  0.84914E+01  0.29442E+02 0.25846E+02 0.15802E+15   8
  0.10472E+02  0.29301E+02 0.36500E+02 0.19384E+15   9
  0.12422E+02  0.29090E+02 0.49189E+02 0.21155E+15  10
  0.14342E+02  0.28861E+02 0.64043E+02 0.21917E+15  11
  0.16233E+02  0.28646E+02 0.81178E+02 0.22394E+15  12
  0.18095E+02  0.28453E+02 0.10048E+03 0.22852E+15  13
  0.19929E+02  0.28274E+02 0.12217E+03 0.23235E+15  14

 ln(kv/kv0) fits experimental data
 sum(kvv0) = kv0 is the prior which normalizes data
 sum(kvv) is used to extrapolate kv

                       kvpv for OH(vp) + O = O2(v) + H

    vp   0            1            2            3            4            5            6            7            8            9            10
 v
  0 0.6219E+13 0.2592E+13 0.1225E+12 0.9461E+09 0.1614E+07 0.7922E+03 0.1420E+00 0.1153E-04 0.5157E-09 0.1515E-13 0.3436E-18
  1 0.4160E+13 0.5120E+13 0.6435E+12 0.1236E+11 0.4972E+08 0.5483E+05 0.2111E+02 0.3527E-02 0.3113E-06 0.1736E-10 0.7184E-15
  2 0.1687E+13 0.6379E+13 0.2137E+13 0.1015E+12 0.9534E+09 0.2339E+07 0.1914E+04 0.6513E+00 0.1124E-03 0.1178E-07 0.8825E-12
  3 0.3963E+12 0.5041E+13 0.4551E+13 0.5324E+12 0.1159E+11 0.6264E+08 0.1079E+06 0.7410E+02 0.2478E-01 0.4838E-05 0.6500E-09
  4 0.6578E+11 0.2517E+13 0.6289E+13 0.1813E+13 0.9087E+11 0.1073E+10 0.3856E+07 0.5291E+04 0.3397E+01 0.1225E-02 0.2928E-06
  5 0.5431E+11 0.7736E+12 0.5680E+13 0.4063E+13 0.4671E+12 0.1196E+11 0.8687E+08 0.2416E+06 0.2950E+03 0.1948E+00 0.8216E-04
  6 0.2427E+11 0.1353E+12 0.3354E+13 0.6064E+13 0.1597E+13 0.8812E+11 0.1344E+10 0.7175E+07 0.1658E+05 0.1982E+02 0.1463E-01
  7 0.6789E+10 0.6532E+11 0.1276E+13 0.6078E+13 0.3685E+13 0.4362E+12 0.1355E+11 0.1410E+09 0.6079E+06 0.1313E+04 0.1683E+01
  8 0.1276E+10 0.3950E+11 0.2987E+12 0.4102E+13 0.5801E+13 0.1471E+13 0.9257E+11 0.1863E+10 0.1492E+08 0.5757E+05 0.1272E+03
  9 0.1680E+09 0.1465E+11 0.6871E+11 0.1851E+13 0.6285E+13 0.3425E+13 0.4346E+12 0.1681E+11 0.2481E+09 0.1699E+07 0.6423E+04
 10 0.1597E+08 0.3648E+10 0.5400E+11 0.5422E+12 0.4707E+13 0.5564E+13 0.1422E+13 0.1051E+12 0.2840E+10 0.3425E+08 0.2200E+06
 11 0.1123E+07 0.6408E+09 0.2593E+11 0.9507E+11 0.2429E+13 0.6365E+13 0.3279E+13 0.4617E+12 0.2270E+11 0.4791E+09 0.5194E+07
 12 0.5960E+05 0.8210E+08 0.8814E+10 0.6390E+11 0.3462E+12 0.5154E+13 0.5378E+13 0.1462E+13 0.1285E+12 0.4715E+10 0.8572E+08
 13 0.2428E+04 0.7863E+07 0.1889E+10 0.3892E+11 0.1901E+12 0.2952E+13 0.6379E+13 0.3245E+13 0.5214E+12 0.3311E+11 0.1003E+10
 14 0.7716E+02 0.5745E+06 0.3165E+09 0.1564E+11 0.6735E+11 0.1182E+13 0.5457E+13 0.5309E+13 0.1536E+13 0.1679E+12 0.8437E+10

   vp     kvp

  0 0.12615E+14
  1 0.22682E+14
  2 0.24508E+14
  3 0.25374E+14
  4 0.26181E+14
  5 0.26651E+14
  6 0.22471E+14
  7 0.10583E+14
  8 0.22118E+13
  9 0.20628E+12
 10 0.95314E+10
```

```
 lamda1= -0.9500000     lamda2= -0.1260325          B4
 T=    2000.000      shift=    27.91000     f=    [illegible]
 Keq(JANAF)=  0.2290500        q-ibOH=     1.084030      q-ibO2=     1.490750

   factor, f, is used to make QCT agree with experiment

                            kvvp for H + O2(v) = OH(vp) + O

      vp  0           1           2           3           4           5           6           7
   v
    0 0.1651E+13 0.6497E+11 0.5672E+09 0.1430E+07 0.1302E+04 0.5204E+00 0.1090E-03 0.1403E-07 [illegible]
    1 0.3798E+13 0.3325E+12 0.6035E+10 0.3015E+08 0.5223E+05 0.3832E+02 0.1424E-01 0.3146E-05 [illegible]
    2 0.6012E+13 0.1188E+13 0.4477E+11 0.4408E+09 0.1443E+07 0.1929E+04 0.1262E+01 0.4726E-03 [illegible]
    3 0.6502E+13 0.2982E+13 0.2343E+12 0.4530E+10 0.2786E+08 0.6736E+05 0.7704E+02 0.4917E-01 [illegible]
    4 0.6026E+13 0.5286E+13 0.8738E+12 0.3311E+11 0.3806E+09 0.1654E+07 0.3284E+04 0.3524E+01 [illegible]
    5 0.2156E+14 0.6599E+13 0.2341E+13 0.1742E+12 0.3726E+10 0.2894E+08 0.9913E+05 0.1777E+03 [illegible]
    6 0.5242E+14 0.5732E+13 0.4529E+13 0.6659E+12 0.2646E+11 0.3654E+09 0.2146E+07 0.6363E+04 [illegible]
    7 0.9075E+14 0.1221E+14 0.6331E+13 0.1865E+13 0.1377E+12 0.3369E+10 0.3375E+08 0.1658E+06 [illegible]
    8 0.1155E+15 0.3441E+14 0.6353E+13 0.3851E+13 0.5308E+12 0.2294E+11 0.3900E+09 0.3140E+07 [illegible]
    9 0.1108E+15 0.6934E+14 0.6818E+13 0.5874E+13 0.1526E+13 0.1165E+12 0.3351E+10 0.4404E+08 [illegible]
   10 0.8164E+14 0.1035E+15 0.2180E+14 0.6600E+13 0.3296E+13 0.4459E+12 0.2163E+11 0.4619E+09 [illegible]
   11 0.4698E+14 0.1174E+15 0.5005E+14 0.5402E+13 0.5364E+13 0.1295E+13 0.1059E+12 0.3663E+10 [illegible]
   12 0.2143E+14 0.1033E+15 0.8568E+14 0.1365E+14 0.6575E+13 0.2874E+13 0.3968E+12 0.2218E+11 [illegible]
   13 0.7846E+13 0.7172E+14 0.1124E+15 0.3498E+14 0.6026E+13 0.4893E+13 0.1147E+13 0.1035E+12 [illegible]
   14 0.2334E+13 0.3962E+14 0.1154E+15 0.6725E+14 0.8624E+13 0.6396E+13 0.2575E+13 0.3754E+12 [illegible]

    deltaE/kT      ln(kv/kv0)       kv0          kv          v

   -0.42484E+01 0.29579E+02 0.24478E+00 0.17165E+13  0
   -0.31287E+01 0.29592E+02 0.58201E+00 0.41369E+13  1
   -0.20260E+01 0.29347E+02 0.13020E+01 0.72445E+13  2
   -0.94016E+00 0.28915E+02 0.26938E+01 0.97231E+13  3
    0.12917E+00 0.28519E+02 0.50266E+01 0.12219E+14  4
    0.11822E+01 0.28929E+02 0.83805E+01 0.30673E+14  5
    0.22191E+01 0.29223E+02 0.12892E+02 0.63372E+14  6
    0.32402E+01 0.29416E+02 0.18641E+02 0.11130E+15  7
    0.42457E+01 0.29465E+02 0.25667E+02 0.16069E+15  8
    0.52359E+01 0.29373E+02 0.34063E+02 0.19447E+15  9
    0.62109E+01 0.29232E+02 0.43827E+02 0.21731E+15 10
    0.71710E+01 0.29047E+02 0.55024E+02 0.22664E+15 11
    0.81164E+01 0.28872E+02 0.67665E+02 0.23393E+15 12
    0.90474E+01 0.28704E+02 0.81767E+02 0.23912E+15 13
    0.99643E+01 0.28545E+02 0.97362E+02 0.24276E+15 14

  ln(kv/kv0) fits experimental data
  sum(kvv0) = kv0 is the prior which normalizes data
  sum(kvv) is used to extrapolate kv

                          kvpv for OH(vp) + O = O2(v) + H

     vp  0          1          2          3          4          5          6
   v
   0 0.5241E+13 0.2690E+13 0.2720E+12 0.7072E+10 0.5922E+08 0.1948E+06 0.3009E+03 0.2867E+00 [illegible]
   1 0.3936E+13 0.4493E+13 0.9444E+12 0.4866E+11 0.7754E+09 0.4681E+07 0.1263E+05 0.1880E+02 [illegible]
   2 0.2068E+13 0.5327E+13 0.2326E+13 0.2362E+12 0.7114E+10 0.7823E+08 0.3776E+06 0.9434E+03 [illegible]
   3 0.7552E+12 0.4517E+13 0.4110E+13 0.8193E+12 0.4635E+11 0.9222E+09 0.7761E+07 0.3291E+05 [illegible]
   4 0.2402E+12 0.2748E+13 0.5261E+13 0.2056E+13 0.2174E+12 0.7772E+10 0.1139E+09 0.8098E+06 [illegible]
   5 0.[illegible]998E+12 0.1197E+13 0.4918E+13 0.3773E+13 0.7425E+12 0.4745E+11 0.1199E+10 0.1424E+08 [illegible]



   6 0.[illegible]565E+12 0.3666E+12 0.3373E+13 0.5113E+13 0.1869E+13 0.2124E+12 0.9203E+10 0.1314E+09 [illegible]
   7 0.[illegible]612E+12 0.2629E+12 0.1698E+13 0.5159E+13 0.3505E+13 0.7054E+12 0.5212E+11 0.1645E+10 [illegible]
   8 0.7506E+11 0.2916E+12 0.6235E+12 0.3897E+13 0.4941E+13 0.1757E+13 0.2204E+12 0.1176E+11 [illegible]
   9 0.[illegible]675E+11 0.2183E+12 0.2486E+12 0.2208E+13 0.5279E+13 0.3317E+13 0.7035E+12 0.6128E+11 [illegible]
  10 0.[illegible]434E+10 0.1229E+12 0.2999E+12 0.9359E+12 0.4300E+13 0.4766E+13 0.1713E+13 0.2425E+12 [illegible]
  11 0.1638E+10 0.5339E+11 0.2636E+12 0.2933E+12 0.2679E+13 0.5322E+13 0.3210E+13 0.7361E+12 [illegible]
  12 0.2902E+09 0.1825E+11 0.1753E+12 0.2679E+12 0.1276E+13 0.4569E+13 0.4674E+13 0.1732E+13 [illegible]
  13 0.4188E+08 0.4993E+10 0.9063E+11 0.2908E+12 0.4609E+12 0.3079E+13 0.5226E+13 0.3165E+13 [illegible]
  14 0.4982E+07 0.1108E+10 0.3719E+11 0.2235E+12 0.2637E+12 0.1609E+13 0.4779E+13 0.4619E+13 [illegible]

   vp      kvp

    0 0.13071E+14
    1 0.22334E+14
    2 0.24641E+14
    3 0.25348E+14
    4 0.25569E+14
    5 0.25434E+14
    6 0.20668E+14
    7 0.10529E+14
    8 0.19994E+13
    9 0.47500E+12
   10 [illegible]E+11
```

```
  lamda1=  -1.510000      lamda2= -0.4198315            B5
  T=   4000.000      shift=    28.33000      f=    3.019020
  Keq(JANAF)=     1.533330      qvibOH=    1.396010     qvibO2=   [illegible]

  factor, f, is used to make QCT agree with experiment

                          kvvp for H + O2(v) = OH(vp) + O

     vp   0            1            2            3            4            5            6
   v
   0 0.1239E+14 0.1718E+13 0.6762E+11 0.9250E+09 0.5263E+07 0.1464E+05 0.2303E+02 [illegible] [illegible]
   1 0.1847E+14 0.4867E+13 0.3490E+12 0.8401E+10 0.6151E+08 0.3755E+06 0.9516E+03 0.1517E+01 [illegible]
   2 0.2070E+14 0.1034E+14 0.1345E+13 0.5664E+11 0.9311E+09 0.7056E+07 0.2862E+05 0.7113E+02 [illegible]
   3 0.1756E+14 0.1666E+14 0.3914E+13 0.2867E+12 0.7936E+10 0.9834E+08 0.6344E+06 [illegible] [illegible]
   4 0.1380E+14 0.2050E+14 0.8686E+13 0.1102E+13 0.5106E+11 0.1028E+10 0.1049E+08 0.6219E+05 [illegible]
   5 0.3370E+14 0.1943E+14 0.1484E+14 0.3247E+13 0.2507E+12 0.8157E+10 0.1307E+09 0.1187E+07 [illegible]
   6 0.6280E+14 0.1428E+14 0.1968E+14 0.7410E+13 0.9487E+12 0.4962E+11 0.1243E+10 0.1719E+08 0.1490E+06
   7 0.9087E+14 0.2261E+14 0.2043E+14 0.1322E+14 0.2795E+13 0.2339E+12 0.9108E+10 0.1907E+09 [illegible]
   8 0.1037E+15 0.4682E+14 0.1670E+14 0.1857E+14 0.6472E+13 0.8623E+12 0.5195E+11 0.1639E+10 [illegible]
   9 0.9449E+14 0.7608E+14 0.1504E+14 0.2072E+14 0.1188E+14 0.2511E+13 0.2330E+12 [illegible] [illegible]
  10 0.6971E+14 0.9846E+14 0.3397E+14 0.1848E+14 0.1742E+14 0.5825E+13 0.8289E+12 0.5853E+11 [illegible]
  11 0.4209E+14 0.1028E+15 0.6082E+14 0.1325E+14 0.2055E+14 0.1086E+14 0.2361E+13 [illegible] 0.1440E+11
  12 0.2102E+14 0.8770E+14 0.8758E+14 0.2444E+14 0.1965E+14 0.1638E+14 0.5426E+13 0.8431E+12 [illegible]
  13 0.8771E+13 0.6178E+14 0.1027E+15 0.4736E+14 0.1530E+14 0.2013E+14 0.1015E+14 [illegible] [illegible]
  14 0.3086E+13 0.3631E+14 0.9930E+14 0.7452E+14 0.1772E+14 0.2031E+14 0.1555E+14 [illegible] [illegible]

   deltaE/kT     ln(kv/kv0)       kv0          kv        v

  -0.21242E+01 0.29280E+02 0.27261E+01 0.14178E+14   0
  -0.15643E+01 0.29395E+02 0.40602E+01 0.23699E+14   1
  -0.10130E+01 0.29334E+02 0.59078E+01 0.32446E+14   2
  -0.47005E+00 0.29154E+02 0.83775E+01 0.38425E+14   3
   0.64583E-01 0.28972E+02 0.11549E+02 0.44141E+14   4
   0.59109E+00 0.29161E+02 0.15468E+02 0.71469E+14   5
   0.11096E+01 0.29282E+02 0.20184E+02 0.10517E+15   6
   0.16201E+01 0.29395E+02 0.25727E+02 0.15016E+15   7
   0.21229E+01 0.29425E+02 0.32121E+02 0.19313E+15   8
   0.26179E+01 0.29356E+02 0.39391E+02 0.22097E+15   9
   0.31054E+01 0.29269E+02 0.47548E+02 0.24474E+15  10
   0.35855E+01 0.29128E+02 0.56608E+02 0.25301E+15  11
   0.40582E+01 0.29005E+02 0.66574E+02 0.26311E+15  12
   0.45237E+01 0.28874E+02 0.77452E+02 0.26885E+15  13
   0.49821E+01 0.28749E+02 0.89243E+02 0.27305E+15  14

  ln(kv/kv0) fits experimental data
  sum(kvv0) = kv0 is the prior which normalizes data
  sum(kvv) is used to extrapolate kv

                          kvpv for OH(vp) + O = O2(v) + H

     vp  0           1            2            3            4            5            6            7
   v
   0 [illegible] 0.2385E+13 0.3194E+12 0.1403E+11 0.2421E+09 0.1931E+07 0.8253E+04 [illegible] [illegible]
   1 [illegible] 0.3659E+13 0.9417E+12 0.7278E+11 0.2142E+10 0.2830E+08 0.1948E+06 0.7996E+03 [illegible]
   2 [illegible] 0.4726E+13 0.2091E+13 0.2827E+12 0.1410E+11 0.3065E+09 0.3376E+07 0.2160E+05 [illegible]
   3 [illegible] 0.4421E+13 0.3536E+13 0.8316E+12 0.6982E+11 0.2482E+10 0.4349E+08 0.4311E+06 [illegible]
   4 0.5944E+12 0.3188E+13 0.4597E+13 0.1872E+13 0.2632E+12 0.1520E+11 0.4211E+09 0.6430E+07 [illegible]
   5 [illegible] 0.1784E+13 0.4639E+13 0.3259E+13 0.7632E+12 0.7123E+11 0.3101E+10 [illegible] [illegible]


   6 [illegible] 0.7808E+12 0.3664E+13 0.4429E+13 0.1720E+13 0.2560E+12 [illegible] [illegible] [illegible]
   7 [illegible] 0.7420E+12 0.2282E+13 0.4740E+13 0.3041E+13 0.7298E+12 0.7720E+11 [illegible] [illegible]
   8 0.5699E+12 0.9295E+12 0.1128E+13 0.4030E+13 0.4259E+13 0.1628E+13 0.2664E+12 0.2164E+11 [illegible]
   9 0.3167E+12 0.9207E+12 0.6194E+12 0.2741E+13 0.4765E+13 0.2889E+13 0.7261E+12 0.6868E+11 [illegible]
  10 [illegible] 0.7318E+12 0.8592E+12 0.1501E+13 0.4291E+13 0.4117E+13 0.1591E+13 0.2892E+12 [illegible]
  11 [illegible] 0.4728E+12 0.9519E+12 0.6658E+12 0.3133E+13 0.4747E+13 [illegible] 0.7574E+12 [illegible]
  12 [illegible] 0.2514E+12 0.8544E+12 0.7654E+12 0.1867E+13 0.4463E+13 0.4016E+13 [illegible] [illegible]
  13 [illegible] 0.1118E+12 0.6291E+12 0.9314E+12 0.9128E+12 0.3445E+13 [illegible] [illegible] [illegible]
  14 [illegible] [illegible] 0.3845E+12 0.9266E+12 0.6683E+12 [illegible] [illegible] [illegible] [illegible]

   vp      kvp

   0 [illegible]E+14
   1 [illegible]E+14
   2 [illegible]E+14
   3 [illegible]E+14
   4 [illegible]E+14
   5 [illegible]E+14
   6 [illegible]E+14
   7 [illegible]E+13
   8 [illegible]E+13
   9 [illegible]E+12
  10 [illegible]E+11
```

```
  lamda1=   -2.000000        lamda2=   -1.39[illegible]       D6
  T=   8000.000       shift=    29.00000      f=    3.77[illegible]
  Keq(JANAF)=     3.007000        qvibOH=     2.19[illegible]      qvibO2=    [illegible].165400

  factor, f, is used to make [illegible] agree with experiment

                          [illegible] for [illegible] = OH(vp) + O

     vp  0              1              2              3              4              5              6
   v
   0 0.2831E+14 0.5668E+13 0.4070E+12 0.1226E+11 0.1786E+09 0.1439E+07 0.7204E+04 [illegible]
   1 0.3938E+14 0.1322E+14 0.1549E+13 0.7427E+11 0.1683E+10 0.2056E+08 0.1526E+06 0.7715E+03 [illegible]
   2 0.4366E+14 0.2443E+14 0.4645E+13 0.3522E+12 0.1232E+11 0.2273E+09 0.2494E+07 [illegible]
   3 0.3696E+14 0.3611E+14 0.1107E+14 0.1320E+13 0.7091E+11 0.1962E+10 0.3160E+08 [illegible]
   4 0.3213E+14 0.4310E+14 0.2118E+14 0.3948E+13 0.3237E+12 0.1336E+11 0.3143E+09 [illegible]
   5 0.5471E+14 0.4190E+14 0.3283E+14 0.9509E+13 0.1183E+13 0.7251E+11 0.2477E+10 [illegible]
   6 0.7587E+14 0.3346E+14 0.4156E+14 0.1861E+14 0.3496E+13 0.3162E+12 0.1561E+11 [illegible]
   7 0.8653E+14 0.4736E+14 0.4335E+14 0.2985E+14 0.8420E+13 0.1118E+13 0.7934E+11 0.3373E+10 [illegible]
   8 0.8192E+14 0.6554E+14 0.3755E+14 0.3956E+14 0.1667E+14 0.3235E+13 0.3283E+12 0.1756E+11 [illegible]
   9 0.6497E+14 0.8228E+14 0.3388E+14 0.4365E+14 0.2735E+14 0.7716E+13 0.1115E+13 0.9270E+11 [illegible]
  10 0.4353E+14 0.8653E+14 0.5496E+14 0.4043E+14 0.3748E+14 0.1530E+14 0.3132E+13 0.3618E+12 [illegible]
  11 0.2485E+14 0.7690E+14 0.7475E+14 0.3166E+14 0.4321E+14 0.2541E+14 0.7338E+13 0.1172E+13 [illegible]
  12 0.1218E+14 0.5822E+14 0.8593E+14 0.4541E+14 0.4223E+14 0.3561E+14 0.1444E+14 [illegible]
  13 0.5161E+13 0.3784E+14 0.8418E+14 0.6594E+14 0.3522E+14 0.4240E+14 0.2405E+14 [illegible]
  14 0.1906E+13 0.2129E+14 0.7080E+14 0.8163E+14 0.3745E+14 0.4319E+14 0.3411E+14 [illegible]

   deltaE/kT      [illegible]        kv0           kv           v

   -0.10621E+01 0.28667E+02 0.12211E+02 0.34401E+14   0
   -0.76217E+00 0.28933E+02 0.14745E+02 0.54221E+14   1
   -0.50651E+00 0.29051E+02 0.17664E+02 0.73101E+14   2
   -0.23504E+00 0.29059E+02 0.20990E+02 0.87542E+14   3
    0.32292E-01 0.29035E+02 0.24738E+02 0.10070E+15   4
    0.29555E+00 0.29210E+02 0.28917E+02 0.14021E+15   5
    0.55478E+00 0.29274E+02 0.33532E+02 0.17334E+15   6
    0.81006E+00 0.29336E+02 0.38586E+02 0.21271E+15   7
    0.10614E+01 0.29346E+02 0.44078E+02 0.24463E+15   8
    0.13090E+01 0.29284E+02 0.50006E+02 0.26106E+15   9
    0.15527E+01 0.29205E+02 0.56363E+02 0.28176E+15  10
    0.17927E+01 0.29140E+02 0.63142E+02 0.285[illegible]E+15  11
    0.20291E-01 0.29074E+02 0.70332E+02 0.29765E+15  12
    0.22619E+01 0.289[illegible]E+02 0.77921E+02 0.30350E+15  13
    0.24911E+01 0.28909E+02 0.85695E+02 0.30836E+15  14

  [illegible] fits experimental data
  sum(kvv0) = kv0 in the prior which normalizes [illegible]
  sum [illegible] is used to extrapolate kv

                       [illegible] for OH(vp) + O = [illegible] + H

     [illegible]            1              2              3              4              5              6
   v
   0 0.4969E+13 0.1889E+13 0.2502E+12 0.1350E+11 0.3430E+09 0.4676E+07 0.3858E+05 [illegible]
   1 0.5220E+13 0.3330E+13 0.7200E+12 0.6185E+11 0.2441E+10 0.5051E+08 0.6187E+06 [illegible]
   2 0.4393E+13 0.4671E+13 0.1638E+13 0.2226E+12 0.1357E+11 0.4237E+09 0.7662E+07 [illegible]
   3 0.2988E+13 0.5[illegible]E+13 0.2977E+13 0.6360E+12 0.5950E+11 0.2788E+10 0.7402E+08 [illegible]
   4 0.1886E+13 0.4809E+13 0.4360E+13 0.1456E+13 0.2079E+12 0.1454E+11 0.5635E+09 0.1355E+08 [illegible]
   5 0.1469E+13 0.359[illegible]E+13 0.5193E+13 0.2695E+13 0.5641E+12 0.6062E+11 0.3412E+10 0.1167E+09 [illegible]


   [illegible] 0.2842E+13 0.2214E+13 0.5073E+13 0.4070E+13 0.1332E+13 0.2040E+12 [illegible]
   7 0.2334E+13 0.2022E+13 0.4099E+13 0.5057E+13 0.2485E+13 0.5589E+12 0.6535E[illegible] [illegible]
   8 0.1718E+13 0.2413E+13 0.2762E+13 0.5212E+13 0.3826E+13 0.1257E+13 0.2103E[illegible] [illegible]
   9 0.1084E+13 0.2561E+13 0.1945E+13 0.4491E+13 0.4901E+13 0.2342E+13 0.5579E+12 0.7439E+11 [illegible]
  10 0.5587E+12 0.2110E+13 0.2473E+13 0.3260E+13 0.5263E+13 0.3639E+13 0.1226E+13 [illegible]
  11 [illegible] 0.1475E+13 0.2646E+13 0.2008E+13 0.4773E+13 0.4754E+13 [illegible]
  12 0.9705E+11 0.8816E[illegible] 0.2401E+13 0.2274E+13 0.3683E+13 0.5259E+13 [illegible]
  13 [illegible] 0.4541E[illegible] 0.1864E+13 0.2616E+13 0.2434E+13 0.4962E+13 [illegible]
  14 [illegible] [illegible] 0.1246E+13 0.2575E+13 0.2057E+13 0.4019E+13 [illegible]

   [illegible]

   [illegible]
   1 [illegible]
   2 0.3[illegible]E+14
   3 0.3[illegible]E+14
   4 [illegible]E+14
   5 [illegible]707[illegible]E+14
   6 [illegible]E+14
   7 0.[illegible]E+13
   8 [illegible]E+13
   9 0.[illegible]E+12
  10 [illegible]E+11
```

Extrap.f

```
      dimension e(10), f(10), x(10), y(10),z(10),zz(10),d(10),g(10,10)
C     open (6,file='kvv.dat', status='new')
      t=298.
      do 6 j=1,10
      e(j) = 2603.7558*(j-1) - 45.221*(j-1)**2 -0.0029*(j-1)**3
    6 e(j) = 1.4388*e(j)
c     a is lamda. It and shift (=lamda0) are best fits to the data.
c     factor adjusts Miller's calculations to fit experiments.
      factor = 1.0000
      eqcon = 4.938e-12
      qvibOH = 1.0000043
      qvibO2 = 1.0000009
      a = 0.16
      shift  = -28.23
      write (6,*) ' '
      write (6,*) ' '
      write (6,*) 'lamda=',a,'T=',t,'shift=',shift,'f=',factor
      write (6,*) 'Keq(JANAF)=',eqcon,' qvibOH=',qvibOH,'qvibO2=',qvibO2
      write (6,*) ' '
      write (6,*) 'factor, f, is used to make QCT agree with experiment'
      write (6,*) ' '
      write (6,*) '                kvvp for H + O2(v) = OH(vp) + O'
      write (6,*) ' '
      write (6,1)  ((m-1), m=1,11)
    1 format (4x,'vp', 10(i3,8x),i3)
      write (6,*) ' v'
      do 7 j = 1,10
      f(j) = 2938.29*(j-1) - 52.4821*(j-1)**2 + 0.2243*(j-1)**3
      f(j) = 1.4388*f(j)
      x(j) = (f(j) - 7859.2057)/t
      z(j) = 0.0
      zz(j) = 0.0
      do 8 k = 1,10
      dd = x(j)/2 - e(k)/2/t
      if (dd.le.0.0) go to 9
      bes2 = bsk0(dd) + 2*bsk1(dd)/dd
      d(k) = dd**2*bes2*exp(dd)*exp(-2*a*dd + shift)*factor
      g(j,k) = d(k)*qvibOH/(eqcon*qvibO2)*exp((e(k)-f(j))/t)
      z(j) = z(j) + dd**2*bes2*exp(dd)*factor
      zz(j) = zz(j) + dd**2*bes2*exp(dd)*exp(-2*a*dd + shift)*factor
      go to 8
    9 if (dd.lt.0.0) go to 10
      d(k) = 2.0*exp(shift)*factor
      g(j,k) = d(k)*qvibOH/(eqcon*qvibO2)*exp((e(k)-f(j))/t)
      z(j) = z(j) + 2.0*factor
      zz(j) = zz(j) + 2.*exp(shift)*factor
```

```
   go to 8
 10 c = abs(dd)
   bes2 = bsk0(c) + 2*bsk1(c)/c
   s = dd**2*bes2*factor
   d(k) = dd**2*bes2*exp(dd-2*a*c + shift)*factor
   g(j,k) = s*qvibOH/(eqcon*qvibO2)*exp((e(k)-f(j))/t+dd-2*a*c+shift)
   z(j) = z(j) + dd**2*bes2*exp(dd)*factor
   zz(j) = zz(j) + dd**2*bes2*exp(dd-2*a*c + shift)*factor
 8 continue
   write (6,4) (j-1), (d(k), k = 1,10)
 4 format (1x, i2, 10e11.4)
   y(j) = alog(zz(j)/z(j))
 7 continue
   write (6,*) ' '
   write (6,*) ' deltaE/kT   ln(kv/kv0)     kv0        kv      v'
   write (6,*) ' '
   write (6,3) (x(j),y(j),z(j),zz(j), (j-1), j = 1,10)
 3 format (1x, 4e12.5, i3)
   write (6,*) ' '
   write (6,*) 'ln(kv/kv0) fits experimental data'
   write (6,*) 'sum(kvv0) = kv0 is the prior which normalizes data'
   write (6,*) 'sum(kvv) is used to extrapolate kv'
   write (6,*) ' '
   write (6,*) '                    kvpv for OH(vp) + O = O2(v) + H'
   write (6,*) ' '
   write (6,1) ((m-1), m=1,11)
   write (6,*) ' v'
   do 5 j = 1,10
 5 write (6,4) (j-1), (g(j,k), k = 1, 10)
   write (6,*) ' '
   write (6,*) ' '
   write (6,*) ' vp    kvp'
   write (6,*) ' '
   do 13 k=1,9
   rev = 0.0
   do 12 j = 1,10
 12 rev = rev + g(j,k)
 13 write (6,14) (k-1), rev
 14 format (1x, i2, e12.5)
   stop
   end
```

Info.f

```
      dimension e(17)
C     open (6,file='rafi.dat', status='new')
      t=4000.
      do 6 j=1,17
      e(j) = 2603.7558*(j-1) - 45.221*(j-1)**2 -0.0029*(j-1)**3
    6 e(j) = 1.4388*e(j)
      do 1 i=1,21
      a = 2.5 + 0.1*(i-11)
      write (6,*) ' '
      write (6,*) ' '
      write (6,*) 'lamda = ', a, 'beta*theta   ln(k/k0)   sum(kvv0)'
      write (6,*) ' '
      if (a.eq.0.0) go to 400
      do 7 j = 1,41
      x = (j-21)*2
      z = 0.0
      zz = 0.0
      do 8 k = 1,17
      dd = x/2 - e(k)/2/t
      if (dd.le.0.0) go to 9
      bes2 = bsk0(dd) + 2*bsk1(dd)/dd
      z = z + dd**2*bes2*exp(dd)
      zz = zz + dd**2*bes2*exp(dd)*exp(-2*a*dd)
      go to 8
    9 if (dd.lt.0.0) go to 10
      z = z + 2.
      zz = zz + 2.
      go to 8
   10 c = abs(dd)
      bes2 = bsk0(c) + 2*bsk1(c)/c
      z = z + dd**2*bes2*exp(dd)
      zz = zz + dd**2*bes2*exp(dd-2*a*c)
    8 continue
      y = alog(zz/z)
    7 write (6,3) x,y,z
    3 format (23x, 3e12.5)
      go to 1
  400 do 11 j = 1,41
      x = (j-21)*2
      y = 0.0
   11 write (6,3) x,y
    1 continue
      stop
      end
```