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Citation: **57**, (1972); doi: 10.1063/1.1678242

View online: <http://dx.doi.org/10.1063/1.1678242>

View Table of Contents: <http://aip.scitation.org/toc/jcp/57/12>

Published by the [American Institute of Physics](#)

Entropy and Chemical Change. II. Analysis of Product Energy Distributions: Temperature and Entropy Deficiency*

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(Received 7 August 1972)

Detailed experimental and theoretical information on the distribution of product energy states resulting from reactive molecular collisions are characterized by their entropy deficiency and temperature. Explicit algorithms are developed both for the case of ultimate resolution (both angular and internal state distribution) which provides the intrinsic (i.e., maximal) entropy deficiency and for the more realistic situations (e.g., chemiluminescence, molecular beam velocity analysis) where only averaged distributions are available and the entropy deficiency is therefore smaller. Twelve "known" product distributions are analyzed. The largest values of the entropy deficiency are found for reactions where there is significant deviation from a simple equilibrium distribution of products. A temperature parameter is introduced as a measure of the deviation from equilibrium. Inverted populations are characterized by a negative value of this temperature. Consideration of a number of isotopic reactions indicate that this temperature is essentially invariant under isotopic substitution. The new temperature parameter introduced in this work is the one appropriate for a finite system and differs from the more familiar (but special) form appropriate for a system coupled to an infinite heat bath. Two new tools are thus proposed for characterizing the deviation of an observed product state distribution (or a computational simulation thereof) from an equilibrium, microcanonical one. These are the temperature parameter (a *differential* measure) and the entropy deficiency (an *integral* one). They measure, respectively, the *local* and the *average* deviation between observed and equilibrium distributions.

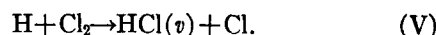
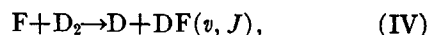
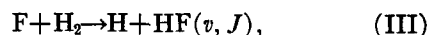
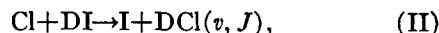
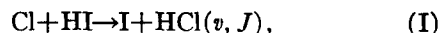
I. INTRODUCTION

On the microscopic level, chemical reactions are characterized not only by their rates (or cross sections) but also by the distribution of the internal energy states of the products. These distributions are not usually measured in conventional bulk experiments due to the rapid relaxation, by subsequent collisions, to the equilibrium distribution of internal states. Indeed, it is required that such relaxation processes be fast compared to the progress of the chemical reaction in order that a conventional reaction rate constant can be well defined.

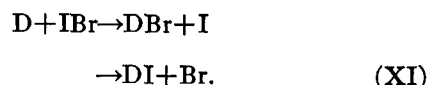
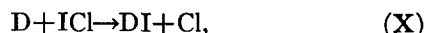
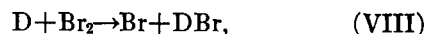
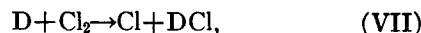
Detailed experimental information on the distribution of the products energy states is currently becoming available from techniques which arrest the secondary relaxation^{1,2} (to a greater or lesser extent). These include the chemiluminescence,^{1,3-6} molecular beam⁷⁻¹⁰ and chemical laser^{11,12} methods. Such studies provide not only information on the dynamics of reactive collisions but are also of interest from a technological point of view.¹³⁻¹⁵

In Paper I of this series² we have considered the general problem of the characterization of the product distribution in terms of its information content¹⁶⁻²⁰ and have introduced the entropy deficiency as a measure of the deviation of the observed product distribution from that expected at equilibrium. In the present paper we illustrate the practical implementation of our approach. We develop the explicit algorithms used in handling realistic experimental data and illustrate the method by applications to specific reactions. The distribution of internal energy states is analyzed for the

reactions



The distribution of the products' (relative) kinetic energy is considered for



For the Reactions (I)–(IV) [and the classical trajectory calculations intended to simulate Reaction (V)] it is shown that the product distribution in any one energy mode (rotational, vibrational, or translational) can be characterized by a temperature.^{21,22}

One problem not explicitly considered in this paper is the role of the reactant energy distribution. Work is in progress on this and on several other aspects of our original formulation, including entropy cycles.

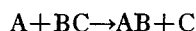
We restrict our attention in this paper to bimolecular

atom-diatom exchange reactions, at a constant total energy E in the center-of-mass (c.m.) system. Experimentally, it is, of course, difficult to have a very well defined reactants' energy and so we consider here exoergic reactions for which (due to the energy release) the uncertainty in the products' total energy is small. This problem does not exist, of course, in the analysis of results of classical trajectory calculations. The other points which require attention are the lack of absolute cross section measurements for most reactions under consideration and the limitations on the product specification. At a given total energy, one can, in principle, specify the final product state not just in terms of the internal state but also in terms of the angular distribution. At the moment, no technique can provide that much detail. The chemiluminescence method that can provide, in favorable cases, complete resolution of product internal states does not provide any angular distribution. The molecular beam approach can, in principle, provide both angular and energy resolution. At the moment however the translational energy resolution is seldom sufficient to resolve the different internal state of the products and all that is usually available²³ is a continuous distribution of the relative translational energy, at any angle.

The discussion begins, in Sec. II with a short summary of our approach with particular emphasis on the concept of entropy deficiency and the degradation of information by lack of resolution. Section III introduces the conditional distribution and the conditional entropy deficiency and considers the intrinsic value of the entropy deficiency, obtained for complete resolution of the final states. The entropy deficiency when only a resolution of the product internal energy states is available is considered in Sec. IV and computed for the Reactions (I)–(V) in Sec. V. The concept of a temperature of a distribution, introduced on empirical grounds in Sec. V, is discussed in Sec. VI. The results of molecular beam velocity analysis are considered in Sec. VII and analyzed for Reactions (VI)–(XI) in Sec. VIII. A discussion of the present approach and a summary (Sec. IX) conclude this paper.

II. INFORMATION AND ENTROPY DEFICIENCY OF A FINAL STATE DISTRIBUTION

In an ultimate experiment the products of the bimolecular reaction



are characterized, in the center-of-mass system, by their internal state n and the momentum $\hbar \mathbf{k}$ of their relative motion.²⁴ With $f \equiv n, \mathbf{k}$ being a label for a particular final state the (missing) information of the product state distribution has been defined² as

$$I[f] = - \sum_f P(f) \lg P(f), \quad (1)$$

where $P(f)$ is the probability (i.e., relative frequency of observation) of a particular final state f ,

$$\sum_f P(f) = 1. \quad (2)$$

We have written the sum (1) (which is a dimensionless, positive number) as $I[f]$ as a reminder that the summation has been over all possible final states. If we take the logarithm in (1) to base e , then (1) defines also the entropy (in units of k per one distribution or R per mole²⁵) of the distribution of final states,²⁶

$$S[f] = -k \sum_f P(f) \log P(f). \quad (3)$$

The maximal value of $S[f]$ is the equilibrium value, S_{eq} . Needless to say, the particular value of S_{eq} depends on the constraints imposed upon the system. In the applications below we shall be mainly concerned with equilibrium subject to a specified total energy. Here, as elsewhere, total energy refers to the total energy per individual collision.

The observed product distribution can deviate from the distribution expected at equilibrium. We characterize this deviation by the entropy deficiency $\Delta S[f]$,

$$\Delta S[f] = S_{eq} - S[f] \geq 0. \quad (4)$$

The larger the entropy deficiency, the greater is the deviation of the experimental product distribution from the equilibrium value. Given the experimental product distribution (or a theoretical-computational prediction) we can compute $S[f]$ and then, subject to the known experimental constraints, obtain S_{eq} and hence $\Delta S[f]$. In the following sections we demonstrate the implementation of this procedure.

In practice, experimental limitations are such that the final states cannot be fully resolved. Rather, what is measured is the distribution of products among groups of states, $P(\gamma)$, where γ is a set of states which are, in principle, indistinguishable under the experimental arrangement. Thus, in the absence of a field the set γ might include all the (degenerate) states which differ only in the value of m_J , the orientation (or magnetic) quantum number for the rotational angular momentum, J , of the diatomic product. In chemiluminescence studies the set γ might include all the final states that differ only in their angular distribution, etc. In general, the poorer is the experimental resolution, the larger is the number of states in the set γ . As shown below, this necessarily implies that with a lower resolution we obtain distributions that are closer to equilibrium.

To obtain $S[\gamma]$ we need to state explicitly our fundamental postulate, which, in fact, was already used implicitly in writing down (1) or (3). This fundamental postulate defines our reference state, or in other words, defines the product state distribution that we would guess in the absence of any experimental evidence. We thus assume that: In the absence of information to the contrary all possible final (quantum) states

are equally probable. In applications, it is necessary to properly identify the existing constraints on the system in order to apply the principle correctly. When all states within the group γ have the same energy we take them as equiprobable and hence, if $g(\gamma)$ is the number of such states, we assign to each state within the group the probability $\bar{P}(f)$ [also denoted $\omega(f)$],

$$\bar{P}(f) = P(\gamma)/g(\gamma). \quad (5)$$

Here $P(\gamma)$ is the probability of the group γ . The representation of the deviation from equilibrium in this fashion was first lucidly discussed by Kinsey.²⁷

The entropy associated with the distribution γ is then

$$\begin{aligned} S[\gamma] &= -k \sum_f \bar{P}(f) \log \bar{P}(f) \\ &= -k \sum_{\gamma} P(\gamma) \log [P(\gamma)/g(\gamma)]. \end{aligned} \quad (6)$$

To obtain the second equality we have broken the summation over f to sums over all states within a given group γ and have used the assumption that all states within the group are equiprobable.²⁸

It follows from the basic principles of information theory that²⁹

$$S[\gamma] \geq S[f] \quad (7)$$

and so

$$\Delta S[\gamma] = S_{\text{eq}} - S[\gamma] \leq S_{\text{eq}} - S[f] = \Delta S[f]. \quad (8)$$

The computed entropy deficiency with the experimental distribution $P(\gamma)$ is thus a lower bound to the intrinsic value, $\Delta S[f]$. Any loss in experimental resolution makes the entropy deficiency smaller, i.e., makes the distribution closer to an equilibrium distribution. In what follows we shall see this principle in operation when we compare high and low resolution distributions for the Reactions (I), (II) and (V)–(VIII).

An important point which will not be considered in this paper is the characterization of the reactants. A preliminary discussion of this point was given in Part I where it was shown that ΔS increases as we sharpen the resolution for selecting the reactants. The considerations of this paper are restricted to a given initial reactants distribution as prepared in the experiment under discussion. The question of inclusive vs detailed experiments² will be taken up in another study which is currently in progress.

III. CONDITIONAL DISTRIBUTIONS AND CONDITIONAL ENTROPY

The discussion in Sec. II was very general and has failed to explicitly consider the physical content of the label f used to specify the final states or the nature of the set of states γ . Explicit expressions for the general final state distribution are obtained in this section where we also consider one additional aspect, namely the special role of the total energy. Essentially, we divide the problem into two parts. One is the product distribution at a given total energy and the other is

the dependence on the total energy. This division, which, in a sense, parallels the experimental approach to this problem, leads us to the concept of conditional entropy, as is discussed later in this section.

To begin with, it is realistic to recognize explicitly that the translational energy for the relative motion of the products is a continuous variable. The final state distribution should thus be characterized by a probability density function (pdf) $P(n, \mathbf{k})$ such that $P(n, \mathbf{k}) d\mathbf{k}$ is the probability for observing products in the internal state n with the relative wave vector $\mathbf{k}$ in the range $\mathbf{k}$ to $\mathbf{k} + d\mathbf{k}$

$$d\mathbf{k} = k^2 dk d\Omega, \quad (9)$$

where Ω is the polar angle specifying the direction of $\mathbf{k}$ ($d\Omega = \sin\theta d\theta d\phi$). Alternatively, the relative translational motion can be discussed in terms of groups of states where the translational energy

$$E_T = \hbar^2 k^2 / 2\mu \quad (10)$$

is in the range E_T to $E_T + dE_T$ and the angle of scattering is in the range Ω to $\Omega + d\Omega$.

In the absence of a preferred direction in space³⁰ the degenerate internal states of the products differing only in orientation quantum numbers (m_J) are indistinguishable, and other limitations may exist on the ability to resolve the internal states completely. Using $\bar{n}$ to designate the internal level of the products, we can measure the pdf $P(\bar{n}, E_T, \Omega)$ such that $P(\bar{n}, E_T, \Omega) dE_T d\Omega$ is the probability of observing the products in the indicated energy and angular range and with an internal state within the (degenerate) group of states $\bar{n}$. In the notation of Eq. (5)

$$\bar{P}(f) \equiv \bar{P}(n, \mathbf{k}) = P(\bar{n}, E_T, \Omega) / \rho(\bar{n}, E_T, \Omega), \quad (11)$$

where $\rho(\bar{n}, E_T, \Omega)$ is the density of states [i.e., $\rho(\bar{n}, E_T, \Omega) dE_T d\Omega$ is the number of final states in the indicated energy and angular range and in the group $\bar{n}$].

It is also convenient to change the energy variable from E_T to the total energy E ,

$$E = E_T + E(\bar{n}), \quad (12)$$

where $E(\bar{n})$ is the internal energy of the (degenerate) states in the group $\bar{n}$. We can then consider the pdf $P(\bar{n}, E, \Omega)$ where, in view of (12),

$$P(\bar{n}, E_T, \Omega) dE_T = P(\bar{n}, E, \Omega) dE. \quad (13)$$

At this point we can explicitly write [cf. Eq. (6)]

$$\begin{aligned} S[\bar{n}, E, \Omega] &= -k \int dE \int d\Omega \sum_{\bar{n}} P(\bar{n}, E, \Omega) \\ &\quad \times \log [P(\bar{n}, E, \Omega) / \rho(\bar{n}, E, \Omega)]. \end{aligned} \quad (14)$$

It is possible to show that the standard expressions for the entropy of the canonical ensemble can be derived from this expression. The present application is, however, to situations where the observed distribution is not the equilibrium one. Moreover, we are often con-

cerned with situations where the total energy is constrained to be in a narrow interval δE about E . It is therefore convenient to carry out the evaluation of $S[\bar{n}, E, \Omega]$ in two stages. First, the entropy at a given total energy is computed and then, if necessary, an average over the distribution in E is performed.

The product distribution at a given total energy, $P(\bar{n}, \Omega | E)$, is defined by

$$P(\bar{n}, \Omega | E) = P(\bar{n}, \Omega, E) / P(E), \quad (15)$$

where, for a given reactant distribution

$$P(E) = \int d\Omega \sum_{\bar{n}}^{\bar{n}^*} P(\bar{n}, \Omega, E) \quad (16)$$

and the summation over $\bar{n}$ is constrained to the range of $\bar{n}$ values for which $E(\bar{n}) \leq E$. $\bar{n}^*$ is the highest allowed value of $\bar{n}$ subject to conservation of energy and any other constraints. With the definition above,

$$\int d\Omega \sum_{\bar{n}}^{\bar{n}^*} P(\bar{n}, \Omega | E) = 1. \quad (17)$$

In the language of probability theory $P(\bar{n}, \Omega, E)$ is the joint distribution of states while $P(\bar{n}, \Omega | E)$ is the conditional distribution, i.e., $P(\bar{n}, \Omega | E)$ is the distribution of states at a given total energy. The introduction of the conditional distribution is necessary and not simply a matter of mathematical elegance. Present day experiments on reactive collisions of neutral species almost invariably give us just the conditional distribution of states. In fact, with a few exceptions, most of the available results are the conditional distributions at one particular energy. The results currently available are often not absolute rates (or cross sections) but only relative values, which are normalized at each total energy. The introduction of a conditional distribution is the theoretical equivalence of the experimental "normalized relative distribution" [cf. Eq. (17)].

The conditional density of states is introduced by an identical procedure

$$\rho(\bar{n}, \Omega | E) = \rho(\bar{n}, \Omega, E) / \rho(E), \quad (18)$$

where $\rho(E)$ is the total density of states at the energy E

$$\rho(E) = \int d\Omega \sum_{\bar{n}}^{\bar{n}^*} \rho(\bar{n}, \Omega, E) \quad (19)$$

and

$$\int d\Omega \sum_{\bar{n}}^{\bar{n}^*} \rho(\bar{n}, \Omega | E) = 1. \quad (20)$$

The conditional density of states is thus a normalized pdf. This normalization is essential in order to prove (26) and other inequalities.

With the definitions (15) and (18) we can rewrite

$S[\bar{n}, \Omega, E]$ as

$$\begin{aligned} S[\bar{n}, \Omega, E] &= -k \int dE P(E) \int d\Omega \sum_{\bar{n}}^{\bar{n}^*} P(\bar{n}, \Omega | E) \\ &\quad \times \log \frac{P(E) P(\bar{n}, \Omega | E)}{\rho(E) \rho(\bar{n}, \Omega | E)} \\ &= S[E] + S[\bar{n}, \Omega | E], \end{aligned} \quad (21)$$

where

$$S[E] = -k \int dE P(E) \log[P(E) / \rho(E)], \quad (22)$$

$$S[\bar{n}, \Omega | E] = \int dE P(E) S[\bar{n}, \Omega | E], \quad (23)$$

and

$$S[\bar{n}, \Omega | E] = -k \int d\Omega \sum_{\bar{n}}^{\bar{n}^*} P(\bar{n}, \Omega | E) \log \frac{P(\bar{n}, \Omega | E)}{\rho(\bar{n}, \Omega | E)}. \quad (24)$$

The right bracket in $S[\bar{n}, \Omega | E]$ is a round bracket to serve as a reminder that E is yet a variable (i.e., an argument of the function) whereas $\bar{n}$ and Ω have been summed over.

The interpretation of the three new entropies introduced in (22), (23), and (24) is as follows: $S[\bar{n}, \Omega | E]$ is the entropy of the conditional distribution (hence "the conditional entropy") at a given total energy E . It is this entropy that we shall be concerned with in the following sections. $S[\bar{n}, \Omega | E]$ is the average value of the conditional entropy, weighted by the reaction probability at each energy and $S[E]$ is the entropy associated with the distribution $P(E)$, i.e., with the distribution of the probability of reaction as a function of the total energy. Currently there is very little information on $P(E)$ and so we are forced to restrict our attention to $\Delta S[\bar{n}, \Omega | E]$. In a subsequent paper, when we consider the energy distribution of the reactants we shall return to the question of averaging over E .

The entropy of the conditional distribution of the products at a given total energy, $S[\bar{n}, \Omega | E]$, is the quantity with which we shall be concerned throughout this paper. The energy dependence of the entropy in the microcanonical ensemble is the analog of the temperature dependence of the entropy in the canonical ensemble, a dependence which is usually not indicated explicitly. Hence we adopt the following *definition*: the conditional entropy in the microcanonical ensemble will be denoted from here on as $S[\bar{n}, \Omega]$ with an *implied* dependence on the total energy. Equation (24) is now rewritten as

$$S[\bar{n}, \Omega] = -k \int d\Omega \sum_{\bar{n}}^{\bar{n}^*} P(\bar{n}, \Omega | E) \log \frac{P(\bar{n}, \Omega | E)}{\rho(\bar{n}, \Omega | E)}. \quad (24)$$

We have defined equilibrium at a given total E as the distribution where all possible final states are equiprobable (a so-called "microcanonical" equilibrium). Therefore, the equilibrium (conditional) distribution

of states $P^0(\bar{n}, \Omega | E)$ is given by [cf. (20)]

$$P^0(\bar{n}, \Omega | E) \equiv \rho(\bar{n}, \Omega | E). \quad (25)$$

For the equilibrium distribution, (24) confirms that $S[\bar{n}, \Omega] = 0$ while in general³¹

$$S[\bar{n}, \Omega] \leq 0, \quad (26)$$

with equality only at equilibrium. It follows from the definition of the entropy deficiency, Eq. (4), that at a given total energy,

$$\Delta S[\bar{n}, \Omega] = -S[\bar{n}, \Omega]. \quad (27)$$

Equation (27) is one fundamental result of this section. The entropy deficiency at a given total E can be directly computed as

$$\Delta S[\bar{n}, \Omega] = k \int d\Omega \sum_{\bar{n}}^* P(\bar{n}, \Omega | E) \log \frac{P(\bar{n}, \Omega | E)}{P^0(\bar{n}, \Omega | E)}, \quad (28)$$

where P and P^0 are the observed and the equilibrium distribution of products, when complete resolution of final states is carried out, in the absence of a preferred direction in space for products' state selection. $\Delta S[\bar{n}, \Omega]$ is the intrinsic value of the entropy deficiency at a given total E in any particular experiment (i.e., for any particular method of reactants selection provided only that no orientation quantum numbers are resolved.

Our next task is to take cognizance of the fact that seldom are experiments performed nowadays with such complete resolution of final states. In the following section we consider the entropy deficiency for the situation of "high" and "low" resolution of product internal energy states when no angular resolution is attempted. We return to the question of angular distribution in Sec. VII.

IV. ENTROPY DEFICIENCY OF A PRODUCT STATE DISTRIBUTION

The distribution of the products' internal energy states (without angular resolution) can be determined experimentally by a number of techniques, most notably, infrared chemiluminescence, chemical lasers and molecular beam product state analysis. Theoretical computations for three dimensional reactive collisions are currently feasible (for realistic systems) only by the use of classical trajectories.³² The entropy deficiency obtained from such results is a lower bound to the intrinsic value due to the averaging implied by the loss of angular information.²⁹ We restrict attention to results obtained at (approximately) constant total energies and consider separately the low resolution results (when only the product diatom vibrational distribution is determined) and the high resolution results (both vibrational and rotational distributions of the product known). The latter results represent the optimal resolution possible (in the absence of reactants orientation state selection) in such experiments.

A. Low Resolution: E and v Determined

In such experiments (or computations) the vibrational distribution is determined for a range of values of the total energy. In principle, if absolute measurement were feasible, one could determine $P(v, E)dE$, the probability of observing the vibrational state v when the total energy is in the range E to $E+dE$. In practice, as discussed in Sec. III, the probability that is actually determined is $P(v | E)$,

$$P(v | E) = P(v, E)/P(E), \quad (29)$$

the normalized relative (i.e., conditional) probability at a given energy.³³

For an experiment (yet to come, but see Ref. 4) over a range of E values we can write as in (21)–(24)

$$S[v, E] = S[E] + S[v | E], \quad (30)$$

where $S[E]$ was defined by (22) and

$$S[v | E] = \int dE P(E) S[v], \quad (31)$$

$$S[v] = -k \sum_{v=0}^{v^*} P(v | E) \log \frac{P(v | E)}{P^0(v | E)}. \quad (32)$$

Here, as usual, v^* is the highest allowed vibrational quantum number of the product at the total energy E ; $P^0(v | E) = \rho(v | E)$ is the conditional density of vibrational states [cf. (25)]. Explicit results for $\rho(v | E)$ are summarized in the Appendix.

The entropy deficiency at a given E for the vibrational distribution is given by [cf. (27)]

$$\Delta S[v] = -S[v] = k \sum_{v=0}^{v^*} P(v | E) \log \frac{P(v | E)}{P^0(v | E)}, \quad (33)$$

where $P^0(v | E) \equiv \rho(v | E)$ is the (conditional) probability at equilibrium. The ratio²⁷

$$\omega(v | E) = P(v | E)/P^0(v | E) = \omega(v, E)/\omega(E) \quad (34)$$

is a convenient measure of the deviation of the experimental distribution from the reference equilibrium value. [Note that while both $P(v | E)$ and $P^0(v | E)$ are normalized, $\omega(v | E)$ is not necessarily bounded by 1.] It is also convenient to introduce the surprisal^{2,34} associated with each v , defined by

$$I(v | E) = -\log \omega(v | E) = -\log [P(v | E)/P^0(v | E)] \quad (35)$$

such that

$$S[v] = k \sum_{v=0}^{v^*} P(v | E) I(v | E). \quad (36)$$

B. High Resolution: E , v , and J Determined

The discussion here closely follows that of the previous case. For an experiment over a range of E values

$$S[v, J, E] = S[E] + S[v, J | E]. \quad (37)$$

When results are available only at one particular value

of E

$$S[v, J] = -k \sum_{v, J} P(v, J | E) \times \log[P(v, J | E)/P^0(v, J | E)] \quad (38)$$

and the entropy deficiency per collision is

$$\Delta S[v, J] = k \sum_{v, J} P(v, J | E) \times \log[P(v, J | E)/P^0(v, J | E)]. \quad (39)$$

We recall again Shannon's lemma³⁵ which implies that $\Delta S[v, J] \geq 0$ with equality only when $P(v, J | E) = P^0(v, J | E)$. Similar remarks apply to subsequent expressions for ΔS since the lemma requires that both P and P^0 be normalized distributions.

We can also define $P(J | E)$

$$P(J | E) = \sum_{v=0}^{v^*} P(v, J | E), \quad (40)$$

as the (conditional) distribution of rotational states at a given E (irrespective of v). The entropy deficiency of this distribution is

$$\Delta S[J] = k \sum_J P(J | E) \log[P(J | E)/P^0(J | E)]. \quad (41)$$

The decrease in entropy deficiency due to averaging is conveniently demonstrated by comparing the results for the high and low resolution studies. We begin with the identity

$$P(v, J | E) = P(J | v, E) P(v | E), \quad (42)$$

where (with $E_{J^*(v)} \leq E - E_v$)

$$\sum_{J=0}^{J^*(v)} P(J | v, E) = 1 \quad (43)$$

or, for the surprisal,

$$I(v, J | E) = I(J | v, E) + I(v | E). \quad (44)$$

Then, using

$$\begin{aligned} \Delta S[v, J] &= k \sum_{J, v} P(v, J | E) [I(v | E) + I(J | v, E)] \\ &= -k \sum_v P(v | E) I(v | E) \\ &\quad - k \sum_v P(v | E) \sum_J P(J | v, E) I(J | v, E) \\ &= \Delta S[v] + \sum_v P(v | E) \Delta S[J | v, E] \\ &= \Delta S[v] + \Delta S[J | v]. \end{aligned} \quad (45)$$

Since entropy deficiency is always nonnegative, we conclude that³⁶

$$\Delta S[v, J] \geq \Delta S[v] \quad (46)$$

with equality only when $\Delta S[J | v, E] = 0$ for all possible v , i.e., when the rotational distribution (for given v and E) is in equilibrium. Examples of (46) will be given in Sec. V (Table I). Similar considerations lead

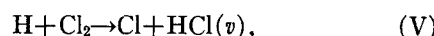
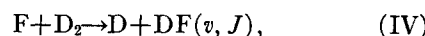
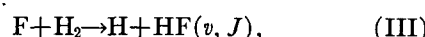
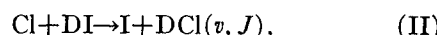
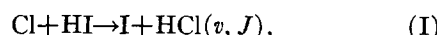
to the inequality

$$\Delta S[v, J] \geq \Delta S[J]. \quad (47)$$

V. ANALYSIS OF EXPERIMENTAL RESULTS FOR PRODUCT STATE DISTRIBUTIONS

A. Entropy of the Product State Distribution

The entropy deficiencies, as defined in the previous section were computed for the exothermic reactions



in an attempt to illustrate most of the points that were discussed. The experimental results are from the infrared chemiluminescence studies of Maylotte *et al.*⁵ [Reactions (I) and (II)], and Polanyi and Woodall⁶ [Reactions (III) and (IV)]. Also considered were the classical trajectory computations by Anlauf *et al.*³⁷ [Reactions (I) and (II)], Muckerman³⁸ [Reaction (III)] and Anlauf *et al.*³⁹ [Reaction (V)].

In analyzing and displaying experimental results it is advantageous to work not with the products' quantum numbers but with the fractions of the total energy in each classical mode, $f_X = E_X/E$, where

$$f_T + f_v + f_R = 1. \quad (48)$$

Using the equilibrium reference distributions derived in the Appendix (the spectroscopic constants ω_e , $\omega_e x_e$, B_e , and α_e are from Herzberg⁴⁰), and Eqs. (39), (33), (45), and (41), the entropy deficiencies $\Delta S[v, J]$, $\Delta S[v]$, $\Delta S[J | v]$, and $\Delta S[J]$ obtained using the experimental results are listed (where ΔS is given per mole, i.e., not per collision) in Table I. The double entries correspond to two alternatives for the rotational distribution as discussed below. The total (i.e., most detailed) entropy deficiency for this type of experiments, $\Delta S[v, J]$, is about 4 cal/deg·mole (eu) for all four examples. The entropy of the vibrational distribution, $\Delta S[v]$, for these reactions which show pronounced vibrational population inversion makes the major contribution to the total entropy and is above 3 cal/deg·mole for all four examples, with the balance made up by the rotational contribution [cf. Eq. (45)].

B. The Vibrational Temperature

The experimental product distributions deviate considerably from the reference (equilibrium) distribution, which tends to favor translational release of the exothermicity. To see this qualitatively consider the RRHO approximation²⁷ [Eq. (A25)], $f_v = E_v/E$,

$$P^0(f_v | E) \propto (1 - f_v)^{3/2}. \quad (49)$$

TABLE I. Chemiluminescence data.^a

Reaction	Cl+HI→HCl+I Ref. 5	Cl+DI→DCI+I Ref. 5	F+H ₂ →HF+H Ref. 6	F+D ₂ →DF+D Ref. 6
<i>E</i> (kcal/mole)	34.0	34.0	34.7	34.4
$\Delta S[v]$ (cal/mole·deg)	3.54	3.25	3.25	2.96
^I $\Delta S[J v]$ (cal/mole·deg)	0.48	0.37	0.75	0.98
^{II} $\Delta S[J v]$ (cal/mole·deg)	0.52	0.49	0.85	1.29
^I $\Delta S[J]$ (cal/mole·deg)	0.89	0.99	1.66	1.64
^{II} $\Delta S[J]$ (cal/mole·deg)	1.62	1.53	2.18	2.36
^I $\Delta S[J, v]$ (cal/mole·deg)	4.02	3.72	4.00	3.95
^{II} $\Delta S[J, v]$ (cal/mole·deg)	4.06	3.84	4.11	4.26
λ_v	-8.0	-8.0	-6.5	-6.4
T_v (°K)	-2100	-2100	-2700	-2700
λ_R		9.5		
T_R (°K)		1800		
$\langle f_v \rangle$	0.70(0.71)	0.69(0.71)	0.66	0.66
$\langle f_R \rangle$	0.13	0.13	0.08	0.08

^a The designations I and II distinguish results based on the extrapolated and actual experimental results, as discussed in the text.

A rather similar functional dependence is found for the more precise VR approximation (Appendix) or even when the conservation of total angular momentum is explicitly taken into account.⁴¹ In view of the strong deviation from the *a priori* expected reference distribu-

tion we have chosen to represent the deviation as

$$P(f_v | E) / P^0(f_v | E) = \omega(f_v | E) = Q^{-1} \exp(-\lambda_v f_v), \quad (50)$$

where Q is a normalizing factor

$$Q = \sum_v P^0(f_v | E) \exp(-\lambda_v f_v) \quad (51)$$

so that the experimental distribution

$$P(f_v | E) = Q^{-1} P^0(f_v | E) \exp(-\lambda_v f_v) \quad (52)$$

remains normalized at every E . The dimensionless parameter λ_v is thus defined (as the derivative of the surprisal):

$$\lambda_v = -[d \log \omega(f_v | E) / df_v] \quad (53)$$

and the average vibrational energy is $E\langle f_v \rangle$ where

$$\langle f_v \rangle = \sum_v f_v P(f_v | E) = -d \log Q / d\lambda_v. \quad (54)$$

Figures 1-4 show the experimental $P(f_v | E)$, the reference distribution $P^0(f_v | E)$ and $-\log \omega(f_v | E)$ for the Reactions (I)-(IV). The pronounced population inversion is indicated by the fact that the most probable f_v is not that for $v=0$ (or, equivalently by the fact that²² $\langle f_v^0 \rangle > 2/7$). The same information is imparted by the value of λ_v . As has already been discussed,²² population inversion corresponds to negative values of the "temperature" parameter λ_v , or of T_v ,

$$T_v = (E/k) / \lambda_v. \quad (55)$$

For all four reactions the plot of $-\log \omega(f_v | E)$ vs f_v is linear⁴² so that λ_v is essentially independent of f_v . It is also clear that λ_v is essentially isotopically invariant.

In contrast to the usual definition of the vibrational temperature, appropriate for an oscillator in equilibrium with an infinite heat bath, the present definition

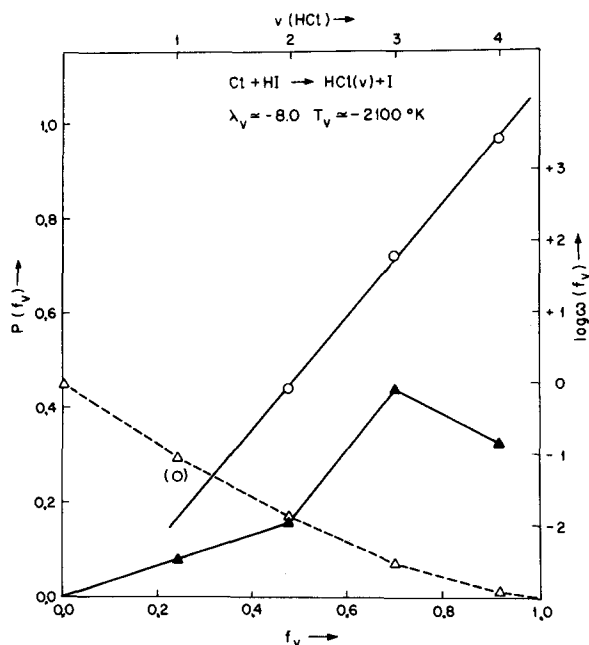


FIG. 1. Distribution of final vibrational states in the reaction $\text{Cl} + \text{HI} \rightarrow \text{HCl}(v) + \text{I}$. $P(f_v) [= P(f_v | E)]$, solid triangles, and $P^0(f_v)$, open triangles are shown vs f_v . (Experimental data from Ref. 5). $E = 34$ kcal/mole, $\Delta S[v] = 3.54$ cal/mole·deg. The extensive population inversion is reflected by the large slope, λ_v , of $\log \omega(f_v)$ (open circles) vs f_v . Points in brackets are uncertain due to a combination of theoretical and experimental errors, as discussed in the text. In this and subsequent figures, the lower two curves are the normalized experimental and reference probability distributions (left ordinate scale) and the upper curve(s) correspond to the surprisal (right ordinate scale).

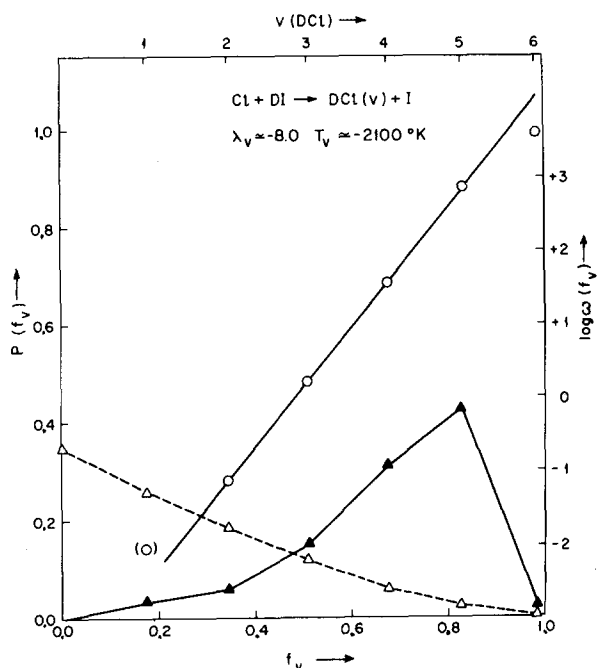


FIG. 2. Distribution of final vibrational states for the isotopic reaction $\text{Cl} + \text{DI} \rightarrow \text{DCl}(v) + \text{I}$. (Experimental data from Ref. 5 and other notation is as in Fig. 1.) Note that λ_v is essentially the same as that of Fig. 1. Other results for this reaction are given in Table I.

does not imply that $P(f_v|E)$ must be a monotonic function of f_v . It is quite clear from Figs. 1–4, that even though $P(f_v|E)$ has a definite maximum, λ_v is essentially constant. This is due to our taking explicit account of the fact that we are dealing with a very finite system and so have to consider the deviation of $P(f_v|E)$ from $P^0(f_v|E)$ and not from the density of states appropriate for an oscillator coupled to an infinite heat bath. This question is further discussed in Sec. VI.

C. The Rotational Distribution

The rotational distribution for each vibrational level, $P(J|v, E)$, was obtained⁴³ by an extrapolation of a series of chemiluminescence runs at decreasing wall temperatures and gas pressures in order to arrest the relaxation of the nascent product state distribution by secondary collisions. As shown in Fig. 5 there still is a considerable difference, for low J values, between the actual experimental (designated II) and the extrapolated (designated I) distributions. For higher J values the difference is more apparent than real, as is indicated by the plots of $-\log \omega(f_R|E)$ vs f_R for the two distributions, which yield an essentially identical rotational temperature (Fig. 5), for Reaction (II). The results for the other reactions appear to be qualitatively similar but the spread in $\log \omega(f_R|E)$ is larger so that λ_R could not be quantitatively determined. For all cases it is positive, indicating the absence of rota-

tional population inversion (at least for the higher J values where the data are more consistent).

The entropies of the rotational distributions were computed for both the extrapolated (O) and actual experimental (Δ) distributions. Higher ΔS values were obtained for the unextrapolated results thereby showing that they are further away from the reference equilibrium state. [Some care is necessary before one draws any final conclusions from this observation. The reference distribution used here is the one appropriate for a given total energy. When secondary collisions are important one should use a reference canonical distribution (i.e., a distribution appropriate for a given temperature).]

As is also discussed in the Appendix, the reference rotational distribution $P^0(J|E)$ is quite sensitive to the "conservation of the total angular momentum" constraint [much more so than $P^0(v|E)$]. It is only when this constraint is disregarded that one obtains the smooth dependence on J shown in Fig. 5. In general, for "angular momentum limited" reactions²¹ the reference angular distribution has to be computed from a proper formulation of the statistical theory^{44–46} which does impose the conservation of both the energy and the total angular momentum.⁴¹

The inequalities (46) and (47) corresponding to the loss of entropy deficiency by averaging are evident from Table I. Even so, for these highly exothermic reactions which produce strongly nonequilibrium distributions no amount of averaging can reduce the entropy deficiency to a near zero value. Simple quasi-

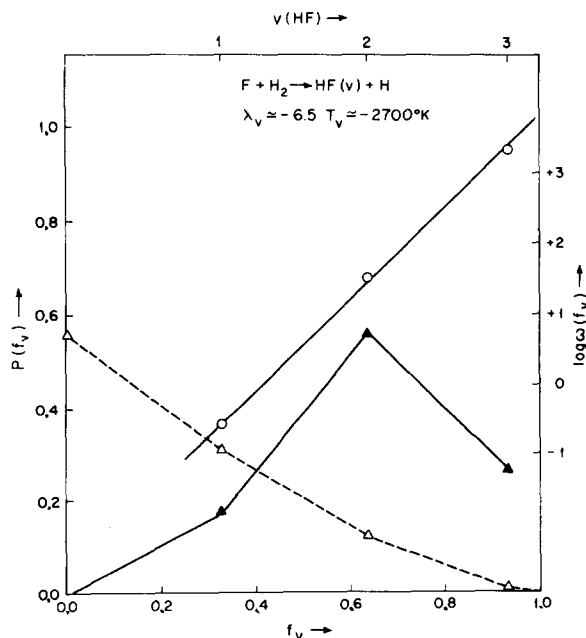


FIG. 3. Distribution of final vibrational states for the reaction $\text{F} + \text{H}_2 \rightarrow \text{HF}(v) + \text{H}$. (Experimental data from Ref. 6; notation is as in Fig. 1.) A summary of the analysis is given in Table I.

TABLE II. Energy dependence for the reaction $\text{Cl} + \text{HI} \rightarrow \text{HCl}(v) + \text{I}$.

	Ref. 5	Ref. 4	Ref. 4	Ref. 4
E kcal/mole	34.0	37.1	38.4	44.4
λ_v	-8.0	-4.9	-4.3	-4.3
T_v (°K)	-2100	-3800	-4500	-5300
$\Delta S[v]$ (cal/deg·mole)	3.54	2.14	1.90	1.41
$\langle f_v \rangle$	0.70	0.58	0.54	0.51

equilibrium theories⁴⁴⁻⁴⁶ cannot therefore be used to describe the distribution of final states, and some dynamic constraints are therefore essential.⁴⁷

D. The Energy Dependence

Cowley, Horne, and Polanyi⁴ have measured the vibrational distribution $P(v|E)$ [or $P(f_v|E)$], at four values of the total energy E , for the Reaction (II). The resulting entropy deficiency $\Delta S[f_v]$ is shown vs E in Fig. 6 and in Table II. It is clear that the character of the vibrational distribution (i.e., the extent of vibrational population inversion) becomes closer to the equilibrium limit with the increase in energy. This conclusion is reinforced by inspection of the plots of $-\log \omega(f_v|E)$ vs f_v as shown in Fig. 7. The vibrational temperature parameter, λ_v , is a decreasing function of the energy, Fig. 8, and while the (negative) temperature T_v , Eq. (55), does increase with E , the increase is slower than linear (indicating that $\langle f_v \rangle$ is a de-

creasing function of E), and reaches a plateau at the highest E value. Clearly, experiments at even higher energies would be exceedingly interesting. There are theoretical indications⁴⁸ that $\langle f_v \rangle$ would continue to decline but experimental evidence is clearly required.

Product state distributions can be determined by other experimental techniques such as chemical lasers¹¹⁻¹² or molecular beam velocity analysis⁴⁹ or product state analysis.⁵⁰⁻⁵² The Reactions (III) and (IV) were studied in the chemical laser work of Parker and Pimentel and Reaction (IV) was subject to molecular beam experiments of Schafer *et al.*⁸ The resulting distributions are however less detailed than those previously discussed. The work of Grice *et al.*⁵² on the rotational distribution of the RbBr from the reaction of $\text{Rb} + \text{Br}_2$ and of Bennewitz *et al.*⁵¹ and Freund *et al.*⁵⁰

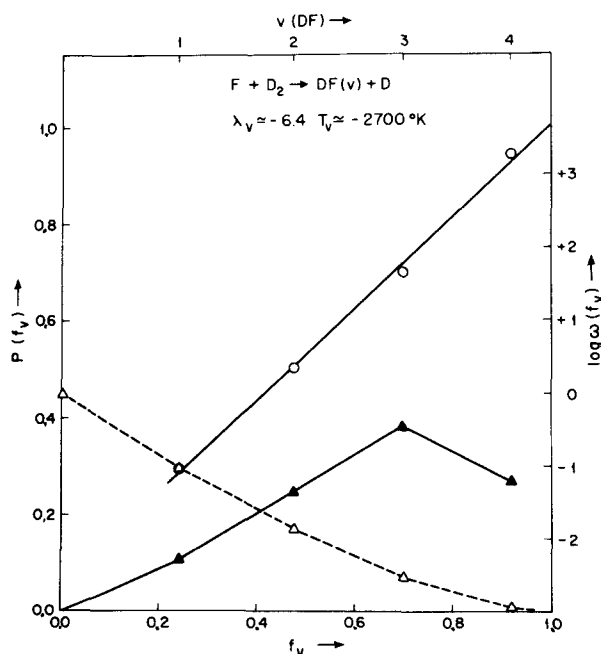


FIG. 4. Distribution of final vibrational states for the isotopic reaction $\text{F} + \text{D}_2 \rightarrow \text{DF}(v) + \text{D}$. (Experimental data from Ref. 6; notation is as in Fig. 1.) A summary of the analysis is given in Table I. For this reaction also, λ_v is essentially invariant under isotopic substitution.

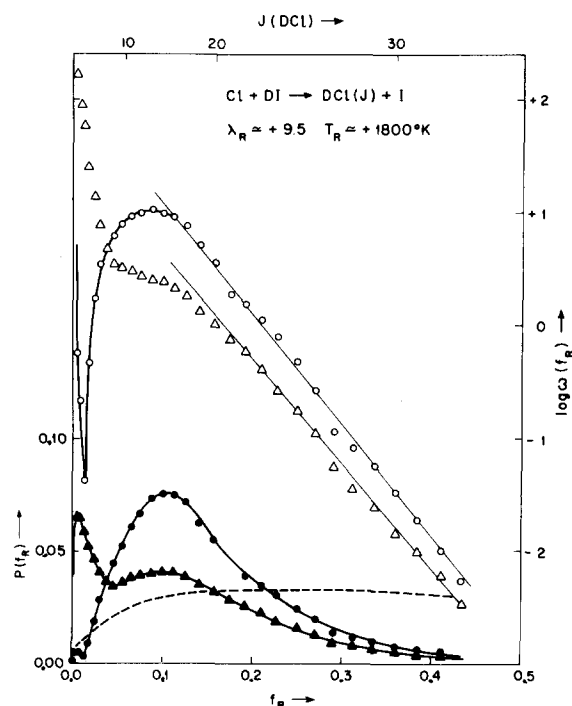


FIG. 5. Distribution of final rotational states for the reaction $\text{Cl} + \text{DI} \rightarrow \text{DCl}(J) + \text{I}$. The triangles and circles represent the actual and extrapolated experimental distributions⁵ as discussed in the text and in Ref. 5. The equilibrium distribution $P^0(f_R|E)$ is shown as a broken line and the actual distributions are shown as a full line. The upper insert shows $\log \omega(f_R)$ vs f_R . The negative slope indicates no population inversion, i.e., $T_R > 0$.

TABLE III. Computer simulation of reactive collisions^a (classical trajectory calculations).

Reaction	Cl+HI→HCl+I Ref. 37	Cl+DI→DCl+I Ref. 37	H+Cl ₂ →HCl+Cl Ref. 38	F+H ₂ →HF+H Ref. 39
<i>E</i> kcal/mole	34	34	46.6	34.7
Δ <i>S</i> [<i>v</i>] (cal/deg·mole)	4.28	3.89	2.09	5.23
λ _{<i>v</i>}	−8.4	−8.4	−5.7	
<i>T_v</i> (°K)	−2000	−2000	−4000	
⟨ <i>f_v</i> ⟩	0.74	0.72	0.59	0.78

^a The results of this table may be compared with the results derived from experimental data (Table I). In general, the trajectory results appear to be farther removed from equilibrium.

on the vibrational distributions in the reactions of Cs+SF₆ and Cs+SF₄ have sought to determine the temperature of the product state distribution, in a manner different from that used here. The definition of the temperature of the distribution will be discussed in the following section.

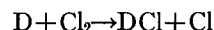
E. Results for Classical Trajectory Computations

Computational results for the product state distributions can be obtained from classical trajectory calculations. Table III summarizes the entropy deficiency analysis of the vibrational state distributions as computed for the Reactions (I)–(V). The results are also shown in Figs. 9–11. For the first two reactions, the trajectory results are in good accord with the experimental distributions, not only in terms of the actual distribution $P(v|E)$ but also in terms of the derived entropy deficiency and vibrational temperature, which here also is essentially isotopically invariant. For Reaction (III) there are only three energetically allowed vibrational states. Out of these, $\omega(f_v|E)$ is very sensitive at $v=1$ to the exact magnitude of $P(f_v|E)$ and at $v=3$ to the exact form of $P^0(f_v|E)$ (since f_3 is nearly unity). One can only draw a tentative conclusion to the effect that the trajectory results show a somewhat higher vibrational population inversion (i.e., larger $\Delta S[v]$ and λ_v) than the experimental results.

The results for the Reaction (V) deserve a separate discussion. The trajectory calculations for an attractive surface³⁹ show a broad vibrational distribution and give a linear $-\log\omega(f_v|E)$ vs f_v plot. Also the computed $\Delta S[v]$ is in the reasonable range for a reaction showing vibrational population inversion. Yet, the experimental distribution⁵³ is markedly different (it peaks strongly at $v=2$ or 3 and shows very little products at $v=5$ or 6). Thus, in contrast to the computer simulation, the experimental distribution does not yield a linear $-\log\omega(f_v|E)$ vs f_v plot.

There are several reasons that one can offer for this behavior and the actual cause is probably a combination of the theoretical and the experimental shortcomings. On the theoretical side, the $P^0(f_v|E)$ used here does not impose the conservation of total angular momentum. This fault is particularly severe at high f_v values

(or low f_T values). We shall encounter this problem again in Sec. VIII when we discuss other reactions involving a large change in the reduced mass.⁵⁴ On the experimental side we should note that for this reaction [as opposed to (I)–(IV)] the vibrational distribution is more sensitive to the external temperature and pressure. Also, the recent molecular beam velocity analysis for the reaction⁹



indicates a somewhat broader distribution of internal energy (mainly in the region of high f_I) than that obtained from the chemiluminescence studies. Clearly more work (both theoretical and experimental) on this reaction is called for.

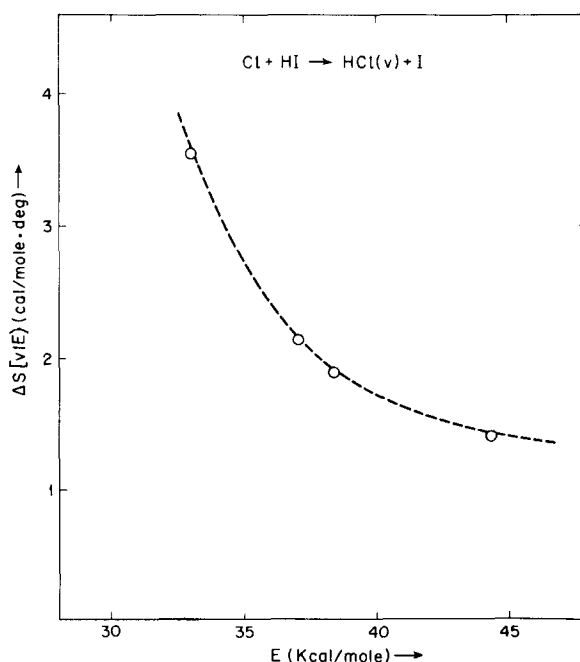
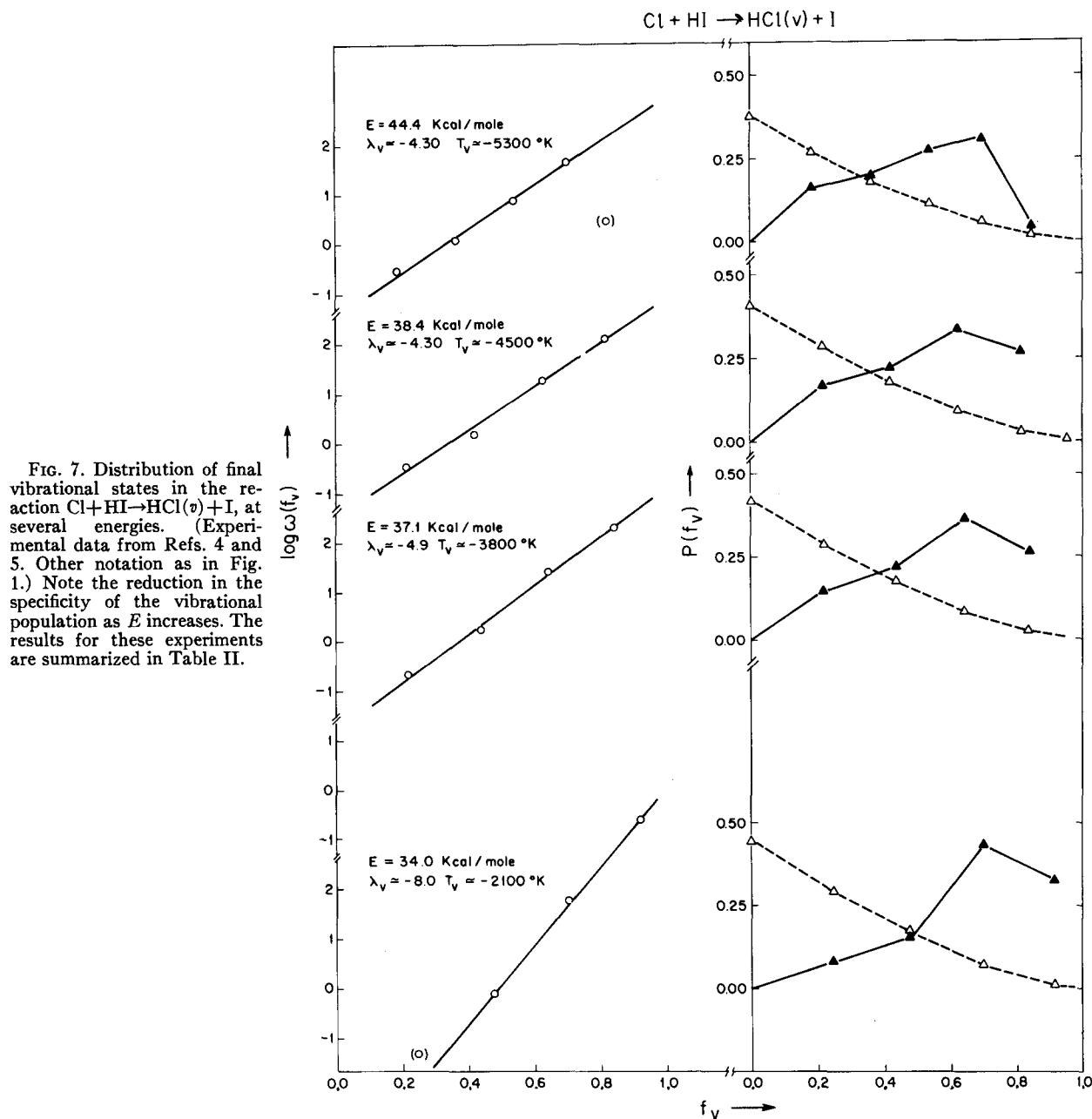


FIG. 6. The energy dependence of the entropy deficiency of the vibrational distribution of the reaction $Cl + HI \rightarrow HCl(v) + I$. Experimental data from Refs. 4 and 5. The decline of $\Delta S[v|E]$ with increasing E indicates an approach to a more uniform distribution of vibrational states as E increases, as evident also from Figs. 7 and 8. (In this figure we have explicitly indicated the energy dependence of the entropy.)



VI. TEMPERATURE

The concept of temperature of a product distribution²² was employed in the previous section as a convenient empirical measure of the deviation of the product distribution from the reference distribution

$$\lambda_X = -d \log \frac{P(f_X | E)/P^0(f_X | E)}{df_X},$$

$$T_X = (E/k)/\lambda_X. \quad (56)$$

Figures 1-5 and 9-12 show the empirical utility of such a parameter. [So much so that we have already

used it as a diagnostic tool in discussing Fig. 8 and Reaction (V) and will do so again in Sec. VIII.]

The essential advantage of the definition (56) from an empirical point of view is that it offers a dimensionless measure of the deviation from the reference state which is independent under any change of variables. Thus, one can use λ_X directly as a measure of the deviation of $f_X^{m.p.}$ from the equipartition value. As is clear from (56)

$$d \log P(f_X | E)/df_X = [d \log P^0(f_X | E)/df_X] - \lambda_X \quad (57)$$

so that $f_X^{m.p.}$ is the solution of

$$\lambda_X = [d \log P^0(f_X | E)/df_X]_{f_X^{m.p.}} \quad (58)$$

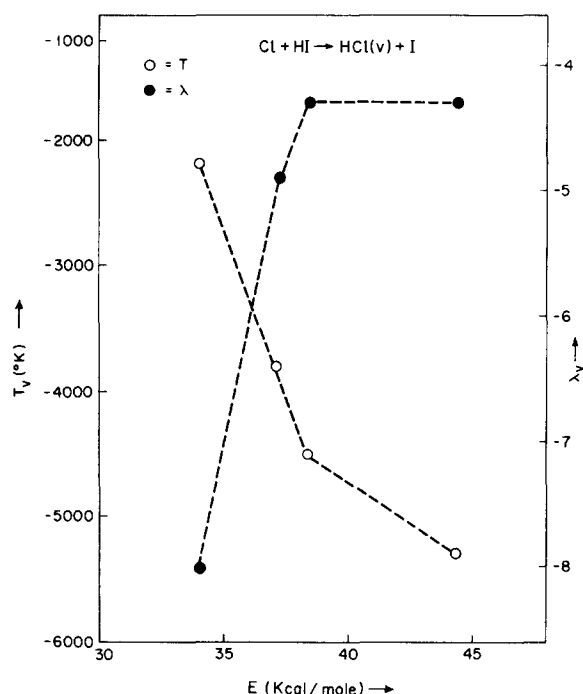


Fig. 8. The vibrational temperature parameter λ_v [and $T_v = E/(k\lambda_v)$] as function of E from the plots in Fig. 7. Note the trend toward a more uniform distribution as E increases.

A positive value of λ_X thus implies a preferential population of the low lying states while a negative value corresponds to population inversion or to $f_X^{m.p.}$ above the equipartition value. Similar conclusions follow when we compare $\langle f_X \rangle$ with the equipartition value $\langle f_X^0 \rangle$ obtained with $\lambda_X = 0$ in (58). For $\lambda_X < 0$, the average energy in the mode X is less than the equipartition value and conversely for $\lambda_X > 0$. The equipartition distribution of energy corresponds to $\lambda = 0$ for all three modes, while the λ parameter characterizing the distribution of $(1 - f_X)$ (say $f_I = 1 - f_T$, etc.) is always of the same magnitude but of opposite sign to λ_X , say

$$\lambda_T + \lambda_I = 0 \quad \text{or} \quad 1/T_T + 1/T_I = 0.$$

The experimental determination of $f_X^{m.p.}$ provides, using (58), a quick estimate of λ_X . This procedure is the analog of the usual equilibrium rules for obtaining the temperature from a known $E_X^{m.p.}$. Taking the translation as an example⁵⁵ [using (58) and (A22)],

$$\lambda_T = (1 - 3f_T^{m.p.}) / [2f_T^{m.p.}(1 - f_T^{m.p.})]. \quad (59)$$

Thus, for the data of Fig. 12, where $f_T^{m.p.} \approx 0.03$ we obtain $\lambda_T \approx 15.5$ vs 15.0 from Fig. 12 and similar estimates can be applied for the other distributions.

Similarly, a quick estimate of ΔS starts with the surprisal $I(f_X | E)$,

$$\omega(f_X | E) = \exp[-I(f_X | E)]. \quad (60)$$

Using a Taylor series expansion

$$I(f_X | E) = I(0 | E) + f_X I'(0 | E) + \dots \quad (61)$$

we can make the identification [cf. (50)–(53)]

$$Q^{-1} = \exp[-I(0 | E)]$$

and

$$\lambda_X = [dI(f_X | E)/df_X]_{f_X=0}. \quad (62)$$

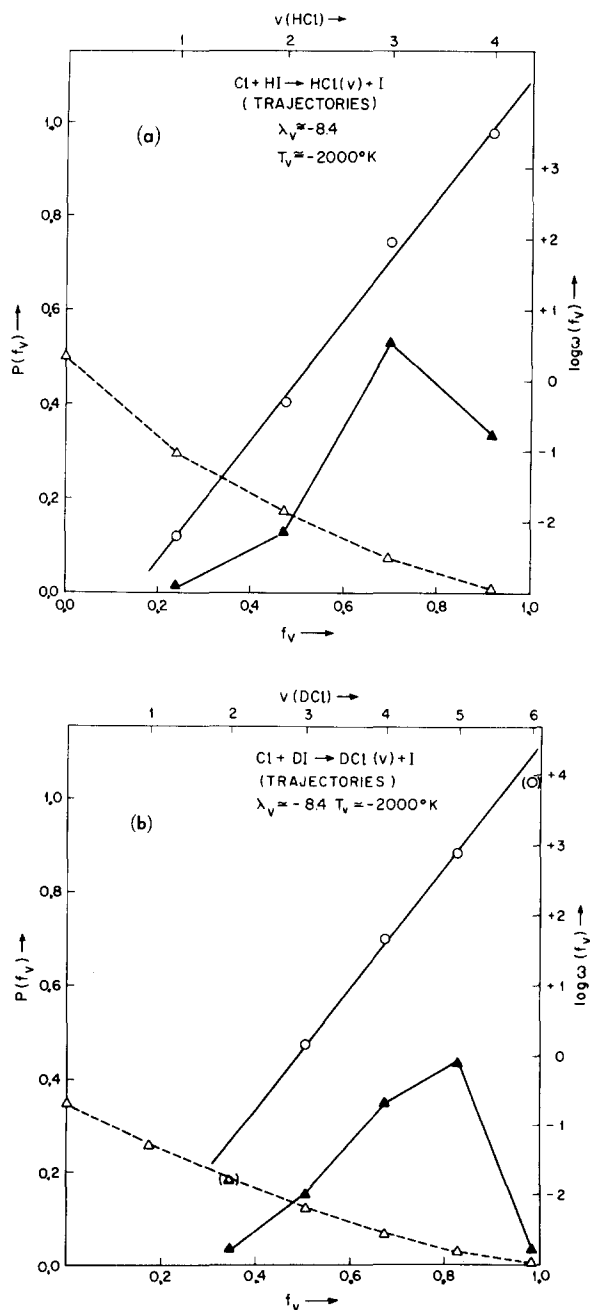


Fig. 9. Analysis of the computer simulation (classical trajectory computations) for the vibrational state distribution of the isotopic reactions (a) $\text{Cl} + \text{HI} \rightarrow \text{HCl}(v) + \text{I}$ and (b) $\text{Cl} + \text{DI} \rightarrow \text{DCl}(v) + \text{I}$. (Results from Ref. 37; notation as in Fig. 1.) A summary of the analysis is given in Table III.

It appears that for exoergic reactions the second derivative of the surprisal is small. In this case we can simply evaluate $S[f_X]$ as

$$S[f_X] = -k \sum_{f_X} P(f_X | E) \log \omega(f_X | E) \\ = k \log Q + k \lambda_X \langle f_X \rangle = k \log Q + \langle E_X \rangle / T_X. \quad (63)$$

There is a difference between the temperature parameter as defined here and the more usual way in which it was sometimes employed,^{49-52,56} i.e.,

$$\gamma_X = -d \log \frac{[P(f_X | E) / \rho_X(f_X)]}{dE_X}, \quad (64)$$

where $\rho_X(f_X)$ is the usual equilibrium density of states⁵⁷ in the mode X . For infinite heat bath⁵⁸ or, in general, when $f_X \rightarrow 0$, the two definitions (64) and (56) are in agreement. This follows from the expressions (A22), (A25), and (A28) or, in general, from the fact that $P^0(f_X | E) \propto \rho_X(f_X) \rho_B(1-f_X)$, where $\rho_B(1-f_X)$ is the density of states of the rest of the system (i.e., of that heat bath). When the heat bath is very large $\rho_B(1-f_X) \propto \exp(-\beta_X f_X)$, as is discussed below. The two definitions differ for a finite system and (56) has the advantage of providing a measure of the deviation from the equipartition reference distribution. What then is measured by γ_X ?

In equilibrium statistical mechanics, temperature is usually introduced as a measure of the deviation of

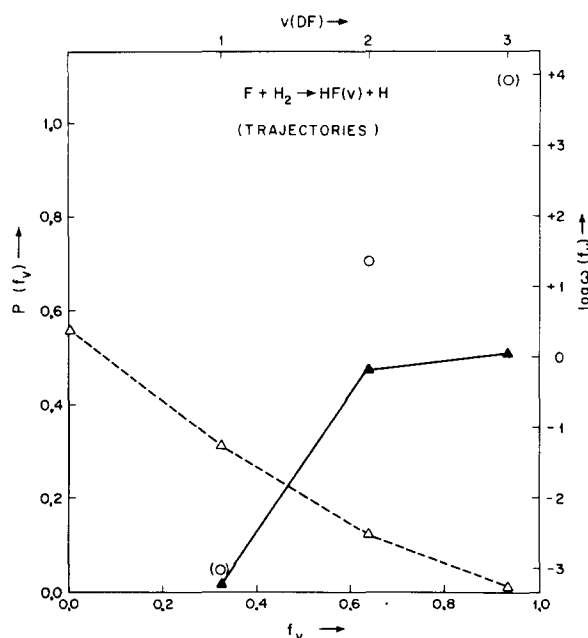


FIG. 10. Classical trajectory results for the vibrational state distribution of the reaction $F + H_2 \rightarrow HF(v) + H$. (Results from Ref. 38 and other notation as in Fig. 1.) The points in brackets are uncertain due to a combination of theoretical and computational errors. The computed $\Delta S[v]$ (Table III) is somewhat larger than the value obtained from the experimental results (Table I).

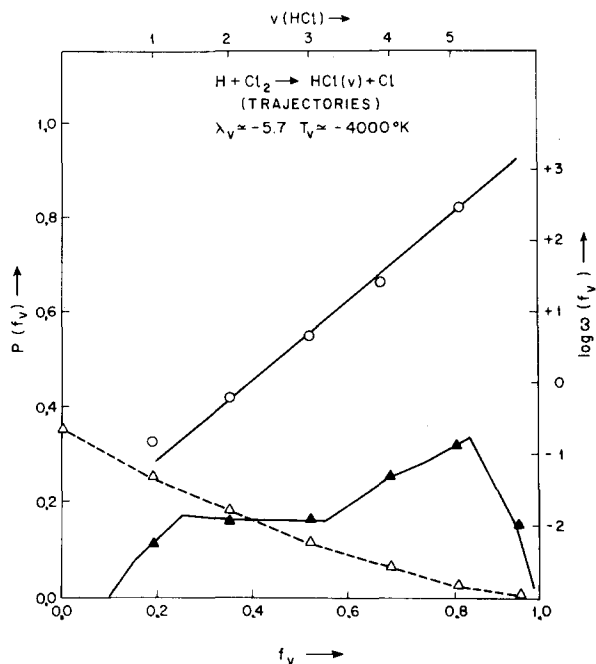


FIG. 11. Trajectory calculations on an attractive surface for the reaction $H + Cl_2 \rightarrow HCl(v) + Cl$. (Results from Ref. 39 and other notation as in Fig. 1.) The experimental distribution for this reaction does not yield a linear $\log \omega(f_v)$ vs f_v plot, as discussed in the text.

$P^0(E_X | E)$ from $\rho_X(E_X)$ for a small subsystem at equilibrium with an infinite heat bath,⁵⁹⁻⁶¹

$$\beta_X = -d \log \frac{[P^0(E_X | E) / \rho_X(E_X)]}{dE_X} \quad (65)$$

so that

$$\gamma_X = \beta_X - \lambda_X / E. \quad (66)$$

When a long-lived complex is formed or, in general, when the available energy is nearly equipartitioned, $\lambda_X \approx 0$ [or $P(E_X | E) \approx P^0(E_X | E)$] and the definition of γ_X reduces to the thermodynamic equilibrium value β_X . For direct reactions, the values of λ_X as determined here imply that γ_X and β_X can be quite different.

One should also note that β_X is independent of E_X only for the case of a small subsystem coupled to a large heat bath. To see this we recall that in the RRHO approximation for a polyatomic⁶²

$$P^0(E_T | E) / \rho_T(E_T) \propto (1-f_T)^{n-1}, \quad (67)$$

where $2n$ is the number of square terms in the Hamiltonian for the internal degrees of freedom, and similar results hold for $X=v$ or R . In the thermodynamic limit, where both n and E become very large, but their ratio remains constant, say $\beta = (n-1)/E$, we find that

$$(1-f_T)^{n-1} \rightarrow \exp[-(n-1)f_T] = \exp(-\beta E_T). \quad (68)$$

For low values of n , the limiting operation (68) is valid for low f_T only. [In the present case this is equivalent to replacing $1-f_T$ by $\exp(-f_T)$.] Thus, for

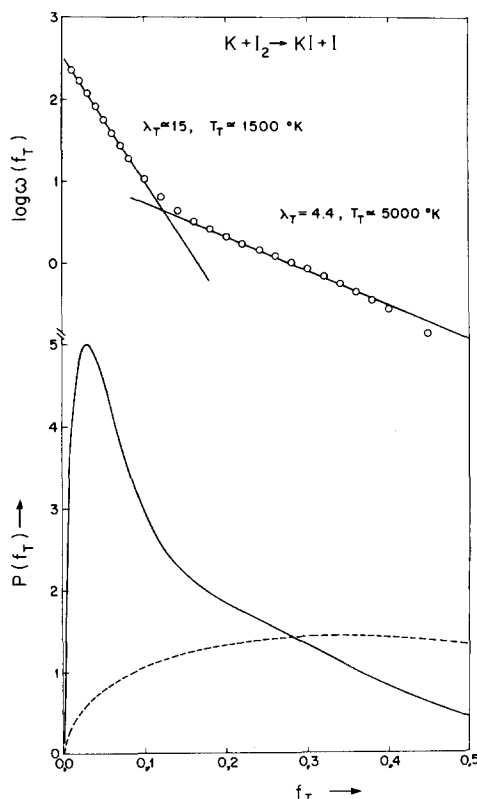


FIG. 12. Translational energy distribution for the reaction $K + I_2 \rightarrow KI + I$. (Experimental results from Ref. 7.) The equilibrium distribution, $P^0(f_T)$, is shown as a broken line while the experimental distribution is a full line. The plot of $\log \omega(f_T)$ vs f_T shows two linear regimes, as discussed in the text. Due to the very low translational exoergicity $\Delta S[f_T]$ is relatively large (Table IV).

a very small finite system β_X is not expected to be independent of E_X .

Our analysis suggests however that, at least for the exothermic reactions here examined, λ_X is essentially independent of E_X . The reason for this empirical result is not immediately obvious, neither should it be completely general and apply to any scattering situation.⁶³ On the other hand, the results of three dimensional classical trajectory calculations on attractive surfaces are also in good accord with the representation

$$\omega(f_X | E) = Q^{-1} \exp(-\lambda_X f_X), \quad (69)$$

where Q is a normalizing factor [cf. Eq. (51)]. Preliminary studies on the interpretation of the vibrational temperature have been reported⁴⁷ and further work is in progress.

The essential difference between the temperature parameter λ_X as used in this paper [Eq. (56)] and the sometimes used parameter γ_X should be clearly understood. The definition of γ_X [Eq. (64)] is appropriate only for a small subsystem coupled to an infinite heat bath. The more fundamental definition is, in fact, (56) and the novelty here is in its application to a system far removed from equilibrium. The advantage is

that λ_X is an obvious measure of the deviation from equilibrium which, as we have shown, can handle inverted populations. Literature results cast in terms of γ_X can be easily converted to λ_X using (66).

VII. ENTROPY DEFICIENCY OF A PRODUCT TRANSLATIONAL AND ANGULAR DISTRIBUTION

The angular and/or translational energy distributions of reaction products are determined using the molecular beam technique, with velocity analysis (for the translational energy distribution), and are usually reported as the differential cross section $d^3\sigma_R/d\Omega dE_T$,

$$d^3\sigma_R/d\Omega dE_T = \sigma_R(E) P(E_T, \Omega | E), \quad (70)$$

where $\sigma_R(E)$ is the total reaction cross section at the energy E . The (conditional) pdf $P(E_T, \Omega | E)$ is defined so that $P(E_T, \Omega | E) d\Omega dE_T$ is the probability of observing products with translational energy and solid angle of scattering in the indicated range at a given total energy. For an atom-diatom collision

$$\begin{aligned} E &= E_T + E_v + E_R, \\ E_I &= E_v + E_R. \end{aligned} \quad (71)$$

Strictly speaking, the internal modes of the diatom are quantized and hence, at a given E , E_T can only assume discrete values. However, when the density of internal states is high, E_T will, for practical purposes, vary continuously. The notation $P(E_T, \Omega | E)$ implies an average over a small range δE_T of translational energies, such that many internal states fall within that interval yet the interval is sufficiently narrow that $P(E_T, \Omega | E)$ hardly varies over the range,

$$\begin{aligned} P(E_T, \Omega | E) &= \sum_n P(n, E_T, \Omega | E) / \delta E_T, \\ E_T &\leq E - E_n \leq E_T + \delta E_T. \end{aligned} \quad (72)$$

Similar comments apply to $P(E_T | E)$,

$$P(E_T | E) = \int d\Omega P(E_T, \Omega | E). \quad (73)$$

The maximal entropy deficiency at a given E is, as usual,

$$\begin{aligned} \Delta S[E_T, \Omega] &= k \int dE_T \int d\Omega P(E_T, \Omega | E) \\ &\quad \times \log[P(E_T, \Omega | E) / P^0(E_T, \Omega | E)]. \end{aligned} \quad (74)$$

To explicitly apply (74) we need to specify the reference (or equilibrium) distribution $P^0(E_T, \Omega | E)$. Considerations of the transformation from final states labeled in terms of k to the specification in terms of E_T and Ω (Sec. II) immediately suggest that, in the absence of information to the contrary, the reference angular distribution should be taken to be an isotropic distribution

$$P^0(\Omega | E_T, E) d\Omega = d\Omega / 4\pi \quad (75)$$

so that

$$\begin{aligned} P^0(E_T, \Omega | E) &= P^0(\Omega | E_T, E) P^0(E_T | E) \\ &= P^0(E_T | E) / 4\pi. \end{aligned} \quad (76)$$

TABLE IV. Molecular beam data.

	K+I ₂ →KI+I Ref. 7	D+Cl ₂ →DCl+Cl Ref. 9	D+Br ₂ →DBr+Br Ref. 9	D+I ₂ →DI+I Ref. 9	D+IBr →DBr+I Ref. 9	D+ IBr →DI+Br Ref. 9	D+ ICl →DI+Cl Ref. 9
<i>E</i> kcal/mole	44.5	55	51	54	44	38	30
¹ Δ <i>S</i> [<i>E_T</i>] ^a cal/deg·mole	1.4	0.11	0.42	0.41	0.60	0.15	0.17
¹¹ Δ <i>S</i> [<i>E_T</i>] ^b cal/deg·mole		0.034	0.45	0.43	0.61	0.21	0.25
¹ Δ <i>S</i> [Ω] ^c cal/deg·mole		0.57	0.24	0.17	0.13	0.24	0.17
¹¹ Δ <i>S</i> [Ω] ^d cal/deg·mole		0.75	0.60	0.73	0.52	0.84	0.74
λ _{<i>T</i>}	15 ^a					2.7 ^b	2.6 ^b

^a Using the original $P(f_T)$ distribution.

^b Using a modified $P(f_T)$ distribution.

^c Using an isotropic reference distribution.

^d Using a collision complex reference distribution.

For certain reactions one may well wish to use alternative reference angular distributions. An obvious example is reactions involving complex formation where, in simple cases,

$$P^0(\Omega | E_T, E) \propto (\sin\theta)^{-1}. \quad (77)$$

Lower values of the entropy deficiencies correspond to more averaged distributions. Thus with

$$\Delta S[E_T] = k \int dE_T P(E_T | E) \log[P(E_T | E)/P^0(E_T | E)] \quad (78)$$

we have [as in (46)] two inequalities

$$\Delta S(E_T, \Omega) \geq \Delta S[E_T] \quad (79)$$

and also

$$\Delta S[E_T, \Omega] \geq \Delta S[\Omega], \quad (80)$$

where $\Delta S[\Omega]$ is obtained from $P(\Omega | E)$, the angular distribution without absence of velocity analysis

$$d^2\sigma_R/d\Omega = \sigma_R(E) P(\Omega | E), \quad (81)$$

$$\Delta S[\Omega] = \int d\Omega P(\Omega | E) \log[P(\Omega | E)/P^0(\Omega | E)]. \quad (82)$$

One particular special case deserves an explicit mention. The lowest order kinematic analysis for lab to c.m. conversion⁶⁴ often uses as a starting point the "uncoupled" approximation⁶⁵

$$P(E_T, \Omega | E) = P(E_T | E) P(\Omega | E), \quad (83)$$

where the product translational and angular distributions are assumed independent. In this case, as follows immediately from (74),

$$\Delta S[E_T, \Omega] = \Delta S[E_T] + \Delta S[\Omega]. \quad (84)$$

VIII. ANALYSIS OF EXPERIMENTAL RESULTS FOR PRODUCTS' TRANSLATIONAL AND ANGULAR DISTRIBUTIONS

We consider a number of examples of molecular beam velocity analysis experiments. Gillen *et al.*⁷ have studied

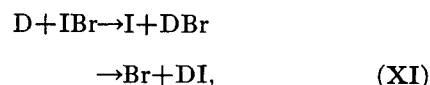
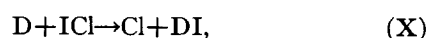
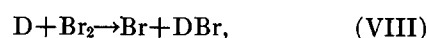
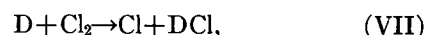
the reaction



and measured the translational and angular distribution $P(E_T, \Omega | E)$ at three different values of E . The translational distribution $P(E_T | E)$ derived for their results⁶⁶ together with the RRHO value of $P^0(f_T | E)$ [Eq. (A22)] yield $\Delta S[E_T] = 1.4$ cal/deg·mole at $E = 44.5$ kcal/mole. This is somewhat lower than the typical values obtained from the chemiluminescence studies. However, $\Delta S[E_T]$ is equivalent to $\Delta S[E_I]$, i.e., the entropy deficiency of the distribution of internal energy, irrespective of the manner of partitioning of E_I among E_v and E_R . As is to be expected²⁹ the distribution in E_I is "nearer to equilibrium" than the distribution in both E_v and E_R (or even in E_v or E_R only).

The plot of $-\log\omega(f_T | E)$ vs f_T (Fig. 12) shows two linear regimes. We have speculated²² that this may well be due to two different mechanisms. A forward (stripping) component with low translational exoergicity (and hence a high λ_T) and a smaller backward (rebound?) component with a much larger translational exoergicity (and hence a lower λ_T). This argument receives further support from the strong θ dependence of the conditional distribution $P(f_T | \Omega, E)$, (cf. Figs. 17–18 of Ref. 7). In the forward direction the large λ_T component is dominant while for $\theta \sim 90^\circ$, the two components are nearly of equal magnitude.

For the D atom reactions



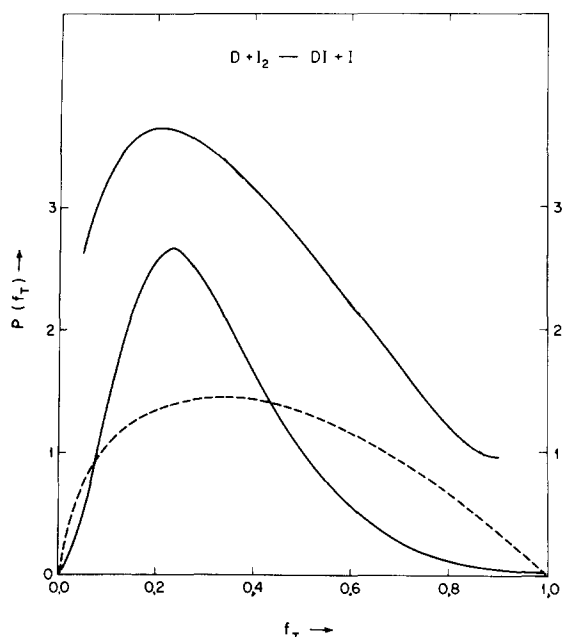


FIG. 13. Distribution of translational energy for the reaction $D + I_2 \rightarrow DI + I$. (Experimental results from Ref. 9, notation as in Fig. 12.) The deviation of the $\log \omega(f_T)$ vs f_T plot from linearity is discussed in the text.

McDonald *et al.*⁹ have determined an approximate, uncoupled angular and translational distribution

$$P(E_T, \Omega | E) = P(E_T | E)P(\Omega), \quad (85)$$

where the angular part was energy independent.⁶⁷ From such an uncoupled distribution the translational and angular contributions to the entropy deficiency are additive [cf. Eq. (84)], and the results are listed in Table IV. There are two entries in each case. For the translational distribution the entry I corresponds to the use of the experimental distribution as stated. On inspection it becomes evident (see Figs. 13–16) that $P(f_T)$ does not tend to zero as $f_T \rightarrow 1$. [The requirement that $P(f_T \rightarrow 1) \rightarrow 0$ was first pointed out by Kinsey²⁷ as a necessary condition for obtaining a finite ω (i.e., a finite surprisal).] To rectify the behavior as $f_T \rightarrow 1$ we have modified the analytic form of $P(f_T)$ by an *ad hoc* addition of the term $-f_T P(f_T = 1)$. This modified distribution yields the entries labeled II for $\Delta S[f_T]$. The effect of this modification is shown in Figs. 15–16. It clearly extends the range of the linear dependence of $-\log \omega(f_T | E)$ on f_T . The failure of this linear dependence for $f_T \rightarrow 0$ is probably due both to the inaccuracy of the RRHO value^{22,54} of $P^0(f_T | E)$ as $f_T \rightarrow 0$ and to the inaccuracy of the analytic (uncoupled) fit of $P(f_T | E)$ at low f_T values. (See Figs. 5 and 6 of Ref. 9.)

The two entries for $\Delta S[\Omega]$ in Table IV correspond to the two choices of the reference angular distribution. The first entry (I) corresponds to the preferred

choice of an *isotropic* reference distribution: $P^0(\Omega | E) = (4\pi)^{-1}$. The second entry (II) is a result of choosing a *symmetrical* reference distribution [$P^0(\Omega | E) = (2\pi^2 \sin \theta)^{-1}$] which is appropriate for linear complex formation.

The entropy deficiency for all D-atom reaction translational distributions is markedly below that found for the $K + I_2$ reaction. This is obvious upon inspection of Figs. 13–16. The $P(f_T)$ distributions for the D atom reactions are broader and tend to peak at about $f_T \sim 1/3$ which is the equilibrium most probable value. In fact, the translational distributions for some of these reactions, say $D + Cl_2$, are very near the equilibrium value as is also indicated by the near independence of $-\log \omega(f_T | E)$ on f_T (Fig. 14). $\lambda_T = 0$ is of course the criterion for an equilibrium distribution of the reaction exoergicity between the translational and the internal modes. The vibrational entropy deficiency of the $H + Cl_2$ reaction is also atypically low. We reiterate our previous remark that the Reactions (V) and (VII) deserve a closer examination, both experimentally and theoretically.

There are several quantitative regularities that one can discern in Table IV. These will be discussed when we consider the question of entropy cycles in a future paper. At this point it is sufficient to say that the entropy deficiency is a compact way of characterizing the products' distribution.

As a final illustration of the importance of the width

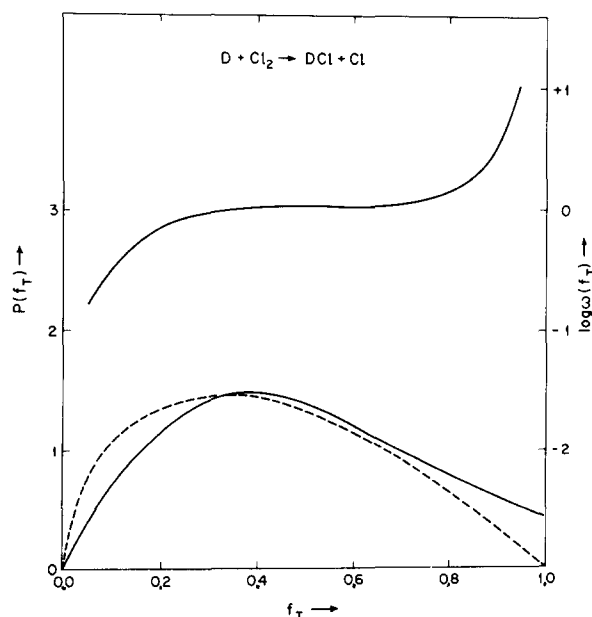


FIG. 14. Translational energy distribution for the reaction $D + Cl_2 \rightarrow DCl + Cl$, as in Fig. 13. Note that over a wide range $\omega(f_T) \simeq 1$, indicating an equilibrium distribution; also the experimental error leading to an "end effect," as first discussed by Kinsey.²⁷

of the distribution in determining the entropy deficiency, we have used an artificial distribution

$$P(f_T | E) = A_n [f_T^{1/2}(1-f_T)]^n \quad (86)$$

(for different n values) to compute $\Delta S[f_T]$. A_n is a normalization constant. As n increases these distributions, which are all peaked at $f_T = 1/3$, become narrower (and hence, due to normalization, of larger maximum). Figure 17 shows the increase of $\Delta S[f_T]$ with the value of $P_m = P(\frac{1}{3} | E)$. Another test made (among many others) showed the effect of the position of the most probable f_T by replacing (86) by $P(f_T | E) = A_n [f_T(1-f_T)^{1/2}]^n$ for which $f_T^{m.p.} = 2/3$, Fig. 17. It is seen that for a given width (i.e., for a given P_m) the entropy deficiency was higher in the latter case, but that the dominant effect is the width of the distribution. When $f_T^{m.p.}$ is arranged to be between $\frac{1}{3}$ and $\frac{2}{3}$, the resulting ΔS (for a given P_m) lies between the two curves in Fig. 17.

IX. CONCLUDING REMARKS

This paper has centered attention on the analysis of the distribution of final states of reactive collisions in terms of the entropy deficiency and the temperature of the distribution. Practical algorithms have been developed and applied to representative examples of direct, exothermic reactions, where there is considerable deviation from simple quasiequilibrium product distributions. The highest values for the entropy de-

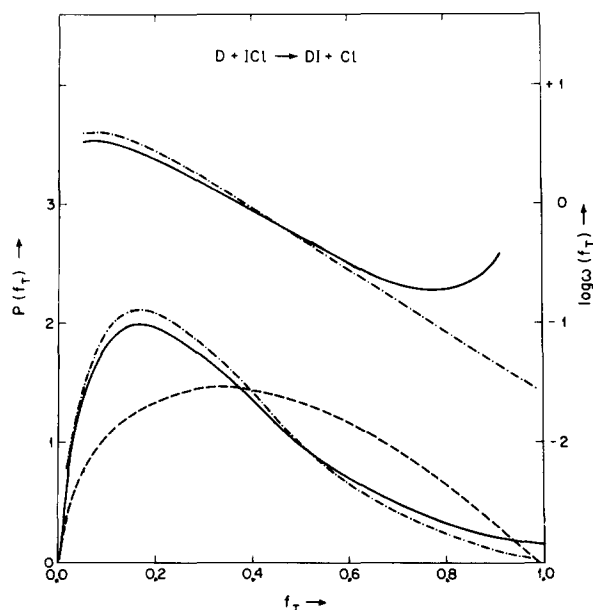


FIG. 15. Translational energy distribution for the reaction $D + ICl \rightarrow DI + Cl$. (Experimental results from Ref. 9, other notation as in Fig. 12.) The modified (---) curves represent a modified $P(f_T)$ [and hence, $\omega(f_T)$] distribution, introduced to insure that $P(f_T \rightarrow 1) \rightarrow 0$, as discussed in the text. Other results for Figs. 12–16 are given in Table IV.

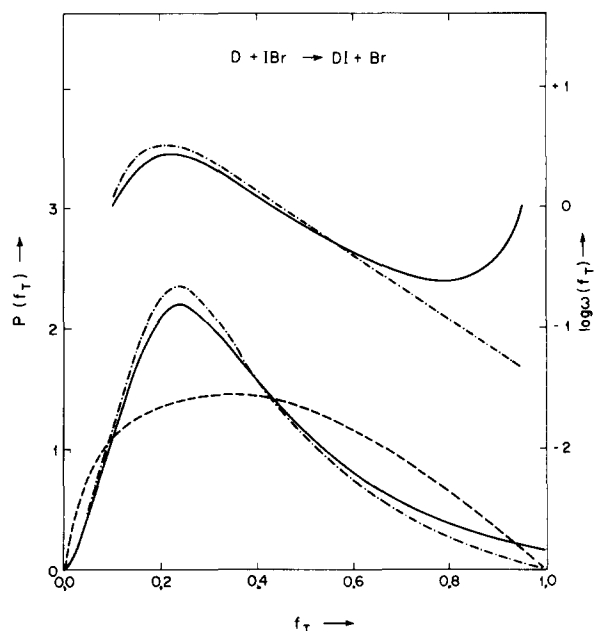


FIG. 16. Distribution of translational energy for the reaction $D + IBr \rightarrow DI + Br$, as in Fig. 15. Here also the modified $P(f_T)$ distribution leads to a more linear $\log \omega(f_T)$ vs f_T plot.

ficiencies were obtained for the high resolution distributions measured by the chemiluminescence experiments. The major contribution to the entropy deficiency was that from the population-inverted vibrational state distribution, which could be characterized by a negative temperature T_v . The entropy deficiencies for translational energy distribution (and for angular distribution) measured by molecular beam velocity analysis were lower, due to the failure to resolve the internal states.

The experiments chosen for analysis in this paper are just a sample of the many recent studies of both atom-diatom and more complex reactions^{68–81}. Not discussed in this paper is the energy partitioning among fragmentation products of energy-rich molecules^{82–92} produced photochemically, by electron impact or by collision with metastable atoms. Often these distributions show significant deviations from a simple equilibrium distribution and the concept of a “restricted phase space” has indeed been invoked⁹³ to interpret such effects. The entropy deficiency is simply a quantitative measure of such deviations from equilibrium; the term “diabatic phase space behavior” has been coined⁴⁷ for such distributions that are neither completely statistical nor entirely adiabatic.

Future work in this series will consider the analysis of “angular momentum limited” reactions,²¹ the analysis of the reactant state distribution, and the question of detailed vs inclusive experiments.² The use of entropy deficiency in analyzing theoretical and computational results and the theoretical significance of the temperature parameter are also under current study.

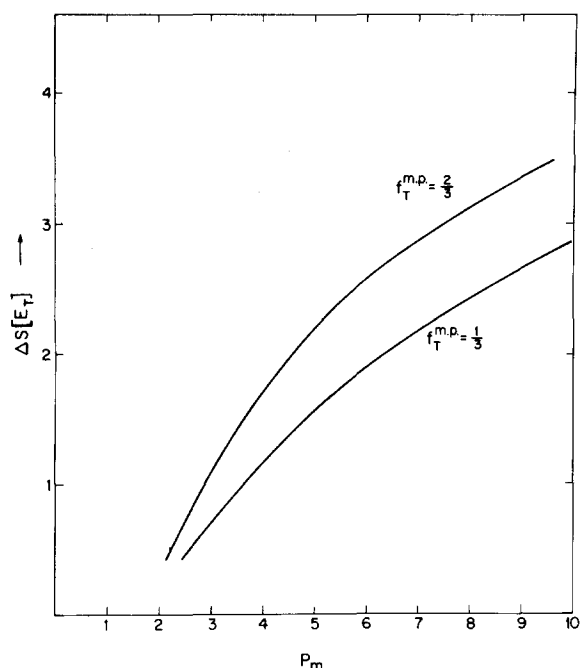


FIG. 17. The effect of the position and width of $P(f_T)$ on the magnitude of $\Delta S(E_T)$. P_m is the maximal value of $P(f_T)$ [and hence, since $P(f_T)$ is normalized, is roughly inversely proportional to the width]. $f_T^{m,p}$ is the position of the maximum. See text for further details.

ACKNOWLEDGMENTS

We appreciate many discussions with our colleagues, particularly Professor G. L. Hofacker and Dr. B. R. Johnson. We thank Mr. Y. Shimoni for his assistance with some of the required computational work.

APPENDIX: DENSITY OF STATES FOR AN ATOM-DIATOM COLLISION

The reference (or equilibrium) distribution of states has been introduced as the distribution of maximal entropy, subject to given experimental conditions. In general, one has to determine the distribution that will maximize the entropy, subject to the known, *a priori* constraints. For the particular case of a given total energy, it follows immediately from the fundamental postulate that in the reference distribution all possible final states are equiprobable. In the discussion below we shall assume only the constraint of conservation of total energy so that the possible states are those having a given total energy. Strictly speaking we should also impose the conservation of total angular momentum. However, unless there is a large change in the reduced mass this restriction is of little practical significance. Work is in progress to incorporate this restriction in the analysis of Reactions (VII)–(XI).

The discussion here follows closely the derivation, by Kinsey,²⁷ of the joint density of states. The only essential (albeit, trivial) difference is that we seek the conditional rather than the joint density.

The (joint) density of final states is obtained by compounding the contributions of the different degrees of freedom. For the translational motion, with an isotropic angular distribution [cf. Sec. III, in particular Eqs. (9)–(10)]

$$\rho(E_T, \Omega) dE_T d\Omega = \rho(E_T) dE_T (d\Omega/4\pi) \quad (A1)$$

with⁹⁴

$$\begin{aligned} \rho(E_T) &= 4\pi\mu P/h^3 = (2^{5/2}\pi\mu^{3/2}/h^3) E_T^{1/2} \\ &= (\mu^{3/2}/2^{1/2}\pi^2\hbar^3) E_T^{1/2} \\ &= A_T E_T^{1/2}. \end{aligned} \quad (A2)$$

Here A_T is a (unit-bearing) constant defined by the last line.

It is possible to modify the angular distribution when one selects the reference state to correspond to a long-lived complex. When the conservation of total angular momentum is neglected,⁹⁵

$$\rho(\Omega) = (2\pi^2 \sin\theta)^{-1}. \quad (A3)$$

The density of states (or, strictly speaking, the degeneracy) of the internal states of the diatom depends on the model selected to approximate the internal motion, as discussed extensively by Kinsey.²⁷ We have used both the rigid-rotor harmonic oscillator approximation⁹⁶ (RRHO) and the vibrating rotor (VR) approximation. For the latter case, the level scheme is

$$E_R = B_v J(J+1) \hbar c, \quad (A4)$$

where

$$B_v = B_e - \alpha_e(v + \frac{1}{2}) \quad (A5)$$

and (measuring energy from the ground state)

$$E_v = \hbar\omega_v[1 - \chi_e(v+1)]. \quad (A6)$$

Putting $\alpha_e = \chi_e = 0$ reduces these expressions to the RRHO level scheme.⁹⁶ In the VR approximation, using the notation of Kinsey,²⁷

$$\rho_J(E_I, v) = (2J+1) (\partial J / \partial E_I)_v = (B_v \hbar c)^{-1}, \quad (A7)$$

where $E_I = E_R + E_v$, and

$$\begin{aligned} \rho_v(E_I, J) &= (\partial v / \partial E_I)_J = \{\hbar\omega[1 - \chi_e(2v+1)] \\ &\quad - \alpha_e J(J+1)\}^{-1}. \end{aligned} \quad (A8)$$

The density of internal levels is then given by

$$\rho_I(E_I) = \sum_{v=0}^{v^*} \rho_J(E_I, v). \quad (A9)$$

A different form is

$$\rho_I(E_I) = \sum_{J=0}^{J^*} (2J+1) \rho_v(E_I, J). \quad (A10)$$

Both expressions yield a continuous dependence of ρ_I on E_I and are identical in the RRHO approximation⁹⁶

$$\rho_I(E_I) = A_I E_I, \quad (A11)$$

where $A_I = (\hbar\omega B_e)^{-1}$. In general, however, (A9) treats

the rotational levels as forming a continuum but treats the vibrational states in a discrete fashion and is thus superior to (A10) which integrates over E_v but sums over J .

For the combined atom-diatom system, we consider the four cases corresponding to the different experimental resolutions considered in the paper.

I. $P^0(v, J | E)$

We consider the density of states at the total energy E for a given internal level. Here E_T is specified implicitly and hence

$$\rho(v, J, E) = (2J+1)\rho_T(E-E_v-E_R) \quad (\text{A12})$$

and the total density of states is

$$\rho(E) = \sum_{v=0}^{J^*(v)} \sum_{J=0}^{J^*(v)} \rho(v, J, E), \quad (\text{A13})$$

where $J^*(v)$ is the maximal value of J , at a given E and v , $E_R(J^*, v) \leq E-E_v$, and $E_{v^*} \leq E$. The VR energy levels (A4) and (A5) were used in the actual analysis. In the RRHO approximation

$$\rho(E) = (4/15)A_I A_T E^{5/2}. \quad (\text{A14})$$

The conditional density is then

$$P^0(v, J | E) = \rho(v, J, E) / \rho(E) \quad (\text{A15})$$

and in the RRHO approximation

$$P^0(v, J | E) = [(2J+1)/A_I] (15/4) (E-E_v-E_R)^{1/2} \quad (\text{A16})$$

or

$$P^0(E_v, E_R | E) = P^0(v, J | E) \left/ \left(\frac{dE_v}{dv} \frac{dE_R}{dJ} \right) \right. \\ = (15/4) (E-E_v-E_R)^{1/2}. \quad (\text{A17})$$

It should be stressed that the RRHO results are not of sufficient accuracy for careful quantitative work. In practice we have computed $P^0(v, J | E)$ from (A12) and (A15) using the VR level scheme with $E_R \equiv E_R(v)$. For the purpose of the comparison between $P(v | E)$ and $P(v, J | E)$ we have used

$$P^0(v, J | E) = P^0(v | E) P^0(J | v, E) \quad (\text{A18})$$

to evaluate $P^0(v | E)$. Less detailed distributions are easily derived. Thus

$$P^0(E_I | E) = \sum_{v=0}^{J^*} P^0(v | E) \sum_{J=0}^{E_R-E_I-E_v} P^0(J | v, E) \quad (\text{A19})$$

and in the RRHO approximation

$$P^0(E_I | E) = (15/4) E_I (E-E_I)^{1/2} E^{-5/2} \quad (\text{A20})$$

or

$$P^0(f_I | E) = (15/4) f_I (1-f_I)^{1/2} \quad (\text{A21})$$

and since $f_I + f_T = 1$,

$$P^0(f_T | E) = (15/4) f_T^{1/2} (1-f_T). \quad (\text{A22})$$

II. $P^0(v | E)$

In this case

$$\rho(v, E) = \sum_{J=0}^{J^*(v)} \rho(v, J, E) \quad (\text{A23})$$

and

$$P^0(v | E) = \rho(v, E) / \rho(E), \quad (\text{A24})$$

where $\rho(E)$ and $\rho(v, J, E)$ are given by (A13) and (A12) respectively. In the RRHO approximation

$$P^0(f_v | E) = \frac{5}{2} (1-f_v)^{3/2} \quad (\text{A25})$$

while in the VR level scheme (but when the rotations are treated as a continuum)

$$P^0(f_v | E) = (1-f_v)^{3/2} / \sum_{v=0}^{J^*} (1-f_v)^{3/2}. \quad (\text{A26})$$

In the strict VR scheme, one simply proceeds from the value of $\rho(v, J, E)$ and evaluates the required summations in (A23) and (A26).

III. $P^0(J | E)$

This case is completely analogous to the previous one

$$\rho(J, E) = \sum_{v=0}^{v'} \rho(v, J, E), \quad (\text{A27})$$

where $E_{v'} \leq E-E_R \leq E_{v'+1}$. In the RRHO approximation

$$P^0(f_R | E) = \frac{5}{2} (1-f_R)^{3/2}. \quad (\text{A28})$$

Work in progress includes the computational study of those reactions involving a large change in the reduced mass and/or a small reaction cross section (i.e.,⁸ $F+D_2 \rightarrow FD+D$) for which the constraint of conservation of total angular momentum is important. For such reactions, $P^0(J | E)$ may show several maxima (cf., for example, Ref. 41).

IV. $P^0(E_T | E)$

In practice we have already indicated the chain of summations leading to $P^0(E_T | E)$ [Eq. (A22)]. It is perhaps worthwhile to reiterate the nature of the approximation leading to this density. Strictly speaking $P^0(E_T | E)$ is not a continuous but a discrete distribution since at a given E , E_T can assume only discrete values,

$$E_T = E - E_I$$

or

$$\rho(E_T, E) = \rho_T(E_T) \sum_I g_I \delta(E - E_T - E_I). \quad (\text{A29})$$

To obtain a continuous distribution we need to average $\rho(E_T, E)$ over a short interval δE_T .³³ With the definition

$$\rho_I(E_I) = \sum_{E_T} g_I / \delta E_T, \quad (\text{A30})$$

$$E_T \leq E - E_I \leq E_T + \delta E_T$$

we have that

$$\langle \rho(E_T, E) \rangle = \int_{E_T}^{E_T + \delta E_T} \rho(E_T, E) dE_T / \delta E_T \\ \simeq \rho_T(E_T) \rho_I(E - E_T). \quad (\text{A31})$$

We thus take

$$P^0(E_T, E) = \rho_T(E_T) \rho_I(E - E_T). \quad (\text{A32})$$

It should be noted that the averaging in (A31) corresponds to the lack of very high resolution in the molecular beam velocity analysis (but see however Ref. 8).

* Work supported by the Air Force Office of Scientific Research, USAF under Grant AFOSR-72-2272, The National Science Foundation under Grant GP-26014 and the Stiftung Volkswagenwerk.

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¹ For a review of recent developments, see T. Carrington and J. C. Polanyi, *International Review of Science: Reaction Kinetics* (MTP, Oxford, 1972), Chap. V.

² R. B. Bernstein and R. D. Levine, *J. Chem. Phys.* **57**, 434 (1972). Part I of this series, where further references can be found.

³ J. C. Polanyi, *Accts. Chem. Res.* **5**, 162 (1972).

⁴ L. T. Cowley, D. S. Horne, and J. C. Polanyi, *Chem. Phys. Letters* **12**, 144 (1971).

⁵ D. H. Maylotte, J. C. Polanyi, and K. B. Woodall, *J. Chem. Phys.* **57**, 1547 (1972), and references therein.

⁶ J. C. Polanyi and K. B. Woodall, *J. Chem. Phys.* **57**, 1574 (1972) and references therein.

⁷ K. T. Gillen, A. M. Rulis, and R. B. Bernstein, *J. Chem. Phys.* **54**, 2831 (1971) and references therein.

⁸ T. P. Schafer, P. E. Siska, J. M. Parson, F. P. Tully, Y. C. Wong, and Y. T. Lee, *J. Chem. Phys.* **53**, 3385 (1970).

⁹ J. D. McDonald, P. R. LeBreton, Y. T. Lee, and D. R. Herschbach, *J. Chem. Phys.* **56**, 769 (1972).

¹⁰ M. E. Gersh and R. B. Bernstein, *J. Chem. Phys.* **55**, 4661 (1971); **56**, 6131 (1972).

¹¹ J. H. Parker and G. C. Pimentel, *J. Chem. Phys.* **51**, 91 (1969); **55**, 857 (1971).

¹² T. D. Padrick and G. C. Pimentel, *J. Chem. Phys.* **54**, 720 (1971).

¹³ R. B. Bernstein, *Israel J. Chem.* **9**, 65 (1971).

¹⁴ J. C. Polanyi, *Appl. Opt. Suppl.* **2**, 109 (1965).

¹⁵ J. C. Polanyi, *Appl. Opt.* **10**, 1717 (1971).

¹⁶ C. E. Shannon and W. Weaver, *The Mathematical Theory of Communication* (University of Illinois Press, Urbana, 1949).

¹⁷ E. T. Jaynes, *Phys. Rev.* **106**, 620 (1957); **108**, 171 (1957).

¹⁸ E. T. Jaynes, 1962 Brandeis Lectures, Vol. 3: *Statistical Physics* (W. A. Benjamin, New York, 1963), p. 181.

¹⁹ A. Katz, *Principles of Statistical Mechanics* (Freeman, San Francisco, 1967).

²⁰ R. Ash, *Information Theory* (Interscience, New York, 1965).

²¹ For the Reactions (V) and (VIII)–(XI), the large change in the reduced mass during the reaction requires that in defining the equilibrium reference state (Appendix) we impose the conservation of total angular momentum. We have neglected this restriction in Appendix, with the result that our reference state is inaccurate for these reactions at high internal excitations. Almost certainly this is responsible for the deviations noted in Figs. 11 and 13–16. This point is under further study.

²² A preliminary report on these results has been published; A. Ben Shaul, R. D. Levine, and R. B. Bernstein, *Chem. Phys. Letters* **15**, 160 (1972).

²³ An exception is the study⁸ of the reaction $F + D_2 \rightarrow DF + D$ where the vibrational states of DF have been resolved, in the angular distribution of DF.

²⁴ R. D. Levine, *Quantum Mechanics of Molecular Rate Processes* (Clarendon, Oxford, 1969).

²⁵ The entropy of independent distributions is simply additive.

Thus the entropy per Avogadro's number (N_0) of independent binary reactive collisions is just N_0 times the entropy of the final state distribution of a single collision.

²⁶ Information is usually defined in terms of logarithms to base 2.

²⁷ J. L. Kinsey, *J. Chem. Phys.* **54**, 1206 (1971).

²⁸ We reiterate again that the present and following discussion apply only to the case of a given total energy. In all other circumstances, the equilibrium reference distribution has to be determined according to the information theoretic rule that the equilibrium distribution is to be chosen so as to maximize $S[f]$, subject to the known constraints on the system (see Refs. 17, 18).

²⁹ Qualitatively, this follows from the interpretation of entropy as "missing information." The division into groups makes the distribution more uniform (since states within each group are considered equiprobable) and hence more information is missing when one wants to predict the result of an experiment. A general mathematical proof is given in p. 21 of Ref. 16. A proof and further discussion of (7) is given in Sec. IV within the specific context of high and low resolution studies. The key concept here, as discussed in Part I, is that any averaging operation of the form $\bar{P}(f) = \sum_j a_{fj} P(j)$, where $\sum_j a_{fj} = \sum_j a_{fj} = 1$, increases the entropy (i.e., reduces the entropy deficiency).

³⁰ In the absence of a field, when one cannot resolve the initial orientation quantum numbers, one cannot resolve the final orientation quantum numbers and the scattering has cylindrical symmetry about the initial $\mathbf{k}$ vector. See, for example, C. N. Yang, *Phys. Rev.* **74**, 764 (1948).

³¹ This follows from the basic lemma of Shannon, cf. Eq. (45) of I. It is also worthwhile to point out that for a distribution in a continuous variable (i.e., a pdf) the entropy is not strictly positive; even so, entropy differences retain their usual significance. See Sec. 2.5 of Ref. 19 and Sec. 8.3 of Ref. 20.

³² D. L. Bunker, *Methods Computational Phys.* **10**, 287 (1971); P. J. Kuntz, *Electronic and Atomic Collision, Invited Papers, VII ICPEAC* (North-Holland, Amsterdam, 1971).

³³ Note that there is usually some spread in the experimental E and strictly speaking we can only obtain $P(v|\bar{E}) = \int P(v, E) \times dE / \int P(E) dE$, where the energy averaging is over the experimental energy spread.

³⁴ M. Tribus, *Thermostatistics and Thermodynamics* (Van Nostrand, New York, 1961).

³⁵ Shannon's lemma is

$$\sum_i P_i \log(P_i / P_i^0) \geq 0,$$

where $\sum_i P_i = \sum_i P_i^0 = 1$, with equality only when $P_i = P_i^0$.

³⁶ The information-theoretic significance of the inequality (46) is easy to see. In computing $\Delta S[v]$ we have no knowledge of the actual distribution of the J, m_J states and so we are forced to assign equal probability to all possible rotational states. On the other hand, when $P(v, J|E)$ is known, we need only average over the different m_J states of each J level. The $P(v, J|E)$ distribution is thus further removed from equilibrium than the $P(v|E)$ distribution.

³⁷ K. G. Anlauf, J. C. Polanyi, W. H. Wong, and K. B. Woodall, *J. Chem. Phys.* **49**, 5189 (1968).

³⁸ J. T. Muckerman, *J. Chem. Phys.* **54**, 1164 (1971); **56**, 2997 (1972). See also R. L. Jaffe and J. B. Anderson, *ibid.* **54**, 2224 (1971).

³⁹ K. G. Anlauf, P. J. Kuntz, D. H. Maylotte, P. D. Pacey, and J. C. Polanyi, *Discussions Faraday Soc.* **44**, 183 (1967). See also, K. G. Anlauf, D. S. Horne, R. G. Macdonald, J. C. Polanyi, and K. B. Woodall, *J. Chem. Phys.* **57**, 1561 (1972).

⁴⁰ G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950), Vol. I, 2nd ed.

⁴¹ This is evident from Fig. 1 of W. H. Wong, *Can. J. Chem.* **50**, 633 (1972).

⁴² The points in Figs. 1–4 which are enclosed in brackets are less reliable because of two sources of errors. In the small f_v region the uncertainty is primarily experimental, due to the low values of $P(f_v|E)$. In the range where $f_v \rightarrow 1$, the uncertainty is due to a combination of factors. The small spread in E is particularly important in this regime as are any approximations made in the level scheme of the diatom, which are reflected in $P^0(f_v|E)$. Due to the considerable margin for error in both $P^0(f_v|E)$ and $P(f_v|E)$ as $f_v \rightarrow 1$, $\omega(f_v|E)$ is rather sensitive at high f_v . These considerations are less important for $\Delta S[f_v]$ since the contribution of $\log \omega(f_v|E)$ is weighted by $P(f_v|E)$ which is small for $f_v \rightarrow 1$.

- ⁴³ J. C. Polanyi and K. B. Woodall, *J. Chem. Phys.* **56**, 1563 (1972).
- ⁴⁴ R. A. Marcus, *J. Chem. Phys.* **53**, 604 (1970), and references therein.
- ⁴⁵ J. C. Light, *Discussions Faraday Soc.* **44**, 14 (1967).
- ⁴⁶ E. E. Nikitin, *Theoret. Exptl. Chem.* **1**, 83, 90 (1965).
- ⁴⁷ G. L. Hofacker and R. D. Levine, *Chem. Phys. Letters* **15**, 165 (1972).
- ⁴⁸ R. D. Levine, *Chem. Phys. Letters* **10**, 510 (1971).
- ⁴⁹ J. H. Birely and D. R. Herschbach, *J. Chem. Phys.* **44**, 1690 (1966).
- ⁵⁰ R. R. Herm and D. R. Herschbach, *J. Chem. Phys.* **43**, 2139 (1965); S. M. Freund, G. A. Fisk, D. R. Herschbach, and W. Klemperer, *ibid.* **54**, 2519 (1971).
- ⁵¹ H. G. Bennewitz, R. Haerten, and G. Müller, *Chem. Phys. Letters* **12**, 335 (1971).
- ⁵² R. Grice, J. E. Mosch, S. A. Safron, and J. P. Toennies, *J. Chem. Phys.* **53**, 3376 (1970).
- ⁵³ K. G. Anlauf, D. S. Horne, R. G. MacDonald, J. C. Polanyi, and K. B. Woodall, *J. Chem. Phys.* **57**, 1561 (1972).
- ⁵⁴ The fact that the $\omega(f_v|E)$ computed from experimental results appears to be too low at high f_v (or low f_T) suggests that our $P^0(f_v|E)$ is too high. In other words, at high f_v values we have counted final states that are "not possible" when conservation of total angular momentum is imposed. We should also note that McDonald *et al.*⁹ have drawn attention to the similarity of the $H+X_2$ translational energy distributions and the photodissociation spectra of the X_2 molecules, expected for a repulsive energy release. It is indeed possible that a different functionality would be more appropriate on a repulsive surface.
- ⁵⁵ Note that for a system coupled to a large heat bath (so that $f_T \ll 1$), (59) reduces to the usual rule $E_T^{m,v} = 1/2\beta$.
- ⁵⁶ J. L. Magee and W. H. Hamill, *J. Chem. Phys.* **31**, 1380 (1959).
- ⁵⁷ Explicitly, in the RRHO approximation, $\rho_v(f_v) = (\hbar\omega)^{-1}$, $\rho_R(f_R) = (Bhc)^{-1}$, and $\rho_T(f_T) = A_T f_T^{1/2}$ (cf. Appendix).
- ⁵⁸ The heat bath is the rest of the system, i.e., all other modes apart from the mode X . The fraction of energy in the heat bath is $1 - f_X$.
- ⁵⁹ A. I. Khinchin, *Mathematical Foundations of Statistical Mechanics* (Dover, New York, 1949).
- ⁶⁰ L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, Oxford, 1969).
- ⁶¹ R. Jancel, *Foundations of Classical and Quantum Statistical Mechanics* (Pergamon, Oxford, 1969).
- ⁶² See, for example, R. H. Fowler, *Statistical Mechanics* (University Press, Cambridge, 1936). For the general case see also Refs. 56, 59, and 60 and also L. Landau, *Physik Z. Sowjet Union* **11**, 556 (1937) and V. F. Weisskopf, *Phys. Rev.* **52**, 295 (1937).
- ⁶³ There is preliminary computational evidence that for reactants where most of the energy is in the internal modes, λ_X may depend on E_X . We are indebted to Dr. C. Rebeck and Dr. S. F. Wu for this observation. Another example of an apparently deviant functionality is the "Gaussian" translational recoil spectra found for the KI formed in the $K+CH_3I$ reaction [A. M. Rulis, Ph.D. thesis, University of Wisconsin, 1972; Report WIS-TCI-476X]. In this case, however, the products ($KI+CH_3$) are not an atom plus diatom, and it might be wrong to force fit the results with the present (Appendix) expressions for P^0 .
- ⁶⁴ See, for example, D. R. Herschbach, *Molecular Beams and Reaction Kinetics*, edited by Ch. Schlier (Academic, New York, 1970), p. 76 and references therein; R. K. B. Helbing, *J. Chem. Phys.* **48**, 472 (1968); T. T. Warnock and R. B. Bernstein, *ibid.* **49**, 1978 (1968); **51**, 4682 (1969).
- ⁶⁵ The uncoupled distribution (83) was first introduced by T. T. Warnock, R. B. Bernstein, and A. E. Grosser, *J. Chem. Phys.* **46**, 1685 (1967) and later used⁷ as the leading term in a general expansion in E and θ . For many reactions (83) is remarkably good.
- ⁶⁶ The experimental⁷ recoil energy distribution was approximated as
- $$P(E_T|E) \propto f_T^{1/2} \exp(-\gamma f_T) \sum_{i=0}^4 a_i P_i(2f_T^{1/2}-1),$$
- where P_i are the Legendre polynomials, $\gamma = 11.8164$ and $a_0 = 2.577$, $a_1 = 4.193$, $a_2 = 3.111$, $a_3 = 0.7748$, $a_4 = -0.2906$, at $E = 44.5$ kcal/mole.
- ⁶⁷ A simple transformation of the results yields
- $$P(f_T) \propto (f_T/f_T^*)^{(n_i-1)/2} \exp\{(n_i/m_i)[1 - (f_T/f_T^*)^{(m_i/2)}]\},$$
- where $i=1$ or 2 for $f_T < f_T^*$ and $f_T > f_T^*$ respectively and f_T^* is the value of E_T/E corresponding to the most probable speed. n and m are constants. Also
- $$P(\Omega) = C_i + (1 - C_i) \exp[-\ln 2(\theta - \theta_i)^2/H_i^2]$$
- $$= 1, \quad \theta_1 < \theta < \theta_2,$$
- where $i=1$ or 2 for $\theta < \theta_1$ and $\theta > \theta_2$ respectively.
- ⁶⁸ For a review on ion-molecule work, see A. Henglein, *Molecular Beams and Reaction Kinetics*, edited by Ch. Schlier (Academic, New York, 1970), p. 139.
- ⁶⁹ M. Chiang, E. A. Gislason, B. H. Mahan, C. W. Tsao, and A. S. Werner, *J. Chem. Phys.* **52**, 2698 (1970).
- ⁷⁰ N. Jonathan, C. M. Melliar-Smith, and D. H. Slater, *J. Chem. Phys.* **53**, 4396 (1970); *Mol. Phys.* **20**, 93 (1971).
- ⁷¹ M. C. Lin and W. H. Green, *J. Chem. Phys.* **53**, 3383 (1970).
- ⁷² K. T. Gillen, C. Riley, and R. B. Bernstein, *J. Chem. Phys.* **50**, 4019 (1969).
- ⁷³ W. B. Miller, S. A. Safron, and D. R. Herschbach, *J. Chem. Phys.* **56**, 3581 (1972).
- ⁷⁴ J. B. Cross and N. C. Blais, *J. Chem. Phys.* **55**, 3970 (1971).
- ⁷⁵ M. J. Berry and G. C. Pimentel, *J. Chem. Phys.* **53**, 3453 (1970).
- ⁷⁶ H. W. Chang, D. W. Setser, M. J. Perona, and R. L. Johnson, *Chem. Phys. Letters* **9**, 587 (1971).
- ⁷⁷ G. Hancock and I. W. M. Smith, *Chem. Phys. Letters* **3**, 573 (1969).
- ⁷⁸ W. Brenner and T. Carrington, *J. Chem. Phys.* **46**, 7 (1967).
- ⁷⁹ J. M. Parson and Y. T. Lee, *J. Chem. Phys.* **56**, 4658 (1972).
- ⁸⁰ A. Lee, R. L. LeRoy, Z. Herman, R. Wolfgang, and J. C. Tully, *Chem. Phys. Letters* **12**, 569 (1972).
- ⁸¹ B. S. Rabinovitch and D. W. Setser, *Advan. Photochem.* **3**, 1 (1964).
- ⁸² R. J. Campbell and E. W. Schlag, *J. Phys. Chem.* **89**, 5103 (1967).
- ⁸³ T. F. Thomas, C. I. Sutin, and C. Steel, *J. Phys. Chem.* **89**, 5107 (1967).
- ⁸⁴ R. C. Mitchel and J. P. Simons, *Discussions Faraday Soc.* **44**, 208 (1967).
- ⁸⁵ K. E. Holdy, L. C. Klotz, and K. R. Wilson, *J. Chem. Phys.* **52**, 4588 (1970).
- ⁸⁶ G. Karl, P. Kruus, and J. C. Polanyi, *J. Chem. Phys.* **46**, 224 (1967).
- ⁸⁷ A. Mele and H. Okabe, *J. Chem. Phys.* **51**, 4789 (1969).
- ⁸⁸ R. D. Levine and R. B. Bernstein, *Chem. Phys. Letters* **15**, 1 (1972).
- ⁸⁹ J. L. Franklin and M. A. Haney, *J. Phys. Chem.* **73**, 2857 (1969).
- ⁹⁰ R. L. LeRoy, *J. Chem. Phys.* **53**, 846 (1970).
- ⁹¹ W. W. Robertson, *J. Chem. Phys.* **44**, 2456 (1966); H. Hotop and A. Niehaus, *Z. Physik* **238**, 452 (1970).
- ⁹² D. H. Stedman and D. W. Setser, *Progr. Reaction Kinetics* **6**, 193 (1971).
- ⁹³ R. A. Marcus, *J. Chem. Phys.* **43**, 1598 (1965); **20**, 355 (1952).
- ⁹⁴ This is the density of translational states, per volume. This is as it should be in order that the entropy include the volume term, $R \log V$. This term cancels, of course, when one considers the entropy deficiency.
- ⁹⁵ D. R. Herschbach, *Discussions Faraday Soc.* **33**, 157 (1962).
- ⁹⁶ We distinguish between the RRHO level scheme, where the levels are given by the rigid-rotor [$E_R = J(J+1)Bhc$] harmonic oscillator [$E_v = (v + \frac{1}{2})\hbar\omega$] energies but are treated as discrete, quantized levels and the RRHO approximation, which not only uses the RRHO level scheme but also considers E_R and E_v to be continuous, classical variables. In obtaining $P^0(f_T|E)$ we have used the RRHO approximation, but this is not recommended when vibrational spacings are large; then one should treat only the rotational energy as continuous, keeping vibrations discrete. In this case, $P^0(f_T|E) \propto \sum_{v=0}^{\infty} v^* f_T^{1/2}$, with $f_v + f_T \leq 1$.