

## THE ROLE OF REAGENT INTERNAL EXCITATION IN COLLISION EXPERIMENTS \*

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Variations in the rates of endoergic reactions due to different reagent excitations at the same total energy are of a limited (positive or negative) range and reflect a dynamical bias. Not so for bulk experiments, where all non-selected degrees of freedom have a thermal distribution.

### 1. Introduction

The role of reagent internal state in chemical reactions can be probed under two distinct types of conditions: (a) single-collision experiments where not only the internal state but also the relative translational energy can be controlled [1–5], and (b) bulk, macroscopic systems where typically all non-selected degrees of freedom have a thermal distribution [6–8]. The purpose of this letter is to contrast the results expected from these two types of experiments with special reference to endoergic reactions where experiments of type (b) will almost invariably lead to more dramatic enhancements of the reaction rate. It may indeed even be the case that at a given total energy, increasing the internal energy will decrease the reaction rate while the same change will significantly enhance the rate in an otherwise thermal experiment.

The different effects of reagent excitation in bulk and single collision experiments reflect two different aspects of the role of energy in chemical reactions. Changing the internal energy at a given total energy alters the dynamics of the collision. Such a change takes the collision through an entirely different region in phase space or, in a more classical language, corresponds to an entirely different set of reactive trajectories. On the other hand, the major effect of changing reagent internal excitation in an otherwise thermal experiment is, in the endothermic regime, to increase the fraction of mole-

cules with energy in excess of the barrier [9–11]. There are, to be sure, dynamical effects also in bulk selection experiments, but the larger role is played by the purely thermochemical effect: In the reaction



regard AB molecules of different internal levels as distinct chemical species [11]. The endoergicity of the reaction from the ground state is  $\Delta E_0$ . The endothermicity for the reaction of AB( $n$ ) is  $\Delta E_0 - E_n$ . Increasing  $E_n$  is thus equivalent to a corresponding decrease in the endothermicity of the reaction.

Experimental results are more readily available on energy disposal in exoergic reactions, e.g. corresponding to (1)



Using detailed balance one can compare the dynamic bias of the forward and reverse reactions and show them to be the same [10–13].

### 2. Detailed balance for single-collision experiments

Consider the state-to-state diatom-atom endoergic reaction



at the total energy  $E$ . Here  $n$  and  $n'$  are labels of either single quantum states or of a group of degenerate states of AB and BC (e.g. the  $g_J = 2J + 1$  quantum states of a

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given  $v, J$  vibrational level). Microscopic reversibility implies that [12–14]

$$g_n \rho_T(E - E_n) k(n \rightarrow n'; E) = g_{n'} \rho_T'(E - \Delta E_0 - E_{n'}) k(n' \rightarrow n, E). \quad (4)$$

Here  $g_n$  is the degeneracy and  $\rho_T(E_T)$  is the density of translational states,  $\rho_T(E_T) = A_T E_T^{1/2}$  [9–13] at the translational energy  $E_T$ . The total energy  $E$  is measured in (4) from the ground state of AB + C. The energy of the ground state of A + BC then equals  $\Delta E_0$ , the endoergicity.

Summing both sides of (4) over  $n'$  leads to the detailed balance relation for reaction (1)

$$z_n \rho_T(E - E_n) k(n \rightarrow ; E) = \rho'(E) k(\rightarrow n, E), \quad (5)$$

where

$$k(\rightarrow n; E) = \sum_{n'} P^0(n'|E) k(n' \rightarrow n; E), \quad (6)$$

$$P^0(n'|E) = g_{n'} \rho_T(E - \Delta E_0 - E_{n'}) / \rho'(E), \quad (7)$$

$$\rho'(E) = \sum_{n'} g_{n'} \rho_T(E - \Delta E_0 - E_{n'}). \quad (8)$$

$k(\rightarrow n, E)$  is the rate constant for the exoergic reaction (2) at the total energy  $E$ . The definition (6) of  $k(\rightarrow n, E)$  in terms of the state-to-state rates  $k(n' \rightarrow n, E)$  is that implied by the canon ("average over initial states").  $P^0(n|E)$  as defined by (7) and (8) is the prior distribution and

$$k(n \rightarrow ; E) = \sum_{n'} k(n \rightarrow n'; E), \quad (9)$$

is the rate constant for the endoergic reaction (1), where the internal energy of AB is  $E_n$  and the relative translational energy of AB( $n$ ) and C is  $E_T = E - E_n$ . The definition (9) follows the canon ("sum over final states"), and is valid whatever the energy distribution in the products A + BC of (2) (except that their total energy is  $E$ ).

The final form of (5) requires one more stage: Summing (4) over both  $n$  and  $n'$

$$\rho(E) k(E) = \rho'(E) k'(E). \quad (10)$$

Here the two rate constants refer to the forward reaction (3) and the reverse reaction



at the total energy  $E$ ,

$$k'(E) = \sum_n k(\rightarrow n; E), \quad (12)$$

$$k(E) = \sum_n P^0(n|E) k(n \rightarrow ; E), \quad (13)$$

$$P^0(n|E) = g_n \rho_T(E - E_n) / \rho(E), \quad (14)$$

$$\rho(E) = \sum_n g_n \rho_T(E - E_n). \quad (15)$$

Using (5), (10), (14) and (15) we obtain the rate constant from AB( $n$ ) at a total energy  $E$  [12,15]

$$k(n \rightarrow ; E) = \rho'(E) k(\rightarrow n; E) / g_n \rho_T(E - E_n) = k(E) P(n|E) / P^0(n|E) \equiv k(E) \exp[-I(n|E)]. \quad (16)$$

Here  $P(n|E)$  is the product state distribution in the exoergic A + BC reaction (2) at the total energy  $E$ .

$$P(n|E) = k(\rightarrow n; E) / k'(E). \quad (17)$$

$P^0(n|E)$  as defined in (14) is the "prior" distribution [13,16] of the product states in the same reaction, and  $I(n|E)$  is the surprisal.

The physical interpretation of (16) is immediate. Any dependence of  $k(n \rightarrow ; E)$ , the rate constant of the AB( $n$ ) + C reaction, on the internal state of AB implies a dynamical bias in the energy disposal of the reversed A + BC reaction and vice versa [11–13]. Hence, on prior grounds, i.e. in the absence of any dynamical bias,  $I(n|E) = 0$ , all AB + C collisions with the same total energy have the same rate, irrespective of the partitioning of the energy between internal and translational degrees of freedom [9].

We would like to emphasize that the result (16) is completely consistent with the conservation of angular momentum. Even such reactions where large changes in the reduced mass take place (e.g. Sr + HF  $\rightarrow$  SrF + H [1], or K + HCl  $\rightarrow$  KCl + H [2]) must still satisfy (16) with  $P^0$  defined as in (14).

### 3. Lower-resolution collision experiments

Much of our knowledge about the role of internal energy in endoergic reactions derives, via detailed balance, from measurements of product state distributions in the reversed, exoergic, processes. In many such experiments the resolution of product internal states is limited to manifolds of states  $\alpha$ . The most obvious cases\* being vibrational levels,  $\alpha = v$ , and translational energy shells,  $(E_T, E_T + \Delta E_T)$  [12,16]. At a given total energy  $E$ , the detailed balance relation for the forward (endoergic) and reverse (exoergic) processes,



is obtained by summing both sides of (5) over the states  $n$  within the group  $\alpha$ ,

$$\rho(\alpha; E)k(\alpha \rightarrow; E) = \rho'(E)k(\rightarrow \alpha; E). \quad (19)$$

Here

$$\rho(\alpha; E) = \sum_n' g_n \rho_T(E - E_n), \quad (20)$$

$$k(\alpha \rightarrow; E) = \sum_n' P^0(n|\alpha)k(n \rightarrow; E), \quad (21)$$

$$P^0(n|\alpha) = g_n \rho_T(E - E_n) / \rho(\alpha; E), \quad (22)$$

$$k(\rightarrow \alpha; E) = \sum_n' k(\rightarrow n; E), \quad (23)$$

where the prime over the summation signifies the restriction to states  $n$  in the group  $\alpha$ . Using (19) and (10) we obtain, in analogy to (16)

$$\begin{aligned} k(\alpha \rightarrow; E) &= k(E)P(\alpha|E)/P^0(\alpha|E) \\ &\equiv k(E) \exp[-I(\alpha|E)], \end{aligned} \quad (24)$$

where

$$P(\alpha|E) = k(\rightarrow \alpha; E) / k'(E), \quad (25)$$

$$P^0(\alpha|E) = \rho(\alpha; E) / \rho(E) \quad (26)$$

\* At a given  $E$  specifying  $v$  corresponds to many translational-rotational states with joint energy  $E_T + E_J = E - E_v$ . Similarly, there are usually many  $v, J$  states within the energy interval  $E - (E_T + \Delta E_T) \leq E_{v,J} \leq E - E_T$ .

are the products " $\alpha$ " distribution in the reverse reaction and the prior distribution, respectively. The relative rate  $k(\alpha \rightarrow; E)/k(E)$ , like  $k(n \rightarrow; E)/k(E)$  cf. (16), depends on any reagent state preparation only if there is a dynamical bias, i.e. if the surprisal  $I(\alpha|E) \neq 0$ .

### 4. Example

The efficacy of different partitions of a given total energy between the different degrees of freedom of the reagents is determined by the surprisal. Enhancement occurs for such initial states whose surprisal is negative while a rate below the average corresponds to initial states of positive surprisal ‡. For endoergic reactions the magnitude of the surprisal can be determined from experimental (or computational) studies of energy disposal in the reversed, exoergic, reactions. The available results of such studies are that the surprisal is seldom larger than a couple of units. Hence the typical dynamical bias provided by nature suffices for at most about two orders of magnitude of variation in the relative rates (at a given total energy).

To emphasize the limited, albeit respectable range of reaction rates possible for different partitions of a given energy we consider the endoergic reaction



The surprisal for the reversed reaction is well characterized [17–21] for thermal reactants. Due to the considerable exoergicity, the spread in the total energy in the products of the  $F + H_2 \rightarrow H + HF$  reaction is small. Hence, to a good approximation the surprisal for  $H + HF$  is known at a given total energy ( $\approx \Delta E_0 + \frac{5}{2}RT + E_a$ , where  $E_a$ , the activation energy is about 1 kcal/mole [22]).

Three choices of  $\alpha$  will be considered:

(i)  $\alpha = v$ . The vibrational surprisal for  $E_v \leq \Delta E_0$  is quite linear

$$I(v|E) \equiv -\ln[P(v|E)/P^0(v|E)] = \lambda_0 + \lambda_v f_v, \quad (28)$$

where  $f_v = E_v/E$  and  $\lambda_v$  is a slowly decreasing function

‡ By the canon,  $k(E)$  is the average rate constant, hence, unless all states react with the same rate, there must be states which react with a smaller than average rate. In other words, if some partitioning of the total energy enhances the rate then, necessarily, some other partitioning decreases the rate.

of  $E$  [20]. From (24) and (28) follows

$$k(v \rightarrow; E)/k(v-1 \rightarrow; E) = \exp(-\lambda_v \Delta f_v), \quad (29)$$

where  $\Delta f_v = f_v - f_{v-1} \approx 0.3$  for the  $\text{H} + \text{HF}(v)$  reaction at  $E$  just above  $\Delta E_0$ , and  $\lambda_v \approx -6.9$  [17-20]. At a given energy the enhancement of the rate by increasing HF internal excitation by a vibrational quantum ( $\approx 11$  kcal/mole) is less than an order of magnitude. By comparison, at 300 K, increasing the HF excitation by a vibrational quantum changes the rate by a factor of  $\approx 10^9$  [10].

Similar conclusions obtain for the role of reagent vibration in other endoergic reactions. The recent report [1] that in the endoergic ( $\Delta E_0 \approx 6$  kcal/mole)  $\text{Sr} + \text{HF} \rightarrow \text{SrF} + \text{H}$  reaction at  $E \approx 13$  kcal/mole, excitation of HF from  $v=0$  to  $v=1$  changed the rate by a factor of 1-10 is therefore consistent with our general expectations. The low enhancement factor is not necessarily indicative of the absence of a dynamical bias. Strict absence of bias requires that the ratio be unchanged and only a strong bias would provide a factor of ten.

(ii)  $\alpha = v, J$  The vibrotational surprisal for  $\text{F} + \text{H}_2$  is well represented by

$$I(v, J|E) = \lambda_v f_v + \theta_R f_R / (1 - f_v) + \lambda_0. \quad (30)$$

Here  $f_R = E_R/E$  is the fraction of the total energy in rotation. For  $\text{F} + \text{H}_2$   $\theta_R \approx 1.75$  corresponding to  $\hat{g}_R = 0.21$  where  $\hat{g}_R$  is the most probable value of  $g_R =$

$f_R/(1 - f_v)$  [21]. The relative rates

$$k(v, J \rightarrow; E)/k(E) = \exp(-\lambda_v f_v - \theta_R f_R - \lambda_0), \quad (31)$$

are shown as a contour plot in fig. 1. The peak is in the vicinity of the  $f_v \rightarrow 1$  apex and the contours decrease by a factor of 2. We are aware that the qualitative shape of our contours differs from what others could have expected. Fig. 1 also shows the more familiar disposal plot of  $P(v, J|E)$ .

(iii)  $\alpha = J$  at constant  $v$  The effect of pure rotational excitation is reflected by the ratio

$$k(v, J \rightarrow; E)/k(v, J-1 \rightarrow; E) = \exp[-\theta_R \Delta f_R / (1 - f_v)]. \quad (32)$$

Since typically  $\theta_R \geq 0$ , rotational excitation will usually decrease the reaction rate. The decline of the rate with increasing rotational state of HF is quite evident in fig. 1. A qualitatively similar decline has recently been reported for the  $\text{K} + \text{HCl}(v=1, J) \rightarrow \text{KCl} + \text{H}$  collision experiments [2].

Exceptions to the unfavourable role of reagent rotation in collision experiments are possible for such rare cases that  $\theta_R < 0$ . Examples are provided by reactions of  $\text{OH}(v, J)$  [23,24], e.g.

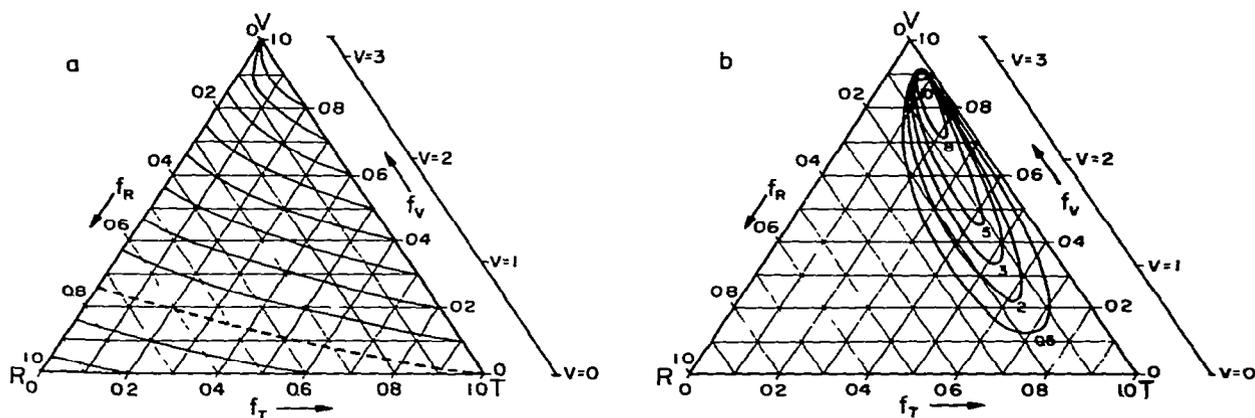
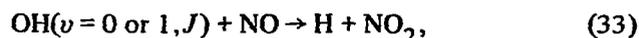
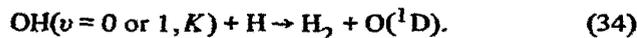


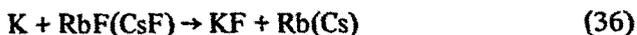
Fig. 1. (a) Contour plot of  $k(v, J \rightarrow; E)/k(E)$  for the  $\text{H} + \text{HF}(v, J)$  reaction at  $E \approx 34$  kcal/mole. Contours shown are connecting different partitionings of the total energy  $E$  which have the same reaction rate according to (31).  $\lambda_v = -6.9$ ,  $\theta_R = 1.75$ . The highest contour is in the uppermost  $f_v \rightarrow 1$  apex and successive contours correspond to a decline of the rate by a factor of 2. The dashed contour is the one of zero surprisal. Partitions of the total energy which are in the region above it enhance the rate, while those which are below correspond to a rate below average. (b) Contour plot of the product  $P(v, J|E)$  distribution in the  $\text{F} + \text{H}_2$  reaction. Note that the two plots are related by the detailed balance equation (24).



Contour plots showing the effects of changing reagent internal (or, equivalently, translational) excitation at a given  $E$  are available for the reaction [12]



and similarly for [25]



### 5. Thermal experiment

The detailed balance relation analogous to (16) for the case where non-selected degrees of freedom have a thermal distribution is [10,11]

$$k(\alpha \rightarrow; T) = k(T)P(\alpha|T)/p(\alpha|T) \quad (37)$$

$P(\alpha|T)$  is the distribution of  $\text{AB}(\alpha)$  molecules in the thermal  $\text{A} + \text{BC}$  reaction.  $p(\alpha|T)$  is the Boltzmann fraction of  $\text{AB}(\alpha)$  molecules at the temperature  $T$ . For a very endoergic reaction, the reversed reaction is very exoergic and hence  $P(\alpha|T) \approx P(\alpha|E)$  at  $E \approx \Delta E_0 + E_\alpha + \frac{5}{2}RT$ . The essential differences between single-collision experiments (24) and bulk experiments (37) is thus in the statistical factors  $P^0(\alpha|E)$  versus  $p(\alpha|T)$ . For exoergic reactions and when  $E_\alpha \leq \Delta E_0$ ,  $P^0(\alpha|E)$  is only a moderately varying function of  $\alpha$  versus the strong dependence of  $p(\alpha|T)$  on  $E_\alpha$  at lower temperatures. As the bulk temperature is increased, the differences between the two types of experiments will diminish.

In the Tolman interpretation [26], the activation energy is the difference between the mean energy of those molecules that react and the mean energy of all molecules. From (37) it follows that

$$E_a(\alpha) \equiv -RT^2 \partial \ln k(\alpha \rightarrow; T) / \partial T \\ = E_a - E_\alpha - RT^2 \partial \ln P(\alpha|T) / \partial T. \quad (38)$$

Here  $E_a$  is the activation energy of the purely thermal reaction, and

$$-E_\alpha \equiv RT^2 \partial \ln p(\alpha|T) / \partial T$$

is the change in energy of all molecules due to selective population of  $\text{AB}(\alpha)$ , while

$$\Delta E_a^\ddagger(\alpha) = -RT^2 \partial \ln P(\alpha|T) / \partial T \quad (39)$$

is the change in the mean energy of those molecules that react. The empirical finding [9] that  $\Delta E_a^\ddagger(\alpha)$  is smaller than  $E_\alpha$  or roughly for  $\alpha = v$ ,

$$\Delta E_a^\ddagger(v) \approx \lambda_v(RT/E)E_v, \quad (40)$$

where  $-\lambda_v(RT/E)$  is typically below 0.25 implies that the primary (>75%) cause for the enhancement of the bulk rate is the increase in the mean energy of all molecules, while the reduction in the mean energy of those molecules that react is a secondary (<25%) effect.

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