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PRODUCT STATE DISTRIBUTION IN EXOERGIC CHEMICAL REACTIONS AND THE CONCEPT OF TEMPERATURE[†]

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The product state distribution in exoergic chemical reactions with respect to any one degree of freedom (*translation, rotation or vibration*) can be characterized by a temperature. The detailed experiments on the reactions of $K + I_2$, $Cl + HI(DI)$ and $F + H_2(D_2)$ are used as examples. For the latter two systems the products have well-defined (negative) vibrational temperatures, essentially isotopically-invariant.

1. Introduction

Detailed experimental results on the distribution of product energy states resulting from reactive molecular collisions are rapidly becoming available from chemiluminescence [1–3], molecular beams [4–8] and chemical lasers [9] studies. The optimal means of characterizing the distribution of products has recently been considered [10,11], and the concept of information content of such a distribution has been put on a quantitative basis [11]. In the course of a detailed study of the application of these concepts to specific systems [12] it has become clear that a very useful parameter is the apparent temperature of the product distribution in any one particular mode (translational, vibrational or rotational). The aim of the present note is to outline the way in which the concept of a "temperature" can be introduced, with particular stress on distributions which are far removed from statistical equilibrium. In particular, it will become evident that the concept is useful even in the extreme case of population-inverting reactions. The three types of reactions chosen here as illustration are

(a) the translational energy distribution for [4]

$$K + I_2 \rightarrow KI + I \; ; \qquad (1)$$

(b) the vibrational state distribution for [2]

$$Cl + HI \rightarrow I + HCl \, ,$$

$$Cl + DI \rightarrow I + DCl \qquad (2)$$

and (c) the vibrational state distribution for [3]

$$F + H_2 \rightarrow H + HF \, ,$$

$$F + D_2 \rightarrow D + DF \, . \qquad (3)$$

Several other systems, including rotational state distributions, have been examined. The only exception to the simplicity of the description afforded by the introduction of a temperature, which we found, is the reaction [13]

$$H + Cl_2 \rightarrow Cl + HCl \, . \qquad (4)$$

Even for this reaction, the results of classical trajectory calculations [14] are however in good accord with our suggested analysis.

The main features of the observed translational energy distributions have been reported for some time [15] as a fit to a distribution of a canonical type,

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$$d\sigma/dE_T \propto g(E_T)\exp(-\beta E_T)\,, \tag{5}$$

where E_T is the final relative translational energy and $g(E_T)$ is, approximately, the equilibrium density of translational states, $g(E_T) \propto E_T^{1/2}$. Also, when a long-living process is formed during the collision, it is natural to expect [8,16,17] that the energy will be equipartitioned between the different degrees of freedom (as in a stable molecule).

The points made in this paper are

(a) that for a *finite* system, at a constant total energy E, the definition of a temperature should be modified compared to the usual definition, appropriate for an *infinite* heat bath, and

(b) that the concept of temperature is useful for all degrees of freedom, even away from statistical equilibrium.

For the latter case (direct reactions), even though the equipartition of energy does not apply, one can still introduce a temperature for each degree of freedom. These temperatures all become equal at equilibrium.

2. Analysis of experimental results

The currently available distributions of product energy states are not absolute cross sections, but only the relative probabilities of the different final states, at a specified total energy E. In this note we examine the distributions in either translation (T) or vibration (v). The final product state is identified by the fraction, f_X, of the total energy in that mode,

$$f_X = E_X/E\,. \tag{6}$$

The relative probabilities of the products are normalized at each energy

$$\sum_v P(f_v) = 1 \tag{7}$$

and

$$\int df_T P(f_T) = 1\,, \tag{8}$$

where we have explicitly distinguished between the vibrational distribution (where E_v is discrete) and the translational distribution. The absolute cross sections are related to the relative distributions[†] by a factor that depends on the total energy only [i.e., the total reaction cross section, $\sigma_R(E)$]. Thus, for the translation

$$d\sigma_R/dE_T = \sigma_R(E)P(E_T) \tag{9}$$

and similarly for the vibration.

As was argued in detail elsewhere [11], it is convenient to characterize the product distributions by their information (i.e., entropy) content. In particular, we defined [11] the surprisal associated with the distribution of products in the mode X by

$$I(E_X|E) = -\ln[P(E_X)/P^0(E_X)]\,. \tag{10}$$

where $P^0(E_X)$ is the equilibrium (microcanonical) distribution, where all quantum states of the products have the same weight. It should be explicitly noted that $P^0(E_X)$ [like $P(E_X)$] is the relative (i.e., conditional) distribution at a given total energy. The appendix outlines the derivation of these $P^0(E_X)$ factors. The final results are:

(a) for the translation, assuming that the product diatomic molecule is a rigid rotor–harmonic oscillator

$$P^0(f_T) = \tfrac{15}{4} f_T^{1/2}(1-f_T)\,; \tag{11}$$

(b) for the vibration, assuming that the rotation can be described by a rigid rotor level scheme

$$P^0(f_v) = (1-f_v)^{3/2} \Big/ \sum_{v=0}^{v^*}(1-f_v)^{3/2}\,, \tag{12}$$

where $f_{v*} \leqslant 1$ (or $E_{v*} \leqslant E$).

It is important to note that (12) does not assume a harmonic oscillator level scheme.

We define the apparent temperature λ_X by the slope of $I(E_X|E)$ versus E_X. We find it convenient to work in reduced units and hence define

$$\lambda_X = -d\ln I(E_X|E)/df_X\,. \tag{13}$$

With this definition

$$\omega(f_X) = \exp(-\lambda_X f_X)\,, \tag{14}$$

or

$$\begin{aligned} P(E_X) &= P^0(E_X)\,\omega(f_X) = P^0(E_X)\exp(-\lambda_X f_X) \\ &= P^0(E_X)\exp(-E_X/kT_X)\,, \end{aligned} \tag{15}$$

[†] In the language of probability theory, $P(E_X)$ is the conditional probability, while $d\sigma/dE_X$ is proportional to the joint probability, $P(E_X,E)$. $P(E_X) \equiv P(E_X|E)$ and $P(E_X|E) = P(E_X,E)/P(E)$.

where

$$T_X = (E/k)/\lambda_X \, . \tag{16}$$

The total energy E appears explicitly in the definition of T_X since λ_X was defined in reduced units, (13). Of course, λ_X may well (and does [12]) depend on E, even though, as will be seen below, it does not depend on E_X.

The most probable final value of f_X is the solution of

$$\mathrm{d} \ln P^0(E_X)/\mathrm{d}f_X = \lambda_X \, . \tag{17}$$

On examining (11) and (12), we obtain

$$\lambda_T = (1-3f_T)/2f_T(1-f_T) \, , \tag{18}$$

so that $\lambda_T > 0$ when $f_T^{\mathrm{m.p.}} < \frac{1}{3}$ and $\lambda_v > 0$ only when the most probable final vibrational state is the $v = 0$ state. It should however be clear that $\lambda_X < 0$ does not imply that $f_X^{\mathrm{m.p.}} = 1$ since $P^0(E_X)$ is a strongly decreasing function of f_X for $f_X \to 1$ and hence counteracts the exponential factor.

Figs. 1–3 show the plots of $-I(E_X|E) = \ln \omega(f_X)$ versus f_X, for the reactions (1)–(3). It is clear that the temperature λ_X is essentially independent of E_X and that for the case of the isotopic variants of the same products, the reduced temperature is the same. It should also be noted that the chemiluminescence data are not at a sharply defined total energy E, but represent reactants in thermal equilibrium. However, due to the large exothermicity, the uncertainty in the total energy is small,

$$E = -\Delta H_0^0 + E_{\mathrm{reac.}} \tag{19}$$

Here $-\Delta H_0^0$ is the zero point to zero point exothermicity (i.e., $-\Delta H_0^0 = 31.7$ kcal mole^{-1} for Cl + HI) and $E_{\mathrm{reac.}}$ is the initial energy of the reactants.

The one exception to the constancy of λ_X are the results for λ_T of K + I_2 where two (rather than one) linear regimes are evident. We would like to argue that this should serve as a diagnostic of this reaction rather than as a defect of the concept of translational temperature. An examination of the experimental data, and in particular of $\mathrm{d}^3\sigma_R/\mathrm{d}^2\omega \mathrm{d}E_T$ (figs. 17 and 18 of ref. [4]) clearly indicates two mechanisms. A forward (stripping) component with a very low Q (and hence high λ_T) and a (somewhat smaller) backward (rebound?) component with a much higher Q (and hence a lower λ_T).

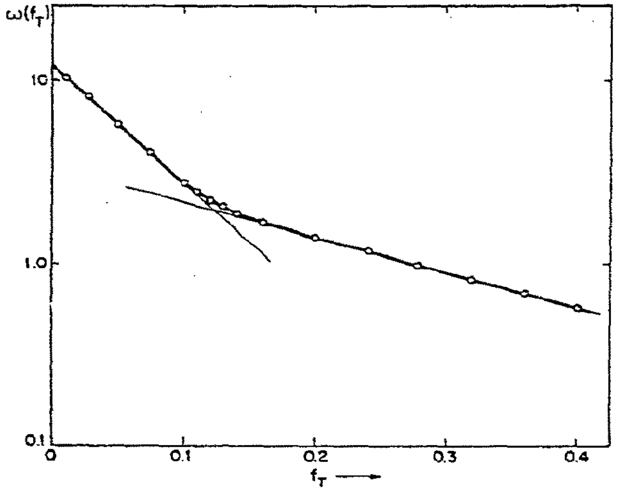

Fig. 1. The translational energy distribution in the reaction K + $I_2 \to$ KI + I. Shown is $\ln \omega(f_T)$ versus f_T using the results of Gillen et al. [4]. E = 44.5 kcal/mole and $P(f_T)$ was obtained by an analytical fit (using least squares) to the observed distribution. The two reduced temperatures are $\lambda_T \approx 14.8$ and $\lambda_T \approx 4.4$, or $T_T \approx 1500$°K and $T_T \approx 5000$°K.

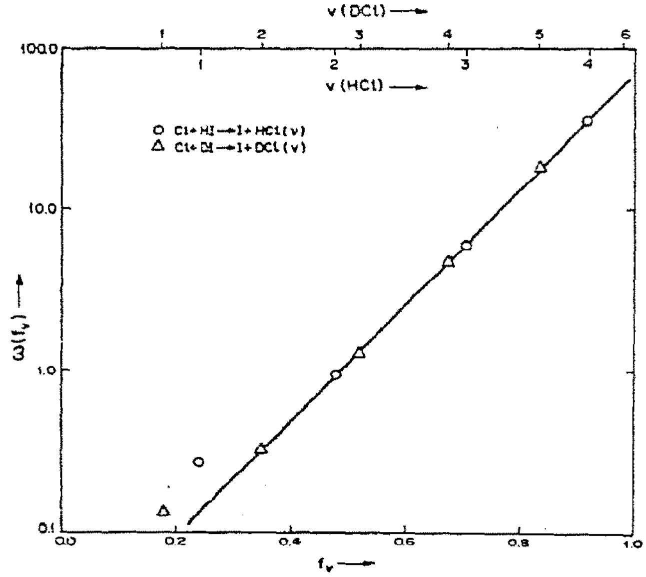

Fig. 2. Vibrational state distribution in the reactions Cl + HI → I + HCl and Cl + DI → I + DCl. Shown is $\ln \omega(f_v)$ versus f_v using the results of Maylotte et al. [2] at E = 34 kcal/mole. For both reactions $\lambda_v \approx -8.3$, or $T_v \approx -2050$°K.

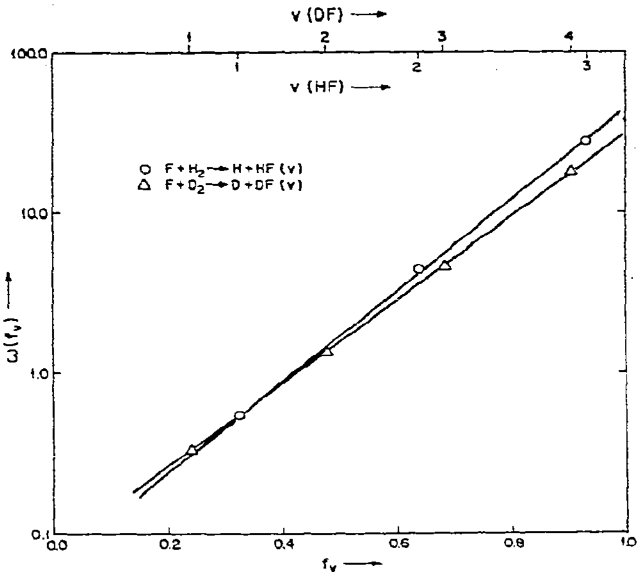

Fig. 3. Vibrational state distribution in the reactions $F + H_2 \rightarrow H + HF$ and $F + D_2 \rightarrow D + DF$. Shown is $\ln \omega(f_v)$ versus f_v, using the results of Polanyi and Woodall [3] at $E(HF) = 34.7$ kcal/mole and $E(DF) = 34.4$ kcal/mole. $\lambda_v(HF) \approx -6.5$, $\lambda_v(DF) \approx -6.0$, or $T_v(HF) \approx -2700°K$, $T_v(DF) \approx -2850°K$.

3. Discussion

The concept of temperature introduced in this note provides a convenient measure of the deviation of the products energy state distribution from the distribution predicted on the basis of a simple statistical theory. In the statistical limit, $\omega(f_X) = 1$ or $P(E_X) = P^0(E_X)$ and so $\lambda_X = 0$ for all three modes and the available energy is equipartitioned[†].

The identification of λ_X as an (inverse) temperature is based on its definition as the energy derivative of the information (i.e., the entropy [11]), as is the definition appropriate for non-equilibrium situation in a finite system. The usual definition [17,18] applies only to a small system in equilibrium with an (infinite) heat bath, at a given total energy. Here one defines

$$\beta_X = -\mathrm{d} \ln[P^0(E_X)/\rho_X(E_X)] / \mathrm{d}E_X \, , \qquad (20)$$

where $\rho_X(E_X)$ is the density of states of the subsystem. If the heat bath is indeed very large, β_X is independent of E_X [17,18]. Thus, if we write

$$-\mathrm{d} \ln[P(E_X)/\rho_X(E_X)] / \mathrm{d}E_X = \beta_X - \lambda_X/E \, , \qquad (21)$$

we see that (21) can be used to define temperature only when the remainder of the system (i.e., the number of the other degrees of freedom) is large, so that β_X is E_X-independent.

An extensive report on the characterization of product state distributions by their information content and their temperature, is in preparation [12]. A companion paper [20] considers the possible dynamic origins of the non-equilibrium features manifested by λ_v being non-zero.

4. Summary

The representation of the distribution of product energy states in the form $P(E_X) = P^0(E_X) \exp(-E_X/kT_X)$ has been considered and illustrated by the experimental results for different reactions. Here $P^0(E_X)$ is the equilibrium (microcanonical) distribution, at a total energy E, where all final states are equiprobable. At statistical equilibrium $P(E_X) = P^0(E_X)$ and the available energy is equipartitioned among the different modes.

Appendix

We derive the (conditional) density of states for E_X at a given total energy.

(a) *Vibration.* The joint density of states $\rho(v,E)$ is defined so that $\rho(v,E)\mathrm{d}E$ is the number of states of an atom–diatom system with a total energy in the interval E to $E + \mathrm{d}E$ and a vibrational quantum number v. Thus [10]

$$\rho(v,E) = \sum_{j=0}^{j^*} (2j+1)\, \rho_T(E - E_v - B_v j(j+1)) . \qquad (A.1)$$

Here $\rho_T(E)$ is the translational density of states and B_v is the rotational constant for the vibrational level v. In practice we found that using a common B_0, appropriate for a Morse oscillator is sufficient for our

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[†] In the statistical limit, $\langle f_T \rangle = 3/7$, $\langle f_v \rangle = 2/7$ and $\langle f_R \rangle = 2/7$ where the angular brackets denote an average over the distribution $P^0(f_X)$.

analysis. j^* (which is a function of v) is the maximal value of j,

$$B_v(j^*+1)(j^*+2) \geqslant E - E_v \geqslant B_v j^*(j^*+1) . \qquad \text{(A.2)}$$

It should be realized that (A.1) does take into account the conservation of the total energy but disregards the conservation of the total angular momentum. For certain reactions (involving a large change in the reduced mass) the failure to conserve the total angular momentum is an unwarranted approximation. (This approximation may account for our failure with reaction (4).)

The conditional density $\rho(v|E) \equiv P^0(E_v)$ is given by

$$\rho(v|E) = \rho(v,E)/\rho(E) , \qquad \text{(A.3)}$$

where

$$\rho(E) = \sum_{v=0}^{v^*} \rho(v,E) . \qquad \text{(A.4)}$$

Using the known results

$$\rho_\mathrm{T}(E_\mathrm{T}) = A_\mathrm{T} E_\mathrm{T}^{1/2} , \qquad \text{(A.5)}$$

where $A_\mathrm{T} = \mu^{3/2}/2^{1/2}\pi^2\hbar^2$ and replacing the summation over j in (A.1) by an integration over $E_j = Bj(j+1)$, we obtain eq. (12) of the text.

(b) *Translation.* Here the joint density of states is defined so that $\rho(E_\mathrm{T},E)\mathrm{d}E_\mathrm{T}\mathrm{d}E$ is the number of states when the total energy is in the interval E to $E + \mathrm{d}E$ and the translational energy is in the interval E_T to $E_\mathrm{T} + \mathrm{d}E_\mathrm{T}$. Thus [10]

$$\rho(E_\mathrm{T},E) = \rho_\mathrm{T}(E_\mathrm{T}) \sum_{v,j} (2j+1)\delta(E - E_\mathrm{T} - E_\mathrm{I}(v,j)) , \qquad \text{(A.6)}$$

where $E_\mathrm{I}(v,j)$ is the internal energy for a given v and j. In the limit of high density of internal states [10] we obtain

$$P^0(E_\mathrm{T}) = \rho(E_\mathrm{T}|E) = \rho(E_\mathrm{T},E)/\rho(E) = \tfrac{15}{4} f_\mathrm{T}^{1/2}(1 - f_\mathrm{T}) , \qquad \text{(A.7)}$$

where

$$\rho(E) = \int_0^E \rho(E_\mathrm{T},E)\,\mathrm{d}E_\mathrm{T} . \qquad \text{(A.8)}$$

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