On entropies and temperature parameters characterizing product distributions in chemical reactions and corresponding thermodynamic quantities

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The relations between the entropy (information content) and temperature parameters characterizing non-relaxed product distributions in chemical reactions and thermodynamic quantities are demonstrated. Two cases of initial reactant distributions—state-selected and thermal—are considered. The entropy change in the passage from non-equilibrium product distributions to partially relaxed distributions and the connection between the two kinds of vibrational temperatures characterizing these stages are treated in detail. An actual 'entropy cycle' is described.

1. INTRODUCTION

The advantages associated with the use of such quantities as 'information content' (or 'entropy') and 'surprisal' for characterizing reactant and product energy distributions in chemical reactions were first recognized by Bernstein and Levine [1]. Since then the approach was extended, new concepts like 'temperature parameters' [2–9] and 'relevance' [6, 8] were defined and many chemical reactions have been analysed. It is now understood that besides providing quantitative means for analysing distributions the information theoretic approach may also yield new insights into the processes of chemical reactions. Obviously, there are many points where refinements and further investigation are required. We here consider in some detail a few of the simplest of these points.

In general, our purpose is to correlate entropies and temperatures characterizing the non-equilibrium microscopic system composed of the atoms taking part in a single reactive collision with corresponding thermodynamic quantities. To this end we shall consider explicitly some well-defined stages specifying the passage from equilibrium reactants to equilibrium products in actual experiments. One of these stages, that of the non-relaxed products is interesting from both theoretical and practical aspects. Thus, for example, when the product state distribution is known many features of the potential hypersurface can be resolved. If the reaction ends up with inverted product population, this knowledge is of primary importance for designing chemical lasers.

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Any product state distribution can be associated with a meaningful entropy function (information content) and in many cases with temperature parameters [1–9]. The entropy of the non-equilibrium products can be considered as one step of an entropy cycle including among others the equilibrium product and reactant states. A general algorithm for constructing entropy cycles of this type and a proof that product entropies are state functions were demonstrated very recently by Levine [8]. We shall therefore confine the corresponding parts in our discussion to apparently special but actually frequent cases. It seems to us that an explicit treatment which points out some stages to which attention must be paid is valuable. We particularly refer to the following points : the connection between the thermodynamic entropy of reaction and the entropy functions characterizing various energy distributions in microscopic arrangements of products or reactants ; the relation between product state entropies corresponding to two differently prepared reactant distributions (and the role of reaction probability) ; the sign and the relative magnitude of the various components of the entropy cycle. In addition we shall discuss the connection between two kinds of vibrational temperatures. The first characterizes the distribution of energy among the various degrees of freedom of the products in a single reactive collision. The second temperature is that of an equilibrium ensemble of diatomic oscillators corresponding to a gas in partial equilibrium. The relation between these two quantities may be of interest for some chemical laser and relaxation studies.

All stages that we shall consider correspond to situations where the colliding species are well separated, either as products or reactants. Therefore such intermediates as ' transition complexes ' which from a dynamical point of view are more interesting will not be considered.

In § 2 we outline a number of essential definitions and relations. Section 3 deals with the relation between microscopic and macroscopic entropies. In § 4 we consider the cases of state-selected and thermal reactant distributions and in § 5 we deal with the resulting product distributions. Section 6 is concerned with reactions characterized by temperature parameters. Partially relaxed distributions and the connection between the two vibrational temperatures is the matter of § 7. In § 8 an actual entropy cycle is demonstrated.

2. Entropy

The functions we are intending to investigate in this work are special cases of the quantity

$$S[i] = - \sum_i P_i \log P_i \tag{1}$$

defined for any system, physical or abstract, for which the probability of being in state i is P_i. (The logarithm may be taken to any basis ; we shall use only the basis e. Square brackets simply denote summation variables and do not involve function arguments). S is called the ' information content ', the ' uncertainty ' or the ' entropy '. It is the most fundamental function in information theory [10]. For macroscopic physical systems the probability distribution function (pdf) which maximizes S subject to some initial conditions (constraints) is the equilibrium pdf and S is the thermodynamic entropy. The maximization procedure, known also as ' Jaynes' principle ' is the basis of

the information theoretic approach to statistical mechanics [11].   In irreversible thermodynamics the development of a non-equilibrium pdf and consequently S in time is governed by the ' Boltzmann H-theorem '.

Here, we shall consider the entropies corresponding to some of the stages in the passage from thermal reactants to thermal products in the reaction $A + BC \rightarrow AB + C$.   (The extension to other types of reactions is in principle not difficult.)   The system of interest is thus a triatomic one.   Disregarding the dynamically unimportant motion of the centre of mass and assuming electronic adiabaticity, the asymptotic reactant and product states are specified by six quantum numbers.   One choice is $\mathbf{k}$, v, j, m_j specifying the momentum of the relative motion and the vibrational, rotational and magnetic quantum numbers of the diatomic, respectively.   Instead we may use ϵ_t; $\Omega \equiv (\theta, \phi)$; v; j; m_j, where $\epsilon_t = \hbar^2 k^2 / 2\mu$ and Ω specify the kinetic energy and orientation of the relative motion, respectively.   In accordance with some experiments (e.g. the chemiluminescence method) we assume that only ϵ_t, v, j or equivalently $\epsilon = \epsilon_t + \epsilon_v + \epsilon_j$, $n \equiv v$, j are determined experimentally.   Thus, our treatment is not designed explicitly for molecular beam experiments where Ω (but rarely n) is resolved. The extension is, however, simple [2, 6, 8].   The appropriate form of S, when continuous variables like ϵ are included in i is [1, 2, 11]

$$S[\epsilon, n] = -\int d\epsilon \sum_{n \leqslant n^*} P(\epsilon, n) \log [P(\epsilon, n)/\rho(\epsilon, n)] \tag{2}$$

where $P(\epsilon, n) \, d\epsilon$ is the probability corresponding to the triatomic system with total energy in the range ϵ to $\epsilon + d\epsilon$ and with the diatomic in state n. n^* is the internal state with the highest energy possible which is lower than ϵ; $\epsilon_{n^*} \leqslant \epsilon$. $\rho(\epsilon, n)$ is the density of states (per unit volume), i.e. $\rho(\epsilon, n) \, d\epsilon$ is the number of internal-translational states compatible with n and ϵ, $\epsilon + d\epsilon$.   Explicitly [2, 12]

$$\rho(\epsilon, n) = g_n \rho^t(\epsilon - \epsilon_n), \tag{3}$$

where g_n is the degeneracy of the internal state and ρ^t is the translational density of states ($\epsilon_t = \epsilon - \epsilon_n$) [2, 12]

$$\rho^t(\epsilon_t) = \mu^{3/2} (2^{1/2} \pi^2 \hbar^3)^{-1} \epsilon_t^{1/2}. \tag{4}$$

Later we use equation (2) for different pdf's of reactants and products.   We shall use the subscript R, and unprimed variables like ϵ, n for reactants and P and primed variables ϵ', n' for products.   A useful decomposition of S results from the following definitions and relations [2] :

$$P(\epsilon, n) = P(\epsilon)P(n|\epsilon), \tag{5}$$

$$\rho(\epsilon, n) = \rho(\epsilon)\rho(n|\epsilon), \tag{6}$$

$$\int d\epsilon p(\epsilon) = \int d\epsilon \sum_{n \leqslant n^*} p(\epsilon, n) = \sum_{n \leqslant n^*} p(n|\epsilon) = 1, \tag{7}$$

$$\sum_{n \leqslant n^*} \rho(\epsilon, n) = \rho(\epsilon) \sum_{n \leqslant n^*} \rho(n|\epsilon) = 1. \tag{8}$$

Thus

$$S[\epsilon, n] = S[\epsilon] + S[n|\epsilon] = -\int d\epsilon \, p(\epsilon) \log [p(\epsilon)/\rho(\epsilon)]$$
$$-\int d\epsilon \, p(\epsilon) \sum_{n \leqslant n^*} p(n|\epsilon) \log [p(n|\epsilon)/\rho(n|\epsilon)]. \tag{9}$$

The joint entropy $S[\epsilon, n]$ and the quantity $S[\epsilon]$ are always non-negative.   The conditional entropy $S[n|\epsilon]$ is always non-positive and vanishes only when

$P(n|\epsilon) = \rho(n|\epsilon)$.   The physical significance of the last equality is that for a given total energy ϵ the occupation probability of the internal state n is proportional to the density of translational states conjugated to it [2].   (From equations (3), (6), (8) we see that the conditional density of states $\rho(n|\epsilon)$ is proportional to $g_n \rho^t(\epsilon - \epsilon_n)$).   In other words, this case corresponds to a situation where all the quantum states consistent with n and ϵ, $\epsilon + \delta\epsilon$ are equally probable or equivalently a microcanonical or statistical distribution.   (Note that ϵ and n alone do not specify the quantum state ; there is always a manifold of translational and degenerate internal states compatible with these requirements.)   As usual a microcanonical distribution maximizes the entropy which in the present case is given by $S[n|\epsilon] = 0$.   In the general case $S[n|\epsilon]$ provides a useful measure of the deviation from statistical behaviour [1, 2].

3. RELATION TO THERMODYNAMIC ENTROPY

The definition of entropy in the previous section applies to triatomic systems (excluding the c.m. motion) characterized by pdf's which are not necessarily equilibrium ones.   Here, with the aid of elementary arguments, we show briefly that the entropy of reaction is simply related to equilibrium ' triatomic entropies ' of the kind as equation (2).   Since reaction entropies are usually expressed as functions of temperature, volume and number of molecules we shall use the formalism of the canonical ensemble.   Using σ to denote macroscopic equilibrium entropies the entropy of reaction $A + BC \rightarrow AB + C$ is $\Delta\sigma = \sigma_P(N, V, \beta) - \sigma_R(N, V, \beta)$. σ_P is the entropy of a system containing N molecules BC in thermal, but not chemical equilibrium with N atoms A in the volume V at temperature $T = (k\beta)^{-1}$.   The definition of σ_R is similar.   Assuming the products and reactants to be ideal gases obeying Boltzmann statistics, the product partition function is

$$Q_P = (q_{AB}q_C)^N V^{2N}/(N!)^2, \tag{10}$$

where q stands for the one-particle partition function per unit volume. q_{AB} can be factorized into its translational and internal parts

$$q_{AB} = q_{AB}{}^{tr}q_{AB}{}^{int} = (m_{AB}/2\pi\beta\hbar^2)^{3/2}q_{AB}{}^{int}. \tag{11}$$

q_C contains only translational contribution.   Since $m_{AB}m_C = \mu M$, where $\mu = m_{AB}m_C/M$ and $M = M_{AB} + M_C$, Q_P can be factorized into q_{CM} involving the c.m. motion and q_P containing the contributions from the relative and internal motions

$$Q_P = (q_{CM}q_P)^N V^{2N}/(N!)^2, \left.\vphantom{\begin{array}{c}a\\b\end{array}}\right\}$$
$$q_P = (\mu_P/2\pi\beta\hbar^2)^{3/2}q_{AB}{}^{int}. \left.\vphantom{\begin{array}{c}a\\b\end{array}}\right\} \tag{12}$$

The entropy of the products (in units of k) is

$$\sigma_P(N, V, \beta) = -\beta(\partial \log Q_P/\partial\beta) + \log Q_P$$
$$= \beta N(\langle\epsilon'_{CM}\rangle + \langle\epsilon'\rangle) + N \log q_{CM}q_P + 2N \log (V/N), \tag{13}$$

where Stirling's formula has been used.   The average energy for a pair of product molecules in the c.m. system is

$$\langle\epsilon'\rangle = -\partial \log q_P/\partial\beta. \tag{14}$$

The c.m. contribution to the entropy is equal for reactants and products. For reactions preserving the number of molecules the terms due to the identity of particles log (N/V) are also equal and we find

$$\Delta\sigma/N = \log\ (q_\mathrm{P}/q_\mathrm{R}) + \beta(\langle\epsilon'\rangle - \langle\epsilon\rangle),\qquad(15)$$

where the energy levels to be used in $q_{\mathrm{AB}}{}^{\mathrm{int}}$ and $q_{\mathrm{BC}}{}^{\mathrm{int}}$ are measured from the zero-point energy of each molecule respectively. (The difference in zero-point energies appears in the energy and free energy of reaction but cancels out in the entropy.)

Although $\Delta\sigma/N$ is not the difference between ' entropies per pair ' (σ/N^2) or equivalently the ' entropy difference per pair ' $(\Delta\sigma/N^2)$ it can be interpreted as the average entropy change per reactive collision. More important from our point of view is that $\Delta\sigma/N$ can be expressed as the difference between two ' triatomic c.m. entropies ' of the form of equation (2). Explicitly

$$\Delta\sigma/N = S_\mathrm{P}{}^\beta[\epsilon', n'] - S_\mathrm{R}{}^\beta[\epsilon, n],\qquad(16)$$

where

$$S_\mathrm{R}{}^\beta[\epsilon, n] = -\int d\epsilon \sum_{n\leqslant n^*} P_\mathrm{R}{}^\beta(\epsilon, n) \log\left[\frac{P_\mathrm{R}{}^\beta(\epsilon, n)}{\rho_\mathrm{R}(\epsilon, n)}\right],\qquad(17)$$

$$P_\mathrm{R}{}^\beta(\epsilon, n) = q_\mathrm{R}{}^{-1}\rho_\mathrm{R}(\epsilon, n)\exp\ (-\beta\epsilon).\qquad(18)$$

We use β as a superscript to denote quantities corresponding to thermal equilibrium. It should be noted again that $S_\mathrm{R}{}^\beta[\epsilon, n]$ is not the entropy for pair of reactants, and that when the number of molecules is changed by the reaction, additional terms should appear in equation (17). To show that q_R of equation (18), i.e.

$$q_\mathrm{R} = \int d\epsilon \sum_{n\leqslant n^*} \rho_\mathrm{R}(\epsilon, n)\exp\ (-\beta\epsilon) = \int d\epsilon\rho_\mathrm{R}(\epsilon)\exp\ (-\beta\epsilon),\qquad(19)$$

is given by equation (12) (for reactants), one has to use equations (3), (4) in equation (19) and the definition $q_{\mathrm{BC}}{}^{\mathrm{int}} = \sum_n g_n \exp\ (-\beta\epsilon_n)$. Regarding equations (5)–(9) we have

$$P_\mathrm{R}{}^\beta(\epsilon) = \rho_\mathrm{R}(\epsilon)\exp\ (-\beta\epsilon)/q_\mathrm{R}\ ;\quad P_\mathrm{R}{}^\beta(n|\epsilon) = \rho_\mathrm{R}(n|\epsilon)\qquad(20)$$

and consequently

$$S_\mathrm{R}{}^\beta[n|\epsilon] = 0,\qquad(21)$$

$$S_\mathrm{R}{}^\beta[\epsilon, n] = S_\mathrm{R}{}^\beta[\epsilon] = \log q_\mathrm{R} + \beta\langle\epsilon\rangle.\qquad(22)$$

Equation (21) reflects the microcanonical character of internal state distributions in any given energy interval. Equations (20), (21) are obvious if we remember that the canonical (thermal) distribution results from the maximization of the entropy subject to the a priori given $\langle\epsilon\rangle$. Since there is no specific constraint regarding the internal states they will be populated in such a way that the entropy is maximal, i.e. $S[n|\epsilon] = 0$ and consequently $S[\epsilon, n]$ depends on $P(\epsilon)$ only. Equation (22) is complementary to equations (16)–(18). The subject of the following sections is the variations in $S[\epsilon, n]$.

4. Non-thermal reactants

The amount of kinetic information provided by a reactive scattering experiment is greater if the reactants are ' state-selected ' rather than thermally distributed [1]. In the present context we consider a ' detailed ' experiment to be

one where the reactants are all prepared with the same internal state $\hat{n}$ and within the energy range $\hat{\epsilon}$, $\hat{\epsilon} + \delta\epsilon$. (In principle more detailed experiments can be performed.) We represent the other extreme, an 'inclusive' [1] experiment, as one where the reactants are thermal. We assume that product distributions can be resolved to the same accuracy in both cases. In accord with other works [1, 2, 6, 8] we use γ to denote the specificity of the experiment with respect to the reactants. Thus by $\gamma \equiv \beta$ we refer to thermal and by $\gamma \equiv \hat{\epsilon}$, $\hat{n}$ to state-selected reactants. The next section is devoted to the rather common case in which there is practically no difference between these two specifications.

The expressions for thermal P_R and S_R were given in the previous section. The pdf corresponding to $\gamma \equiv \hat{\epsilon}$, $\hat{n}$ is

$$P_R^{\hat{\epsilon}\hat{n}}(\epsilon, n) = \begin{cases} \delta_{n, \hat{n}}(1/\delta\epsilon) & \hat{\epsilon} < \epsilon < \hat{\epsilon} + \delta\epsilon \\ \\ 0 \end{cases} \tag{23}$$

where $\delta_{n, \hat{n}}$ is the Kronecker symbol. Thus

$$P_R^{\hat{\epsilon}\hat{n}}(\epsilon) = (1/\delta\epsilon) \quad P_R^{\hat{\epsilon}n}(n|\epsilon) = \delta_{n, \hat{n}} \tag{24}$$

for ϵ within $\hat{\epsilon}$ to $\hat{\epsilon} + \delta\epsilon$ and zero everywhere else. The entropy is

$$S_R^{\hat{\epsilon}\hat{n}}[\epsilon, n] = \log [\rho_R(\hat{\epsilon}, \hat{n})\delta\epsilon]$$
$$= \log [\rho_R(\hat{\epsilon})\delta\epsilon] + \log \rho_R(\hat{n}|\epsilon). \tag{25}$$

The second line here corresponds to the decomposition as in equation (9). We note that the first term has the formal appearance of a microcanonical entropy. The second is always negative and describes deviations from 'microcanonicality' in $\hat{\epsilon}$. The whole expression corresponds to a restricted microcanonical-like entropy, where all states compatible with $\hat{\epsilon}$, $\hat{n}$ within $\delta\epsilon$ are equally probable. Note that while for macroscopic systems the canonical and microcanonical ensembles are effectively equivalent, $S^\beta[\epsilon]$ and $S^{\hat{\epsilon}\hat{n}}[\epsilon]$ are usually different. In some cases, however the difference is small (see the next section).

There is a fundamental theorem from information theory stating that any averaging (doubly stochastic) transformation $\bar{P}_i = \sum_j a_{ij}P_j$ ($\sum_i a_{ij} = \sum_j a_{ij} = 1$; $a_{ij} \geqslant 0$) implies $\bar{S} \geqslant S$ with S, $\bar{S}$ defined by equation (1) [1, 10]. It is possible (not very easily, however) to extend this theorem to the case where $i \equiv \epsilon$, n. Then with appropriately defined $a(\epsilon, n ; \epsilon'n')$ it is possible to identify

$$\bar{P}(\epsilon, n) \equiv P_R^\beta(\epsilon, n) ; \quad P(\epsilon, n) \equiv P_R^{\hat{\epsilon}\hat{n}}(\epsilon, n)$$

and to apply the theorem to entropies defined by equation (2). The result†

$$S_R^\beta[\epsilon, n] \geqslant S_R^{\hat{\epsilon}\hat{n}}[\epsilon, n] \tag{26}$$

is in agreement with our interpretation of S as a measure for 'disorder' or 'uncertainty'. The significance of (26) to our case is that state selection of reagents from thermal distribution is associated with entropy decrease [1] (the reverse process would be called relaxation or equilibration).

Another fundamental theorem states that the entropy corresponding to a pdf which is a superposition of other pdf's is greater than the corresponding

† See note added in proof.

superposition of the entropies [1, 10]. In the present connection the inequality is

$$S_R^\beta[\epsilon, n] \geqslant \langle S_R^{\hat{\epsilon}\hat{n}}[\epsilon, n] \rangle_\beta, \tag{27}$$

where the averaging is over the thermal distribution

$$\langle S_R^{\hat{\epsilon}\hat{n}}[\epsilon, n] \rangle_\beta = \int d\hat{\epsilon} \sum_{n \leqslant n^*} P_R^\beta(\hat{\epsilon}\hat{n}) S_R^{\hat{\epsilon}\hat{n}}[\epsilon, n]. \tag{28}$$

A more interesting variant of inequality (27) regarding product distributions will be discussed in the next section.

5. NON-EQUILIBRIUM PRODUCT DISTRIBUTIONS

The pdf corresponding to the products $AB + C$ prior to any relaxation is proportional to the rate constant (cross section) into ϵ', n'. This non-equilibrium pdf depends upon the initial reactant distribution. Using $k(\epsilon'n' ; \gamma)$ to denote the rate constants (normalized according to equation (7)) corresponding to reactant pdf specified by γ, the product distribution entropy is defined by [1, 2]

$$S[\epsilon', n' ; \gamma] = -\int d\epsilon' \sum_{n' \leqslant n'^*} k(\epsilon', n' ; \gamma) \log [k(\epsilon', n' ; \gamma)/\rho_P(\epsilon'n')]. \tag{29}$$

To distinguish from entropies corresponding to other stages we do not use here any subscript (R or P). Thus even when γ is omitted, by non-subscripted k we refer to completely non-relaxed product pdf's. The general relations between the entropies corresponding to different γ's are discussed elsewhere [1, 2]. We shall here consider in more detail the two cases above. We use $\pi(\epsilon, n)$ to denote the reaction probability, i.e. in a collision specified initially by BC in state n and total collision energy $\epsilon = \epsilon_t + \epsilon_n$ within ϵ to $\epsilon + d\epsilon$ $\pi(\epsilon, n)$ is the probability for reactive collision (averaged over all quantum numbers compatible with ϵ, n). This quantity is proportional to the total reactive cross section out of ϵ, n. Note that the normalization of $\pi(\epsilon, n)$ is only via $\pi(\epsilon, n) + \tilde{\pi}(\epsilon, n) = 1$, where $\tilde{\pi}$ is the probability for a non-reactive collision. The relation between the two product distributions is then

$$k(\epsilon'n' ; \beta) = [\pi(\beta)]^{-1} \int d\epsilon \sum_{n \leqslant n^*} P_R^\beta(\epsilon, n) \pi(\epsilon, n) k(\epsilon'n' ; \epsilon, n), \tag{30}$$

where

$$\pi(\beta) = \int d\epsilon \sum_{n \leqslant n^*} P_R^\beta(\epsilon, n) \pi(\epsilon, n) \tag{31}$$

is the average probability for reactive collision in the canonical ensemble. (In the last equations and other obvious cases, we use ϵ, n instead of $\hat{\epsilon}, \hat{n}$). $P_R^\beta \pi$ is the distribution of ' reactive reactants '.

There is no inequality analogous to (26) relating $S[\epsilon'n' ; \beta]$ and $S[\epsilon'n' ; \hat{\epsilon}\hat{n}]$. Thus, for instance, the first kind of product entropy will be larger if for the particular reactant specification $\hat{\epsilon}\hat{n}$ the product pdf is a ' very non-statistical ' one compared to other choices of ϵ, n. It will be smaller in the opposite case i.e. when $\hat{\epsilon}\hat{n}$ leads to a statistical distribution. There is, however, an inequality similar to (27), that is

$$S[\epsilon'n' ; \beta] \geqslant \langle S[\epsilon'n' ; \epsilon, n] \rangle_\beta, \tag{32}$$

where now

$$\langle S[\epsilon'n' ; \epsilon n] \rangle_\beta = [\pi(\beta)]^{-1} \int d\epsilon \sum_{n < n^*} P_R^\beta(\epsilon, n) \pi(\epsilon, n) S[\epsilon'n' ; \epsilon, n]. \tag{33}$$

The physical content of (32) is the following [1] : $S[\epsilon'n' \; ; \; \beta]$ can be computed with the aid of experimental results for product distributions resulting from thermal reactants. $\langle S[\epsilon'n' \; ; \; \epsilon n]\rangle_\beta$ is known when the detailed distributions $k(\epsilon'n' \; ; \; \epsilon, n)$ and the reaction probabilities are given. Obviously the second type of experiment provides more dynamical information and consequently gives rise to smaller entropy (uncertainty). Therefore the difference

$$R = S[\epsilon'n' \; ; \; \beta] - \langle S[\epsilon'n' \; ; \; \epsilon, n]\rangle_\beta \tag{34}$$

is a measure of the information gained when detailed experiments are performed. Moreover, R is a measure of the influence of reactant specification on the product distribution. When $k(\epsilon'n' \; ; \; \epsilon, n)$ is independent of ϵ, n, $R = 0$. Bernstein and Levine have introduced this quantity to the field of chemical reactions and have given it the name ' relevance ' [6]. (In the context of information theory it is known as ' the information processed by a channel ', its maximum with respect to different initial distributions is the ' channel capacity ' determining the most efficient coding scheme [10].)

6. Exoergic reactions, temperatures

Exothermic reactions are especially interesting for product entropy analysis, because of the large number of available internal states (open channels). In some cases, mainly for reactions involving hydrogenic molecules, when the reactants are at room temperature and the exothermicity is high, there is no essential difference between the two kinds of γ specification [13]. In these cases it can be assumed that the reactants populate only one (or mostly few) internal states $\hat{n}$ and that most collisions take place with translational energy centred in $\delta\epsilon$ around $\hat{\epsilon}_t = \hat{\epsilon} - \hat{\epsilon}_n$ with $\delta\epsilon \ll D$ the zero temperature exothermicity. Thus, one may write

$$P_R{}^\beta(\epsilon, n) \approx P_R{}^{\hat{\epsilon}\hat{n}}(\epsilon, n). \tag{35}$$

The width $\delta\epsilon$ can be estimated from

$$q_R{}^{tr} \approx \rho_R{}^t(\hat{\epsilon}_t) \exp(-\beta\hat{\epsilon}_t)\delta\epsilon \tag{36}$$

with $\hat{\epsilon}_t \approx \frac{3}{2}\beta^{-1}$. Using equations (4), (12) we find $\delta\epsilon \sim 2\beta^{-1}$. The assumption above implies also

$$k(\epsilon'n' \; ; \; \beta) \approx k(\epsilon'n' \; ; \; \hat{\epsilon}\hat{n}) \tag{37}$$

and

$$S[\epsilon'n' \; ; \; \beta] \approx S[\epsilon'n' \; ; \; \hat{\epsilon}\hat{n}] \approx \langle S[\epsilon'n' \; ; \; \epsilon n]\rangle_\beta. \tag{38}$$

As in equation (9) we can write

$$S[\epsilon'n' \; ; \; \gamma] = S[\epsilon' \; ; \; \gamma] + S[n'|\epsilon' \; ; \; \gamma]$$

$$= -\int d\epsilon' \, k(\epsilon' \; ; \; \gamma) \log [k(\epsilon' \; ; \; \gamma)/\rho_P(\epsilon')]$$

$$- \int d\epsilon' \, k(\epsilon' \; ; \; \gamma) \sum_{n' \leqslant n'^*} k(n'|\epsilon' \; ; \; \gamma) \log [k(n'|\epsilon' \; ; \; \gamma)/\rho_P(n'|\epsilon)]. \tag{39}$$

The sum in the second term measures the deviations from statistical (micro-canonical) product distribution and has been extensively investigated [2]. For

many exothermic reactions, where equations (35)–(38) are adequate, $k(n'|\epsilon')$ was found to be expressible by means of a convenient and meaningful formula. To write it down, we need some changes in the notation. Remembering that $n' = \nu'j'$ and that γ is in the present case unimportant, the vib-rotational pdf for a given ϵ', i.e. $k(\nu'j'|\epsilon')$ will be denoted as $k(\nu'j')$. For a given ϵ' it is common to use the variables $f_\nu' = \epsilon_\nu'/\epsilon$, $f_j' = \epsilon'_j/\epsilon$ (in our case $\epsilon' = \hat{\epsilon}' \approx \hat{\epsilon} + D$) and the rate constants $k(f_\nu', f_j')$ or $k(f_\nu', j')$ where every k is normalized with respect to its arguments. In this notation the vibrational pdf is

$$k(f_\nu') = \sum_{j' \leqslant j'^*(\nu)} (2j'+1)k(f_\nu', j'), \tag{40}$$

where $\epsilon_j'^*(\nu) \lesssim \epsilon' - \epsilon_\nu'$. For many exoergic reactions it was found that [2–9]

$$k(f_\nu') = \rho_P(f_\nu') \exp(-\lambda_V f_\nu')/z_V. \tag{41}$$

Here, $\rho_P(f_\nu') = \sum (2j'+1)\rho_P(f_\nu', j'|\epsilon')$ is a conditional density of states, i.e. a normalized function. If the diatomic is approximated as a rigid rotor and j is considered to be continuous then $\rho(f_\nu) \propto (1 - f_\nu)^{3/2}$ [2, 12]. If in addition it is assumed that the molecule is a harmonic oscillator and ν and f_ν are continuous variables (the RRHO approximation) then [2, 12]

$$\rho_P(f_\nu') = \tfrac{5}{2}(1 - f_\nu')^{3/2}. \tag{42}$$

In equation (41) λ_V is a constant independent of ν which, following the analogy between equation (41) and canonical pdf's was called 'the (reciprocal) vibrational temperature'. z_V is a normalization constant or partition function. λ_V is a measure for deviations from statistical distributions. If $\lambda_V = 0$ than $z_V = 1$, $S[\nu'|\epsilon'] = 0$ and the vibrational levels are populated in proportion to the corresponding density of rotational–translational states. For many exoergic reactions it was found that $-\lambda_V$ ranges between 5 and 10. Such high negative values indicate a high degree of vibrational population inversion. Some more properties of λ_V and equation (41) will be mentioned in the next section. Extensive discussions concerning the validity and the theoretical background of equation (41) are given elsewhere [2–9]. For a number of reactions it was found that equations similar to equation (41) can be used to describe the more detailed vib-rotational distribution $P(f_\nu', j')$. In some cases, no additional parameters are required and the distribution corresponds to an equipartion of the non-vibrational energy among the translational and rotational modes (' R–T microcanonical equilibrium ') [5, 7]. In general, additional rotational temperature parameters are useful in describing vib-rotational distributions [4, 6].

The conditional entropy $S[\nu'j'|\epsilon']$ can be further decomposed into $S[\nu'|\epsilon']$ and $S[j'|\nu', \epsilon']$ [2, 6]. The second quantity accounts for deviations from equipartition of the non-vibrational energy. In the following, we shall assume for simplicity that such R–T equipartition does exist and consequently that $S[j'|\nu'\epsilon'] \approx 0$ or equivalently $S[\nu'j'|\epsilon'] \approx S[\nu'|\epsilon']$. With this assumption and using equations (35)–(41) we find

$$S[\epsilon'n'] = \log[\rho_P(\hat{\epsilon} + D)\delta\epsilon] + \log z_V + \lambda_V \langle f_\nu' \rangle. \tag{43}$$

In the derivation of equation (43) the conservation of energy during the collision was taken into account via $k(\epsilon'; \hat{\epsilon}\hat{n}) = P_R^{\hat{\epsilon}\hat{n}}(\epsilon) = (1/\delta\epsilon)$ as given by

equations (23)–(24).   The average fraction of the total energy $\langle f_V' \rangle$ is a measurable quantity.   With the aid of equation (41) we find

$$\langle f_\nu' \rangle = -\frac{\partial \log z_V}{\partial \lambda_V}. \tag{44}$$

This is the analogue of the thermodynamic identity $\langle E \rangle = -\partial \log Q/\partial\beta$.   The analogue of $k\beta = \partial\sigma/\partial E$ (σ is the thermodynamic entropy) is

$$\lambda_V = \partial S[f_\nu']/\partial\langle f_\nu' \rangle,$$

where $S[f_\nu'] = S[\nu'|\hat{e}']$ and $S[\nu'|\epsilon'] \equiv \int d\epsilon' k(\epsilon') S[\nu'|\epsilon')$ [2].

7. Partially relaxed distribution, vibrational temperatures

Besides the physical significance of equation (41), the use of a single temperature parameter to characterize product distributions is practical.   One immediate application of equation (41) is for calculating gain factors in chemical lasers [7].   In the conventional description of chemical lasers, however, a vibrational temperature of a different kind, T_V, is used [14].   This section lends itself to explore the relation between T_V and λ_V.

On the basis of experimental observations it is usually assumed that the relaxation of an excited diatomic gas occurs on two separate time scales.   First the fast V→V (vibration to vibration) and R→T, R transfer processes take place and only then the slow V→T, R exchange establishes the final equilibrium distribution.   This assumption implies that the first relaxation step leads to a partial equilibrium condition characterized by a vibrational temperature T_V and a translational–rotational temperature T.   The validity of the assumption above and the values of T_V and T depend on the molecular composition of the relaxing medium.   In general, the V→V process will be an efficient one if resonant or near-resonant vibrational energy transfer, as in collisions between harmonic oscillators, can take place [15].   (For a general treatment of anharmonic effects see [16].)

Consider now the excited AB products immediately after the reaction.   In many cases, mainly if not very high vibrational levels are involved, they can be approximated as harmonic oscillators.   In actual experimental situations the excited AB molecules are usually surrounded by molecules of other kinds.   Therefore, the efficient V→V exchange which can take place only via collisions between AB molecules might be appreciably hindered due to collisions with the host molecules.   (In some cases e.g. the $F + H_2 \rightarrow HF + H$ laser where HF and H_2 have similar vibrational spacing, efficient energy exchange may also occur through collision between unlike molecules).   This and other considerations, like the possibility of interfering V→R, T processes set limits on the quantitative significance of T_V in real conditions.   Still, T_V is a commonly used and meaningful concept and it is therefore interesting to see how λ_V and T_V are related to each other.   For this we assume that vibrational energy exchange can take place only by collisions between AB molecules and that rotational and translational energies can be exchanged also with the heat bath.   (In the next section we briefly mention another type of partial equilibrium.)   In addition, it is assumed that AB is a harmonic oscillator.   The vibrational energy distribution after the fast relaxation step is

$$P(\nu') = \exp\left(-\beta_V \epsilon_\nu'\right)/q_V, \tag{45}$$

where q_V is the ordinary vibrational partition function corresponding to one oscillator in thermal equilibrium with other oscillators at temperature $T_V = (k\beta_V)^{-1}$. (For simplicity we do not write here $P_P{}^{\beta_V}(\nu')$. A remark concerning $P(\epsilon', \nu')$ is given below.)

Prior to evaluating the explicit relation connecting λ_V and T_V it should be emphasized again that these two quantities have entirely different origin and meaning. λ_V specifies the distribution of the total collision energy among the states of a single triatomic c.m. system $AB + C$ prior to any deactivation. Consequently λ_V is a microscopic non-equilibrium parameter. β_V on the other hand, is a pure equilibrium parameter characterizing a macroscopic system of oscillators. From the information theoretic point of view both quantities are Lagrangian multipliers resulting from entropy maximation [11]. λ_V is due to the maximization of $S[n'|\epsilon']$ (the sum in the second term of equation (39)) subject to an *a priori* given $\langle f_\nu' \rangle$ [3, 5, 9]. β_V results from the maximization of the entropy of the oscillator ensemble subject to a given average energy per oscillator $\langle \epsilon_\nu' \rangle$ or, equivalently, a given temperature [11]. In both cases the resulting distributions have a Boltzmannian form (equations (41), (45)).

According to our assumptions the average vibrational energy per molecule does not change in the first relaxation step. Therefore, using obvious notation, we find $\langle \epsilon_\nu' \rangle_{\beta_V} = \bar{\epsilon}' \langle f_\nu' \rangle_{\lambda_V}$, where $\bar{\epsilon}' = \bar{\epsilon} + D$ and where $\langle f_\nu' \rangle_{\lambda_V}$ is given by equation (44). Since $\langle \epsilon_\nu' \rangle_{\beta_V} = - \partial \log q_V / \partial \beta_V$ we have

$$\frac{\partial \log q_V}{\partial \beta_V} = \bar{\epsilon}' \frac{\partial \log z_V}{\partial \lambda_V}. \tag{46}$$

If ϵ_ν' is measured from the ground vibrational state then $q_V = [1 - \exp(-\beta_V \hbar \omega)]^{-1}$, where ω is the vibrational frequency. Unfortunately, z_V cannot be expressed in a simple closed form even in the RRHO approximation. Remembering, however, the semi-quantitative character of T_V an approximate expression connecting λ_V and T_V will be sufficient.

Using the RRHO expression equation (42) we find

$$z_V = \tfrac{5}{2} \int_0^1 df_\nu' (1 - f_\nu')^{3/2} \exp(-\lambda_V f_\nu')$$

$$= \tfrac{5}{2} \lambda^{-5/2} \exp(\lambda) \gamma(\tfrac{5}{2}; \lambda), \tag{47}$$

where $\gamma(a; b)$ is the incomplete gamma function. Equation (47) was written for the more frequent and interesting case of negative λ_V, $\lambda = -\lambda_V$. From equations (46), (47) and the explicit form of q_V mentioned above we obtain

$$\hbar \omega [\exp(\beta_V \hbar \omega) - 1]^{-1} = \bar{\epsilon}' [1 - \tfrac{5}{2\lambda} + \lambda^{3/2} \exp(-\lambda) / \gamma(\tfrac{5}{2}; \lambda)]. \tag{48}$$

We demonstrate the applicability of this equation by two specific examples. For the reaction $Cl + HI \rightarrow HCl + I$ (and the isotopic analogue with deuterium) we have $\bar{\epsilon}' \approx 34$ kcal mol^{-1}† [17], $-\lambda_V = \lambda = 8 \cdot 0$ [2] and the most populated vibrational level of HCl after reaction is $\nu_{mP}' = 3$. For $F + H_2 \rightarrow HF + H$ (and the isotopic reaction) $\bar{\epsilon}' \approx 34 \cdot 7$ kcal mol^{-1}, $\lambda = 6 \cdot 5$ and $\nu_{mP}' = 2$ [2, 18]. For such high values $\gamma(\tfrac{5}{2}; \lambda) \sim \Gamma \tfrac{5}{2} = 3\sqrt{(\pi/4)}$ where Γ is the gamma function, and therefore the third term in the square brackets in equation (48) is small. In

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† cal $= 4 \cdot 184$ J.

order to test the accuracy of equation (48) we may compare the experimental value $\langle f_\nu' \rangle = 0.71$ for the first reaction above with the right-hand side of equation (48). When γ is replaced by Γ this leads to $\langle f_\nu' \rangle = 0.70$. For the second reaction the values are 0.66 and 0.64 respectively. Considering the inaccuracy of the RRHO approximation and the experimental error, we may conclude that equation (48) is a reasonable approximation.

A quick estimation of β_V is obtained if the high temperature expression for $\langle \epsilon_\nu' \rangle$, i.e. $\langle \epsilon_\nu' \rangle = \beta_V^{-1}$, is used. This is approximately true even for the two examples above. (ω_{HCl} and ω_{HF} are large, but $\nu_{mp}' = 3$ and 2 for the two reactions respectively, thus $(\beta_V \hbar \omega)^{-1} \sim 3$ and 2). If in addition the last term on the right-hand side of equation (48) is neglected, we find

$$T_V \sim k^{-1} \bar{\epsilon}''[1 - \tfrac{5}{2\bar{\lambda}}]. \tag{49}$$

Using equation (49) we find $T_V \sim 13\,500$ K for $Cl + HI \rightarrow HCl + I$ and $T_V \sim 15\,000$ K for $F + H_2 \rightarrow HF + F$. A cruder estimate is obtained if we take $\langle f_\nu' \rangle = f_{\nu_{m.p.}}' \sim 1 - \tfrac{3}{2\bar{\lambda}}$ (see equations (41, 42)) and a better one if equation (48) is used.

In chemical laser studies the necessary lasing conditions are usually expressed in terms of the ratio between T_V and the gas kinetic temperature T [14]. Some of the shortcomings associated with the use of T_V were mentioned above. More important is the fact that for an efficient lasing action the vibrational population must be completely inverted. Unless T_V is negative, such populations where higher vibrational levels are more populated than lower levels cannot be described by equation (45). In this case, equation (45) loses its physical meaning as representing a partially relaxed population. Moreover, one has to assign different T_V's to different ν's. For these reasons it was suggested that for chemical lasers based on pumping reactions with well-defined λ_V, gain factors and lasing conditions should be expressed in terms of λ_V rather than T_V [7].

The entropy corresponding to the partially relaxed AB + C gas is given by a formula similar to equation (13). The only difference is that of using two temperatures, T_V for the vibration and T for the rotation and translation. For one AB + C pair in the c.m. system, i.e. excluding the c.m. and the mixing contributions to σ, the corresponding expression to S_P of equations (17), (22) is

$$S_P^{\beta \beta_V}[\epsilon_t', \nu', j'] = \log \left[q_P^{tr}(\beta) q_{AB}^{rot}(\beta) \right] + \beta \langle \epsilon_t' + \epsilon_j' \rangle_\beta$$

$$+ \log q_{AB}^{vib}(\beta_V) + \beta_V \langle \epsilon_\nu' \rangle_{\beta V}. \tag{50}$$

Here, we have used ϵ_t', ν', j' in the square brackets for emphasizing that, to distinguish from equation (9), equation (50) corresponds to the decomposition

$$S_P^{\beta, \beta_V}[\epsilon_t' \nu' j'] = S_P^{\beta}[\epsilon_t' j'] + S_P^{\beta_V}[\nu'].$$

It is clear, however, that summation over ϵ_t', ν', j' is equivalent to summation over $\epsilon' n'$ i.e. $S[\epsilon_t' \nu' j'] = S[\epsilon' n']$. We could perform a decomposition similar to equation (9) by using the explicit form of $P_P^{\beta \beta_V}(\epsilon', n')$ in $S[\epsilon' \nu'] = S[\epsilon'] + S[\nu' | \epsilon']$. The result is that both terms depend upon β and β_V and due to lack of energy equipartitioning $S[\nu' | \epsilon'] \neq 0$. In any case, no new features of the entropy which are not obvious from equation (50) will result from such a decomposition.

8. EXAMPLE OF ENTROPY CYCLE

The entropy change in the reaction—equation (16)—can be decomposed into any number of steps corresponding to changes in the pdf and the entropy of the triatomic system. In order to have some idea about these entropy changes, we consider an almost classical example, namely the reaction $Cl + HI \rightarrow HCl + I$. This is one of the reactions that have been extensively investigated by Polanyi and his coworkers both by the arrested relaxation-infra-red chemiluminescence method [17] and by classical trajectory computations [19]. In addition, this is one of the reactions for which the thermal reactant distribution can be approximated by equations (35)–(38) [13] and for which equation (41) is in excellent agreement with experiment [2]. The data for this reaction are $T \approx 300$ K, $\hat{\epsilon} \approx \epsilon_k + 5RT/2 \approx 2 \cdot 3$ kcal mol^{-1}, $\hat{\epsilon}' = \hat{\epsilon} + D \approx 34$ kcal mol^{-1}, $\langle f_\nu' \rangle = 0 \cdot 71$, $\langle f_j' \rangle = 0 \cdot 13$, $-\lambda_V = 8 \cdot 0$, $S[\nu'|\epsilon'] = -3 \cdot 54$ cal mol^{-1} K^{-1} or $-1 \cdot 57$ k per reactive collision† $S[j'|\nu_a'] \approx -0 \cdot 5$ cal mol^{-1} K^{-1} or $-0 \cdot 25$ k [2, 17]. Considering that $S[j'|\nu'\epsilon']$ is much smaller than $S[\nu'|\epsilon']$ and that the R–T equilibrium assumption leads within the limits of experimental error to the observed vib-rotational distribution [4, 5], we may assume $S[j'|\nu'\epsilon'] \approx 0$. The overall entropy change in the reaction is given by equation (15). Considering the high characteristic vibrational temperatures of HI and HCl we find $\langle \epsilon' \rangle \sim \langle \epsilon \rangle \sim \frac{5}{2}RT$ so that $\Delta\sigma/N \approx \log (q_P/q_R)$. Since for the present reaction $\mu_P \approx \mu_R$ the entropy change is very small and is mainly due to the rotation

$$\Delta\sigma/N \approx \log (B_R/B_P) = 0 \cdot 2 \ k, \tag{51}$$

where $B_R \equiv B_{HI}$ is the rotational constant. We now calculate the entropy changes for the triatomic c.m. system corresponding to the stages described in the previous sections (see also the figure).

8.1. *Thermal to state-selected reactants*

The entropy change is $S_R^{\hat{\epsilon}\hat{n}}[\epsilon, n] - S_R^{\beta}[\epsilon, n]$. It was assumed, however, that equations (35)–(38) are valid, i.e. that this difference is only slightly smaller than zero. The exact value cannot be accurately determined since $\delta\epsilon$ is not well defined. In fact, for HI at room temperature several rotational levels $(j \sim 2$–$5)$ rather than one are populated $(\nu \neq 0$ are effectively not populated). However, the contribution to S^β is mostly from the translation and if $\delta\epsilon$ is estimated from equation (36) the translational contributions to $S_R^{\hat{\epsilon}\hat{n}}[\epsilon, n]$ and $S_R^{\beta}[\epsilon, n]$ are identical. The absolute value of the entropy is

$$S_R^{\hat{\epsilon}\hat{n}}[\epsilon, n] \approx S_R^{\beta}[\epsilon, n] = S_R^{\beta}[\epsilon] = 60 \cdot 0 \ k, \tag{52}$$

where equation (22) was used and $\beta\langle\epsilon\rangle$ was taken as $\frac{5}{2}$, (rotation + translation).

8.2. *Thermal (or state-selected) reactants to non-relaxed products*

As in the former stage the γ specification is redundant and equations (37, 38) can be used. The contribution of $S[\nu'|\epsilon']$ to the non-equilibrium product entropy was calculated previously [2] and was cited above as $-1 \cdot 57 \ k$. The

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† k (Boltzmann constant) $\approx 1 \cdot 380 \ 622 \times 10^{-23}$ J K^{-1}.
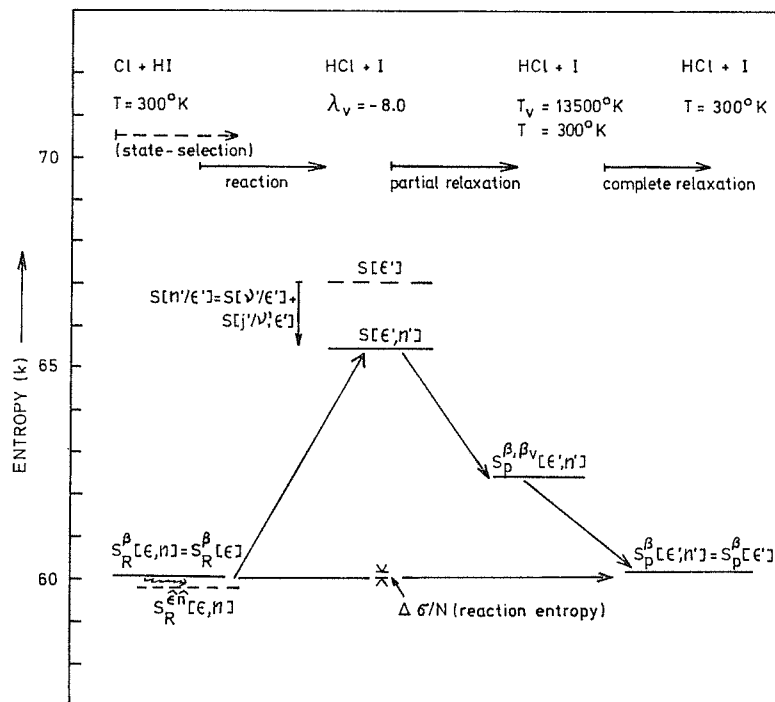
An entropy cycle for the reaction Cl + HI → HCl + I. Experimental data from reference [17] (see text).

main contribution to $S[\epsilon'n']$ is however from $S[\epsilon']$ as given by the first term in equation (43). Using the explicit formula

$$\rho_P(\tilde{\epsilon}') = \mu_P{}^{3/2}(2^{1/2}\pi^2\hbar^4\omega_P B_P)^{-1}(\tilde{\epsilon}')^{5/2} \quad [2, 12]$$

we find

or

$$\left.\begin{array}{l} S[\epsilon'] = 67 \cdot 0 \ k \\[2mm] S[\epsilon'] - S_R[\epsilon'] = 7 \ k. \end{array}\right\} \tag{53}$$

The accuracy of this value should be considered subject to the accuracy of the experimental values of $\tilde{\epsilon}$ and D. We note that the most significant quantity from a dynamical point of view, i.e. $S[n'|\epsilon'] \simeq -1 \cdot 6 \ k$, is only a small fraction of $S[\epsilon'n']$. The total entropy change in this step is

$$S[\epsilon'n'] - S_R[\epsilon, n] = 5 \cdot 4 \ k. \tag{54}$$

This is mainly due to the increase in the density of states associated with the sudden change in the energy from $\tilde{\epsilon}$ to $\tilde{\epsilon}' = \tilde{\epsilon} + D$. $\quad(\rho_P(\tilde{\epsilon} + D) \sim \rho_R(\tilde{\epsilon} + D) \gg \rho_R(\tilde{\epsilon}))$.

8.3. Non-equilibrium products to partially relaxed products with vibrational temperature $T_V = 13\,500$ K and translational–rotational temperature $T = 300$ K

The entropy of one HCl + I pair (excluding the c.m. motion) of the partially relaxed products is given by equation (50). The values of the various terms in this equation are approximately 57·7 ; 2·5 ; 1·1 and 1·0 respectively. Thus

$S_P{}^{\beta\beta v}[\epsilon'n'] = 62 \cdot 3 \; k$ and

$$S_P{}^{\beta, \; \beta v}[\epsilon'n'] - S[\epsilon'n'] = -3 \cdot 1 \; k. \tag{55}$$

The negative value of the entropy difference associated with this relaxation step is due to the ' cooling ' of the rotational and translational degrees of freedom. Before the relaxation the energy of these modes was $\langle f_t' + f_j' \rangle = 1 - \langle f_v' \rangle = 0 \cdot 3$ or $\langle \epsilon_t' + \epsilon_j' \rangle = 0 \cdot 3 \times 34 = 10 \cdot 2 \; \mathrm{kcal \; mol^{-1}}$. After relaxation the energy is

$$\langle \epsilon_t' + \epsilon_j' \rangle_\beta \simeq 5RT/2 \simeq 1 \cdot 5 \; \mathrm{kcal \; mol^{-1}}.$$

This energy decrease for one $HCl + I$ pair is associated with corresponding entropy decrease. The entropy which increases in the course of the relaxation is that of the gas and the heat bath together. Obviously there is a positive contribution to the ' triatomic entropy ' resulting from the vibrational energy exchange between the molecules (the negative total value shows that, in absolute value, the vibrational contribution to the change in entropy is smaller than that due to rotation and translation). The statement that the relaxation from a vibrational distribution given by equation (41) to one which is given by equation (45) leads to a positive entropy change does not require an explicit proof. Adopting the information theoretic approach, for instance, the statement is understood on the basis of the following arguments. Since we have assumed that the average vibrational energy per molecule does not change in the first relaxation stage, the only constraint on the entropy of the oscillator gas is that $\langle \epsilon_v \rangle$ should be conserved. Equation (45) is exactly the one which maximizes $S[\nu']$ with respect to this constraint. The constraint $\langle f_v' \rangle = \mathrm{constant}$ which leads to equation (41) has a similar form, but the system under consideration here is the triatomic $AB + C$ system and not the ensemble of AB molecules.

8.4. *Partial to complete relaxation*

The only change in entropy here is due to the reduction of the vibrational temperature from $T_V = (k\beta_V)^{-1}$ to $T = (k\beta)^{-1}$. Since for HCl $\beta\hbar\omega \gg 1$ the vibrational contribution to $S_P{}^\beta[\epsilon'n']$ is negligible and thus there is a net decrease in the entropy of the triatomic system

$$S_P{}^\beta[\epsilon'n'] - S_P{}^{\beta, \; \beta v}[\epsilon'n'] = -2 \cdot 1 \; k \tag{56}$$

with $S_P{}^\beta[\epsilon'n'] = 60 \cdot 2 \; k$.

In principle, we could enrich our entropy cycle by considering other intermediate stages. For instance, one may imagine an hypothetical experiment in which the products $AB + C$ are collected immediately after the reaction into an isolating container. Then, due to the exothermicity of the reaction, the rotational and translational modes will first equilibrate at some $T' > T$ and later, together with the vibration, at T'', $T_V > T'' > T'$. The entropies corresponding to such situations are easily calculable. One only has to include the c.m. motion in the energy repartitioning. Remembering, however, the general purpose of this paper, we think that inclusion of such intermediates in the entropy cycle is of minor interest.

The figure shows an entropy cycle of the form suggested by Levine. In our case, however, only a few stages are shown. The calculation of other possible paths from reactants to products requires additional experimental or theoretical information. The purpose of this diagram is to demonstrate the relative magnitude

and sign of the various entropy changes and in particular to show where and how $S[n' | \epsilon']$ is located in the entropy cycle.

9. Summary

We have considered in detail some simple points associated with the information theoretic approach to chemical reactions. The general purpose was to investigate the relation between entropies and temperature parameters and their ordinary thermodynamic analogues. There are still many aspects of the approach which must be carefully tested. Some of them are : the connection to other statistical theories ; the role of constraints ; the development of entropy along the reaction path and the possibility of extending the approach beyond the scope of the reaction $A + BC \rightarrow AB + C$.

Note added in proof.—A sufficient condition for the existence of inequality (26) is that $\delta\epsilon$ (equations (23)–(25)) should be smaller than the width of the thermal distribution $P_R{}^\beta$ whose $\langle \epsilon \rangle = \hat{\epsilon}$ (equations (14), (23)). A rigorous (and lengthy) proof of this inequality is given elsewhere [20]. In the same work [20] which deals, among others, with entropy cycles in a generalized fashion the interpretation of $P_R{}^{\hat{\epsilon}\hat{n}}(\epsilon, n)$ (equations (23), (24)) and of $\pi(\epsilon, n)$ (§ 5) are somewhat different.

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