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LETTERS

Reversibility Relationship in Collision-Complex-Forming Bimolecular Reactions

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We present both intuitive and formal justification for the common assumption that the forward and reverse rate coefficients for bimolecular reactions proceeding through a collision complex are related by the equilibrium constant for reactants and products, regardless of the effects of third-body collisional relaxation of the intermediate.

I. Introduction

One of the most basic equations in chemical thermodynamics relates the rate coefficients for the forward and reverse directions of a reaction

$$\mathrm{A} + \mathrm{B} \underset{k_\mathrm{r}}{\overset{k_\mathrm{f}}{\rightleftarrows}} \mathrm{C} + \mathrm{D}$$

via the equilibrium constant

$$\frac{k_\mathrm{f}}{k_\mathrm{r}} = K_\mathrm{eq} = \frac{Q_\mathrm{C}Q_\mathrm{D}}{Q_\mathrm{A}Q_\mathrm{B}}\,\mathrm{e}^{-\Delta H^\circ/k_\mathrm{B}T} \qquad (1)$$

where Q_i is the partition function for species i, ΔH° is the enthalpy change for the reaction at 0 K (i.e., the difference between the zero-point energies of products and reactants), and the other symbols take their usual meanings. Ab initio estimates of reaction enthalpies, even at a high level of theory, are rarely reliable to within 2 kcal mol^{-1} for open shell systems. Partition functions can generally be accurately computed either from spectroscopic or ab initio data, however, so that if the equilibrium constant is known, a more precise estimation of the reaction enthalpy can be made. Experimental measurement of forward and reverse rate coefficients is an important route to the determination of equilibrium constants, since the residence time in flow reactors is often considerably shorter than that which would be required for equilibrium to be attained, so that it is much easier to measure the forward and reverse kinetics than it is to achieve the equilibrium measurement. In this manner, databases of experimentally measured rate coefficients enable estimation and cross-validation of heats of formation of individual chemical species, crucial data for the estimation of abundances in atmospheric[1] or interstellar environments.[2]

This picture is not quite so straightforward in the case where the reaction proceeds via a collision complex, in which case the finite lifetime of the complex introduces the possibility of collisions with surrounding bath gases prior to dissociation and hence possible stabilization of the complex. If the well is

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shallow, then the lifetime of the complex is very short and so there is no problem since collisions do not interfere on this time scale. On the other hand, if the well is deep, then stabilization of the complex represents an additional pathway for the reaction. Further complications arise when there are other possible dissociation pathways for the complex, leading to different sets of products. The qualitative effect of pressure on such systems is well understood in terms of the classic falloff behavior of multichannel unimolecular reactions (although quantitative modeling remains a demanding and important challenge). This may be summarized as follows: (1) at high pressures, an effective Boltzmann population distribution of the collision complex is maintained and stabilization dominates; (2) at low pressures collisions do not interfere with the forward and reverse reaction processes; (3) at intermediate pressures there is competition between collisional relaxation and dissociation, producing a nonequilibrium population distribution of the collision complex as a function of energy and angular momentum and leading to branching ratios that are very difficult to model quantitatively.

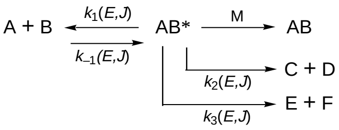
The question that we address in this Letter is whether measurements of forward and reverse rate coefficients for bimolecular reactions proceeding through a collision complex can still be used in the manner summarized above to infer equilibrium constants and hence enthalpies of reaction, regardless of the effect of collisions in modifying the population distribution of the collision complex in a way that depends on pressure. As we shall see below, there are strong intuitive grounds for suggesting that the simple relationship of eq 1 above should be valid independent of pressure. However, to the best of our knowledge it has never been proven through a master equation analysis that the nonequilibrium forward and reverse rate coefficients are indeed exactly related as in eq 1. As shown below, a careful examination of the formal solution of the master equation shows that eq 1 does indeed hold for a very wide range of conditions.

We begin with a simple *gedanken* experiment that provides a strong intuitive argument for the validity of the eq 1, independent of pressure. Consider a reversible bimolecular system proceeding through a collision complex

$$\mathrm{A} + \mathrm{B} \leftrightarrow \mathrm{AB}^* \leftrightarrow \mathrm{C} + \mathrm{D}$$

and assume that, as indicated, the system has equilibrated initially at very low pressures, such that forward and reverse bimolecular rate coefficients are related exactly by the equilibrium constant. We also know that for an equilibrated system at high pressures the same relationship must hold, the difference being that in the latter case the stable energy levels of the molecular species AB are fully populated, whereas in the former case only the metastable levels of the collision complex above the lowest dissociation threshold of the molecule are populated. Now gradually increase the pressure so that collisions between bath gases and the metastable collision complexes begin to induce the formation of stable molecular species AB. Does the formation of the stable species AB with increasing pressure disturb the equilibrium ratio of species {A,B} and {C,D}? One does not expect so, since in the long-time limit, when equilibrium of the molecular species AB with respect to separated fragments is attained, the population ratios of {A,B} and {C,D} are still given by the equilibrium constant. Hence, one expects on intuitive grounds that, whatever the actual values of the forward and reverse bimolecular rate coefficients in the presence of stabilization, they should still be related by the equilibrium constant. Indeed, if the equilibrium ratio of {A,B} and {C,D} were to be disturbed, this would appear to violate the second law of thermodynamics.

The argument based on the hypothetical experiment above is strongly suggestive; however, the initial conditions envisaged are not the same as those that usually apply. Hence, we proceed now to consider the master equation for a bimolecular reaction proceeding through a collision complex where initially there are only reactants present, i.e., no intermediate species or products. The reactants are assumed to be dilute in a bath gas, as is generally the case (by design) in experimental measurements of this sort. To allow for some more generality, we shall consider a three-channel system (i.e., reactants and two bimolecular product channels) We make the usual assumptions of a statistical collision complex with a reasonably high density of states, so that the standard master equation description is appropriate for the kinetics (see, e.g., ref 3). The evolution of the population distribution, $g(E,J)$, of the molecular species AB (including the levels of the collision complex) over energies E and angular momenta J is then given by



$$\frac{\mathrm{d}g(E,J)}{\mathrm{d}t} = [\mathrm{M}]\int\int [R(E,J;E',J')\, g(E',J') - R(E',J';E,J)\, g(E,J)]\mathrm{d}E'\, \mathrm{d}J' - k(E,J)\, g(E,J) + k_{-1}(E - \Delta H_1^\circ,J)\, f_{\mathrm{A,B}}(E - \Delta H_1^\circ,J)[\mathrm{A}(t)][B(t)] \quad (2)$$

where [M] is the concentration of the bath gas M, $R(E,J;E',J')$ is the bimolecular rate coefficient for energy and angular momentum transfer from initial values (E',J') to final values (E,J) during collisions with the bath gas, $k(E,J) = \sum_{i=1}^{3} k_i(E,J)$ is the sum of the microcanonical dissociation rate coefficients for each of the channels (reactants and two product channels), and $f_{\mathrm{A,B}}(E - \Delta H_1^\circ,J)$ is the normalized thermal equilibrium population of reactants. The reactant channel is denoted as channel 1, and $k_{-1}(E - \Delta H_1^\circ,J)$ is the microcanonical capture rate coefficient, related to $k_1(E,J)$ by detailed balance. $[\mathrm{A}(t)]$ and $[\mathrm{B}(t)]$ are the time-dependent concentrations of reactants A and B, respectively. Note that eq 2 describes the irreversible kinetics that occur when the concentration of products is small and hence formation of complex by recombination of "products" C + D or E + F may be neglected, as is the usual situation in flow reactors.

II. Strong Collision Approximation

The solution of the master equation for the (generally oversimplified) case where stabilization of the complex by collisions with the surrounding bath gas is assumed to be irreversible and to occur at the collision rate (i.e., the strong collision assumption) is well-known (e.g., ref 4). Inspection reveals that the forward and reverse bimolecular rate coefficients resulting from this simple approximation do obey the relation of eq 1. For this case, the steady-state solution for the collision complex population distribution, $g^*(E,J)$, is given by

$$g^*(E,J) = \frac{[\mathrm{A}(t)][\mathrm{B}(t)]}{Q_{\mathrm{A}}Q_{\mathrm{B}}}\, \mathrm{e}^{-(E-\Delta H_1^\circ)/k_{\mathrm{B}}T} \frac{W_1(E,J)}{h[\omega + k(E,J)]}$$

$$= [\mathrm{A}(t)][\mathrm{B}(t)]K_{\mathrm{eq}}(\mathrm{A,B}|\mathrm{AB})\, f(E,J)\frac{k_1(E,J)}{[\omega + k(E,J)]} \quad (3)$$

where $K_{\mathrm{eq}}(\mathrm{A,B}|\mathrm{AB})$ is the equilibrium constant for the molecule AB relative to reactants A and B,

$$K_{\rm eq}({\rm A,B}|{\rm AB}) = \frac{Q_{\rm AB}}{Q_{\rm A}Q_{\rm B}}\, {\rm e}^{\Delta H_1^0/k_{\rm B}T} \qquad (4)$$

$f(E,J) = \rho(E,J)\exp(-E/k_{\rm B}T)/Q$ is the equilibrium population of AB, $W_1(E,J)$ is the sum of states evaluated at the transition state for the entrance channel (i.e., that which governs the capture flux), and ω is the frequency of collisions with the bath gas. Hence, the forward bimolecular rate coefficient for formation of products C and D is

$$k_{\rm f} = K_{\rm eq}({\rm A,B}|{\rm AB})\int\!\!\int {\rm d}E\,{\rm d}J\, f(E,J)\frac{k_2(E,J)\,k_1(E,J)}{[\omega + k(E,J)]} \qquad (5)$$

The reverse rate coefficient, $k_{\rm r}$, for formation of products A and B from reactants C and D is given similarly by

$$k_{\rm r} = K_{\rm eq}({\rm C,D}|{\rm AB})\int\!\!\int {\rm d}E\,{\rm d}J\, f(E,J)\frac{k_1(E,J)\,k_2(E,J)}{[\omega + k(E,J)]} \qquad (6)$$

hence the ratio $k_{\rm f}/k_{\rm r}$ follows directly as in eq 1.

III. General Case: Time-Independent Rate Coefficients

It remains to verify by examination of the formal solution of the master equation that relationship 1 holds more generally, i.e., when irreversible stabilization of the complex by a single collision with a bath gas molecule is not assumed. It is useful to write the discretized version of eq 2 in matrix form as

$$\frac{{\rm d}\mathbf{g}}{{\rm d}t} = \mathbf{J}\mathbf{g} + \frac{K_{\rm eq}[{\rm A}(t)][{\rm B}(t)]}{Q_{\rm AB}}\mathbf{r} \qquad (7)$$

where $r_i = k_1(E,J)\,\rho(E,J)\exp(-E/k_{\rm B}T)$, and $K_{\rm eq}$ is to be read as $K_{\rm eq}({\rm A,B}|{\rm AB})$ here and below unless otherwise indicated. For notational convenience, when referring to the elements of vectors or matrixes we use a single index i to refer to the (discretized) energy and angular momentum (E,J). In eq 7, $\mathbf{g}$ is the population vector whose elements are the $g(E,J)$ of eq 2; the matrix $\mathbf{J}$ contains all of the collisional transition rates $R(E,J;E',J')$ and the microcanonical dissociation rate coefficients $k(E,J)$ of eq 2, and the term involving $\mathbf{r}$ describes the influx terms of eq 2. Because the collisional transition probabilities contained in $\mathbf{J}$ must satisfy the detailed balance requirement, the matrix is related to a real symmetric matrix $\mathbf{B}$ by the transformation[5]

$$\mathbf{B} = \mathbf{S}^{-1}\mathbf{J}\mathbf{S} \qquad (8)$$

where the diagonal matrix $\mathbf{S}$ has elements $S_{ii} = \delta_{ij}\,[\rho(E,J)\exp(-E/k_{\rm B}T)]^{1/2}$. The solution to this "chemical activation" master equation has been examined in somewhat different ways by Schranz and Nordholm,[6] by Troe,[7] and by Smith et al.[8] The general solution to eq 7 has the following form

$$\mathbf{g}(t) = \mathbf{g}(t{=}0) + \frac{K_{\rm eq}}{Q_{\rm AB}}\int_0^t {\rm d}s[{\rm A}(s)][{\rm B}(s)]{\rm e}^{\mathbf{J}(t-s)}\mathbf{r} \qquad (9)$$

where $\mathbf{g}(t{=}0)$ will be 0 if there are no AB molecules present at the start of the reaction (typically, calculations are carried out with the real symmetric matrix $\mathbf{B}$ rather than $\mathbf{J}$ itself). In their study, Smith et al.[8] showed that for the case of a reasonably deep potential well and not-too-high temperatures (i.e., conditions where a time-independent stabilization rate coefficient is well-defined), there exists a clear separation between the lowest eigenvalue of the matrix $\mathbf{J}$ and its higher eigenvalues and the population distribution of eq 9 splits into two terms. One of these terms ($\mathbf{g}^*$) is directly proportional to $[{\rm A}(t)][{\rm B}(t)]$ and may be identified as the steady-state population distribution of the collision complex, and the other ($\mathbf{g}_{\rm s}$) rises slowly with time and may be associated with the build-up of population of the stabilized molecule. Thus

$$\mathbf{g} = \mathbf{g}_{\rm s} + \mathbf{g}^* \qquad (10a)$$

where

$$\mathbf{g}_{\rm s} = \frac{K_{\rm eq}}{Q_{\rm AB}}\,\frac{k_{\rm uni}^1\sum_i x_i^1}{\sum_i[(x_i^1)^2/b_i]}\,\mathbf{x}^1\int_0^t {\rm d}s\,{\rm e}^{-k_{\rm uni}(1-s)}\,{\rm A}(s)\,{\rm B}(s) \qquad (10b)$$

and

$$\mathbf{g}^* = \frac{K_{\rm eq}}{Q_{\rm AB}}\left[\eta - \frac{k_{\rm uni}^1\sum_i x_i^1}{k_{\rm uni}\sum_i[(x_i^1)^2/b_i]}\mathbf{x}^1\right]{\rm A}(t)\,{\rm B}(t) \qquad (10c)$$

In eq 10, $b_i = \rho(E,J)\exp(-E/k_{\rm B}T)$, $\mathbf{x}^1$ is the eigenvector of $\mathbf{J}$ corresponding to the eigenvalue of smallest absolute magnitude, $-k_{\rm uni}$, which gives the total thermal unimolecular dissociation rate coefficient for fragmentation through *all* channels, and $k_{\rm uni}^1$ is the thermal unimolecular dissociation rate coefficient for formation of A and B. Finally, $\eta = -\mathbf{J}^{-1}\mathbf{r}$ is the steady-state population distribution corresponding to long times where there would be no net stabilization. Analysis of the stabilized population $\mathbf{g}^{\rm s}(t)$ leads to the result[8] that the stabilization rate coefficient is given by

$$k_{\rm s} = K_{\rm eq}k_{\rm uni}^1 f_{\rm ne} \qquad (11)$$

with The fraction $f_{\rm ne}$ is found in practice to be unity for all

$$f_{\rm ne} = \frac{(\sum_i x_i^1)^2}{Q\sum_i[(x_i^1)^2/b_i]} \qquad (12)$$

except very high temperatures or weakly bound species, i.e., the usual conditions under which the eigenvalue separation mentioned above is valid. Examination of the steady-state complex population $\mathbf{g}^*$ yielded the following result for the forward bimolecular rate coefficient (from channel 1 to channel j)

$$k_{\rm f}^{1\to j} = \frac{K_{\rm eq}({\rm A,B}|{\rm AB})}{Q_{\rm AB}}\left(\sum_i k_i^j\eta_i - \left\{\frac{k_{\rm uni}^1\sum_i x_i^1}{k_{\rm uni}\sum_i[(x_i^1)^2/b_i]}\right\}\sum_i k_i^j\,x_i^1\right)$$

$$= k_{\rm ss}^{1\to j} - \frac{K_{\rm eq}({\rm A,B}|{\rm AB})f_{\rm ne}k_{\rm uni}^1\,k_{\rm uni}^j}{k_{\rm uni}} \qquad (13)$$

where $k_{\rm ss}^{1\to j}$ is the steady-state bimolecular rate coefficient (i.e., that which obtains when there is no longer any net stabilization). Likewise, the reverse rate coefficient *from* channel j *to* channel 1 will be given as

$$k_{\mathrm{r}}^{j\rightarrow 1} = k_{\mathrm{ss}}^{j\rightarrow 1} - \frac{K_{\mathrm{eq}}(\mathrm{C,D|AB}) f_{\mathrm{ne}} k_{\mathrm{uni}}^{j}\, k_{\mathrm{uni}}^{1}}{k_{\mathrm{uni}}} \qquad (14)$$

Clearly, the second terms in eqs 13 and 14 will give the simple ratio of equilibrium constants that we are seeking to establish. It is necessary therefore to examine the expression for the steady-state rate coefficients (the first terms) more closely. For this purpose, we note that $k_{\mathrm{ss}}^{1\rightarrow j}$ can be written using the following matrix notation

$$k_{\mathrm{ss}}^{1\rightarrow j} = -\frac{K_{\mathrm{eq}}(\mathrm{A,B|AB})}{Q_{\mathrm{AB}}}(\mathbf{k}^{j})^{\mathrm{T}}\mathbf{J}^{-1}\mathbf{S}^{2}\mathbf{k}^{1} \qquad (15)$$

where $\mathbf{k}^{i}$ is a column vector containing the microcanonical dissociation rate coefficients $k^{i}(E,J)$, and we have used the fact that $\mathbf{r} = \mathbf{S}^{2}\mathbf{k}^{1}$. Substituting for $\mathbf{J}$ in terms of the real symmetric matrix $\mathbf{B}$, we then have

$$\begin{aligned} k_{\mathrm{ss}}^{1\rightarrow j} &= -\frac{K_{\mathrm{eq}}(\mathrm{A,B|AB})}{Q_{\mathrm{AB}}}[(\mathbf{k}^{j})^{\mathrm{T}}(\mathbf{SBS}^{-1})^{-1}\mathbf{S}^{2}\mathbf{k}^{1}] \\ &= -\frac{K_{\mathrm{eq}}(\mathrm{A,B|AB})}{Q_{\mathrm{AB}}}[(\mathbf{k}^{j})^{\mathrm{T}}(\mathbf{SB}^{-1}\mathbf{S}^{-1})\mathbf{S}^{2}\mathbf{k}^{1}] \qquad (16) \\ &= -\frac{K_{\mathrm{eq}}(\mathrm{A,B|AB})}{Q_{\mathrm{AB}}}[(\mathbf{k}^{j})^{\mathrm{T}}(\mathbf{SB}^{-1}\mathbf{S})\mathbf{k}^{1}] \end{aligned}$$

The reverse steady-state rate coefficient, $k_{\mathrm{ss}}^{j\rightarrow 1}$, is likewise given by

$$k_{\mathrm{ss}}^{j\rightarrow 1} = -\frac{K_{\mathrm{eq}}(\mathrm{C,D|AB})}{Q_{\mathrm{AB}}}[(\mathbf{k}^{1})^{\mathrm{T}}(\mathbf{SB}^{-1}\mathbf{S})\mathbf{k}^{j}] \qquad (17)$$

The terms in the square brackets of eqs 16 and 17 are identical, however, since $\mathbf{B}$, $\mathbf{B}^{-1}$, and hence the matrix $\mathbf{SB}^{-1}\mathbf{S}$ are real symmetric. Hence the ratio of forward and reverse steady-state bimolecular rate coefficients also follows the simple relationship of eq 1, which completes the proof.

IV. General Case: Time-Dependent Rate Coefficients

In the above arguments, we have dealt with the commonly encountered case of a suitably deep potential well and temperatures that are not too high. Under these conditions there is a clear separation of the lowest eigenvalue of the matrix $\mathbf{J}$ from the rest of its spectrum so that one has well-defined, time-independent rate coefficients for both stabilization and formation of bimolecular products. The relative size of these will depend strongly on pressure: at high pressures stabilization dominates, whereas at low pressures the formation of bimolecular products will dominate (either way, if the well is deep it may take a very long time for eventual equilibrium to be achieved). When these conditions do not apply, however, the separation of the lowest eigenvalue from the rest of the spectrum of $\mathbf{J}$ will not be so pronounced, leading to more complex, time-dependent kinetics. Examination of the more general time-dependent solution in eq 9 shows, however, that the simple relation of eq 1 still holds (although the experimental interpretation of the time-dependent kinetics might be more problematic). To see this, we substitute for $\mathbf{J}$ in terms of the real symmetric $\mathbf{B}$ in eq 9 and explicitly assume that at zero time the population of the molecular species is zero

$$\mathbf{g}(t) = \frac{K_{\mathrm{eq}}(\mathrm{A,B|AB})}{Q_{\mathrm{AB}}}\int_{0}^{t}\mathrm{d}s[\mathrm{A}(s)][\mathrm{B}(s)]\mathrm{e}^{\mathbf{SBS}^{-1}(t-s)}\mathbf{r} \qquad (18)$$

Expanding the exponential operator as a polynomial series, one notes that $\mathbf{J}^{n} = (\mathbf{SBS}^{-1})^{n} = \mathbf{SB}^{n}\mathbf{S}^{-1}$, and hence the matrixes $\mathbf{S}$ and $\mathbf{S}^{-1}$ can be factored out on either side of the exponential, yielding

$$\mathbf{g}(t) = \frac{K_{\mathrm{eq}}(\mathrm{A,B|AB})}{Q_{\mathrm{AB}}}\int_{0}^{t}\mathrm{d}s[\mathrm{A}(s)][\mathrm{B}(s)]\mathbf{S}\mathrm{e}^{\mathbf{B}(t-s)}\mathbf{S}\mathbf{k}^{1} \qquad (19)$$

where we have again used the fact that $\mathbf{r} = \mathbf{S}^{2}\mathbf{k}^{1}$. Writing the forward flux as $R^{1\rightarrow j}(t)$, we have

$$R^{1\rightarrow j}(t) = \frac{K_{\mathrm{eq}}(\mathrm{A,B|AB})}{Q_{\mathrm{AB}}}\int_{0}^{t}\mathrm{d}s[\mathrm{A}(s)][\mathrm{B}(s)](\mathbf{k}^{j})^{\mathrm{T}}(\mathbf{S}\mathrm{e}^{\mathbf{B}(t-s)}\mathbf{S})\mathbf{k}^{1} \qquad (20)$$

The reverse flux $R^{j\rightarrow 1}(t)$ follows immediately as Provided the

$$R^{j\rightarrow 1}(t) = \frac{K_{\mathrm{eq}}(\mathrm{C,D|AB})}{Q_{\mathrm{AB}}}\int_{0}^{t}\mathrm{d}s[\mathrm{C}(s)][\mathrm{D}(s)](\mathbf{k}^{1})^{\mathrm{T}}(\mathbf{S}\mathrm{e}^{\mathbf{B}(t-s)}\mathbf{S})\mathbf{k}^{j} \qquad (21)$$

populations of C and D in the reverse reaction are set up appropriately to match those of A and B in the forward reaction, the integrals of eqs 20 and 21 will be identical because the matrix $\mathbf{S}\mathrm{e}^{\mathbf{B}(t-s)}\mathbf{S}$ is real symmetric. Hence the ratio of the time-dependent fluxes for the forward and reverse reactions still obeys eq 1 even in the case of a shallow well and/or high temperatures, where time-independent rate coefficients may not be well-defined.

The above discussion provides both intuitive and formal justification for the common practice of assuming that the forward and reverse bimolecular rate coefficients in collision-complex-forming reactions are related by the equilibrium constant of reactants and products in order to infer thermodynamic data from experimental measurements. We have shown this to be so (1) regardless of the pressure, (2) regardless of the presence of additional product channels, and (3) even under non-steady-state conditions. The generalization of the proof to multiple-well problems is transparent and hence will not be dealt with here.

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