Some Considerations on the Fundamentals of Chemical Kinetics: Steady State, Quasi-Equilibrium, and Transition State Theory

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ABSTRACT: The elementary reaction sequence $A \rightleftharpoons I \longrightarrow$ Products is the simplest mechanism for which the steady-state and quasi-equilibrium kinetic approximations can be applied. The exact integrated solutions for this chemical system allow inferring the conditions that must fulfil the rate constants for the different approximations to hold. A graphical approach showing the behavior of the exact and approximate intermediate concentrations might help to clarify the use of these methods in the teaching of chemical kinetics. Finally, the previously acquired ideas on the approximate kinetic methods lead to the proposal that activated complexes in steady state rather than in quasi-equilibrium with the reactants might be a closer to reality alternative in the mathematical development of Transition State Theory (TST), leading to an expression for the rate constant of an elementary irreversible reaction that differs only in the factor $1-\kappa$ (κ being the transmission coefficient) with respect to that given by conventional TST, and to an expression for the equilibrium constant of an elementary reversible reaction more compatible with that predicted by chemical thermodynamics.

■ A LITTLE HISTORY

When deriving the rate law corresponding to the mechanism of a complex chemical reaction in order to compare it with the one found in the laboratory, it is often mandatory to eliminate the concentrations of the reaction intermediates, expressing them as a function of the concentrations of other chemical species experimentally accessible (reactants, products, and potential catalysts or inhibitors). To do so, we have two main alternatives: the steady-state and quasi-equilibrium approximations.

The steady-state approximation was first proposed by Chapman and Underhill in 1913 for the photochemically induced reaction between chlorine and hydrogen in the gas phase.[1] Afterwards, the potential value of this method was progressively accepted: it was soon realized that in many kinetic studies the rate law experimentally found in the laboratory matched the one obtained from a chemically-acceptable proposed mechanism provided that the concentrations of the chemical species involved as very reactive intermediates (I) were eliminated by equalling their rate of formation to their rate of disappearance. This would mean that $d[I]/dt \cong 0$.[2-4] Several physical chemistry[5-8] and chemical kinetics[9] textbooks deal with this topic in some depth.

In this contribution it will be defended that a graphical approach might be the best solution to explain to students at the advanced undergraduate level not only the steady-state approximation but also that of the quasi-equilibrium. Finally, the ideas developed in the former sections will be applied in order to discuss whether the steady state or the quasi-equilibrium is the best choice of approximate method for the activated complex of an elementary reaction involved in Transition State Theory (TST).

■ A SIMPLE MECHANISM WITH EXACT KINETIC INTEGRATED SOLUTIONS

The Exact Solutions

Let us start considering the following simple mechanism:

$$A \quad \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \quad I \quad \xrightarrow{k_2} \quad Products \tag{1}$$

Since the three reactions involved in that mechanism are unimolecular, the differential laws corresponding to the reactant and intermediate concentrations are, respectively:

$$\frac{d[A]}{dt} = - k_1 [A] + k_{-1} [I] \tag{2}$$

$$\frac{d[I]}{dt} = k_1 [A] - k_{-1} [I] - k_2 [I] \tag{3}$$

The advantage of illustrating the conditions required for the steady-state and quasi-equilibrium approximations to hold with a sequence of unimolecular (instead of bimolecular) reactions is that we know in this case the exact analytical solutions for the concentrations of the reactant and intermediate at different instants during the course of the reaction:

$$[A] = \frac{[A]_o}{\omega_1 - \omega_2} [(k_1 - \omega_2) e^{-\omega_1 t} - (k_1 - \omega_1) e^{-\omega_2 t}] \tag{4}$$

$$[I] = \frac{k_1 [A]_o}{\omega_1 - \omega_2} (e^{-\omega_2 t} - e^{-\omega_1 t}) \tag{5}$$

where parameters ω_1 and ω_2 are algebraic combinations of the three rate constants involved:

$$\omega_1 = \frac{1}{2} \{k_1 + k_{-1} + k_2 + \left[(k_1 + k_{-1} + k_2)^2 - 4\, k_1\, k_2 \right]^{\frac{1}{2}} \} \tag{6}$$

$$\omega_2 = \frac{1}{2} \{k_1 + k_{-1} + k_2 - \left[(k_1 + k_{-1} + k_2)^2 - 4\, k_1\, k_2 \right]^{\frac{1}{2}} \} \tag{7}$$

The integrated laws (eqs 4 and 5) have been obtained by integration of the corresponding differential laws (eqs 2 and 3) using a matrix-based method.[10] The validity of these exact solutions can be verified by consulting different sources,[11,12] and they have been experimentally confirmed for the oxidation of thiols by Cr(VI).[13-16] Otherwise, the integrated laws can be checked straightforwardly by differentiation, leading to the differential laws derived from the mechanism considered (eq 1).

An interesting parameter to discuss later the application of the steady-state and quasi-equilibrium approximations is the time elapsed when the intermediate reaches its maximum concentration. By obtaining d[I]/dt from eq 5 and equating the result to zero, it can be inferred that:

$$t_{max} = \frac{1}{\omega_1 - \omega_2} \ln \frac{\omega_1}{\omega_2} \tag{8}$$

First Approximation

According to eqs 6 and 7, both parameters ω_1 and ω_2 are positive, but with $\omega_1 > \omega_2$. This means that the exponential function whose exponent is $-\omega_1 t$ approaches the zero value much

faster than the function whose exponent is $-\omega_2 t$ (Figure 1). Thus, there exists an instant that we may call t_2 so that for $t \geq t_2$ the only exponential function still different enough from zero will be the second, and then eqs 4 and 5 can be approximated to:

$$[A] \cong \frac{(\omega_1 - k_1)\,[A]_o}{\omega_1 - \omega_2}\, e^{-\omega_2 t} \tag{9}$$

$$[I] \cong \frac{k_1\,[A]_o}{\omega_1 - \omega_2}\, e^{-\omega_2 t} \tag{10}$$
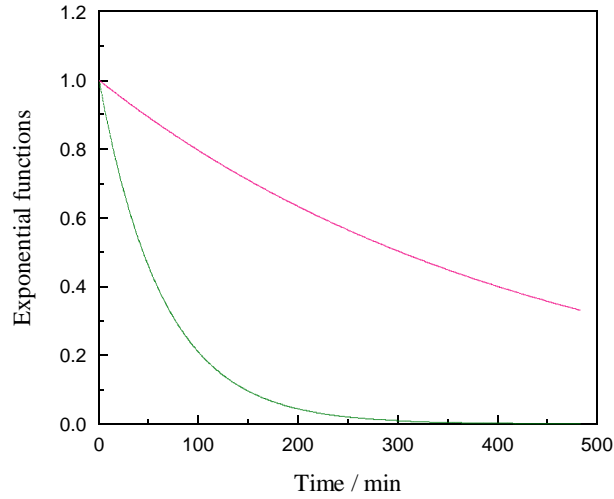
Figure 1. Dependence of the exponential functions $e^{-\omega_1 t}$ (green plot) and $e^{-\omega_2 t}$ (purple plot) for the mechanistic scheme formed by two unimolecular consecutive reactions, the first reversible and the second irreversible, with $k_1 = k_{-1} = k_2 = 1.00 \times 10^{-4}$ s^{-1}.

Since the approximations that will be developed in the following sections (steady state and quasi-equilibrium) will assume the fulfilment of eqs 9 and 10, it is important to notice that these new approximations can be applied only after a certain instant of the reaction course ($t \geq t_2$) and never from the beginning itself. As we will see later, this happens after the instant at which the intermediate attains its maximum concentration ($t_2 = t_{max}$).

■ STEADY-STATE APPROXIMATION

Mathematical Approach to the Steady-State Method

Let us consider firstly the particular case corresponding to the mechanism for which the first, reversible step is slow in the forward direction and fast in the backward direction, whereas the second, irreversible step is also fast, that is $k_{-1} \gg k_1$ and $k_2 \gg k_1$. Under these conditions, we can approximate:

$$\left[(k_1 + k_{-1} + k_2)^2 - 4\,k_1 k_2 \right]^{\frac{1}{2}} \cong k_{-1} + k_2 \tag{11}$$

Replacing this result into eqs 6 and 7:

$$\omega_1 \cong k_{-1} + k_2 \tag{12}$$

$$\omega_2 \cong \frac{1}{2}\,k_1 \tag{13}$$

and the new results into eqs 9 and 10 (remember that k_1 is negligible against both k_{-1} and k_2):

$$[A] \cong [A]_o\, e^{-\frac{1}{2} k_1 t} \tag{14}$$

$$[I] \cong \frac{k_1\,[A]_o}{k_{-1} + k_2}\, e^{-\frac{1}{2} k_1 t} \tag{15}$$

From eqs 14 and 15:

$$[\text{I}] \ \cong \ \frac{k_1}{k_{-1} + k_2} \ [\text{A}] \qquad\qquad (16)$$

Finally, from eq 16:

$$k_1 \, [\text{A}] - (\, k_{-1} + k_2 \,) \, [\text{I}] \ \cong \ 0 \qquad\qquad (17)$$

and from eq 3:

$$\frac{d[\text{I}]}{dt} \ \cong \ 0 \qquad\qquad (18)$$

which is precisely the equation serving as definition for the steady-state approximation. We can thus conclude that application of this approximate method to a particular intermediate requires that it disappear in steps much faster than the one corresponding to its formation (for the particular case considered here, $k_{-1} \gg k_1$ and $k_2 \gg k_1$). Thus, an intermediate in steady state always is present in the reacting system in minute concentrations, since its tendency to disappear (reactivity) is much higher than its tendency to be formed. Small free radicals would be an excellent example of steady-state intermediates indeed.

Graphical Approach to the Steady-State Method

Now, we can represent the exact solution of [I] at different instants during the course of the reaction (eq 5) and compare it with the approximate solution provided by the steady-state condition (eq 16):

$$[I]_{ss} = \frac{k_1}{k_{-1} + k_2} [A] \tag{19}$$

Since both [I] (exact solution) and $[I]_{ss}$ (steady-state approximate solution) are directly proportional to $[A]_o$, it will be enough to compare the exact ratio (from eq 5):
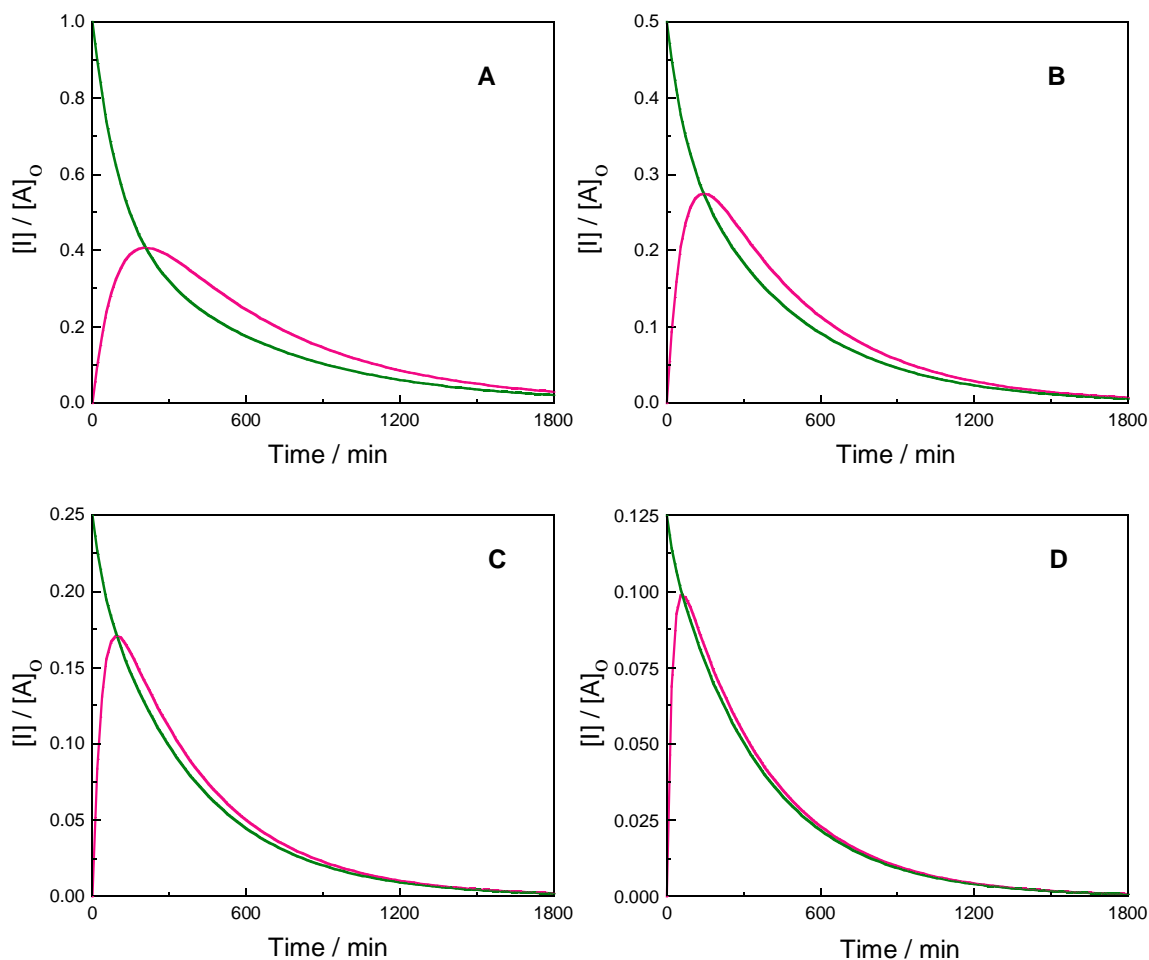
$$\frac{[I]}{[A]_o} = \frac{k_1}{\omega_1 - \omega_2} (e^{-\omega_2 t} - e^{-\omega_1 t}) \tag{20}$$

with the steady-state approximate ratio (from eqs 4 and 19):

$$\frac{[I]_{ss}}{[A]_o} = \frac{k_1}{k_{-1} + k_2} \frac{1}{\omega_1 - \omega_2} f(t) \tag{21}$$

involving the function of time:

$$f(t) = (k_1 - \omega_2) e^{-\omega_1 t} - (k_1 - \omega_1) e^{-\omega_2 t} \tag{22}$$

Figure 2. Comparison between the kinetic plots showing the [Intermediate]/[Reactant]$_o$ ratio as obtained using either the steady-state approximation (green plots) or the exact rate law (purple plots) for the mechanistic scheme formed by two unimolecular consecutive reactions, the first reversible and the second irreversible, with $k_1 = 1.00 \times 10^{-4}$ s^{-1}, and $k_{-1} = k_2 = 5.00 \times 10^{-5}$ s^{-1} (A), 1.00×10^{-4} s^{-1} (B), 2.00×10^{-4} s^{-1} (C) and 4.00×10^{-4} s^{-1} (D).

In order to reach conclusions about the relative values that must take the rate constants of the elementary reactions (k_1, k_{-1}, and k_2) for the steady state approximation to hold, k_1 has been kept constant, whereas the other two rate constants have been progressively increased keeping $k_{-1} = k_2$. In Figure 2, the four bell-shaped curves showing a maximum (in purple)

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correspond to the exact concentration ratio (eq 20), whereas the four continuously-decreasing curves (in green) correspond to the steady-state approximate concentration ratio (eqs 21 and 22). We can see that, for each set of rate constants, the exact and approximate curves cross exactly at the maximum of the intermediate concentration, given that eq 18 (the steady-state condition) is only exact at that maximum (the only point with a horizontal tangent). We can also see that each time rate constants k_{-1} and k_2 are multiplied by a factor of 2 (keeping k_1 constant), the approximate curve gets closer and closer to the exact curve after its maximum. For the case $k_{-1} = k_2 = 4\,k_1$ (Figure 2, D) the steady-state approximate curve is almost coincidental with the exact curve once the maximum is reached, meaning that the steady-state condition qualifies as an excellent approximation for this set of rate constants. Thus, we can consider that the time necessary for the steady-state condition to be fulfilled is coincident with the time elapsed when the intermediate concentration reaches its maximum value $(t_2 \cong t_{\max})$

The ratio between the exact and approximate intermediate concentrations increases with time, reaching a plateau when $t \to \infty$ (Figure 3). The asymptotic value of the ratio is (from eqs 9, 10 and 19):

$$\lim_{t \to \infty} \frac{[I]}{[I]_{ss}} = \frac{k_{-1} + k_2}{\omega_1 - k_1} \tag{23}$$

and, from eq 12, it can be inferred that:

$$\lim_{k_{-1}, k_2 \to \infty} \left(\frac{k_{-1} + k_2}{\omega_1 - k_1} \right) = 1 \tag{24}$$
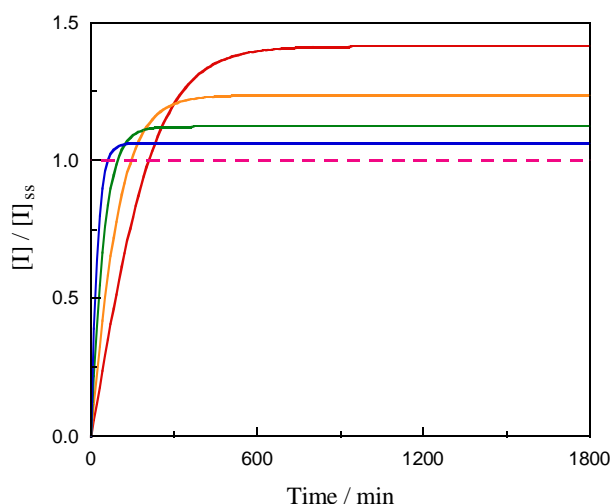
Figure 3. Ratio between the exact intermediate concentration ([I]) and that obtained using the steady-state approximation ([I]$_{ss}$) for the mechanistic scheme formed by two unimolecular consecutive reactions, the first reversible and the second irreversible, with $k_1 = 1.00 \times 10^{-4}$ s^{-1}, and $k_{-1} = k_2 = 5.00 \times 10^{-5}$ s^{-1} (red), 1.00×10^{-4} s^{-1} (orange), 2.00×10^{-4} s^{-1} (green) and 4.00×10^{-4} s^{-1} (blue). The dashed line shows the limit corresponding to a perfect fulfilment of the steady-state approximation ([I] = [I]$_{ss}$).

In other words, when k_1 is kept constant and both k_{-1} and k_2 are gradually increased, the limit of the asymptotic value of the ratio [I]/[I]$_{ss}$ decreases approaching unity (Figure 4, bottom), corresponding to a perfect fulfilment of the steady-state-approximation. Simultaneously, the time elapsed when the intermediate reaches its maximum concentration (coincident with the time interval required for the steady-state approximation to hold) also decreases approaching zero (Figure 4, top). We can, therefore, define an intermediate in steady state as a very reactive intermediary chemical species that has already reached its maximum concentration.

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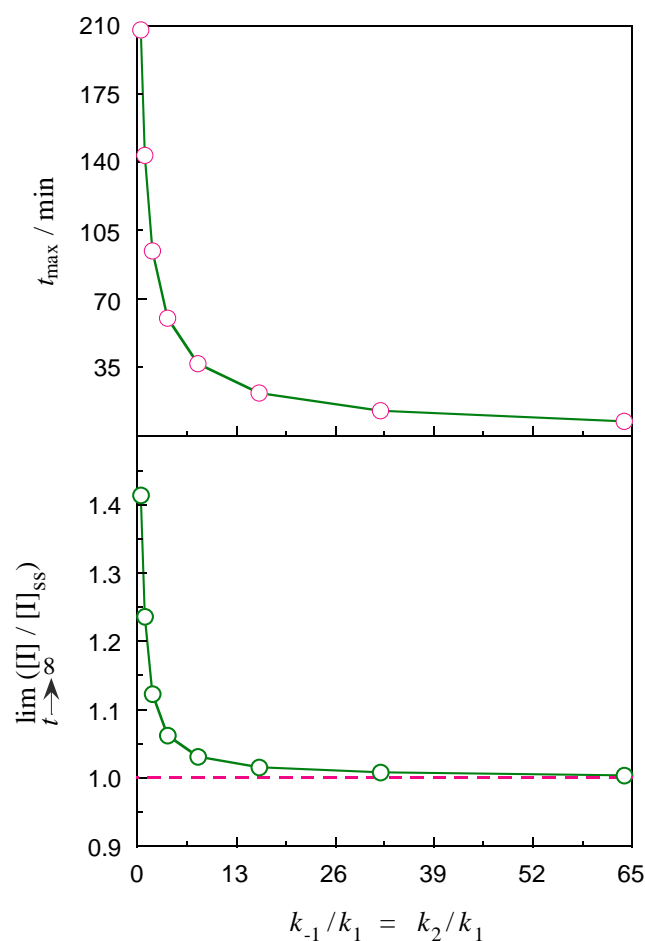
Figure 4. Dependencies of the time elapsed when the intermediate reaches its maximum concentration (top) and the limit at infinite time of the ratio between the exact intermediate concentration ([I]) and that obtained using the steady-state approximation ([I]$_{ss}$) (bottom) on the fast/slow ratio of rate constants (keeping $k_{-1} = k_2$) for the mechanistic scheme formed by two unimolecular consecutive reactions, the first reversible and the second irreversible. The dashed line shows the limit corresponding to a perfect fulfilment of the steady-state approximation ([I] = [I]$_{ss}$).

■ QUASI-EQUILIBRIUM APPROXIMATION

Mathematical Approach to the Quasi-Equilibrium Method

Let us consider as a second particular case the one corresponding to the mechanism (eq 1) for which the first, reversible step is fast in both directions whereas the second, irreversible step is slow, that is $k_1 \gg k_2$ and $k_{-1} \gg k_2$. Under these conditions, we can approximate:

$$\left[(k_1 + k_{-1} + k_2)^2 - 4\, k_1 k_2 \right]^{\frac{1}{2}} \cong k_1 + k_{-1} \tag{25}$$

and replacing this result into eqs 6 and 7:

$$\omega_1 \cong k_1 + k_{-1} \tag{26}$$

$$\omega_2 \cong \frac{1}{2}\, k_2 \tag{27}$$

and the new results into eqs 9 and 10 (remember that this time k_2 is negligible against both k_1 and k_{-1}):

$$[A] \cong \frac{k_{-1}\,[A]_o}{k_1 + k_{-1}}\; e^{-\frac{1}{2} k_2 t} \tag{28}$$

$$[I] \cong \frac{k_1\,[A]_o}{k_1 + k_{-1}}\; e^{-\frac{1}{2} k_2 t} \tag{29}$$

From eqs 28 and 29:

$$[\text{I}] \cong \frac{k_1}{k_{-1}}[\text{A}] \tag{30}$$

Since the equilibrium constant (referred to concentrations instead of to activities) associated to the first, reversible step of the mechanism considered (eq 1) can be expressed as the ratio of the rate constants corresponding to the forward and backward elementary reactions:

$$K_c = \frac{k_1}{k_{-1}} \tag{31}$$

eq 30 can also be written as:

$$K_c \cong \frac{[\text{I}]}{[\text{A}]} \tag{32}$$

which is precisely the equation obtained when the quasi-equilibrium approximation is applied to the first, reversible step of the mechanism considered. We can thus conclude that this approximate method requires that the reversible step to which is applied be fast in both directions with respect to the rate-determining step of the mechanism (for the particular case considered here, $k_1 \gg k_2$ and $k_{-1} \gg k_2$). In other words, this method is useful for intermediates formed in very fast, reversible reactions only. Those formed in acid-base reactions (both reversible and fast) would be an excellent example of quasi-equilibrium intermediates indeed.

Graphical Approach to the Quasi-Equilibrium Method

We can represent the exact solution for [I] at different instants during the course of the reaction (eq 5) and compare it with the approximate solution provided by the quasi-equilibrium condition (eq 30):

$$[I]_{qe} \quad = \quad \frac{k_1}{k_{-1}} \; [A] \tag{33}$$
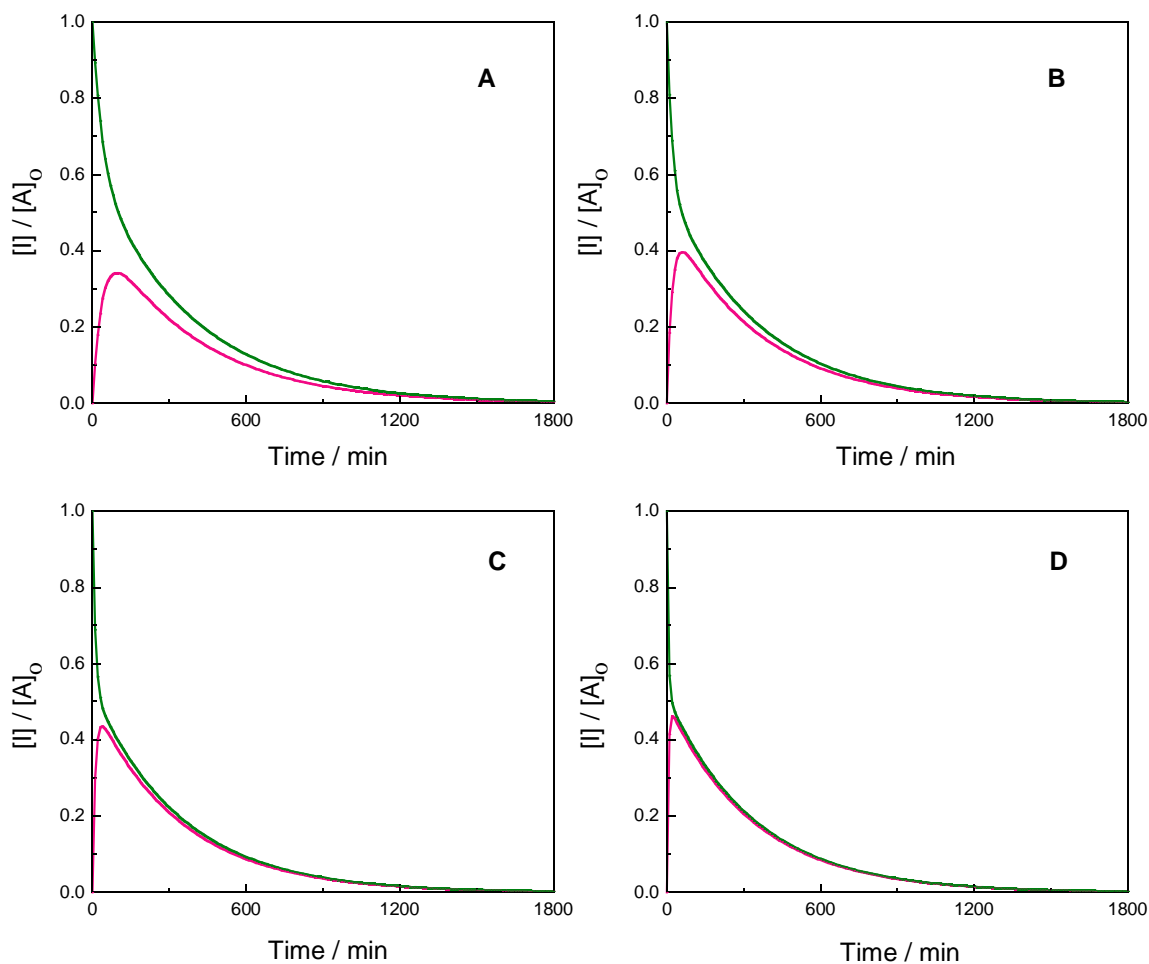
Figure 5. Comparison between the kinetic plots showing the [Intermediate]/[Reactant]$_o$ ratio as obtained using either the quasi-equilibrium approximation (green plots) or the exact rate

law (purple plots) for the mechanistic scheme formed by two unimolecular consecutive reactions, the first reversible and the second irreversible, with $k_1 = k_{-1} = 2.00 \times 10^{-4}$ s^{-1} (A), 4.00×10^{-4} s^{-1} (B), 8.00×10^{-4} s^{-1} (C) and 1.60×10^{-3} s^{-1} (D) , and $k_2 = 1.00 \times 10^{-4}$ s^{-1}.

Since both [I] (exact solution) and [I]$_{qe}$ (quasi-equilibrium approximate solution) are directly proportional to [A]$_o$, it will be enough to compare the exact ratio (eq 20) with the quasi-equilibrium approximate ratio (from eqs 4 and 33):

$$\frac{[I]_{qe}}{[A]_o} = \frac{k_1}{k_{-1}} \frac{1}{\omega_1 - \omega_2} f(t) \tag{34}$$

where $f(t)$ has the same meaning than in eq 22.

In order to reach conclusions about the relative values that must have the rate constants of the elementary reactions (k_1, k_{-1} and k_2) for the quasi-equilibrium approximation to hold, k_2 has been kept constant, whereas the other two rate constants have been progressively increased keeping $k_1 = k_{-1}$. In Figure 5, the four bell-shaped curves showing a maximum (in purple) correspond to the exact concentration ratio (eq 20), whereas the four continuously-decreasing curves (in green) correspond to the quasi-equilibrium approximate concentration ratio (eq 34). We can see that each time rate constants k_1 and k_{-1} are multiplied by a factor of 2 (keeping k_2 constant), the approximate curve gets closer and closer to the exact curve after its maximum. For the case $k_1 = k_{-1} = 16\ k_2$ (Figure 5, D) the quasi-equilibrium approximate curve is almost coincidental with the exact curve once the maximum is reached, meaning that the quasi-equilibrium condition qualifies as an excellent approximation for this set of rate constants. Thus, we can consider again (as happened with the steady-state condition) that the

time necessary for the quasi-equilibrium condition to be fulfilled is coincident with the time elapsed when the intermediate concentration reaches its maximum value $(t_2 \cong t_{max})$. Incidentally, we can infer from these plots that the quasi-equilibrium approximation does not require (as the steady-state approximation does) that the intermediate be present in minute concentration, provided that it is formed in a fast, reversible step.
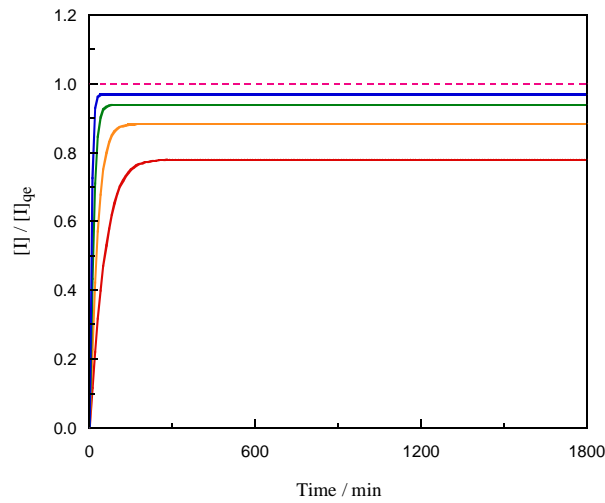
Figure 6. Ratio between the exact intermediate concentration ([I]) and that obtained using the quasi-equilibrium approximation ([I]$_{qe}$) for the mechanistic scheme formed by two unimolecular consecutive reactions, the first reversible and the second irreversible, with $k_1 = k_{-1} = 2.00 \times 10^{-4}$ s^{-1} (red), 4.00×10^{-4} s^{-1} (orange), 8.00×10^{-4} s^{-1} (green) and 1.60×10^{-3} s^{-1} (blue), and $k_2 = 1.00 \times 10^{-4}$ s^{-1}. The dashed line shows the limit corresponding to a perfect fulfilment of the quasi-equilibrium approximation ([I] = [I]$_{qe}$).

The ratio between the exact and approximate intermediate concentrations increases with time, reaching a plateau when $t \rightarrow \infty$ (Figure 6). The asymptotic value of the ratio is (from eqs 9, 10 and 33):

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$$\lim_{t \to \infty} \frac{[I]}{[I]_{qe}} = \frac{k_{-1}}{\omega_1 - k_1} \tag{35}$$

and, from eq 26, it can be inferred that:

$$\lim_{k_1, k_{-1} \to \infty} \left(\frac{k_{-1}}{\omega_1 - k_1} \right) = 1 \tag{36}$$

In other words, when k_2 is kept constant and both k_1 and k_{-1} are gradually increased, the limit of the asymptotic value of the ratio $[I]/[I]_{qe}$ increases approaching unity (Figure 7, bottom), corresponding to a perfect fulfilment of the quasi-equilibrium approximation. Simultaneously, the time elapsed when the intermediate reaches its maximum concentration (coincident with the time interval required for the quasi-equilibrium approximation to hold) decreases approaching zero (Figure 7, top). We can, therefore, define an intermediate in quasi-equilibrium with the reactants as an intermediary chemical species formed in a fast, reversible step and that has already reached its maximum concentration.
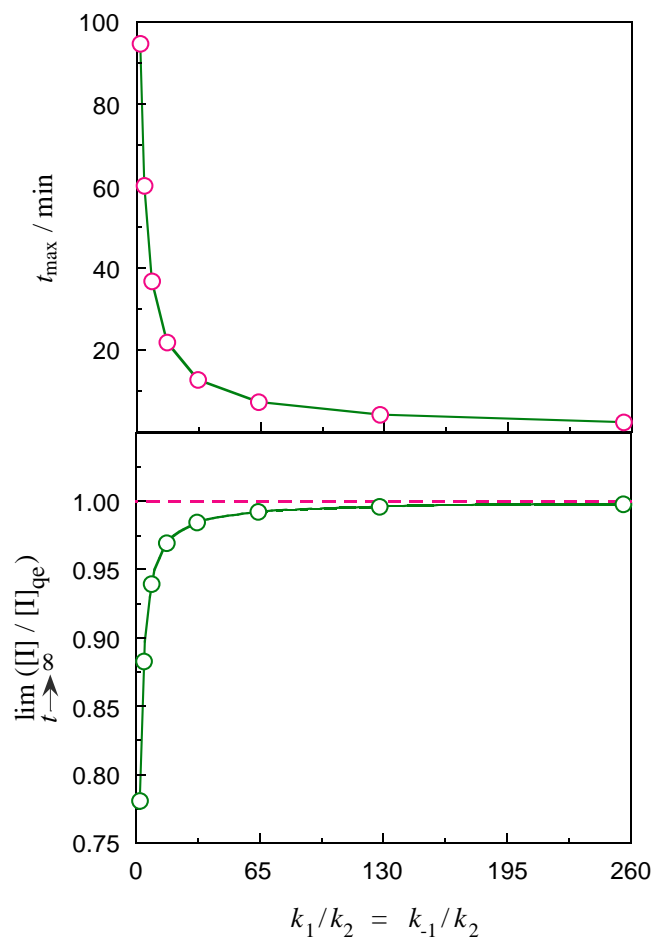
Figure 7. Dependencies of the time elapsed when the intermediate reaches its maximum concentration (top) and the limit at infinite time of the ratio between the exact intermediate concentration ($[I]$) and that obtained using the quasi-equilibrium approximation ($[I]_{qe}$) (bottom) on the fast/slow ratio of rate constants (keeping $k_1 = k_{-1}$) for the mechanistic scheme formed by two unimolecular consecutive reactions, the first reversible and the second irreversible. The dashed line shows the limit corresponding to a perfect fulfilment of the quasi-equilibrium approximation ($[I] = [I]_{qe}$).
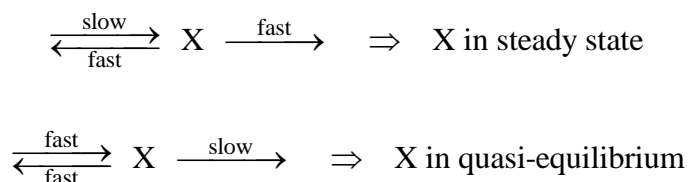
■ TRANSITION STATE THEORY

Activated Complexes: in Quasi-Equilibrium or in Steady State?

The thermodynamic formulation of TST assumes as a basic hypothesis that the activated complex of an elementary reaction is in quasi-equilibrium with the reactants. However, we have seen that, in the simple mechanism considered (eq 1), the combination of rate constants $k_1 \ll k_{-1}, k_2$ leads to the steady-state approximation, whereas the combination $k_1, k_{-1} \gg k_2$ leads to the quasi-equilibrium approximation. This situation is illustrated in Scheme 1.

Scheme 1. Combinations of Slow/Fast Steps Leading to Each Approximation

$$\xrightleftharpoons[\text{fast}]{\text{slow}} \ X \ \xrightarrow{\text{fast}} \quad \Rightarrow \quad X \text{ in steady state}$$

$$\xrightleftharpoons[\text{fast}]{\text{fast}} \ X \ \xrightarrow{\text{slow}} \quad \Rightarrow \quad X \text{ in quasi-equilibrium}$$

Since, in the case of TST, the energy barrier is associated with the forward direction of the reversible step leading to the formation of the activated complex, whereas decomposition of the latter either in the direction of the reactants or in that of the products does not imply any energetic requirement, we may wonder whether the activated complex is actually in quasi-equilibrium or in steady state instead. At first view, and taking into account the information given in Scheme 1, it seems that the steady-state alternative might be more reasonable: formation of the activated complex is expected to be the slow step, whereas its decompositions in both the reactant and product directions are expected to be rather fast.

The mathematical expression obtained from TST (thermodynamic formulation) for the rate constant of an elementary reaction is the well-known Eyring equation:

$$k \;=\; \kappa \; \frac{k_{\mathrm{B}} T}{h} \; (c^{\mathrm{o}})^{1-n} \; e^{\frac{\Delta S^{\mathrm{o}}_{\neq}}{R}} \; e^{-\frac{\Delta H^{\mathrm{o}}_{\neq}}{RT}} \tag{37}$$

where κ is the transmission coefficient, n is the kinetic order of the elementary reaction (molecularity), c^{o} is the standard-state concentration (arbitrarily taken as 1 mol dm^{-3}), $\Delta H^{\mathrm{o}}_{\neq}$ and $\Delta S^{\mathrm{o}}_{\neq}$ are the standard activation enthalpy and entropy, whereas k_{B}, h and R are the Boltzmann, Planck and ideal gas universal constants, respectively. The factor $(c^{\mathrm{o}})^{1-n}$ did not appear in the original Eyring equation, but more recently it has been incorporated in order to assure its dimensional homogeneity.[17]

Let us now consider the case of an elementary reaction, for instance (although not necessarily) that of a bimolecular process involving two different reactants, written as:

$$\mathrm{A} + \mathrm{B} \;\; \underset{k^{*}_{-1}}{\overset{k^{*}_{1}}{\rightleftharpoons}} \;\; [\mathrm{A-B}]_{\neq} \;\; \xrightarrow{k^{*}_{2}} \;\; \mathrm{P} + \mathrm{Q} \tag{38}$$
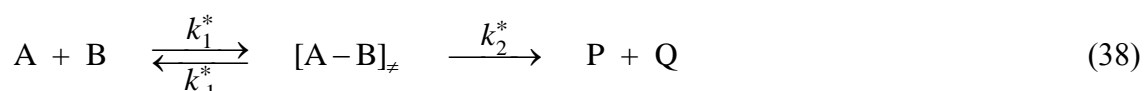
where A and B are the reactants, $[\mathrm{A-B}]_{\neq}$ the activated complex, and P and Q the reaction products. The symbols above and below the arrows carry an asterisk in order to emphasize that they are not true rate constants, although there units are the ones corresponding to either second-order (k^{*}_{1}, in M^{-1} s^{-1}) or first-order (k^{*}_{-1} and k^{*}_{2}, in s^{-1}) rate constants. We may designate these new parameters (k^{*}_{1}, k^{*}_{-1}, and k^{*}_{2}) as microscopic rate constants to differentiate them from the macroscopic rate constant for the elementary reaction (k).

If we consider now that the activated complex of the elementary reaction is in steady state rather than in quasi-equilibrium (what would be more consistent with the situation reflected in Scheme 1), we can write that the derivative $d[(A-B)_{\neq}]/dt$ equals zero:

$$k_1^* \, [A] \, [B] \; - \; k_{-1}^* \, [(A-B)_{\neq}] \; - \; k_2^* \, [(A-B)_{\neq}] \;\; = \;\; 0 \tag{39}$$

allowing to isolate the activated complex concentration as:

$$[(A-B)_{\neq}] \;\; = \;\; \frac{k_1^* \, [A] \, [B]}{k_{-1}^* + k_2^*} \tag{40}$$

The equilibrium constant of formation of the activated complex from the reactants (referred to concentrations, in M^{-1}) can be expressed as:

$$K_{\neq} \;\; = \;\; \frac{k_1^*}{k_{-1}^*} \tag{41}$$

and from eqs 40 and 41:

$$[(A-B)_{\neq}] \;\; = \;\; \frac{k_{-1}^* \, K_{\neq} \, [A] \, [B]}{k_{-1}^* + k_2^*} \tag{42}$$

On the other hand, we can consider three alternative fates the activated complex may suffer in a particular vibration of the normal mode of frequency $\nu_{\neq}$: (i) the activated complex

breaks down into the reaction products (forward direction, probability κ_f), (ii) the activated complex breaks down into the reactants (backward direction, probability κ_b), (iii) the oscillation is not energetic enough for the breakdown to take place (probability κ_o). The three probabilities are interrelated by:

$$\kappa_f + \kappa_b + \kappa_o = 1 \tag{43}$$

According to TST parameters k_{-1}^*, and k_2^* can be calculated as:

$$k_{-1}^* = \kappa_b \, \nu_{\neq} = (1 - \kappa_f - \kappa_o) \, \nu_{\neq} \tag{44}$$

$$k_2^* = \kappa_f \, \nu_{\neq} \tag{45}$$

and from eqs 42, 44 and 45:

$$[(A-B)_{\neq}] = \frac{(1 - \kappa_f - \kappa_o) \, K_{\neq} \, [A] \, [B]}{1 - \kappa_o} \tag{46}$$

The rate of formation of products can be expressed in two alternative ways, the first being a phenomenological law from chemical kinetics and the second a theoretical law from TST:

$$\frac{d[P]}{dt} = k \, [A] \, [B] \tag{47}$$

$$\frac{d[P]}{dt} = k_2^* \, [(A-B)_{\neq}] \tag{48}$$

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Using eqs 45-48:

$$ k = \frac{(1-\kappa_{\mathrm{f}}-\kappa_{\mathrm{o}})\,\kappa_{\mathrm{f}}\,\nu_{\neq}\,K_{\neq}}{1-\kappa_{\mathrm{o}}} \tag{49} $$

Finally, TST allows us to write:

$$ \nu_{\neq}\,K_{\neq} = \frac{k_{\mathrm{B}}T}{h}\,(c^{\mathrm{o}})^{1-n}\,e^{\frac{\Delta S_{\neq}^{\mathrm{o}}}{R}}\,e^{-\frac{\Delta H_{\neq}^{\mathrm{o}}}{RT}} \tag{50} $$

and replacing into eq 49:

$$ k = \frac{(1-\kappa_{\mathrm{f}}-\kappa_{\mathrm{o}})\,\kappa_{\mathrm{f}}}{1-\kappa_{\mathrm{o}}}\,\frac{k_{\mathrm{B}}T}{h}\,(c^{\mathrm{o}})^{1-n}\,e^{\frac{\Delta S_{\neq}^{\mathrm{o}}}{R}}\,e^{-\frac{\Delta H_{\neq}^{\mathrm{o}}}{RT}} \tag{51} $$

TST for Reversible Elementary Reactions: Activated Complex in Quasi-Equilibrium

Consider now the following elementary reversible reaction (not involving any intermediate species):

$$ \mathrm{A} + \mathrm{B} \;\underset{k_{-1}^{*}}{\overset{k_{1}^{*}}{\rightleftarrows}}\; [\mathrm{A-B}]_{\neq} \;\underset{k_{-2}^{*}}{\overset{k_{2}^{*}}{\rightleftarrows}}\; \mathrm{P} + \mathrm{Q} \tag{52} $$
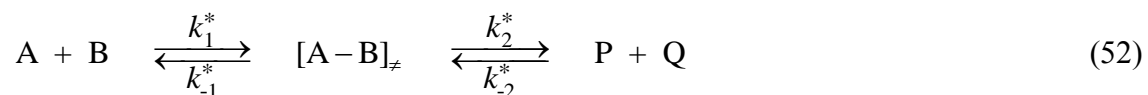
TST can be applied to the forward and backward reactions, assuming that the activated complex is in quasi-equilibrium with the reactants and products, respectively, and the following expressions for the corresponding rate constants are derived:

$$k_f \;=\; \kappa_f \; \frac{k_B T}{h} \; (c^o)^{1-n_f} \; e^{\frac{\Delta S^o_{\neq,f}}{R}} \; e^{-\frac{\Delta H^o_{\neq,f}}{RT}} \tag{53}$$

$$k_b \;=\; \kappa_b \; \frac{k_B T}{h} \; (c^o)^{1-n_b} \; e^{\frac{\Delta S^o_{\neq,b}}{R}} \; e^{-\frac{\Delta H^o_{\neq,b}}{RT}} \tag{54}$$

From eqs 53 and 54, we obtain for the equilibrium constant of the reversible reaction (referred to concentrations):

$$K_c \;=\; \frac{k_f}{k_b} \;=\; \frac{\kappa_f}{\kappa_b} \; (c^o)^{n_b - n_f} \; e^{\frac{\Delta S^o}{R}} \; e^{-\frac{\Delta H^o}{RT}} \tag{55}$$

the standard reaction enthalpy and entropy being related to the activation parameters corresponding to the forward and backward reactions by:

$$\Delta H^o \;=\; \Delta H^o_{\neq,f} - \Delta H^o_{\neq,b} \tag{56}$$

$$\Delta S^o \;=\; \Delta S^o_{\neq,f} - \Delta S^o_{\neq,b} \tag{57}$$

In addition, the equilibrium constant referred to activities is related to that referred to concentrations by the equation:

$$K_{\mathrm{a}} \;=\; K_{\mathrm{c}} \, (c^{\mathrm{o}})^{n_{\mathrm{f}} - n_{\mathrm{b}}} \prod_{i=1}^{n_{\mathrm{f}} + n_{\mathrm{b}}} \gamma_{i,e}^{\nu_i} \tag{58}$$

where $\gamma_{i,e}$ are the activity coefficients of reactants and products at equilibrium, and ν_i the corresponding stoichiometric coefficients ($\nu_i < 0$ for reactants and $\nu_i > 0$ for products). Assuming that the reacting mixture is dilute enough ($\gamma_{i,e} \approx 1$), eqs 43, 55, and 58 lead to:

$$K_{\mathrm{a}} \;=\; \frac{\kappa_{\mathrm{f}}}{\kappa_{\mathrm{b}}} \, e^{\frac{\Delta S^{\mathrm{o}}}{R}} \, e^{-\frac{\Delta H^{\mathrm{o}}}{RT}} \tag{59}$$

The latter equation is not consistent with the well-known thermodynamic expression for the equilibrium constant unless we assume that $\kappa_{\mathrm{f}} = \kappa_{\mathrm{b}}$. This assumption might be too far-reaching because the chemical bonds that must break down for the reaction products to be generated from the activated complex are different from those involved for the generation of the reactants.

Moreover, if the activated complex is in quasi-equilibrium with both reactants and products of the reversible reaction, we can write:

$$[\mathrm{A{-}B}]_{\neq} \;=\; K_{\neq,1} \, [\mathrm{A}] \, [\mathrm{B}] \;=\; \frac{k_1^*}{k_{-1}^*} \, [\mathrm{A}] \, [\mathrm{B}] \tag{60}$$

$$[\mathrm{A{-}B}]_{\neq} \;=\; K_{\neq,2} \, [\mathrm{P}] \, [\mathrm{Q}] \;=\; \frac{k_{-2}^*}{k_2^*} \, [\mathrm{P}] \, [\mathrm{Q}] \tag{61}$$

where $K_{\neq,1}$ and $K_{\neq,2}$ are the equilibrium constants (referred to concentrations) for the formation of the activated complex from the reactants and from the products, respectively.

Since, according to eq 60, the concentration of the activated complex should decrease as the reaction advances (due to the decrease in the reactant concentrations), whereas, according to eq 61, it should increase (due to the increase in the product concentrations), these two equations are mutually incompatible unless we contemplate the existence of two activated complexes, one in quasi-equilibrium with the reactants (crossing the activation barrier from reactants to products) and the other in quasi-equilibrium with the products (crossing the activation barrier from products to reactants). However, this interpretation might be in conflict with the principle of microscopic reversibility.

TST for Reversible Elementary Reactions: Activated Complex in Steady State

If we consider now that the activated complex of the elementary reversible reaction (eq 52) is in steady state rather than in quasi-equilibrium (what would be certainly more consistent with the situation reflected in Scheme 1), application of eqs 43 and 51 yields for the rate constants of the forward and backward reactions:

$$k_f = \frac{\kappa_b \, \kappa_f}{1 - \kappa_o} \, \frac{k_B T}{h} \, (c^o)^{1-n_f} \, e^{\frac{\Delta S^o_{\neq,f}}{R}} \, e^{-\frac{\Delta H^o_{\neq,f}}{RT}} \tag{62}$$

$$k_b = \frac{\kappa_f \, \kappa_b}{1 - \kappa_o} \, \frac{k_B T}{h} \, (c^o)^{1-n_b} \, e^{\frac{\Delta S^o_{\neq,b}}{R}} \, e^{-\frac{\Delta H^o_{\neq,b}}{RT}} \tag{63}$$

and for the equilibrium constants of the reversible reaction referred to concentrations (from eqs 62 and 63):

$$K_c = \frac{k_f}{k_b} = (c^o)^{n_b - n_f} \, e^{\frac{\Delta S^o}{R}} \, e^{-\frac{\Delta H^o}{RT}} \tag{64}$$

and to activities (from eqs 58 and 64, assuming again that $\gamma_{i,e} \approx 1$):

$$K_a = e^{\frac{\Delta S^o}{R}} \, e^{-\frac{\Delta H^o}{RT}} \tag{65}$$

the latter equation being identical to the one predicted by chemical thermodynamics (unlike eq 59).

We can see that the notable symmetry of eqs 62 and 63 with respect to the probability coefficients corresponding to the breakdown of the activated complex in the product or reactant directions (k_f is directly proportional to $\kappa_b \, \kappa_f$ and k_b to $\kappa_f \, \kappa_b$) makes that the equilibrium constant be independent of them. Thus, application of the steady state instead of the quasi-equilibrium as approximate method in TST leads to a higher degree of compatibility between chemical kinetics and chemical thermodynamics (total if activity coefficients are excluded).

Moreover, by application of the steady-state condition to the activated complex involved in the elementary reversible reaction considered (eq 52), we can write that the derivative $d[(A-B)_{\neq}]/dt$ equals zero:

$$k_1^* \, [A] \, [B] + k_{-2}^* \, [P] \, [Q] - k_{-1}^* \, [(A-B)_{\neq}] - k_2^* \, [(A-B)_{\neq}] = 0 \tag{66}$$

$$[(A-B)_{\neq}] = \frac{k_1^* \, [A] \, [B] + k_{-2}^* \, [P] \, [Q]}{k_{-1}^* + k_2^*} \tag{67}$$

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We can see that eq 67 does not raise any compatibility problem as eqs 60 and 61 do. Assuming that the activated complex is present in steady state rather than in quasi-equilibrium, there is no need to invoke the existence of two activated complexes: one crossing the energy barrier in the forward direction and the other in the backward direction. The latter hypothesis seems to be incompatible with the very nucleus of TST itself: this theory admits that the activated complex can go in the two directions since, even in the case of an elementary irreversible reaction, the formation of the activated complex from the reactants is assumed to be a reversible process (see eq 38).

Simplification of the Modified Eyring Equation

Given that the vibrational energy required to break the activated complex is rather low (only weak chemical bonds must be broken to go forward to the reaction products or backward to the reactants), eq 51 can be simplified by assuming that $\kappa_{\mathrm{o}} \cong 0$:

$$k \quad = \quad \kappa \, (1-\kappa) \, \frac{k_{\mathrm{B}} T}{h} \, (c^{\mathrm{o}})^{1-n} \, e^{\frac{\Delta S_{\neq}^{\mathrm{o}}}{R}} \, e^{-\frac{\Delta H_{\neq}^{\mathrm{o}}}{RT}} \tag{68}$$

where, according to the definition of transmission coefficient, it has been taken into account that $\kappa_{\mathrm{f}} = \kappa$. Thus, the equation obtained assuming that the activated complex is in steady state (eq 68) is identical to the one given by conventional TST (eq 37) except for the factor $1-\kappa$. Therefore, the value of the rate constant now obtained shows the same temperature dependence than that obtained from conventional TST but it is numerically lower (since $1-\kappa$ < 1). This is indeed an expected result because the quasi-equilibrium approximation can be

inferred from eq 42 simply by assuming that $k_{-1}^* \gg k_2^*$. This situation would correspond to an activated complex being simultaneously in steady state and in quasi-equilibrium with the reactants. Thus, conventional TST tends to ignore the decrease in the concentration of the activated complex caused by its decomposition into the reaction products (contribution of parameter k_2^*), considering only the one caused by its decomposition into the reactants (contribution of parameter k_{-1}^*). The value of parameter k_2^* might not be negligible after all against that of k_{-1}^* as required by conventional TST. In other words, although the new factor $1-\kappa$ would be unimportant provided that $\kappa \ll 1$ ($k_{-1}^* \gg k_2^*$ in eq 42), this condition might be difficult to reach in most cases.

Boltzmann Distribution Approach

Some textbooks[18] avoid the application of the quasi-equilibrium condition by assuming that the energies of the activated complex quasi-molecules and of the reactant molecules follow a Boltzmann distribution. However, this solution might be misleading. In fact, the final equations obtained from the quasi-equilibrium approach and from the Boltzmann distribution approach are identical (both converge into eq 37). Thus, the Boltzmann approach would also lead to eq 59 for the equilibrium constant of an elementary reversible reaction, in clear incompatibility with the prediction made by chemical thermodynamics. The apparent reason is the fact that the Boltzmann distribution of energies would require that the system composed by the reactant molecules and activated complexes be, not only in thermal equilibrium, but also of fixed composition. The latter condition requires a chemical equilibrium between the reactant molecules and activated complex quasi-molecules. The existence of a process

converting the activated complex into the reaction products (contribution of k_2^* in eq 42) renders this condition impossible to reach in the case of elementary irreversible reactions.

Convergence of the Three Different Approaches

Only for an elementary reversible reaction and only once the chemical equilibrium state is reached, application of both the quasi-equilibrium hypothesis and the Boltzmann distribution law to the activated complex would give completely satisfactory results. Effectively, application in this case of eq 67 at $t = \infty$ leads to:

$$[(A-B)_{\neq}]_e \;=\; \frac{k_1^* \, [A]_e \, [B]_e \;+\; k_{-2}^* \, [P]_e \, [Q]_e}{k_{-1}^* \;+\; k_2^*} \tag{69}$$

and, since the equilibrium constant referred to concentrations associated to the elementary reversible reaction considered (eq 52) can be expressed as:

$$K_c \;=\; \frac{k_1^* \, k_2^*}{k_{-1}^* \, k_{-2}^*} \;=\; \frac{[P]_e \, [Q]_e}{[A]_e \, [B]_e} \tag{70}$$

by combining eqs 69 and 70:

$$[(A-B)_{\neq}]_e \;=\; \frac{k_1^*}{k_{-1}^*} \, [A]_e \, [B]_e \;=\; \frac{k_{-2}^*}{k_2^*} \, [P]_e \, [Q]_e \tag{71}$$

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From eqs 60, 61 and 71 it follows that both the quasi-equilibrium and steady-state treatments lead to the same prediction for the concentration of the activated complex of an elementary reversible reaction at equilibrium ($t = \infty$). This situation can be considered as the only state for which the three different approaches potentially applicable in TST (quasi-equilibrium, Boltzmann distribution, and steady state) converge.

Concluding Remark

We have seen that the steady-state approximate method is a good choice for the activated complexes involved in elementary reactions (both irreversible and reversible), since the only condition required by this approximation is that the intermediary species to which it is applied be in minute concentration (provided that the reaction time t be such that $t \geq t_{max}$, where t_{max} is the time at which the highly reactive intermediate attains its maximum concentration). Certainly, if we are looking for examples of chemical species in steady state, the activated complex should be regarded as the perfect candidate.

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Notes

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