Time-Dependent Statistical Mechanics
10. Classical theory of chemical kinetics

Hans C. Andersen

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One of the most recent applications of classical linear response theory is to the theory of chemical reaction rate constants, although this is one of the more important and interesting applications of time dependent statistical mechanics, from a chemistry point of view. At first glance it looks like an unusual and unphysical way of constructing a theory, but in fact it is valid.

Lecture
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Before discussing this, we want to review and extend some remarks we made about a linear response situation that we discussed briefly a few lectures ago.

1 Macroscopic description of first order reaction kinetics

Recall that in getting a microscopic expression for the self diffusion coefficient as an equilibrium time correlation function we compared the predictions of the macroscopic diffusion equation with the predictions of the microscopic equations of motion and assume that both were valid for long enough time scales and distance scales.

We now want to do the same thing for chemical reaction rate constants.

For simplicity, we shall restrict our attention to first order reactions, but the discussion could certainly be generalized to more complicated reactions.

1.1 Chemical rate equations

Let's suppose that the reaction involves conversion of an A molecule to a B molecule and vice versa.

$$\mathrm{A} \xrightarrow{k_f} \mathrm{B}$$

$$\mathrm{B} \xrightarrow{k_r} \mathrm{A}$$

The forward and reverse rate constants are k_f and k_r.

The chemical rate equations are

$$\frac{dN_A}{dt} = -k_F N_A + k_r N_B$$

$$\frac{dN_B}{dt} = k_F N_A - k_r N_B$$

At equilibrium, each of these derivatives is zero, and we have

$$-k_f N_A + k_r N_B = 0$$

$$\frac{N_{B.eq}}{N_{A,eq}} = \frac{k_f}{k_r} = K$$

where K is the equilibrium constant of the reaction.

Suppose the system is close to equilibrium, but the concentrations are not quite at their equilibrium values. We want to obtain the time dependence of the numbers of molecules of each type.

Let $\delta N_A(t) = N_A(t) - N_{A,eq}$ and $\delta N_B(t) = N_B(t) - N_{B,eq}$. Note that because of conservation of molecules, $\delta N_A(t) = -\delta N_B(t)$. Then

$$\begin{aligned}\frac{d\delta N_B(t)}{dt} &= k_f\left(N_{A,eq} + \delta N_A(t)\right) - k_r\left(N_{B,eq} + \delta N_B(t)\right) \\ &= -(k_f + k_r)\delta N_B(t)\end{aligned}$$

Therefore

$$\delta N_B(t) \propto \exp\left(-(k_f + k_r)t\right)$$

Hence

$$\delta N_B(t) = \delta N_B(0)\exp\left(-(k_f + k_r)t\right)$$

Let's let $k = k_f + k_r$. Then

$$\delta N_B(t) = \delta N_B(0) \exp(-kt) \tag{1}$$

Similarly, we have

$$\delta N_A(t) = \delta N_A(0) \exp(-kt)$$

1.2 Comments on the validity of chemical rate equations

Simple kinetic equations based on first order kinetics, second order kinetics, etc., are valid only if there is a separation of time scales between the characteristic times for the motions of the reactant molecules to move around among their accessible states and the time scale for the chemical reaction to take place.

For example, consider a first order process that involves breaking a chemical bond. In the reactant molecule, there is presumably a vibrational mode of the molecule that involves the relative motion of the two atoms in the bond. That vibration has a frequency and a time scale associated with it. Moreover, there are other important time scales for the motion of the molecule, e.g. internal rotations, motions relative to nearby solvent molecules, etc. When you assume first order kinetics you assume that all reactant molecules are equally likely to undergo reaction in the next time time interval. Moreover, you are in effect assuming that the reaction takes place instantaneously. But the reaction itself takes a certain amount of time to take place; i.e. it takes some time for the atoms to move from a configuration in which the bond exists to one in which the bond is broken.

Let's use the symbol t_{mol} to denote a typical molecular time that represents the time scale for the motions mentioned above. In general, it is of the order of picoseconds or shorter, depending on the complexity of the reactive species.

The fact that the kinetic equations regard the reaction as instantaneous is the clue that they hold only on a long time scale. This is analogous to the situation with self diffusion, where the diffusion equation holds on a long time scale but not for very shortest times characteristic of the motion of the molecule.

Thus the solutions to the kinetic equations give a meaningful description of the time dependence of the numbers of reactant molecules only if the reaction is slow on a microscopic time scale. In the present case, this means that k^{-1}, k_f^{-1} and k_r^{-1}, which are the characteristic times for the chemical reaction to take place to an appreciable extent, must all be times large compared with the microscopic time t_{mol}, which is of the order of picoseconds.

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Time scales

molecular (microscopic) time scale: τ_{mol}

e.g. vibrational period, rotational time, time it takes a molecule to come apart once it has enough energy to do so

typically picoseconds or less

macroscopic time scale: k^{-1}, k_f^{-1}, k_r^{-1}

characteristic time for the relaxation of the concentrations of reactants and products to equilibrium

Typical conditions for the validity of chemical rate equations

$$\tau_{mol} << k^{-1}$$

$$\tau_{mol} << t$$

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Perturbation of a chemically reactive system

Suppose we have the system at chemical equilibrium.

We do something to perturb the equilibrium just slightly.

As a result, $N_B/N_A \neq K$.

We watch the system relax back to equilibrium.

There are a variety of ways in which to do this, some of them physical and some unphysical.

- We could add a little extra reactant or product to the system and stir.
- We could raise the temperature slightly by heating or by microwave radiation.
- We could apply a field that lowers the energy of the reactants without lowering the energy of the products and without affecting the entropy of either. This will shift the equilibrium to having more A molecules. Then we turn off the field.

The first two are physical, and the third is unphysical.

No matter which of these we do, we are confident that the relaxation of the system back to equilibrium will be in accordance with the chemical rate equation above, if this relaxation takes place a time scale mentioned above in which the chemical rate laws are valid.

When we apply linear response theory to calculate the rate constants, we will use the third method.

2 Microscopic description of first order reaction kinetics

2.1 Classical mechanics description of the reactive system

We now want to set up a microscopic description of the chemically reactive system we have been discussing. We shall consider one special case, but the methods we develop can be applied to more general situations.

We suppose that A and B correspond to different forms of what is essentially the same molecule. E.g., they might be different conformational isomers or geometric isomers, or they might differ by an internal proton transfer.

We suppose that we have one such molecule in the system that also contains solvent molecules.

We suppose that we can construct a coordinate system for the reactive molecule such that there is one specific coordinate, called the reactive coordinate q, such that when $q < q^*$ the molecule is an A (reactant) molecule and when $q > q^*$ the molecule is a B (product) molecule. The value $q = q^*$ corresponds to the transition state between reactants and products.[1] The momentum conjugate to q will be called p. All the other coordinates and momenta will be called Q, P. This includes other coordinates and momenta associated with the reactive molecule and all the coordinates and momenta associated with the solvent molecules.

We suppose that the overall Hamiltonian for the system is

$$H(q,p,Q,P) = \frac{p^2}{2m} + V(q,Q,P) + H_0(Q,P)$$

Thus we are assuming that the reactive coordinate is basically a Cartesian

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[1] It may seem unreasonable to think that one can be that precise in specifying the boundary between where the molecule is A and where it is B. It is as if we are saying that the molecule changes abruptly from an A molecule to a B molecule the instant it crosses from $q < q^*$ to $q > q^*$. If you examine closely the way the effects this assumption has on the development of the theory, you will find that it does not affect the calculated value of the rate constant, provided that there is the separation of time scales mentioned above.

coordinate (rather than, for example, an angle).[2]

We need a dynamical variable, i.e. a function of q, p, Q, P that represents the number of reactant molecules in the system, n_A. The choice is an obvious one. This variable should involve only q and should be of the form

$$\begin{aligned} n_A(q,p,Q,P) &= 1 \quad \text{if } q < q^* \\ &= 0 \quad \text{if } q > q^* \end{aligned}$$

Similarly

$$\begin{aligned} n_B(q,p,Q,P) &= 1 \quad \text{if } q > q^* \\ &= 0 \quad \text{if } q < q^* \end{aligned}$$

Note that

$$n_A(q,p,Q,P) + n_B(q,p,Q,P) = 1$$

for all states of the system, as it should be. The total number of reactive molecules is 1.

The equilibrium distribution function is

$$P_{eq}(q,p,Q,P) = (const.) \times \exp\left(-H(q,p,Q,P)/k_B T\right)$$

Next we want to get the microscopic analog of the equilibrium constant relationship. The ensemble average $\langle n_A \rangle$ is the average number of reactant molecules in the system.

$$\langle n_A \rangle = \int dqdpdQdP\, n_A(q) P_{eq}(q,p,Q,P) = \int_{-\infty}^{q^*} dq \int dpdQdP\, n_A(q) P_{eq}(q,p,Q,P)$$

Similarly

$$\langle n_B \rangle = \int dqdpdQdP\, n_B(q) P_{eq}(q,p,Q,P) = \int_{q^*}^{\infty} dq \int dpdQdP\, n_B(q) P_{eq}(q,p,Q,P)$$

The ratio should be the equilibrium constant.

$$K = \frac{\langle n_B \rangle}{\langle n_A \rangle} = \frac{\int dqdpdQdP\, n_B(q) \exp\left(-H(q,p,Q,P)/k_b T\right)}{\int dqdpdQdP\, n_B(q) \exp\left(-H(q,p,Q,P)/k_b T\right)}$$

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[2] The choice of coordinates for any specific problem is a complicated technical matter that we won't go into. Other choices must sometimes be made. The example we are discussing is sufficient for discussing the general principles associated with the theory of chemical reaction rates.

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Classical mechanics description of the reactive system

Consider one special case, but the methods we develop can be applied to more general situations:

A and B correspond to different forms of what is essentially the same molecule.

They might be different conformational isomers or geometric isomers, or they might differ by an internal proton transfer.

We suppose that we have one such molecule in the system that also contains solvent molecules. The system is of macroscopic size.

Coordinates and momenta. Choose a coordinate system for the reactive molecule such that there is one specific coordinate, called the reactive coordinate q, such that:

when $q < q^*$ the molecule is an A (reactant) molecule, and

when $q > q^*$ the molecule is a B (product) molecule.

The value $q = q^*$ corresponds to the transition state between reactants and products.

The momentum conjugate to q will be called p.

The set of all the other coordinates and momenta will be called Q, P. This includes those associated with the reactive molecule and all the solvent molecules.

Hamiltonian

$$H(q, p, Q, P) = \frac{p^2}{2m} + V(q, Q, P) + H_0(Q, P)$$

We are assuming that the reactive coordinate is basically a Cartesian coordinate (rather than, for example, an angle).

Dynamical variables of special interest. We need a dynamical variable that represents the number of reactant molecules in the system, n_A. The choice is an obvious one.

$$\begin{aligned} n_A(q,p,Q,P) &= 1 \quad \text{if } q < q^* \\ &= 0 \quad \text{if } q > q^* \end{aligned}$$

Similarly

$$\begin{aligned} n_B(q,p,Q,P) &= 1 \quad \text{if } q > q^* \\ &= 0 \quad \text{if } q < q^* \end{aligned}$$

Note that

$$n_A(q,p,Q,P) + n_B(q,p,Q,P) = 1$$

for all states of the system, as it should be. The total number of reactive molecules is 1.

The equilibrium distribution function

$$P_{eq}(q,p,Q,P) = (const.) \times \exp\left(-H(q,p,Q,P)/k_B T\right)$$

The microscopic analog of the equilibrium constant relationship

$$\langle n_A \rangle = \int dqdpdQdP\, n_A(q) P_{eq}(q,p,Q,P) = \int_{-\infty}^{q^*} dq \int dpdQdP\, n_A(q) P_{eq}(q,p,Q,P)$$

Similarly

$$\langle n_B \rangle = \int dqdpdQdP\, n_B(q) P_{eq}(q,p,Q,P) = \int_{q^*}^{\infty} dq \int dpdQdP\, n_B(q) P_{eq}(q,p,Q,P)$$

The ratio should be the equilibrium constant.

$$K = \frac{\langle n_B \rangle}{\langle n_A \rangle} = \frac{\int dqdpdQdP\, n_B(q) \exp\left(-H(q,p,Q,P)/k_b T\right)}{\int dqdpdQdP\, n_B(q) \exp\left(-H(q,p,Q,P)/k_b T\right)}$$

Modifications needed to describe a very dilute solution of reacting molecules.

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2.2 Linear response theory

We want to invent an external field that can perturb the concentration of reactants and products. It is relatively straightforward to do this. We invent a field that couples to n_A. We add $-g(t)n_A(q)$ to the Hamiltonian of the system.

Let's specify that $g(t)$ has the following behavior. We turn it on slowly at negative times and by the time $t = 0$ the system has adjusted to the presence of that additional field. The effect of this adjustment will be to have more reactant and less product than when the field is absent and the system is at equilibrium. Then we turn off the field and watch the concentrations relax back to those given by the equilibrium constant relation.

Comparison with our general linear response theory show that:

- the variable to which the field coupled in the general theory was called B, and in the special case under consideration, it is n_A;
- the variable whose time evolution was observed was called A, and in the special case is n_A.

Applying our result for the time dependence after abruptly turning off a steady field, we get

$$\langle n_A(t)\rangle = \langle n_A\rangle_{eq} + \frac{g_0}{k_B T} C_{\delta n_A \delta n_A}(t)$$

or

$$\langle n_A(t)\rangle - \langle n_A\rangle_{eq} = \frac{g_0}{k_B T} C_{\delta n_A \delta n_A}(t)$$

Also, for $t = 0$,

$$\begin{aligned}\langle n_A(0)\rangle - \langle n_A\rangle_{eq} &= \frac{g_0}{k_B T} C_{\delta n_A \delta n_A}(0)\\ &= \frac{g_0}{k_B T} \langle (\delta n_A)^2\rangle_{eq}\end{aligned}$$

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Linear response theory

We want to invent an external field that can perturb the concentration of reactants and products.

We invent a field that couples to n_A. We add $-g(t)n_A(q)$ to the Hamiltonian of the system.

Choose $g(t)$ to have the following behavior.

- We turn it on slowly at negative times.
- When $t = 0$ the system has adjusted to the presence of that additional field. The effect of this adjustment will be to have more reactant and less product than when the field is absent and the system is at equilibrium.
- We turn off the field and watch the concentrations relax back to those given by the equilibrium constant relation.

Comparison with linear response theory for classical systems

- the variable to which the field coupled in the general theory was called B, and in the special case under consideration, it is n_A;
- the variable whose time evolution was observed was called A, and in the special case is n_A.

Applying our general result for this case, we get

$$\langle n_A(t)\rangle = \langle n_A\rangle_{eq} + \frac{g_0}{k_BT} C_{\delta n_A \delta n_A}(t)$$

or

$$\langle n_A(t)\rangle - \langle n_A\rangle_{eq} = \frac{g_0}{k_BT} C_{\delta n_A \delta n_A}(t)$$

Also, for $t = 0$,

$$\begin{aligned}
\langle n_A(0)\rangle - \langle n_A\rangle_{eq} &= \frac{g_0}{k_BT} C_{\delta n_A \delta n_A}(0) \\
&= \frac{g_0}{k_BT} \langle (\delta n_A)^2\rangle_{eq}
\end{aligned}$$

end of slide

3 Comparison of microscopic and macroscopic descriptions of the linear response

Let's collect the two results we obtained.

$$\delta N_A(t) = \delta N_A(0) \exp\left(-kt\right)$$

$$\langle n_A(t) \rangle - \langle n_A \rangle_{eq} = \frac{g_0}{k_B T} C_{\delta n_A \delta n_A}(t)$$

There are some unimportant differences between the two scenarios. One is that in the macroscopic description there were a large number of reactive molecules that did not influence each others chemical reaction. In the microscopic description, there is only one reactive molecule. But if we take this microscopic result and scale it up by increasing the number of molecules, it should be of the same form if the reactive molecules do not influence each others chemical reaction.

Now, as we were in the case of self diffusion, we have two different descriptions of the same process. The microscopic description works on all time scales. The macroscopic description works on time scales of the order of the reaction time, but not on microscopic time scales. Hence we can conclude that

$$\frac{g_0}{k_B T} C_{\delta n_A \delta n_A}(t) = \delta N_A(0) \exp\left(-kt\right) \tag{2}$$

but this is valid only for times long compared with microscopic times. In particular, we consider times t that are such that

$$t >> t_{mol}$$

and Eq. (2) holds in this time range.

We also use the microscopic theory to calculate $\delta N_A(0)$. We get

$$\delta N_A(0) = \langle \delta n_A(0) \rangle = \frac{g_0}{k_B T} \langle (\delta n_A)^2 \rangle_{eq} = \frac{g_0}{k_B T} C_{\delta n_A \delta n_A}(0)$$

(Thus, we see that Eq. (2) holds at $t = 0$. Note however, that there is a range of times between 0 and some time large compared with t_{mol} in which Eq. (2) does not hold.)

Putting these two together, we get

$$C_{\delta n_A \delta n_A}(t) = C_{\delta n_A \delta n_A}(0) \exp(-kt) \quad \text{for } t >> t_{mol}$$

This is a remarkable result. For times long compared with molecular times, the relaxation of concentration functions in a reactive system obeys the macroscopic rate equations and decays exponentially with the same time constant as macroscopic concentration fluctuations.

We want an expression for k. So differentiate with regard to time.

$$\dot{C}_{\delta n_A \delta n_A}(t) = -kC_{\delta n_A \delta n_A}(0) \exp(-kt) \quad \text{for } t >> t_{mol}$$

Now, choose a Δt with the following characteristics:

$$t_{mol} << \Delta t << k^{-1}$$

If there is a separation of time scales, such a Δt can be found. The equation above is valid for $t = \Delta t$. So we get.

$$\dot{C}_{\delta n_A \delta n_A}(\Delta t) = -kC_{\delta n_A \delta n_A}(0)$$

$$\begin{aligned} k &= -\frac{\dot{C}_{\delta n_A \delta n_A}(\Delta t)}{C_{\delta n_A \delta n_A}(0)} \\ &= -\frac{1}{\langle (\delta n_A)^2 \rangle_{eq}} \frac{d}{dt} \langle \delta n_A(\Delta t) \delta n_A(0) \rangle_{eq} \\ &= -\frac{1}{\langle (\delta n_A)^2 \rangle_{eq}} \langle \delta \dot{n}_A(\Delta t) \delta n_A(0) \rangle_{eq} \end{aligned}$$

Thus we have a microscopic expression for the rate constant in terms of correlation functions of concentration fluctuations in a chemically reactive system at equilibrium.

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Comparison of microscopic and macroscopic descriptions of the linear response

Let's collect the two results we obtained.

$$\delta N_A(t) = \delta N_A(0)\exp(-kt)$$

$$\langle n_A(t)\rangle - \langle n_A\rangle_{eq} = \frac{g_0}{k_B T} C_{\delta n_A \delta n_A}(t)$$

The left sides both refer to essentially the same thing.

An unimportant difference between the two results

- In the macroscopic description there were a large number of reactive molecules that did not influence each others chemical reaction.
- In the microscopic description, there is only one reactive molecule.

But if we take this microscopic description and scale it up by increasing the number of reactive molecules, it should be of the same form if the reactive molecules do not influence each others chemical reaction.

An important difference between the two results

- The microscopic description works on all time scales.
- The macroscopic description works on time scales of the order of the reaction time, but not on microscopic time scales.

$$\begin{aligned}
\delta N_A(t) &= \delta N_A(0)\exp(-kt) && \text{for } t = 0 \text{ and } t >> \tau_{mol} \\
\langle n_A(t)\rangle - \langle n_A\rangle_{eq} &= \frac{g_0}{k_B T} C_{\delta n_A \delta n_A}(t) && \text{for all } t \geq 0
\end{aligned}$$

Hence

$$\frac{g_0}{k_B T} C_{\delta n_A \delta n_A}(t) = \delta N_A(0)\exp(-kt) \quad \text{for } t = 0 \text{ and } t >> \tau_{mol}$$

or

$$C_{\delta n_A \delta n_A}(t) = C_{\delta n_A \delta n_A}(0)\exp(-kt) \quad \text{for } t = 0 \text{ and } t >> t_{mol}$$

For times long compared with molecular times, the relaxation of concentration functions in a reactive system obeys the macroscopic rate equations and decays exponentially with the same time constant as macroscopic concentration fluctuations.

We want an expression for k. Differentiate with regard to time.

$$\dot{C}_{\delta n_A \delta n_A}(t) = -k C_{\delta n_A \delta n_A}(0) \exp(-kt) \quad \text{for } t >> t_{mol}$$

Now, choose a Δt with the following characteristics:

$$t_{mol} << \Delta t << k^{-1}$$

If there is a separation of time scales, such a Δt can be found. The equation above is valid for $t = \Delta t$. So we get.

$$\dot{C}_{\delta n_A \delta n_A}(\Delta t) = -k C_{\delta n_A \delta n_A}(0)$$

$$\begin{aligned}
k &= -\frac{\dot{C}_{\delta n_A \delta n_A}(\Delta t)}{C_{\delta n_A \delta n_A}(0)} = -\frac{1}{\langle(\delta n_A)^2\rangle_{eq}} \frac{d}{dt} \langle \delta n_A(\Delta t) \delta n_A(0)\rangle_{eq} \\
k &= -\frac{1}{\langle(\delta n_A)^2\rangle_{eq}} \langle \delta \dot{n}_A(\Delta t) \delta n_A(0)\rangle_{eq}
\end{aligned}$$

Thus we have a microscopic expression for the rate constant in terms of correlation functions of concentration fluctuations in a chemically reactive system at equilibrium.

end of slide

4 Simplification of the correlation function formula for the reaction rate constant

To understand this result and its implications, we must manipulate it a bit and simplify it.

Simplifying the denominator. The denominator is

$$\left\langle (n_A - \langle n_A \rangle)^2 \right\rangle$$

But in a system with one reactive molecule $\langle n_A \rangle = x_A$, where x_A is the equilibrium mole fraction of A. So this is equal to

$$\left\langle (n_A - x_A)^2 \right\rangle = \left\langle n_A^2 - 2x_A n_A + x_A^2 \right\rangle = \left\langle n_A^2 \right\rangle - 2x_A \langle n_A \rangle + x_A^2$$

But n_A only has values 0 or 1, so $n_A^2 = n_A$. Thus this is equal to

$$x_A - 2x_A^2 + x_A^2 = x_A - x_A^2 = x_A(1 - x_A) = x_A x_B$$

Thus we have

$$k = \frac{1}{x_A x_B} \langle \delta \dot{n}_A(\Delta t) \delta n_A(0) \rangle_{eq}$$

Manipulating the location of the time derivative. We now want to get the numerator into a form in which the time derivative appears with a time argument of zero.

To do this, we need some elementary properties of correlation function. The first is that[3]

$$\dot{C}_{XY}(t) = C_{\dot{X}Y}(t)$$

The second is that[4]

$$\dot{C}_{XY}(t) = -C_{X\dot{Y}}(t)$$

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[3] The proof is straightforward.

$$\begin{aligned} \dot{C}_{XY}(t) &= \frac{d}{dt} C_{XY}(t) = \frac{d}{dt} \int d\Gamma\, P_{eq}(\Gamma) X(t,\Gamma) Y(\Gamma) \\ &= \int d\Gamma\, P_{eq}(\Gamma) \frac{\partial X(t,\Gamma)}{\partial t} Y(\Gamma) \\ &= \int d\Gamma\, P_{eq}(\Gamma) \dot{X}(t,\Gamma) Y(\Gamma) = C_{\dot{X}Y}(t) \end{aligned}$$

[4] This proof is just slightly more complicated.

$$\begin{aligned} \dot{C}_{XY}(t) &= \frac{d}{dt} C_{XY}(t) = \frac{d}{dt} \int d\Gamma\, P_{eq}(\Gamma) X(t,\Gamma) Y(\Gamma) \\ &= \frac{d}{dt} \int d\Gamma\, P_{eq}(\Gamma) X(\Gamma) Y(-t,\Gamma) \end{aligned}$$

Putting these two together, we get

$$C_{\dot{X}Y}(t) = -C_{X\dot{Y}}(t)$$

These hold for any dynamical variables X and Y.

Then

$$k = \frac{1}{x_A x_B} \langle \delta n_A(\Delta t) \delta \dot{n}_A(0) \rangle_{eq}$$

$$\begin{aligned}
&= \int d\Gamma\, P_{eq}(\Gamma) X(t,\Gamma) \frac{\partial Y(-t,\Gamma)}{\partial t} \\
&= -\int d\Gamma\, P_{eq}(\Gamma) X(t,\Gamma) \dot{Y}(-t,\Gamma) \\
&= \int d\Gamma\, P_{eq}(\Gamma) X(t,\Gamma) \dot{Y}(-t,\Gamma) = -C_{X\dot{Y}}(t)
\end{aligned}$$

In getting the third equality, we used the fact that equilibrium time correlation functions depend only on the time interval between the two arguments.

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Manipulating the location of the time derivative. We now want to get the numerator into a form in which the time derivative appears with a time argument of zero.

Some elementary properties of correlation function. The first is that

$$\dot{C}_{XY}(t) = C_{\dot{X}Y}(t)$$

The second is that

$$\dot{C}_{XY}(t) = -C_{X\dot{Y}}(t)$$

Putting these two together, we get

$$C_{\dot{X}Y}(t) = -C_{X\dot{Y}}(t)$$

These hold for any dynamical variables X and Y.

Then

$$k = \frac{1}{x_A x_B}\langle \delta n_A(\Delta t)\delta \dot{n}_A(0)\rangle_{eq}$$

end of slide

Evaluating $\delta\dot{n}_A$ We have

$$n_A(q, p, Q, P) = \Theta(q^* - q)$$

Therefore

$$\dot{n}_A(q, p, Q, P) = \delta(q^* - q)\,(-\dot{q}) = -\dot{q}\delta(q^* - q) = -\frac{p}{m}\delta(q - q^*)$$

The time derivative of n_A is sometimes called a flux.

We see that $\dot{n}_A$ is nonzero only if the reaction variable is right at the transition value of q^*.

If $p > 0$, the flux is negative, corresponding to a decrease in n_A.

If $p < 0$, the flux is negative.

Then

$$k = -\frac{1}{x_A x_B}\langle \delta n_A(\Delta t)\dot{q}\delta(q - q^*)\rangle_{eq}$$

Switching the emphasis to products. Note that $\delta n_A = -\delta n_B$.

So we have

$$k = \frac{1}{x_A x_B} \langle \delta n_B(\Delta t) \dot{q} \delta(q - q^*) \rangle_{eq}$$

Also $\delta n_B = n_B - x_B$.

Since $\langle \dot{q} \delta(q - q^*) \rangle_{eq} = m^{-1} \langle p \rangle_{eq} \langle \delta(q - q^*) \rangle_{eq} = 0$, we can replace δn_B by n_B.

Thus we have

$$k = \frac{1}{x_A x_B} \langle n_B(\Delta t) \dot{q} \delta(q - q^*) \rangle_{eq}$$

An expression for the forward rate constant. Recall

$$K = \frac{k_f}{k_r} = \frac{x_B}{x_A}$$

$$k = k_f + k_r$$

Solve for k_f in terms of k.

$$k = k_f + \frac{x_A}{x_B} k_f = \left(1 + \frac{x_A}{x_B} k_f\right) = \frac{k_f}{x_B}$$

The final result is

$$k_f = \frac{1}{x_A} \langle n_B(\Delta t) \dot{q} \delta(q - q^*) \rangle_{eq}$$

The rate constant is the correlation function of:

- the flux along the reactive coordinate at the transition state at zero time and
- the population of product at time Δt.

The derivation has been for a system with a single reactive molecule. But if the system contains a large number of reactive molecules at high dilution, the same result is obtained.

This is an exact expression for the forward rate constant of a reaction in terms of a time correlation function for a system at equilibrium. In particular, the system is at chemical equilibrium.

This is the form of the result for the rate constant that is most easy to discuss physically.

5 Discussion of the correlation function formula for the rate constant

Each of the quantities in the average are dynamical variables. We can write the result as an integral over phase space in the following way.

$$k_f = \frac{1}{x_A} \int d\Gamma \, P_{eq}(\Gamma) n_B(\Delta t; \Gamma) \dot{q}(0; \Gamma) \delta \left(q(0; \Gamma) - q^* \right)$$

The only states that contribute to the integral are those whose q coordinate is right at the boundary between reactants and products. There is a factor of P_{eq}, so one important factor that governs the rate is what is the probability of being at that boundary in an equilibrium system. We shall call that boundary the 'transition state' or the transition surface. In fact, in equilibrium the system spends most of its time in low energy states well on the reactant or product side of the boundary. The boundary surface is often at high energy compared to the predominant states of reactants and products. Thus this expression will automatically contain a factor related to the exponential of the negative of the energy of at the transition state.

All states with $q = q^*$ potentially contribute to the integral. However, we see that there is a factor of $n_B(\Delta t; \Gamma)$. Thus the only states that contribute are those that are on the transition surface and that are such that at some time Δt in the future the system is on the product side of that surface.

The contribution that a state Γ makes is also proportional to the value of $\dot{q}$. Thus it is positive for positive $\dot{q}$ and negative for negative $\dot{q}$.

Thus we have the following result:

- Points on the transition surface that have positive $\dot{q}$ (i.e. that are moving from reactants to products at time 0) and that will end up as products at time Δt contribute positively to the rate constant.

- Points on the transition surface that have negative $\dot{q}$ (i.e. that are moving from products to reactants at time 0) and that nevertheless end up as products at time Δt contribute negatively to the rate constant).

slide

Discussion. Write the result as an integral over phase space.

$$k_f = \frac{1}{x_A} \int d\Gamma \, P_{eq}(\Gamma) n_B(\Delta t; \Gamma) \dot{q}(0; \Gamma) \delta\left(q(0; \Gamma) - q^*\right)$$

The $\delta\left(q(0;\Gamma) - q^*\right)$ factor. The only states that contribute to the integral are those whose q coordinate is right at the boundary between reactants and products, which is the transition state.

The $P_{eq}(\Gamma)$ factor. The boundary surface is often at high energy compared to the predominant states of reactants and products.

Thus this expression will automatically contain a factor related to the exponential of the negative of the energy at the transition state.

The $n_B(\Delta t; \Gamma)$ factor. The only states that contribute are those such that at time Δt in the future the system will be on the *product* side of that surface.

The $\dot{q}(0; \Gamma)$ factor. The contribution that a state Γ makes is positive for positive $\dot{q}$ and negative for negative $\dot{q}$.

Thus

- Points on the transition surface that have positive $\dot{q}$ (i.e. that are moving from reactants to products at time 0) and that will end up as products at time Δt contribute positively to the rate constant.
- Points on the transition surface that have negative $\dot{q}$ (i.e. that are moving from products to reactants at time 0) and that nevertheless end up as products at time Δt contribute negatively to the rate constant).

end of slide

6 Two limiting case pictures of chemical reaction dynamics

This formally exact result for the rate constant leads naturally to a classical version of the traditional transition state theory of rate constants. This theory is most often associated with the name of Eyring in the chemistry literature, but it also owed much to a Wigner, who was a very famous physicist.

To lead into this discussion, let's consider two limiting situations. The reaction is taking place in a multidimensional phase space. Let's consider just the coordinate variables. The space whose axes represents the coordinates is called configuration space. The space is still multidimensional. Let's imagine a diagram in configuration space that has contours of constant energy. We can indicate this schematically in two dimensions. There are deep basins corresponding to reactants and products. These basins are separated, in general, by a region of higher energy. We draw an imaginary dividing plane that separates reactants and products. The reaction coordinate q is some coordinate perpendicular to that plane. One can imagine that on this surface there are one or more saddle points (or mountain passes) that are the lowest energy points on the surface. It is likely that trajectories that cross the surface cross near such saddle points, because more energy is required to cross at other points.

Let's for simplicity assume that there is one such mountain pass. Then it would be convenient to regard the reaction coordinate as the coordinate that corresponds to going over that pass along a minimum energy path. There are very many coordinate directions that are perpendicular to that reaction coordinate, corresponding to the other degrees of freedom of the molecule and the degrees of freedom of the other molecules in the system.

6.1 The first limiting case

The first limiting case to consider would be one in which the mountain pass has steep sides in all directions, falling down sharply in the direction of the reaction coordinate but rising sharply in the other directions. The motion of the system will be like that of a particle sliding on such a surface.

If the system has $\dot{q} > 0$ at $t = 0$ it will be moving toward the product side and will rather quickly experience forces that pull it downhill toward products. It is unlikely that the system will return to the transition surface; instead it will fall into the part of configuration space of products. Eventually, after staying there for a while, it may recross, but that will be at a time much larger than Δt. Thus, we expect $n_B(\Delta t) = 1$ for such a system.

On the other hand, if the system has $\dot{q} < 0$ at $t = 0$, it will be moving toward reactants and will probably fall into the reactant well, and so $n_B(\Delta t) = 0$.

6.2 The second limiting case

The second limiting case is one in which the solvent molecules and other degrees of freedom of the system have an important influence on the way the system crosses the transition state. For example, suppose the solvent molecules are continually influencing the motion of the reaction coordinate, perhaps even making it undergo something like Brownian motion. So the motion is not like sliding or rolling on some surface as much as like undergoing diffusive motion on the surface. The reaction coordinate is subject to repeated changes in its velocity, even repeated changes in the sign of its velocity. As a result, if it starts out at $q = q^*$ with positive $\dot{q}$, it is still likely to cross the surface many times in the future before finally falling into the product or reactant wells.

6.3 Comparison of the two cases

The important difference between these two limiting cases is related to the question of whether a trajectory that crosses the transition surface at time 0 is likely or unlikely to cross it again within a time Δt before falling decisively into the reactant or product basins. Strong interactions with a solvent can make recrossings more likely. They are less likely when the solvent does not have much effect on the reaction coordinate or when there is little or no solvent.

End of lecture 7 10/13/09

7 Classical transition state theory

Lecture 8 10/15/09

The assumption that is the basis for transition state theory. Classical transition state theory is applicable in the first of these limiting situations.

The basic assumption of classical transition state theory is that:

- a trajectory that crosses the transition surface will not cross it again for a very long time (much longer than Δt).

This is a physical assumption about the dynamics of trajectories.

This is the formulation that, I think, Wigner came up with. It is rather different in spirit from that of Eyring, which you may be more familiar with.

If we make this assumption, we can go far to evaluating the rate constant. In the integral, if Γ is such that $q = 0$ and $\dot{q} > 0$ at time 0, then the system is crossing from reactant to product and hence it will stay on the reactant side for some time and so $n_B(\Delta t) = 1$. If Γ is such that $q = 0$ and $\dot{q} < 0$, then the system is crossing from product to reactant and so $n_B(\Delta t) = 0$. Thus, it follows from this assumption that

$$n_B(\Delta t) = \Theta(\dot{q}(0))$$

In other words, for a system that starts at $q = 0$ at $t = 0$, whether the system will be reactant of product at time Δt is determined solely by the sign of its velocity at $t = 0$. Thus we have

$$k_{f,TST} = \frac{1}{x_A}\langle\Theta(\dot{q}(0))\dot{q}(0)\delta(q(0) - q^*)\rangle_{eq} = \frac{1}{x_A}\langle\Theta(\dot{q})\dot{q}\delta(q - q^*)\rangle_{eq} \qquad (3)$$

The remarkable thing about this is that it is of the form of a static equilibrium average that can be calculated in principle using only equilibrium statistical mechanics. The assumption that a trajectory that crosses the transition surface does so once and does not come back to the surface for a very long time simplifies the expression for the rate constant significantly.

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This assumption allows us to simplify the expression for k_f.

If the initial state is such that $q = 0$ and $\dot{q} > 0$ at time 0, then the system is crossing from reactant to product and hence it will stay on the reactant side for some time and so $n_B(\Delta t) = 1$.

If the initial state is such that $q = 0$ and $\dot{q} < 0$ at time 0, then the system is crossing from product to reactant and so $n_B(\Delta t) = 0$.

Thus, in both cases

$$n_B(\Delta t) = \Theta(\dot{q}(0))$$

Thus we have

$$k_{f,TST} = \frac{1}{x_A}\langle\Theta(\dot{q}(0))\dot{q}(0)\delta(q(0) - q^*)\rangle_{eq} = \frac{1}{x_A}\langle\Theta(\dot{q})\dot{q}\delta(q - q^*)\rangle_{eq}$$

This is of the form of a static equilibrium average that can be calculated in principle using only equilibrium statistical mechanics.

end of slide

Further manipulation of the result. Let's manipulate this a little further to get it into a more familiar form.

$$\begin{aligned} k_{f,TST} &= \frac{1}{x_A}\int d\Gamma\, P_{eq}(\Gamma)\Theta(\dot{q}(0))\dot{q}(0;\Gamma)\delta\left(q(0;\Gamma) - q^*\right) \\ &= \frac{1}{x_A}\int dqdpdQdP\, P_{eq}(q,p,Q,P)\Theta(p)\frac{p}{m}\delta\left(q - q^*\right) \end{aligned}$$

The equilibrium distribution function is

$$\begin{aligned} P_{eq}(q,p,Q,P) &= (const.) \times \exp\left(-H(q,p,Q,P)/k_BT\right) \\ &= \frac{1}{\mathcal{Q}_{cl}}\exp\left(-H(q,p,Q,P)/k_BT\right) \\ &= \frac{1}{\mathcal{Q}_{cl}}\exp\left(-\left(\frac{p^2}{2m} + V(q,Q,P) + H_0(Q,P)\right)/k_BT\right) \end{aligned}$$

where

$$\mathcal{Q}_{cl} = \int dqdpdQdP\, \exp\left(-H(q,p,Q,P)/k_BT\right)$$

is a classical partition function. If we substitute this into the expression for k_{TST}, then then integral factors into a number of factors.

- The q integral is trivial, because of the delta function. We get rid of the integration and of the delta function, and q is replaced elsewhere in the integral by q^*.
- The p integral is straightforward. It is

$$\int_{-\infty}^{\infty} dp\, \Theta(p) \frac{p}{m} \exp(-p^2/2mkT) = \int_0^{\infty} dp\, \frac{p}{m} \exp(-p^2/2mkT) = k_B T$$

Thus we get

$$k_{f,TST} = \frac{k_B T}{x_A \mathcal{Q}_{cl}} \int dQdP\, \exp\left(-\left(V(q^*, Q, P) + H_0(Q, P)\right)/k_B T\right)$$

The integral that remains looks like a partition function, but note that it does not contain an integration over the reaction coordinate or its conjugate momentum. The reaction coordinate is held fixed at q^*, and the integral for the momentum conjugate to it has factored out and been evaluated. It is really a partition function for a system with one fewer degree of freedom than the original system. It is a partition function for all the other degrees of freedom, but these other degrees of freedom are subject to a potential energy that corresponds to holding the reaction coordinate fixed at q^*. This is what is ordinarily described as the partition function for the 'activated complex' or the partition function of the transition state.

Let's define

$$\mathcal{Q}_{cl}^{\ddagger} \equiv \int dQdP\, \exp\left(-\left(V(q^*, Q, P) + H_0(Q, P)\right)/k_B T\right)$$

Then we have

$$k_{f,TST} = \frac{k_B T \mathcal{Q}_{cl}^{\ddagger}}{x_A \mathcal{Q}_{cl}}$$

We can also write

$$K = \frac{x_B}{x_A} = \frac{\langle n_B \rangle}{\langle n_A \rangle} = \frac{\int dqdpdQdP\, n_B(q) \exp\left(-H(q, p, Q, P)/k_b T\right)}{\int dqdpdQdP\, n_A(q) \exp\left(-H(q, p, Q, P)/k_b T\right)} = \frac{\mathcal{Q}_{cl,B}}{\mathcal{Q}_{cl,A}}$$

where we have defined separate classical partition functions for reactants and products. Note that

$$\mathcal{Q}_{cl,A} + \mathcal{Q}_{cl,B} = \mathcal{Q}_{cl}$$

Also it is easily shown that $\mathcal{Q}_{cl,A} = x_A \mathcal{Q}_{cl}$.

Then we have

$$k_{f,TST} = \frac{k_B T \mathcal{Q}^{\ddagger}_{cl}}{\mathcal{Q}_{cl,A}} \tag{4}$$

The forward rate constant is proportional to the ratio of the partition function of the transition state to the partition function of the reactant states.

In statistical mechanics, the partition function of a system is related to its free energy in the following way.

$$A = -k_B T \ln \mathcal{Q}$$

where $\mathcal{Q}$ is the canonical partition function. However, this is true only when you use the correct quantum mechanical partition function. If you simply use the classical partition function, you don't get the right answer.

However, the correct quantum mechanical partition function is closely related to the classical partition function when the temperature is high enough for quantum effects to be unimportant. The relationship is of the following form:

$$\mathcal{Q} = \frac{1}{h^M} \frac{1}{(\text{symmetry numbers})} \mathcal{Q}_{cl}$$

where M is the number of degrees of freedom and h is Planck's constant. The symmetry numbers are numerical factors related to the number of identical molecules in the system and the symmetries of individual molecules.

This allows us to calculate the free energy A of reactants or products from the corresponding classical partition function. Let us use this also to *define* the free energy of the transition state.[5]

If we use this to calculate $\mathcal{Q}^{\ddagger}/\mathcal{Q}_A$, we get

$$\frac{\mathcal{Q}^{\ddagger}}{\mathcal{Q}_A} = h \frac{\sigma_A}{\sigma^{\ddagger}} \frac{\mathcal{Q}^{\ddagger}_{cl}}{\mathcal{Q}_{A,cl}}$$

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[5] Partition functions and free energies of transition states do not arise in ordinary statistical thermodynamics. We are free to define them as we are doing, as long as we do not attribute any thermodynamic significance to the resulting quantities.

We get one factor of h, since there is one fewer degree of freedom in the transition state than in the overall system. σ_A is the symmetry number of the reactant molecule A. $\sigma^\ddagger$ is the symmetry number of the transition state. The symmetry numbers associated with the solvent molecules cancel because they are the same in the two partition functions. Hence

$$\frac{\mathcal{Q}^\ddagger_{cl}}{\mathcal{Q}_{A,cl}} = \frac{\sigma^\ddagger \mathcal{Q}_A}{h\sigma_A \mathcal{Q}^\ddagger}$$

Let us restrict our attention to the special case that the two symmetry numbers are equal.[6] Then, substituting this result into our expression for $k_{f,TST}$ gives

$$k_{f,TST} = \frac{k_B T \mathcal{Q}^\ddagger}{h\mathcal{Q}_A} = \frac{k_B T}{h} e^{-\Delta A^\ddagger / k_B T}$$

where

$$\Delta A^\ddagger = -k_B T \ln\left(\frac{\mathcal{Q}^\ddagger}{\mathcal{Q}_A}\right)$$

is called the free energy of activation (i.e. the free energy change for going from the set of reactant states to the transition state).

In transition state theory, the factor of $k_B T/h$ is sometimes called the 'frequency factor', and its appearance in some of the less rigorous derivations of transition state theory can be especially mysterious. Here it arose in a straightforward way.

- The factor of $k_B T$ arose from doing the integration over the momentum associated with the reaction coordinate. The result was so simple because of the simplifying assumptions we made about the form of the Hamiltonian.
- The factor of h arose from expressing the classical partition functions in terms of the quantum partition functions. Introducing quantum partition functions into a classical theory may seem unnecessary, and it is. But if you really want to introduce the idea of free energy of activation,

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[6] The correct handling of symmetry numbers is a technical detail that is very important in getting the right answer for any particular problem. It is tied up with other technical aspects of the calculation as well. These considerations are best handled on an individual basis rather than giving general formulas.

> then it is necessary since only in quantum statistical mechanics is there the correct relationship between partition functions and free energies.

If one does not like to see factors of h in a classical theory, they can be avoided simply by deciding not to introduce free energies. Eq. (4) then is a perfectly acceptable expression for the classical transition state theory, as is Eq. (3).[7]

slide

Further manipulation of the result

$$\begin{aligned} k_{f,TST} &= \frac{1}{x_A}\int d\Gamma\, P_{eq}(\Gamma)\Theta(\dot{q}(0))\dot{q}(0;\Gamma)\delta\left(q(0;\Gamma)-q^*\right) \\ &= \frac{1}{x_A}\int dqdpdQdP\, P_{eq}(q,p,Q,P)\Theta(p)\frac{p}{m}\delta\left(q-q^*\right) \end{aligned}$$

The equilibrium distribution function is

$$\begin{aligned} P_{eq}(q,p,Q,P) &= (const.)\times\exp\left(-H(q,p,Q,P)/k_BT\right) \\ &= \frac{1}{\mathcal{Q}_{cl}}\exp\left(-H(q,p,Q,P)/k_BT\right) \\ &= \frac{1}{\mathcal{Q}_{cl}}\exp\left(-\left(\frac{p^2}{2m}+V(q,Q,P)+H_0(Q,P)\right)/k_BT\right) \end{aligned}$$

where

$$\mathcal{Q}_{cl} = \int dqdpdQdP\,\exp\left(-H(q,p,Q,P)/k_BT\right)$$

is a classical partition function.

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[7] If the symmetry numbers of the reactant, product, and transition state are all the same, then one can blithely use classical statistical mechanics for calculating rates and one will get the correct classical limit of the quantum result, provided one has the factor of h in the frequency factor. If the symmetry numbers are not all the same, they must be taken into account in the calculation of either the rate constant or the equilibrium constant or both.

$$
\begin{aligned}
&k_{f,TST} \\
&\quad = \frac{1}{x_A \mathcal{Q}_{cl}} \int dqdpdQdP \\
&\qquad \times \exp\left(-\left(\frac{p^2}{2m} + V(q,Q,P) + H_0(Q,P)\right)/k_BT\right)\Theta(p)\frac{p}{m}\delta\left(q-q^*\right)
\end{aligned}
$$

- The q integral is trivial, because of the delta function. We get rid of the integration and of the delta function, and q is replaced elsewhere in the integral by q^*.
- The p integral is straightforward. It is

  $$\int_{-\infty}^{\infty} dp\,\Theta(p)\frac{p}{m}\exp(-p^2/2mkT) = \int_0^{\infty} dp\,\frac{p}{m}\exp(-p^2/2mkT) = k_BT$$

The result is

$$k_{f,TST} = \frac{k_BT}{x_A \mathcal{Q}_{cl}} \int dQdP\, \exp\left(-\left(V(q^*,Q,P) + H_0(Q,P)\right)/k_BT\right)$$

Let's define

$$\mathcal{Q}_{cl}^{\ddagger} \equiv \int dQdP\, \exp\left(-\left(V(q^*,Q,P) + H_0(Q,P)\right)/k_BT\right)$$

Then we have

$$k_{f,TST} = \frac{k_BT\mathcal{Q}_{cl}^{\ddagger}}{x_A \mathcal{Q}_{cl}}$$

We can also write

$$K = \frac{x_B}{x_A} = \frac{\langle n_B \rangle}{\langle n_A \rangle} = \frac{\int dqdpdQdP\, n_B(q) \exp\left(-H(q,p,Q,P)/k_bT\right)}{\int dqdpdQdP\, n_A(q) \exp\left(-H(q,p,Q,P)/k_bT\right)} = \frac{\mathcal{Q}_{cl,B}}{\mathcal{Q}_{cl,A}}$$

where we have defined separate classical partition functions for reactants and products. Note that

$$\mathcal{Q}_{cl,A} + \mathcal{Q}_{cl,B} = \mathcal{Q}_{cl}$$

Also it is easily shown that $\mathcal{Q}_{cl,A} = x_A \mathcal{Q}_{cl}$.

Then we have

$$k_{f,TST} = \frac{k_B T \mathcal{Q}_{cl}^{\ddagger}}{\mathcal{Q}_{cl,A}}$$

The partition function of a system is related to its free energy in the following way.

$$A = -k_B T \ln \mathcal{Q}$$

where $\mathcal{Q}$ is the canonical partition function (i.e. the correct quantum mechanical partition function).

The correct quantum mechanical partition function is:

$$\mathcal{Q} = \frac{1}{h^M} \frac{1}{(\text{symmetry numbers})} \mathcal{Q}_{cl}$$

where M is the number of degrees of freedom and h is Planck's constant. The symmetry numbers are numerical factors related to the number of identical molecules in the system and the symmetries of individual molecules.

Use this to calculate $\mathcal{Q}_{cl}^{\ddagger}/\mathcal{Q}_{cl,A}$.

$$\frac{\mathcal{Q}^{\ddagger}}{\mathcal{Q}_A} = h \frac{\sigma_A}{\sigma^{\ddagger}} \frac{\mathcal{Q}_{cl}^{\ddagger}}{\mathcal{Q}_{cl,A}} \qquad \frac{\mathcal{Q}_{cl}^{\ddagger}}{\mathcal{Q}_{cl,A}} = \frac{\sigma^{\ddagger} \mathcal{Q}_A}{h \sigma_A \mathcal{Q}^{\ddagger}}$$

Restrict our attention to the special case that the two symmetry numbers are equal. Then

$$k_{f,TST} = \frac{k_B T \mathcal{Q}^{\ddagger}}{h \mathcal{Q}_A} = \frac{k_B T}{h} e^{-\Delta A^{\ddagger}/k_B T}$$

where

$$\Delta A^{\ddagger} \equiv -k_B T \ln \left(\frac{\mathcal{Q}^{\ddagger}}{\mathcal{Q}_A} \right)$$

is called the free energy of activation (i.e. the free energy change for going from the set of reactant states to the set of transition states).

In transition state theory, the factor of $k_B T/h$ is sometimes called the 'frequency factor'.

- The factor of $k_B T$ arose from doing the integration over the momentum associated with the reaction coordinate.
- The factor of h arose from expressing the classical partition functions in terms of the quantum partition functions.

end of slides

Transition state theory as an upper bound to the exact rate constant

Let's return to the exact classical expression for the rate constant.

$$k = \frac{1}{x_A x_B} \int d\Gamma \, P_{eq}(\Gamma) n_B(\Delta t, \Gamma) \dot{q}(0;\Gamma) \delta \left(q(0;\Gamma) - q^* \right)$$

Suppose we consider a given H and P_{eq}, and suppose we don't know $n_B(\Delta t, \Gamma)$ for all Γ. But we do know that $n_B(\Delta t, \Gamma)$ for any Γ can only have the values of 0 or 1.

Subject to these restrictions, what form of $n_B(\Delta t, \Gamma)$ will give the largest value of k? It is clear that for initial states for which $\dot{q} > 0$, we will want $n_B(\Delta t, \Gamma)$ to always be 1 (rather than sometimes be 1 and sometimes 0), and for initial states for which $\dot{q} < 0$, we will want $n_B(\Delta t, \Gamma)$ to be always 0 (rather than sometimes 0 and sometimes 1). But this is what follows from the transition state theory assumption.

It follows that

$$k \leq k_{TST}$$

The transition state theory rate constant provides an upper bound to the exact classical rate constant. This is a truly remarkable result.[8]

What it means physically is that anything that would affect the dynamics in such a way as to cause trajectories to cross the surface many times will cut

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[8] The quantum transition state theory is on a less firm basis, and in fact there are several different theories that have the characteristics that one might call 'quantum transition state theory'. However, for none of them has it been shown that the theory gives an upper bound to the correct rate.

down the rate of the reaction, possibly to much smaller values than what is predicted by transition state theory.

slides

Transition state theory as an upper bound to the exact rate constant. The exact classical expression for the rate constant

$$k = \frac{1}{x_A x_B} \int d\Gamma \, P_{eq}(\Gamma) n_B(\Delta t, \Gamma) \dot{q}(0; \Gamma) \delta \left(q(0; \Gamma) - q^* \right)$$

We know that $n_B(\Delta t, \Gamma)$ for any Γ can only have the values of 0 or 1.

Question: What formula for $n_B(\Delta t, \Gamma)$ will give the largest value of k?

Answer:

- For initial states for which $\dot{q} > 0$, we will want $n_B(\Delta t, \Gamma)$ to always be 1 (rather than sometimes be 1 and sometimes 0)
- For initial states for which $\dot{q} < 0$, we will want $n_B(\Delta t, \Gamma)$ to be always 0 (rather than sometimes 0 and sometimes 1).

But this is what follows from the transition state theory assumption.

It follows that

$$k \leq k_{TST}$$

The transition state theory rate constant provides an upper bound to the exact classical rate constant.

end of slides

8 Variational transition state theory

The fact that the transition state theory provides an upper bound to the exact rate constant let's us provide a satisfying answer to following question, which may have occurred to you.

How does one choose the appropriate value of q^*? More generally, how does one divide the configuration space into regions corresponding to reactants A and products B?

In some sense it does not make any difference precisely where the dividing surface is placed. The average of the dynamical variable n_A is insensitive to the choice, so any choice works equally well, as long as the dividing surface is somewhere between the A and B parts of the phase space and in a region where there is very little equilibrium probability. Moreover, if the theory is correct, as it is, the same final result (i.e. the correct result) for the rate constant should be obtained from any choice.

The fact that k_{TST} is an upper bound to the true rate constant suggests that the appropriate thing to do is choose the surface so that the calculated value of k_{TST} is as small as possible. This is known as 'variational transition state theory'. A surface chosen this way is in some sense the best because it makes the transition state approximation as accurate as it can be. Lecture 8 10/15/09 continued in N10B