

Foundations of Chemical Kinetics Lecture 10: Transition-state theory in practice

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The TST rate constant revisited

First-order reactions

- For a first-order reaction $R \xrightleftharpoons{K^\ddagger} \text{TS} \xrightarrow{k^\ddagger} P$,

$$k = \frac{k_B T}{h} \frac{q^\ddagger}{q_R} \exp\left(-\frac{\Delta\epsilon^\ddagger}{k_B T}\right)$$

- Units of k : s^{-1}
- The units of the partition functions cancel out, so you can use any convenient partition function: q, q, \hat{q}

The TST rate constant revisited

Gas-phase second-order reactions

- In the previous lecture, we derived

$$k = \frac{k_B T}{c^\circ h} \frac{q^\ddagger}{q_X q_Y} \left(\frac{N}{V} \right) \exp \left(-\frac{\Delta \epsilon^\ddagger}{k_B T} \right)$$

- We would normally use a pressure-based standard state for gas-phase thermodynamics. If we use pressures instead of concentrations in the rate law as well, we get

$$k = \frac{k_B T}{p^\circ h} \frac{q^\ddagger}{q_X q_Y} \left(\frac{N}{V} \right) \exp \left(-\frac{\Delta \epsilon^\ddagger}{k_B T} \right)$$

- Since $N/V = p^\circ/k_B T$ in the standard state,

$$k = \frac{1}{h} \frac{q^\ddagger}{q_X q_Y} \exp \left(-\frac{\Delta \epsilon^\ddagger}{k_B T} \right)$$

- Units of q : m^{-3}
- Units of k : $\text{J}^{-1} \text{m}^{-3} \text{s}^{-1} \equiv \text{Pa}^{-1} \text{s}^{-1}$

The TST rate constant revisited

Gas-phase second-order reactions (continued)

- Suppose that you want conventional units for the second-order rate constant of $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$.

- $\frac{p}{n/V} = RT$ (units: $\text{Pa m}^3 \text{mol}^{-1}$)

$$k = \frac{RT}{h} \frac{q^\ddagger}{q_X q_Y} \exp\left(-\frac{\Delta\epsilon^\ddagger}{k_B T}\right)$$

The TST rate constant revisited

Gas-phase second-order reactions (continued)

- Suppose we want to use the Gaussian-style partition functions $\hat{q} = \hat{V}q$, with $\hat{V} = k_B T / p^\circ$.

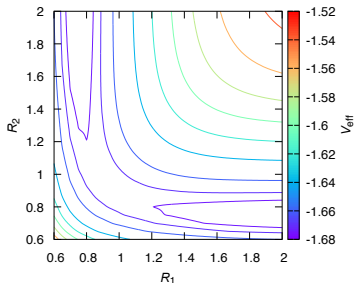
$$\begin{aligned} k &= \frac{Lk_B T}{h} \frac{\hat{q}^\ddagger}{\hat{q}_X \hat{q}_Y} \left(\frac{k_B T}{p^\circ} \right) \exp \left(-\frac{\Delta\epsilon^\ddagger}{k_B T} \right) \\ &= \frac{L(k_B T)^2}{p^\circ h} \frac{\hat{q}^\ddagger}{\hat{q}_X \hat{q}_Y} \exp \left(-\frac{\Delta\epsilon^\ddagger}{k_B T} \right) \end{aligned}$$

- Units of k : $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$

The H + H₂ reaction

Collecting preliminary information

- We had previously calculated the PES for the collinear reaction of H + H₂:



- This shows a saddle point near $R_{AB} = R_{BC} = 0.95$ Å.

A computational issue: Basis-set superposition error

- To get accurate energy differences, it is critical to use the same basis set.
- For situations where we want to compare separated subsystems (e.g. atom + molecule) to something that is at least weakly bound (e.g. the TS), in the bound configuration, there is a sharing of basis functions between fragments, which is lost when the fragments are separated.
In effect, the basis set is bigger for the bound system.
- If you know about counterpoise corrections, you can't use these for transition states.
- Solutions:
 - DFT methods may be less sensitive to basis set size than Hartree-Fock+.
 - Use the biggest basis set you can afford.
 - In an ideal world, use extrapolation methods to extrapolate to the infinite basis-set limit.

The H + H₂ reaction

Finding the transition state

- We are going to calculate the rate constant at 1000 K.
- I want a starting geometry with $R_{AB} = R_{BC} \approx 0.95 \text{ \AA}$.
- I don't necessarily want an exactly collinear geometry. I will let Gaussian optimize the angle in the transition state.
- Set up an Opt+Freq calculation, but this time, select Optimize to a TS (Berny). Also choose Force Constants: Calculate at all points.
- We're going to do a DFT calculation using the ω B97X-D functional with an unrestricted-spin wavefunction and the aug-cc-pVQZ basis set.
- Add `pressure=0.986923 temperature=1000` to the Additional Keywords.

The H + H₂ reaction

Finding the transition state

- The optimized transition state is essentially linear (angle = 179.7°), suggesting that the transition state may be exactly linear.
- Restart calculation with an exactly linear geometry.
Reason: From the point of view of calculating partition functions, it makes a difference whether a molecule is linear or not. If the TS really is linear, we have to make sure that we have the correct geometry.
- | | | |
|------------------------|-----------------|-----------------------------|
| Energy, slightly bent: | -1.6650 hartree | |
| Energy, linear: | -1.6652 hartree | lower energy: more accurate |

The H + H₂ reaction

Transition-state data

- Thermodynamic data for the transition state:

- $\epsilon_{\text{TS}} = -1.6652$ hartree

- $\hat{q}^\ddagger = 3.833 \times 10^7$ (“Total Bot” value)

Note: Gaussian leaves out the imaginary (reactive) mode when computing the vibrational partition function, which is exactly what we want.

The H + H₂ reaction

Data for H₂ and H

- Don't forget to set pressure=0.986923
temperature=1000!
- Thermodynamic data for H₂:
 - $\epsilon_{\text{H}_2} = -1.1771$ hartree
 - $\hat{q}_{\text{H}_2} = 5.568 \times 10^5$
- Thermodynamic data for H:
Note: It turns out you can get partition function values by doing a Frequency calculation.
 - $\epsilon_{\text{H}} = -0.5029$ hartree
 - $\hat{q}_{\text{H}} = 1.660 \times 10^6$

The H + H₂ reaction

TST rate constant

$$\begin{aligned}\Delta\epsilon^\ddagger &= \epsilon_{TS} - (\epsilon_{H_2} + \epsilon_H) \\ &= -1.6652 - [-1.1771 + (-0.5029)] \text{ hartree} = 0.0148 \text{ hartree} \\ &\equiv (0.0148 \text{ hartree})(4.359\,744 \times 10^{-18} \text{ J hartree}^{-1}) \\ &= 6.45 \times 10^{-20} \text{ J.}\end{aligned}$$

The H + H₂ reaction

TST rate constant (continued)

$$\begin{aligned}
 k &= \frac{L(k_B T)^2}{p^\circ h} \frac{\hat{q}^\ddagger}{\hat{q}_X \hat{q}_Y} \exp\left(-\frac{\Delta\epsilon^\ddagger}{k_B T}\right) \\
 &= \frac{(6.022\,141 \times 10^{23} \text{ mol}^{-1}) [(1.380\,649 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})]^2}{(10^5 \text{ Pa})(6.626\,070 \times 10^{-34} \text{ J Hz}^{-1})} \\
 &\quad \times \frac{3.833 \times 10^7}{(5.568 \times 10^5)(1.660 \times 10^6)} \\
 &\quad \times \exp\left(\frac{-6.45 \times 10^{-20} \text{ J}}{(1.380\,649 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})}\right) \\
 &= 6.71 \times 10^5 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}
 \end{aligned}$$

The H + H₂ reaction

TST rate constant (continued)

- Experimental value: $(2.1 \pm 0.6) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
- Calculated value:

$$\begin{aligned}
 k &= 6.71 \times 10^5 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \\
 &\equiv \frac{(6.71 \times 10^5 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1})(100 \text{ cm m})^3}{(6.022 \, 141 \times 10^{23} \text{ mol}^{-1})} \\
 &= 1.11 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
 \end{aligned}$$

- Main source of error: tunneling, which is particularly significant for light particles

TST's strong points

- The thermodynamic formalism of transition-state theory connects well to other parts of physical chemistry, making the theory conceptually useful.
- For very simple reactions, transition-state theory often gives fairly good values.
- Even when the theory doesn't do a great job of predicting the value of a rate constant, it often predicts the relative effect of various factors on the rate constant correctly, e.g. isotope effects.
- It's an important starting point for understanding reactions under non-ideal conditions, e.g. the effect of ionic strength.

TST's weak points

- Transition-state theory often badly overestimates rate constants.

This is thought to result from trajectories that cross the saddle point and then turn around and come back, which are not properly accounted for in the theory.

- This is sometimes fixed by multiplying transition-state rate constants by a **transmission coefficient** (κ), which is unfortunately not much more than a fudge factor.

E.g.:

$$k = \kappa \frac{L(k_B T)^2}{p^\circ h} \frac{\hat{q}^\ddagger}{\hat{q}_X \hat{q}_Y} \exp\left(-\frac{\Delta\epsilon^\ddagger}{k_B T}\right)$$

TST's weak points

- One part of transition-state theory, the idea of passage through the transition state from reactants to products, is an irreducibly classical mechanical idea.

Of course, molecules are quantum mechanical objects, so the idea of a trajectory through the transition state can't be right.

This leads to a number of difficulties which have not, to this day, been resolved.

- What exactly do we mean by passage “through” the transition state?
- Tunneling is important in reactions involving motions of light particles (electron-transfer reactions, proton-transfer reactions, etc.).
- Separability of the reaction coordinate is not guaranteed.

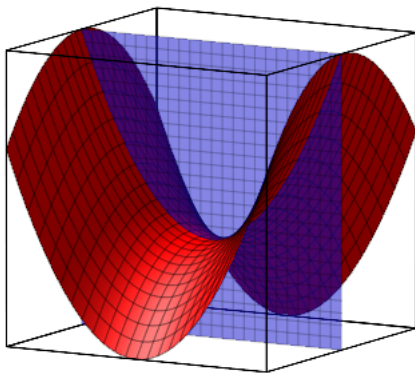
TST's weak points

- The equilibrium approximation at the heart of transition-state theory is only valid for high barriers.
- In most reactions, the reactants have to be in a fairly specific quantum state to react (e.g. one specific vibrational mode has to have enough energy, and the energy in the other modes doesn't matter).

This will tend to have the effect of creating a non-equilibrium (i.e. non-Boltzmann) distribution of energy. If this effect is sufficiently strong, perhaps because molecules energized in the correct vibrational mode react very quickly, then again the equilibrium approximation might not be valid, regardless of the height of the barrier.

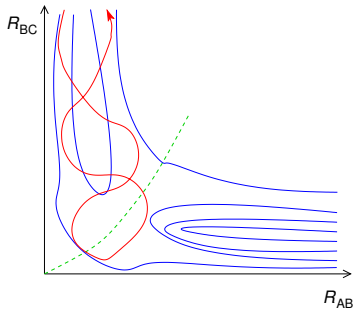
In either of the above cases, transition-state theory might give results that are not even qualitatively correct.

Transition-state dividing surface (TSDS)



The recrossing problem

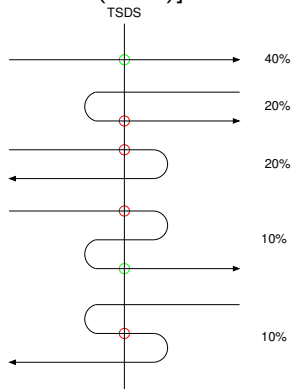
- To go beyond ordinary TST, we need to think in phase space, i.e. the space of particle positions and momenta.
- In the first instance, we only want to count trajectories crossing in the reactant-to-product direction.
- That may not be enough. “Caroming” on the PES can result in trajectories that cross the TSDS then return.



- These effects are highly momentum-dependent.

The transmission coefficient

Suppose that, in the vicinity of the transition state, typical trajectories that cross the TSDS at least once in the reactant to product direction have the following qualitative appearance and frequencies [Adapted from Truhlar and Garrett, *Acc. Chem. Res.* **13**, 440 (1980)]:

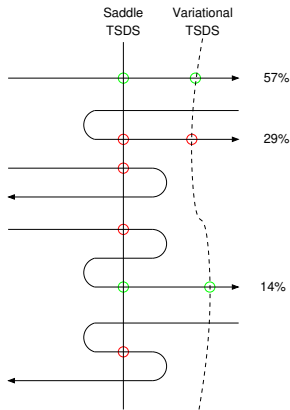


- Standard TST counts all the reactant-to-product (circled) crossings.
- Only the crossings circled in green should count.
- In conventional TST, we would need a transmission coefficient of $\kappa = \frac{40+10}{110} = 0.45$.

Variational transition-state theory

- In conventional TST, the TSDS is chosen to be perpendicular to the classical reaction coordinate.
In phase space, because momentum is not taken into account in defining the TSDS, the surface is parallel to the momentum subspace.
- In variational TST (VTST), we choose a TSDS in the full phase space (coordinates + momenta) to **minimize the computed rate constant**.

Variational transition-state theory (continued)



- Many fewer events are being counted.
- Assuming the trajectory statistics given previously, $\kappa = \frac{40+10}{70} = 0.71$.
- **But we will probably do better** because we are optimizing the surface location in the full phase space (hard to picture).

- In the simplest version of the theory, the calculation machinery is similar to that in conventional TST, except that we Boltzmann average over points in the variational TSDS in the full phase space.