

Reaction Paths and Transition States

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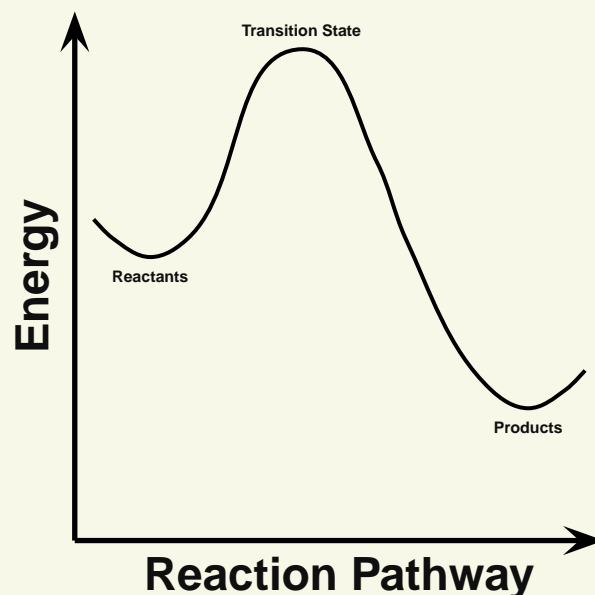


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Reaction Paths and Transition States

Very early in the study of Chemistry, we are introduced to the idea of a reaction coordinate diagram:



Description of Reaction Coordinate Diagram

- The reactants and products are stable molecules and are shown along the reaction coordinate.
- They are connected by a transition state (TS) which is unstable with respect to motion along the reaction coordinate and is represented as an energy maximum.

Obtaining Information From a Reaction Coordinate Diagram

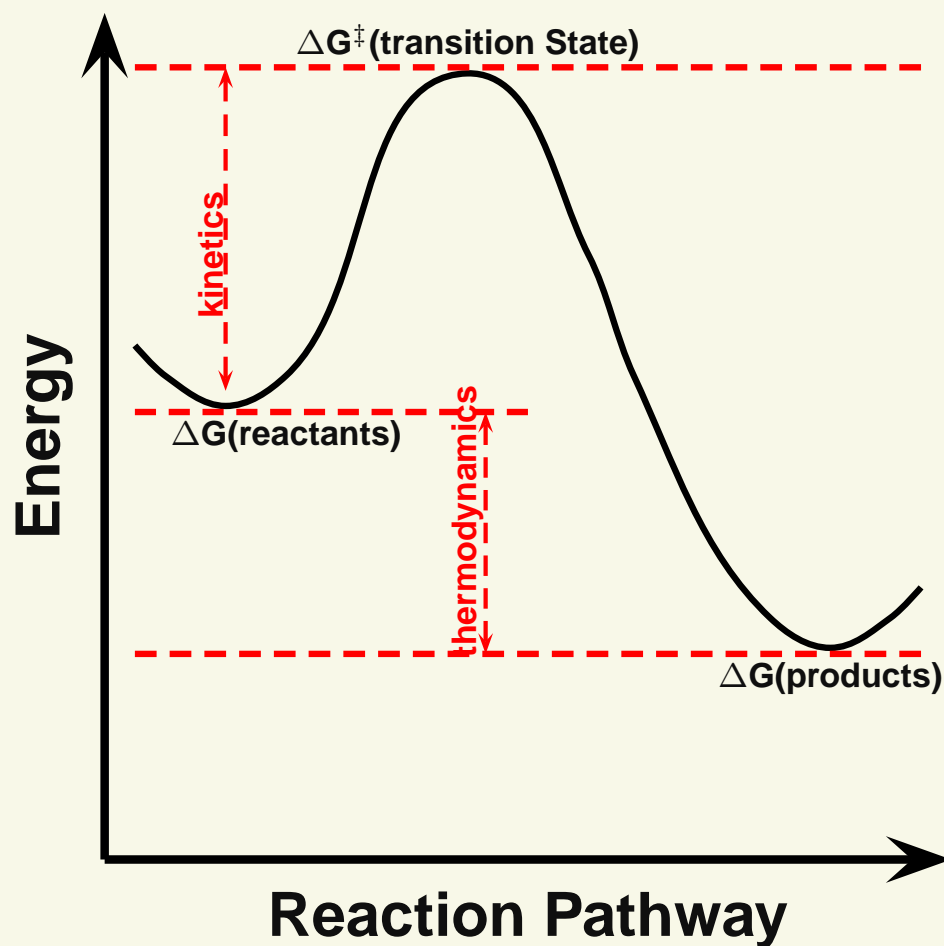
- Defines the geometries of reactant, transition state, and product along the reaction coordinate.
- Provides information about the thermochemistry of the reaction:

$\Delta G_{\text{product}} < \Delta G_{\text{reactant}} \rightarrow$ reaction exothermic, and thermodynamics suggests that there will eventually be more product than reactant.

$\Delta G_{\text{product}} > \Delta G_{\text{reactant}} \rightarrow$ reaction endothermic, and thermodynamics suggests that there will eventually be more reactant than product.

Reaction Paths and Transition States

The reaction coordinate diagram tells us something about the kinetics (or rate) of a reaction: the higher the transition state (TS) relative to the reactant (activation energy, ΔG^\ddagger), the slower the reaction is to proceed.



Role of Calculations in Determining Reaction Pathways

Calculations provide a direct handle on all important details of the potential energy surface (PES) for a Chemical reaction:

- They provide geometries of stable reactants and products, short-lived intermediates, and transition states.
- Unlike experiment, calculations can deal with any arrangement of atoms.
- Calculated minima on the PES provide relative thermochemical stabilities.
- Energies of transition states relative to reactants relate to kinetic stabilities.
- The high reactivity and short lifetimes of reactive intermediates make the direct experimental observation of these species impossible or, at best, very difficult.

Computer modelling of reactive intermediates is no more difficult than modelling stable compounds.

- Computer models are naturally long-lived, can manipulate the molecular and electronic structure, explore the properties of new and unusual reactive intermediates, and predict the properties for which experimental data is limited or unavailable.

Computer simulation of chemical reactions is an invaluable tool for experimental chemists faced with the problem of interpreting experimental results.

Most chemists now view computer modelling as a full partner with experiment for the study of molecular structure, chemical reactions, and properties of molecules.

Distinguishing Between Minima, Maxima, and Saddle Points on a PES

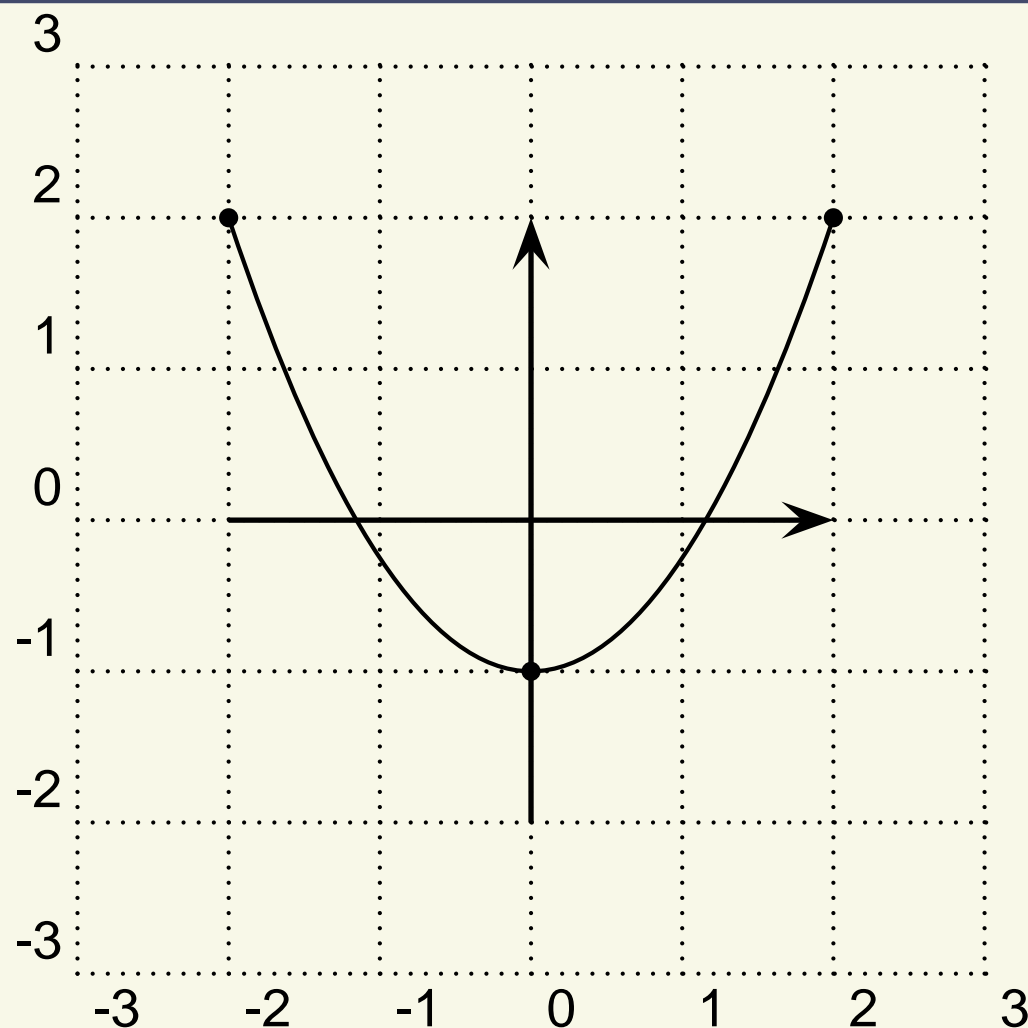
As a system moves from one minimum to another, the energy increases to a maximum at the TS and then falls. We need a way to find the geometry of the transition state structure.

For a reaction pathway, we need to describe both the path between minima and the manner in which the geometry of the system changes.

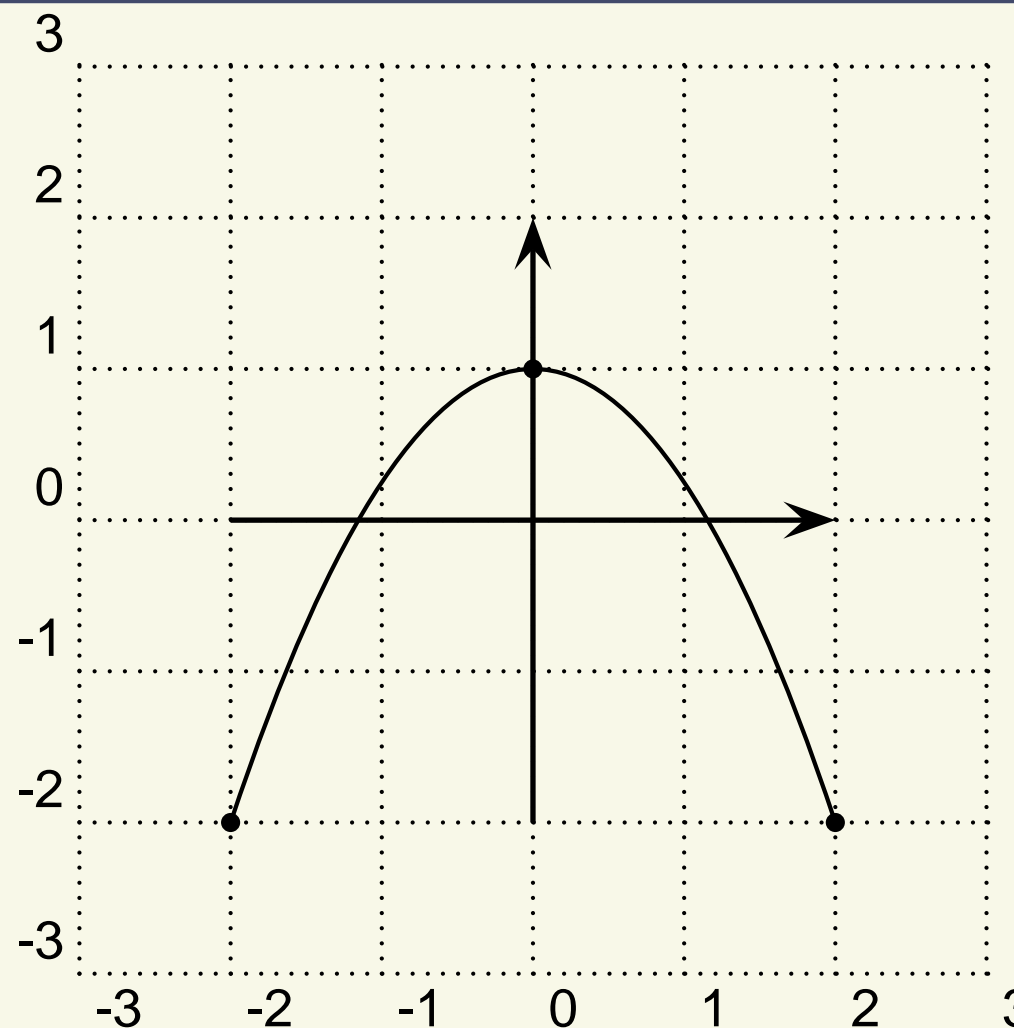
A configuration at which all the first derivatives are zero, $f'(x) = 0$ need not necessarily be a minimum because this holds at both maxima and saddle points as well.

From simple Calculus, we know that the second derivative of a function, $f''(x) > 0$, at a minimum, and $f''(x) < 0$ at a maximum.

Distinguishing Between Minima, Maxima, and Saddle Points on a PES



$$\begin{aligned}f(x) &= x^2 - 1 \\f'(x) &= 2x \\f'(0) &= 0 \text{ at } x = 0 \\f''(x) &= 2\end{aligned}$$



$$\begin{aligned}f(x) &= 1 - x^2 \\f'(x) &= -2x \\f'(0) &= 0 \text{ at } x = 0 \\f''(x) &= -2\end{aligned}$$

Distinguishing Between Minima, Maxima, and Saddle Points on a PES

The Hessian or Second Derivative Matrix

It is necessary to calculate the eigenvalues of the Hessian matrix of second derivatives of all the coordinates to distinguish between minima, maxima, and saddle points.

- A minimum corresponds to 6 zero eigenvalues (3 translation + 3 rotation) and $3N-6$ positive eigenvalues for $3N$ Cartesian coordinates.
- A maximum corresponds to 6 zero eigenvalues (3 translation + 3 rotation) and $3N-6$ negative eigenvalues for $3N$ Cartesian coordinates.
- A saddle point has one or more eigenvalues that are negative.

Distinguishing Between Minima, Maxima, and Saddle Points on a PES

An Example Involving the Hessian

Consider the function:

$$f(x, y) = x^4 + 4x^2y^2 - 2x^2 - 2y^2$$

and the Hessian matrix is

$$\mathcal{H} = \begin{pmatrix} H_{xx} & H_{yx} \\ H_{xy} & H_{yy} \end{pmatrix} = \begin{pmatrix} 12x^2 + 8y^2 - 4 & 16xy \\ 16xy & 8x^2 + 4 \end{pmatrix}$$

It turns out there two minima for this function at the points (1,0) and (-1,0)

- For the minimum at (1,0), the eigenvalues are +4 and +8 which are both positive, and this is a minimum.
- For the minimum at (-1,0), the eigenvalues are both positive, and this is also a minimum.
- But at the point (0,0), the eigenvalues are -4 and +4, so this is a saddle point.

The vectors for these eigenvalues are

$$+4 \rightarrow \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad -4 \rightarrow \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

Distinguishing Between Minima, Maxima, and Saddle Points on a PES

The Saddle Point

At a saddle point, the first derivatives of the PES with respect to all the coordinates equals zero. This is also true at all the minima along the reaction pathway.

For a first order saddle point, the energy passes through a maximum for displacements between two minima in one direction, but is a minimum for displacement in all other directions along the reaction pathway.

There is one negative eigenvalue (which can be related to the force constant) of the Hessian matrix and referred to as an imaginary frequency:

$$\Delta E = h\nu = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}}; \quad k = \text{force constant}; \quad \mu = \text{reduced mass.}$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}; \quad k < 0 \rightarrow \nu \text{ is an imaginary frequency}$$

Transition State versus Transition Structure

The transition structure is the point of highest potential energy along the reaction pathway and is usually the result of a calculation.

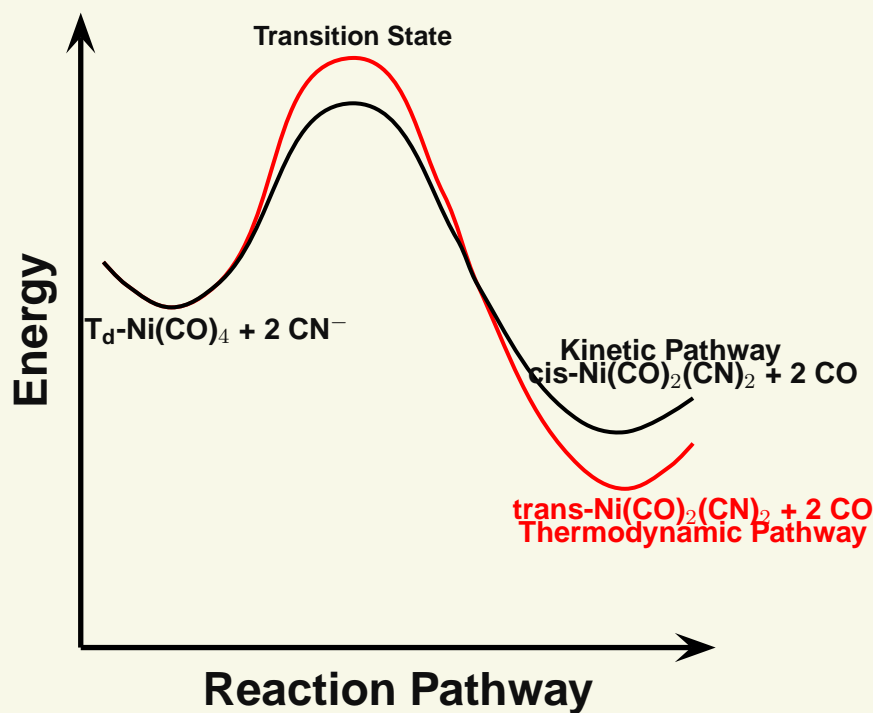
The transition state is the geometry of the molecule at the peak in the free energy profile.

The two are usually similar, but, if the free energy of activation (ΔG^\ddagger) contains energy contributions from other sources, they could be different. For example, if the transition state is temperature dependent, then entropic factors are important.

Thermodynamic versus Kinetic Control of a Reaction

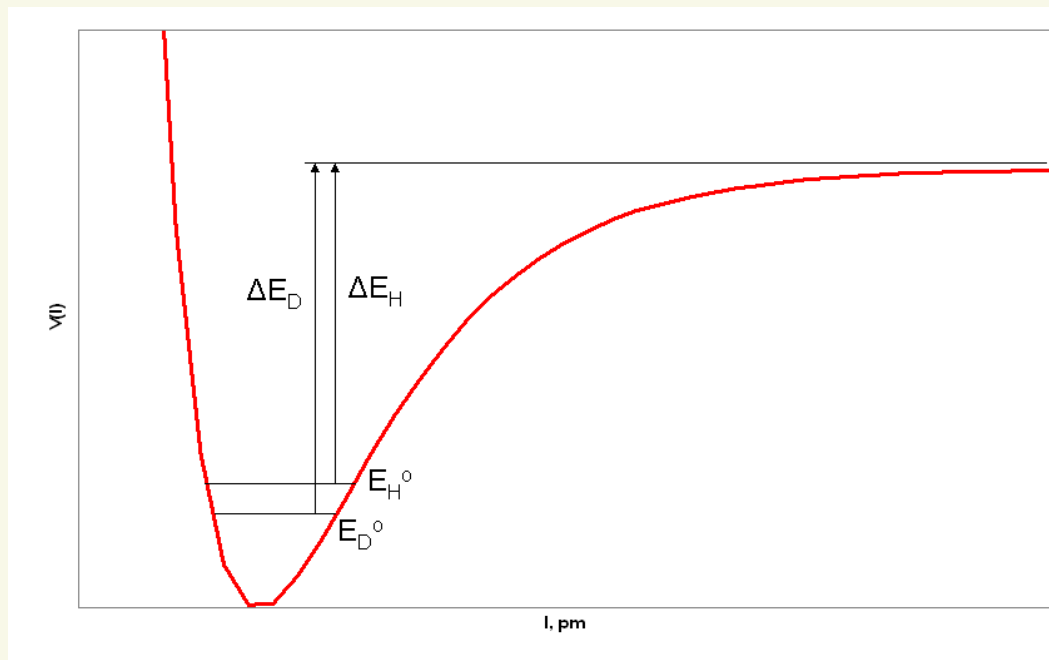
Knowledge of the minimum points on an energy surface enables the thermodynamic data to be interpreted.

For kinetics, it is necessary to investigate the nature of the energy of structures away from the minimum points.



Zero Point Energy (ZPE)

Below is an example of a potential energy curve of energy versus internuclear separation with the zero point vibrational energies of two isotopic molecules. An example would be X-H and X-D, where X is a group/atom that is much heavier than H or D.



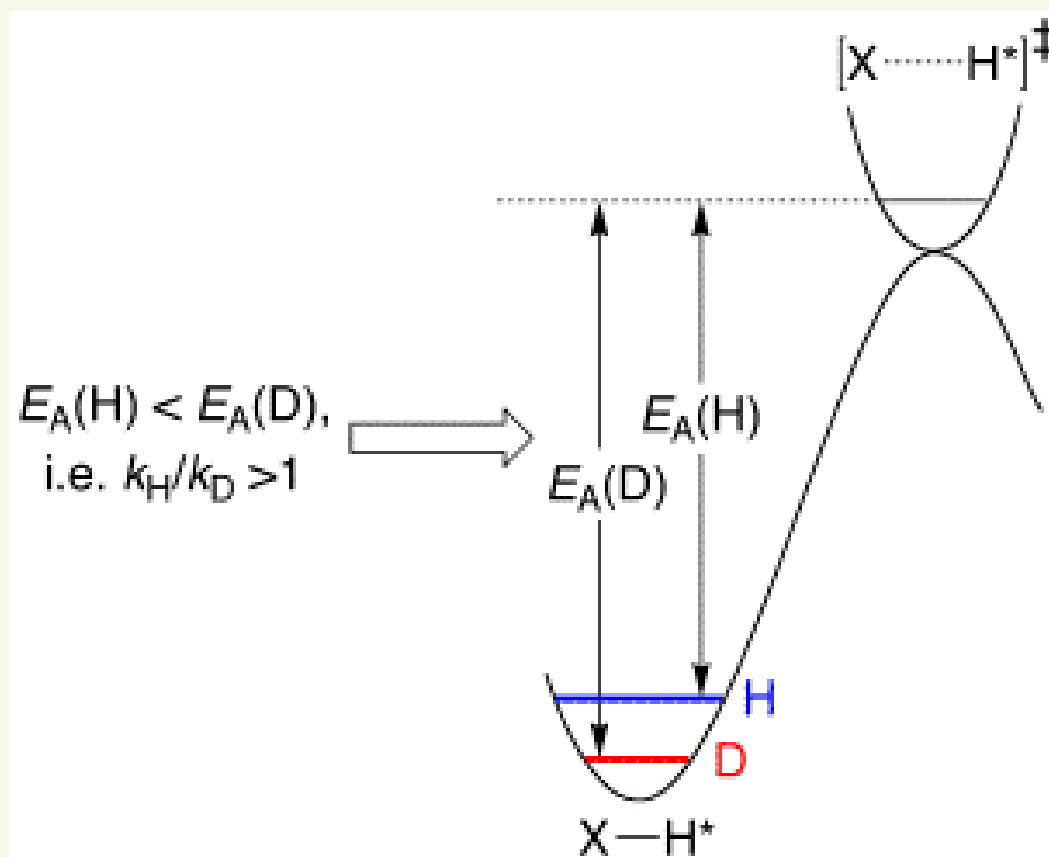
E_D^0 and E_H^0 correspond to the zero point energies of deuterium and hydrogen. The zero point energy is the lowest possible energy of a molecule. and is dependent upon the reduced mass of the molecule.

The heavier the molecule or atom, the lower the frequency of vibration and the smaller the zero point energy. Lighter molecules or atoms have a greater frequency of vibration and a higher zero point energy. As shown in the figure, deuterium is heavier than hydrogen and therefore has the lower zero point energy.

Kinetic Isotope Effect

The lower zero point energy for deuterium results in a larger bond dissociation energy (X-D) for deuterium than for hydrogen (X-H).

This difference in energy because of isotopic replacement results in differing rates of reaction, an effect which is measured in kinetic isotope effects (KIE).



Kinetic Isotope Effect

It is possible to use a predicted ΔG^\ddagger to calculate a unimolecular rate constant, k_i by using the equation

$$k_i = \frac{k_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}}$$

where k_B is the Boltzmann constant, and ΔG^\ddagger is the activation energy, E_A .

Rates of reaction are determined, in part, by the energy barrier for the reaction (ΔG^\ddagger) which involves changes in both the potential energy surface and the zero point energy.

$$\Delta G^\ddagger \approx (\text{PE}^\ddagger - \text{PE}_{\text{Reactant}}) + (\text{ZPE}^\ddagger - \text{ZPE}_{\text{Reactant}})$$

Since the zero point energy is isotope sensitive, the magnitude of the barrier may also be isotope dependent, and a kinetic isotope effect may be observed.

The potential energy surface is the same for all isotopic derivatives, and the kinetic isotope effect can be given as

$$\frac{k_i}{k_j} = e^{-\frac{(\Delta \text{ZPE}_i - \Delta \text{ZPE}_j)}{RT}}$$

One can measure the kinetic isotope effect in reactions for

$$\frac{k_{\text{H}}}{k_{\text{D}}}, \quad \frac{k_{12\text{C}}}{k_{13\text{C}}}, \quad \frac{k_{14\text{N}}}{k_{15\text{N}}}, \quad \frac{k_{35\text{Cl}}}{k_{37\text{Cl}}}, \quad \frac{k_{32\text{S}}}{k_{34\text{S}}}, \quad \frac{k_{79\text{Br}}}{k_{81\text{Br}}}$$

as well as other isotopes and compare them to calculated values.