COMMONWEALTH OF AUSTRALIA

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Liquids: Chemical kinetics

Lecture 29

Liquids: Diffusion and Randomness

Lecture 30

Liquids: Chemical kinetics

Lecture 31

Kinetics: Elementary processes and reaction mechanisms

Rate laws – a few reminders

In chemical kinetics we are interested in determining how the concentration of a species changes over time as we proceed from an initial state to equilibrium. This may be expressed as EITHER:

A differential rate law, showing the rate of change of concentration as a function of concentrations of one or more species. E.g. $\frac{d[A]}{dt} = -k[A]$

$$\frac{\mathrm{d}[\mathrm{HBr}]}{\mathrm{d}t} = \frac{k_a[\mathrm{H_2}][\mathrm{Br_2}]^{\frac{3}{2}}}{[\mathrm{Br_2}] + k_b[\mathrm{HBr}]}$$

OR, an integrated rate law, showing concentration as a function of time. E.g. $[A] = [A]_0 \exp(-kt)$

If we know the differential rate law, then we can determine the integrated rate law analytically for simple cases, or numerically otherwise.

E.g. If the reaction A → B has a simple "first order" rate law: $\frac{d[A]}{dt} = -k[A]$

We can integrate this expression to give [A] as a function of time: $\int \frac{d[A]}{[A]} = \int -k dt$

As $[A] = [A]_0$ at t = 0, this gives $\ln([A]) = -kt + \ln([A]_0)$

or $\ln\left(\frac{[A]}{[A]_0}\right) = -kt$

or $[A] = [A]_0 \exp(-kt)$

Plotting ln([A]) vs t gives a straight line with a gradient, –k.

Other simple rate laws

	0th order	1st order	2nd order
Rate equation	$\frac{d[A]}{dt} = -k$	$\frac{d[A]}{dt} = -k[A]$	$\frac{d[A]}{dt} = -k[A]^2$
Integrated rate equation	$[A] = [A]_0 - kt$	$[A] = [A]_0 \exp(-kt)$ $\ln([A]) = -kt + \ln([A]_0)$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
Plot to test for linearity and determine *k*	$[A]$ vs t	$\ln([A])$ vs t	$\frac{1}{[A]}$ vs t
Half life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{\ln(2)}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

Diffusion-Controlled Reactions

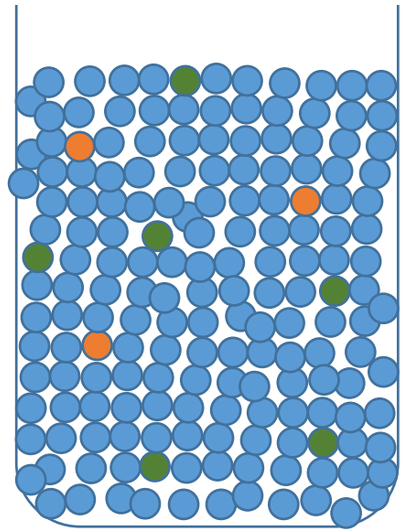
- Imagine a reaction in solution that occurs every time an **orange** and a **green** molecule come into contact with one another.
- How fast/often does this occur?
- How long τ does it take for an orange molecule to exchange with a neighbouring solvent molecule?
  - Recall the average time to diffuse a distance x:

$$time = \frac{x^2}{2D}$$ (Einstein-Smoluchowski)

  - If all molecules have radius r, then $x = 2r$ and we have

$$\tau = \frac{(2r)^2}{2D} = \frac{2r^2}{D}$$

  - In a time period Δt, we expect $\Delta t/\tau$ exchanges for each orange particle.



volume V
concentration $c_o = n_o/V$
concentration $c_g = n_g/V$
Solvent molecules are blue

Diffusion-Controlled Reactions (cont.)

Q1

- The probability of encountering a green neighbour after each exchange is related to the number of neighbours (~12 in 3d), and the proportion of all sites that are green:

$$\mathrm{P}\sim 12\,\frac{n_g \cdot V_g}{V} = 12\,\frac{n_g \cdot \frac{4\pi}{3} r^3}{V}$$

- The successful number of collisions in time Δt is then:

$$\mathrm{Z} = n_o \cdot \frac{\Delta t}{\tau} \cdot P = \frac{n_o n_g}{V} \cdot 4\pi \cdot 2r \cdot D \cdot \Delta t$$

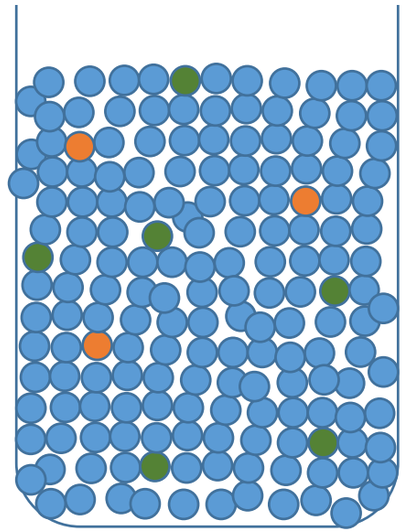
- Allowing green particles to diffuse as well, and different radii:

$$\mathrm{Z} = \frac{n_o n_g}{V} \cdot 4\pi \cdot \left(r_o + r_g\right) \cdot \left(D_o + D_g\right) \cdot \Delta t$$

- So, the overall instantaneous rate of reaction:

$$\frac{dc_o}{dt} = -k c_o c_g \qquad \leftarrow \text{differential rate law}$$

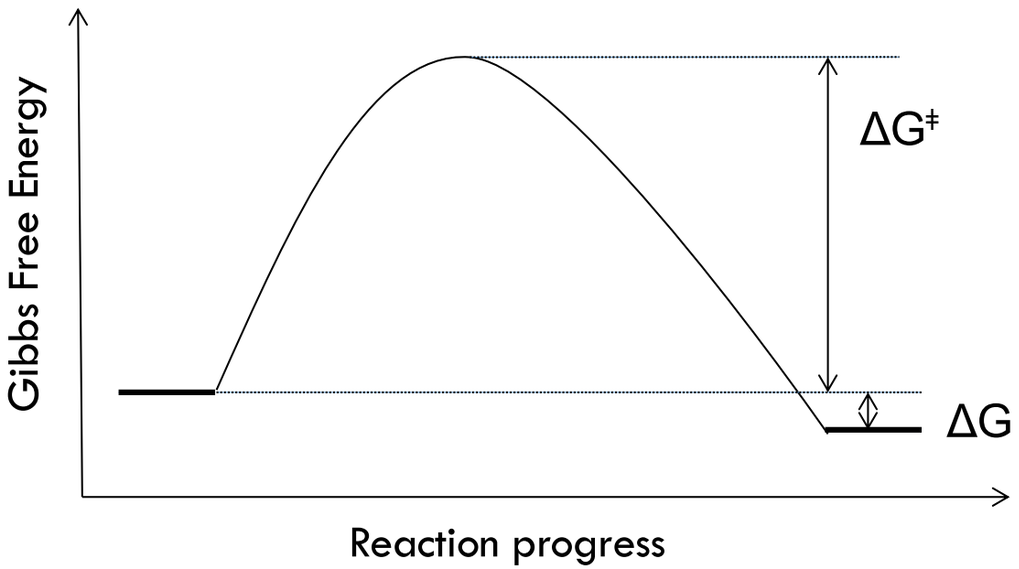
where $\quad k = 4\pi \cdot \left(r_o + r_g\right) \cdot \left(D_o + D_g\right) \cdot N_A \qquad \leftarrow$ rate coefficient



The reaction rate of a diffusion-controlled reaction depends on the diffusion coefficients of the reaction partners ($D_o + D_g$), and the distance at which the reactants touch and are able to react ($r_o + r_g$).

Activated reactions

Q2

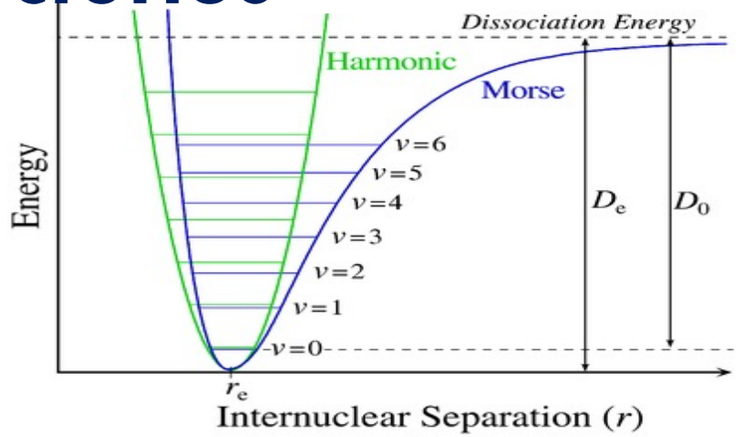


- Most reactions don't occur every time the reactants collide. They need the energy and steric orientation to pass through a transition state (sometimes called an "activated complex").
- Since the energy of molecules is very sensitive to the temperature of the system, we need to reduce our diffusion-controlled rate by a temperature-sensitive factor.
- Svante Arrhenius proposed in 1889 that the temperature dependence of rate constants follows a relationship:

$$k = A \exp(-E_a/RT)$$

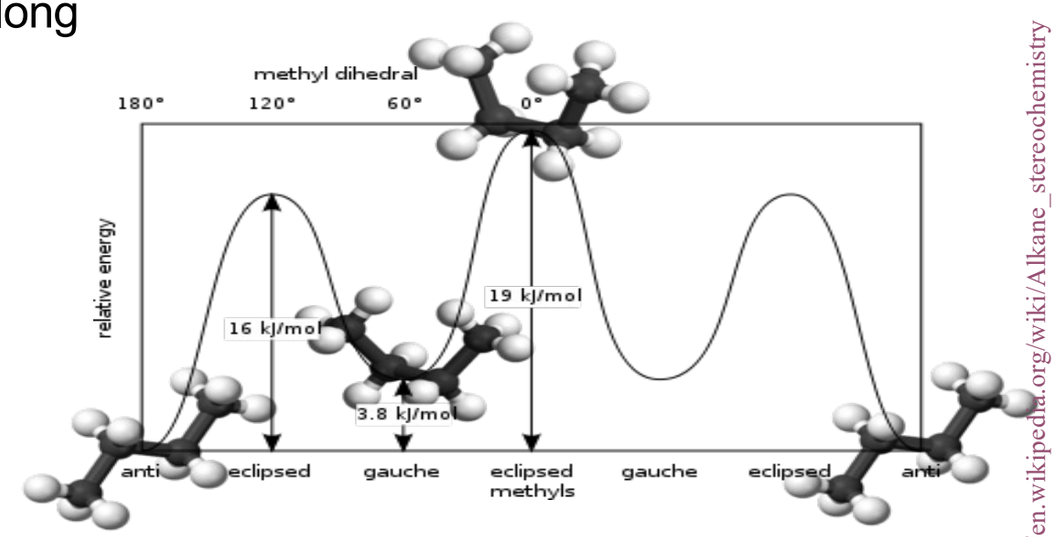
Activated chemical reactions as trajectories

Dissociation is a bond stretching vibrational mode. For a simple diatomic, we can express this as a one-dimensional graph of potential energy versus internuclear separation or bond length.



Dimerisation starts out as translation, but at small distances intermolecular forces come into play as a bond forms. The force acting on an atom or molecule is the derivative of the potential energy along that reaction coordinate.

Internal rotations of organic molecules are also one-dimensional graphs of potential energy versus dihedral angle (assuming no bonds stretch during rotation).



In this classical picture, a reaction can be regarded as movement along a potential energy curve.

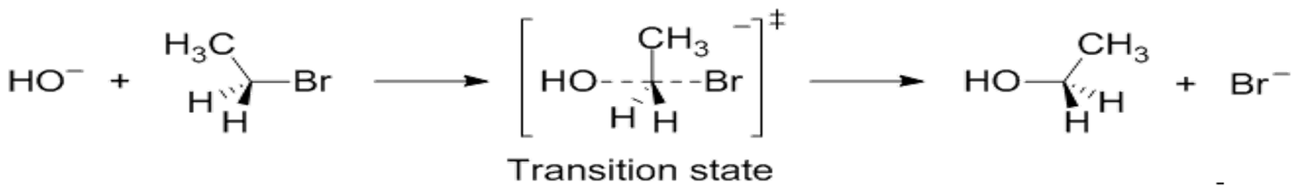
http://en.wikipedia.org/wiki/File:Morse-potential.png

http://en.wikipedia.org/wiki/Alkane_stereochemistry

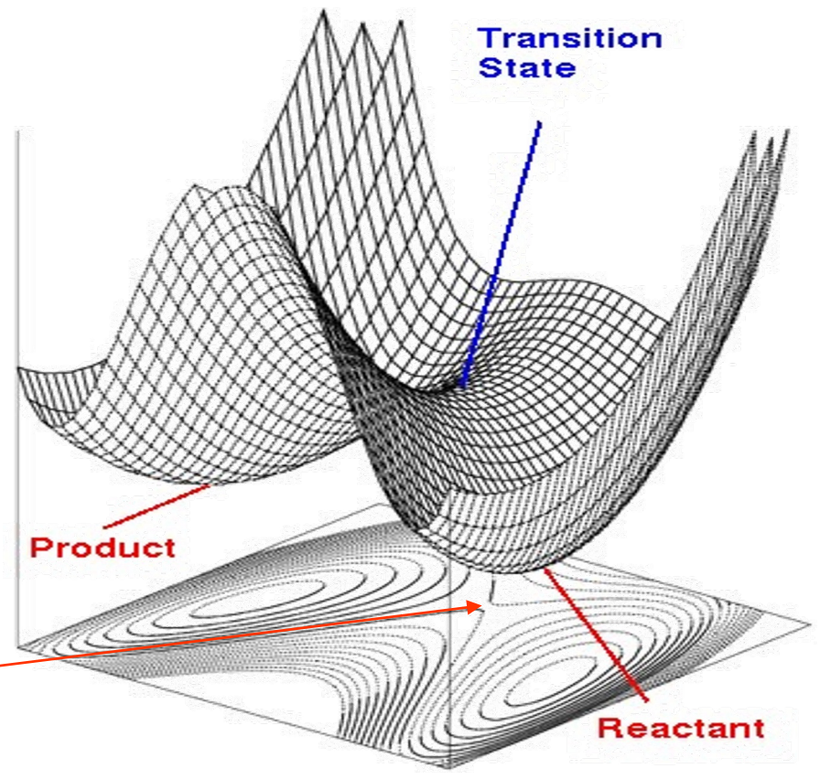
The Potential Energy Surface and the Transition State

A reaction may involve movement along more than one coordinate. For two coordinates, the potential energy function is a surface. Even though it is hard to visualise for more than two coordinates, we still talk about a potential energy surface.

The transition state is a particular configuration of reactants along the reaction trajectory.



It corresponds to the saddle point of the potential energy surface. For example



The potential energy surface can be pictured in 2D using a contour plot where each line connects points of equal potential energy (i.e. 'height').

Note how the saddle point looks in the contour plot.

http://www.chm.bris.ac.uk/pt/harvey/msci_pract/back_qm.html

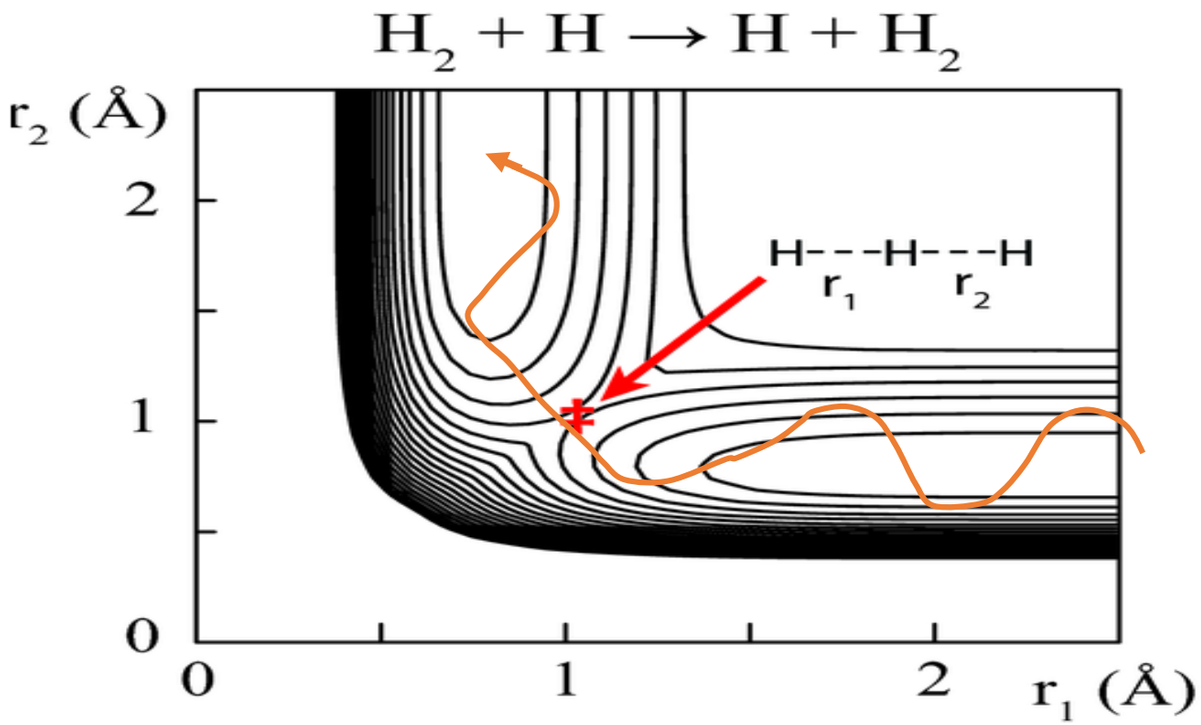
The simplest reaction: Hydrogen Exchange

Any bimolecular process is a variation on this simple reaction describing the exchange of a hydrogen atom in a hydrogen molecule, i.e.

$$H_a + H_b\text{-}H_c \rightarrow H_a\text{-}H_b + H_c$$

Studied by Eyring and Polanyi in 1931

Worksheet



The orange curve represents a reactive trajectory.

Note that reactive trajectories are forced to pass close to the saddle point (the 'mountain pass') between the reactant and product 'valleys'.

Transition State Theory

Transition state theory considers an equilibrium between reactants and the transition state, and expresses the equilibrium constant $K^{\ddagger}$ in terms of the Gibbs free energy difference between the transition state and the reactants ($\Delta G^{\ddagger}$), which can be decomposed into an enthalpic ($\Delta H^{\ddagger}$) and entropic ($\Delta S^{\ddagger}$) component.

$$K^{\ddagger} = \exp(-\Delta G^{\ddagger}/RT) = \exp(-\Delta H^{\ddagger}/RT)\exp(\Delta S^{\ddagger}/R)$$

Once at the transition state, a very fast rate coefficient k_p describes the microscopic dynamics of moving off the transition state. This is given by $k_p = k_B T/h$, where h is Planck's constant.

TST then obtains an expression for the rate constant *k*

$$k_{TST} = k_p K^{\ddagger}/2 = k_B T/2h \exp(\Delta S^{\ddagger}/R)\exp(-\Delta H^{\ddagger}/RT)$$

This gives the temperature dependence of reaction rates first described by Arrhenius in 1889. $\Delta H^{\ddagger}$ is often written as E_a, the *activation energy*.

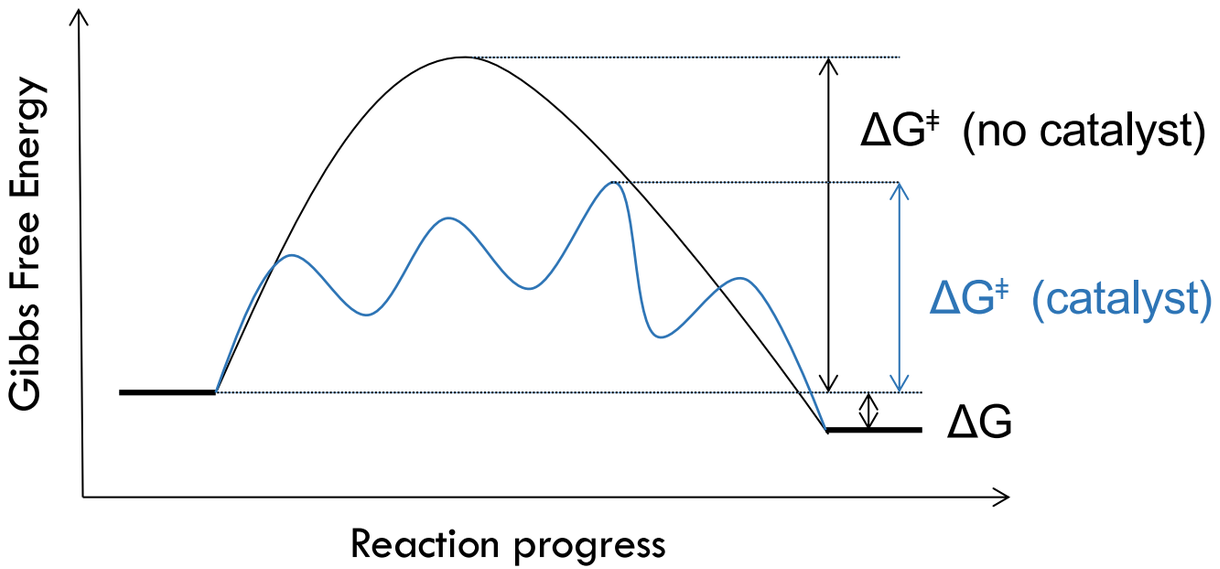
$$k_{TST} = A\exp(-E_a/RT) \qquad A = k_B T/2h \exp(\Delta S^{\ddagger}/R)$$

We can use quantum mechanics with statistical thermodynamics to calculate (via computer) the properties of the transition state and hence the rate constant, in the same way as we would for any other molecular structure.

Transition States and Catalysis

Q3

While the specific mechanism by which a catalyst acts may be complicated, the general explanation for the increase in the rate constant is simply that the Gibbs free energy of activation $\Delta G^{\ddagger}$ has been decreased. This can occur either by a change in $\Delta H^{\ddagger}$ (sometimes written as E_a), or by a change in $\Delta S^{\ddagger}$.



Learning outcomes

After this lecture you should be able to:

- Explain the factors affecting the kinetics of a diffusion-controlled reaction.
- Recognise integrated and differential rate laws for simple 0th, 1st, and 2nd-order reactions.
- Write down the relationship between the rates of formation and consumption of reactants and products in a balanced reaction.
- Understand the connection between the properties of the transition state and the temperature, and the reaction rate coefficient
- Explain the concept of catalysis, and provide a microscopic description of how it can enhance reaction rates