Development of Complex Curricula for Molecular Bionics and Infobionics Programs within a consortial* framework**

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**Molekuláris bionika és Infobionika Szakok tananyagának komplex fejlesztése konzorciumi keretben

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INTRODUCTION TO BIOPHYSICS

(Bevezetés a biofizikába)

DERIVATION OF THE RATE CONSTANT

(A sebességi együttható származtatása)

GYÖRFFY DÁNIEL, ZÁVODSZKY PÉTER

Introduction

- The temperature dependence of the rate constant is described by the empirical Arrhenius equation
- Several theories were established for calculating the value of rate constant and explaining the temperature dependence of the rate constant
- The collision theory considers reactions between atoms or molecules as collisions between rigid spheres

- Only collisions with sufficiently large kinetic energy along the straight line connecting the centres of colliding molecules or atoms lead to reaction
- Results from collision theory are in only qualitative agreement with the experimental results
- Transition state theory is based on free energies of different states
- The state with the highest free energy along the reaction path is called the transition state

- The difference in free energy between the initial state and the transition state is the activation energy
- Some improvements of transition state theory were carried out by Eyring
- The crucial assumption of Eyring's theory is that transition state itself is also in a free energy valley
- The transition state theory provides some quantitatively useful predictions

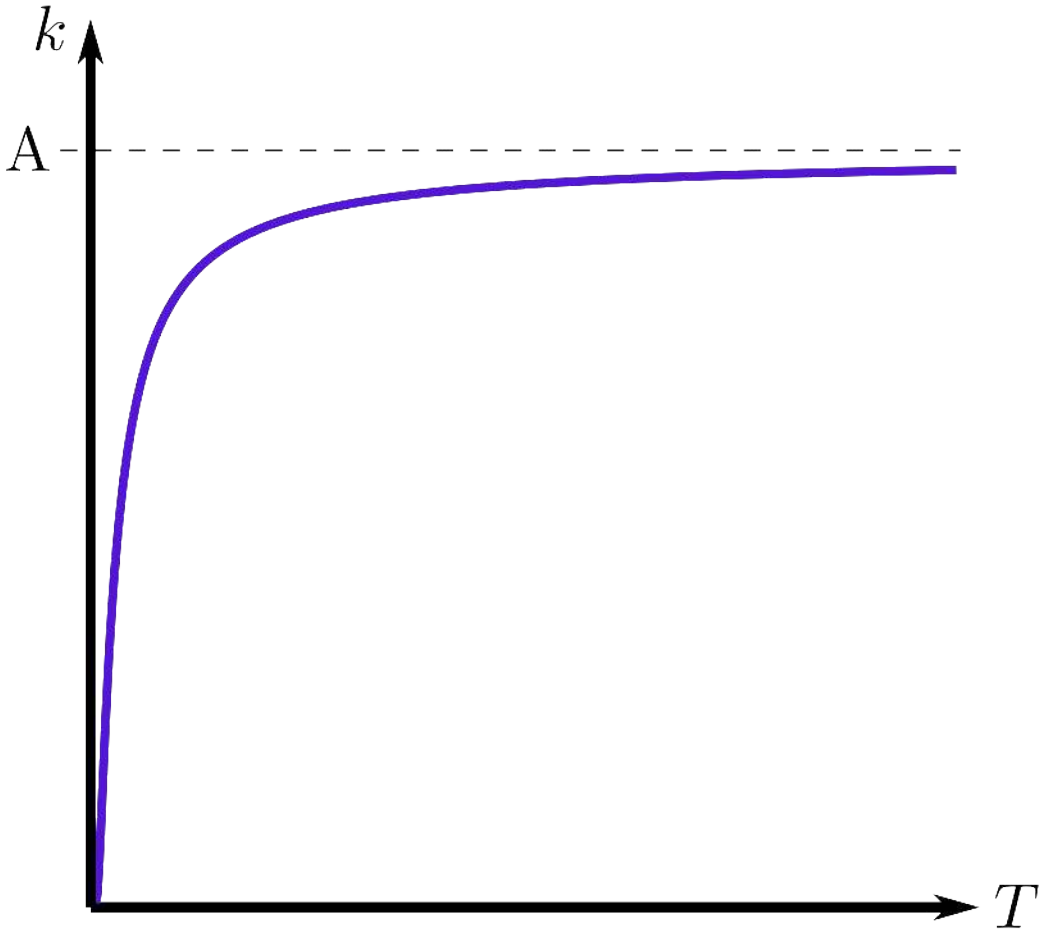
Arrhenius equation

- It was known that the rate of reaction depends on the temperature:
  - Warming speeds up and
  - Cooling slows down the reactions
- Arrhenius describes this relation in his famous equation

$$k = A\, e^{-E_A / RT}$$

where k is the rate constant, E_A is the activation energy, R=8.314 J·mole^{-1}·K^{-1} the gas constant, T is the temperature and A is the so called *pre-exponential factor* which can be different for different reactions and its value can be measured

The temperature dependence of the rate constant



Svante Arrhenius (1859-1927)

Determination of activation energy

- We can calculate the activation energy from the temperature dependence of the rate constant
- To make this calculation simpler, we derive a linear relationship from the Arrhenius equation

- Let us set out from the original form of the Arrhenius equation

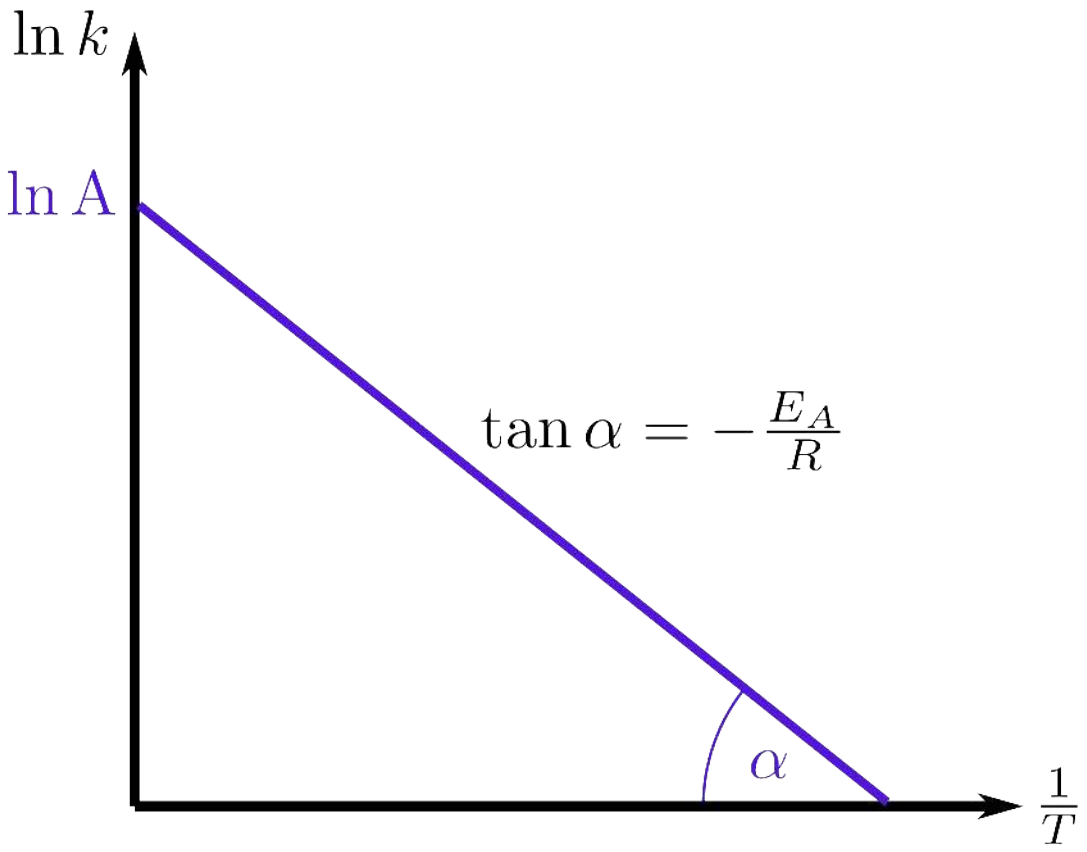
$$k = A\, e^{-E_A / RT}$$

- Let us take its logarithm

$$\ln k = \ln A - \frac{E_A}{RT}$$

- Now we would like to determine the activation energy of a particular reaction
- Let us measure the velocity of the reaction at different temperatures
- Let us plot ln k against $1/T$ to get a linear relationship

Linear form of Arrhenius plot



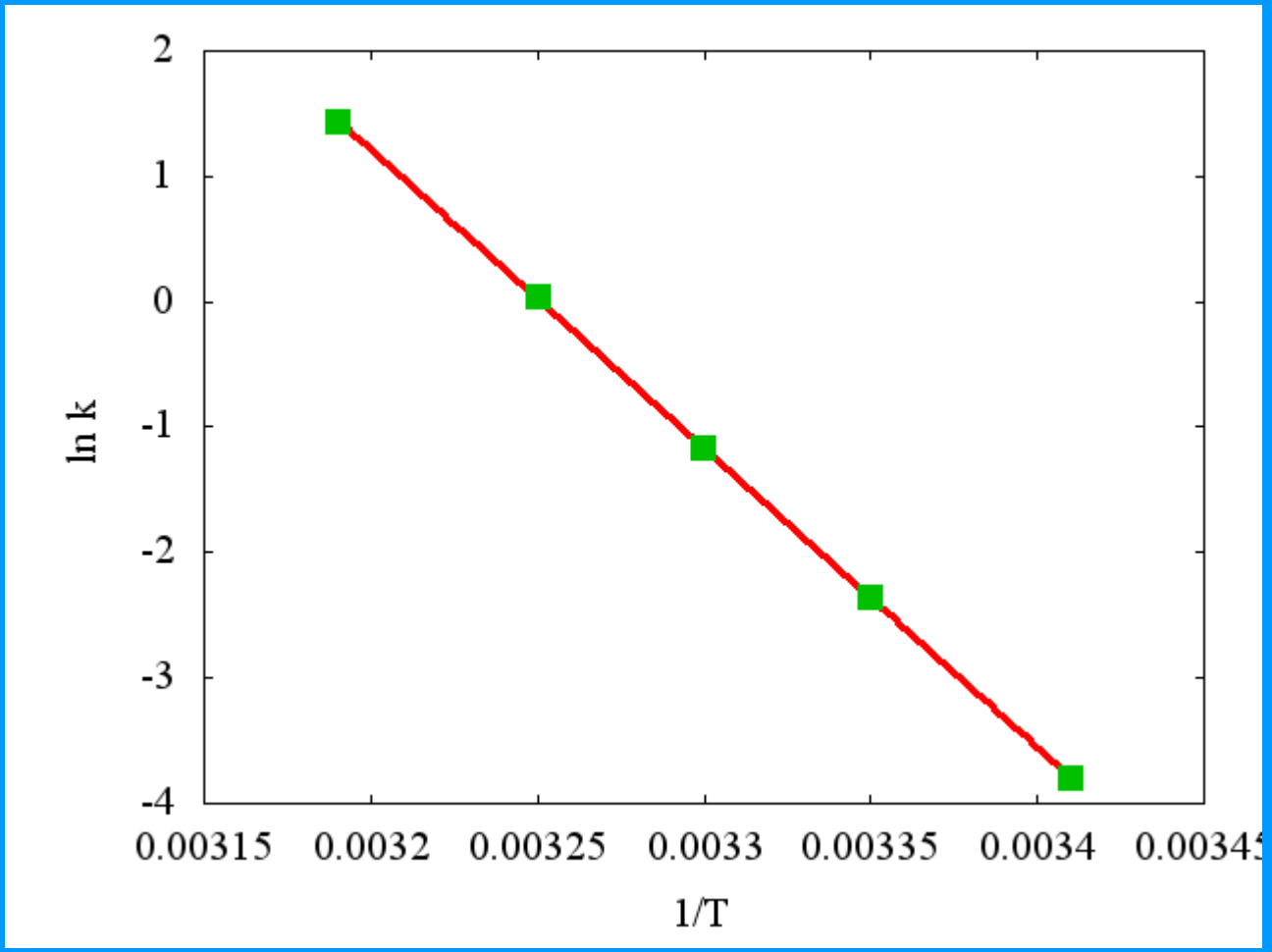
Problem 1

- We wonder what the activation energy of a given reaction is
- The values of the rate constant *k* as a function of the temperature were measured

The rate constant against temperature

T (K)	1/T (1/K)	ln k (ln 1/s)	k (1/s)
293	$3.41 \cdot 10^{-3}$	-3.8	$2.25 \cdot 10^{-2}$
298	$3.35 \cdot 10^{-3}$	-2.36	$9.44 \cdot 10^{-2}$
303	$3.30 \cdot 10^{-3}$	-1.16	$3.13 \cdot 10^{-3}$
308	$3.25 \cdot 10^{-3}$	0.04	1.04
313	$3.19 \cdot 10^{-3}$	1.44	4.39

The ln *k* vs. 1/*T* plot



- The slope of the fitted straight line can be read from the plot

$$slope = -\frac{E_A}{R} \approx -24000\ K^{-1}$$

- Thus the activation energy is

$$E_A \approx 200\ kJ/mol$$

The Maxwell-Boltzmann distribution

- Collision theory derives the rate constant from the number of collisions
- We can count collisions only if we know the velocities of atoms
- We do not know the velocities of all atoms but we know their probability distribution
- Velocities of atoms follow the Maxwell-Boltzmann distribution

- We already know that energies of particles follow the Boltzmann distribution

$$p(E)=\Omega(E)\frac{e^{-E/k_B T}}{\sum_j \Omega(E_j)\, e^{-E_j/k_B T}}$$

where *p(E)* is the probability that a particle has energy *E* or in other words, the ratio of particles with energy *E; Ω(E)* is the density of states of energy *E,* i.e. the number of states with energy *E* and $k_B=1.38\cdot10^{-23}$ J·K^{-1} is the *Boltzmann constant*

- To get the distribution of particle velocities, we have to determine a relationship between velocity and energy
- The kinetic energy of particles depends on velocity of those particles

$$E_k = \frac{m v^2}{2}$$

where E_k is the kinetic energy, v is the velocity and m is the mass of the particle

- First of all, let us reduce the problem to one dimension and consider only the component of velocity in the *x* direction
- According to the Boltzmann distribution

$$p(\mathbf{v}_x) = \frac{e^{-\varepsilon(\mathbf{v}_x)/k_B T}}{\int_{-\infty}^{\infty} e^{-\varepsilon(\mathbf{v}_x)/k_B T}} = \frac{e^{-m\mathbf{v}_x^2/2\,k_B T}}{\int_{-\infty}^{\infty} e^{-m\mathbf{v}_x^2/2\,k_B T}}$$

where $p(\mathbf{v}_x)$ is the probability that the *x* component of the velocity of a particle is $\mathbf{v}_x$, $\varepsilon(\mathbf{v}_x)$ is the kinetic energy corresponding to the *x* component of velocity

- Considering the integral

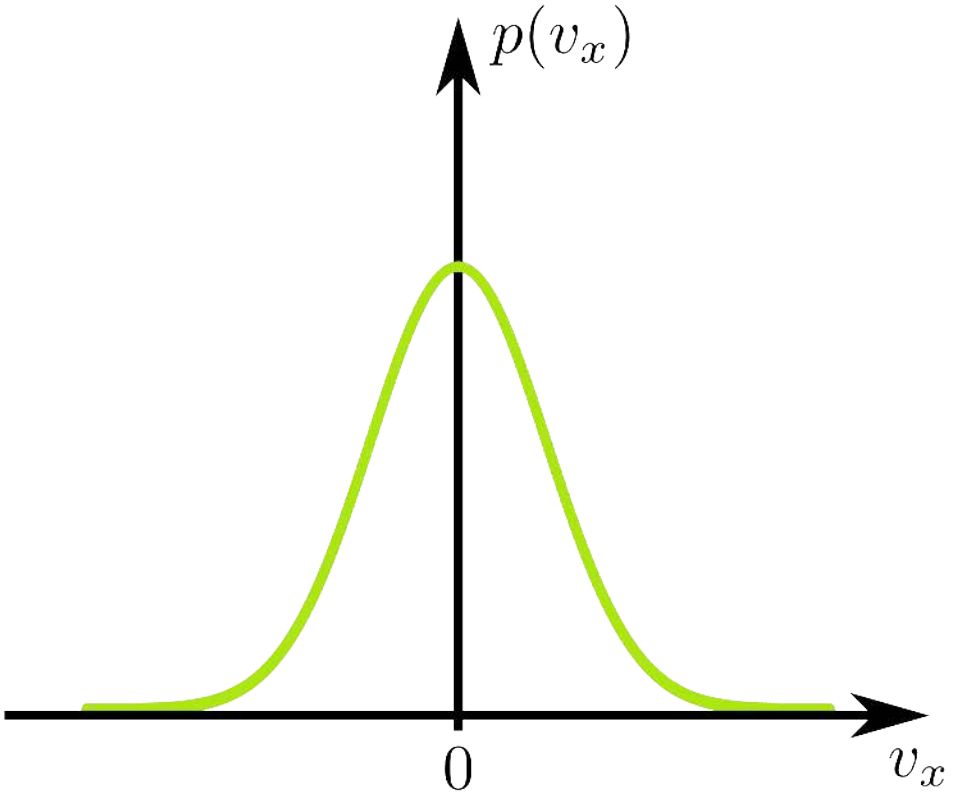
$$\int_{-\infty}^{\infty} e^{-a x^2}\, dx = \sqrt{\frac{\pi}{a}}$$

the probability is

$$p(\mathbf{v}_x) = \sqrt{\frac{m}{2\pi k_B T}}\, e^{-m \mathbf{v}_x^2 / 2 k_B T}$$

- This expression is the *Maxwell-Boltzmann distribution* for one component of the velocity

One-dimensional Maxwell-Boltzmann distribution



- Based on the results for one direction, let us build the expression for the total velocity vector
- The three dimensional velocity is

$$\mathbf{v}^2 = \mathbf{v}_x^2 + \mathbf{v}_y^2 + \mathbf{v}_z^2$$

- In an ideal gas, the one-dimensional components of velocity are independent of each other so the probability that the velocity vector is **v** is

$$p(\mathbf{v}) = p(\mathbf{v}_x)\, p(\mathbf{v}_y)\, p(\mathbf{v}_z)$$

- The probability that the particle has velocity characterized by the vector **v** is

$$p(\mathbf{v}) = \sqrt{\frac{m}{2\pi k_B T}}^{3} e^{-m(\mathbf{v}_x^2+\mathbf{v}_y^2+\mathbf{v}_z^2)/2k_B T} = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-m\mathbf{v}^2/2k_B T}$$

- The above expression only tells us what the probability of a particle with the velocity vector $\mathbf{v}(\mathbf{v}_x,\mathbf{v}_y,\mathbf{v}_z)$ is but we are interested in the distribution of absolute values i.e. the lengths of vectors

- The end points of vectors of identical lengths and beginning at the same point lie on the surface of a sphere with radius *v*
- so

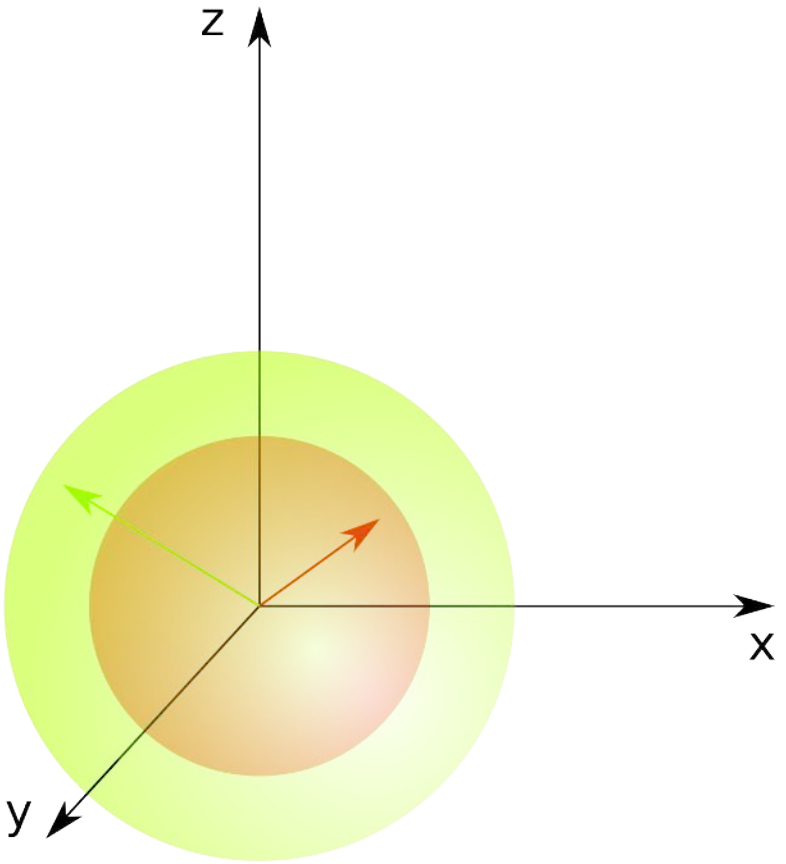
$$N_v \propto 4\pi v^2$$

where N_v is the number of vectors with length *v*

- Thus the probability distribution for *v* is

$$p(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T}$$

Number of vectors of length v



- Based on the distribution, we can obtain the average speed i.e. the expected value of *v*

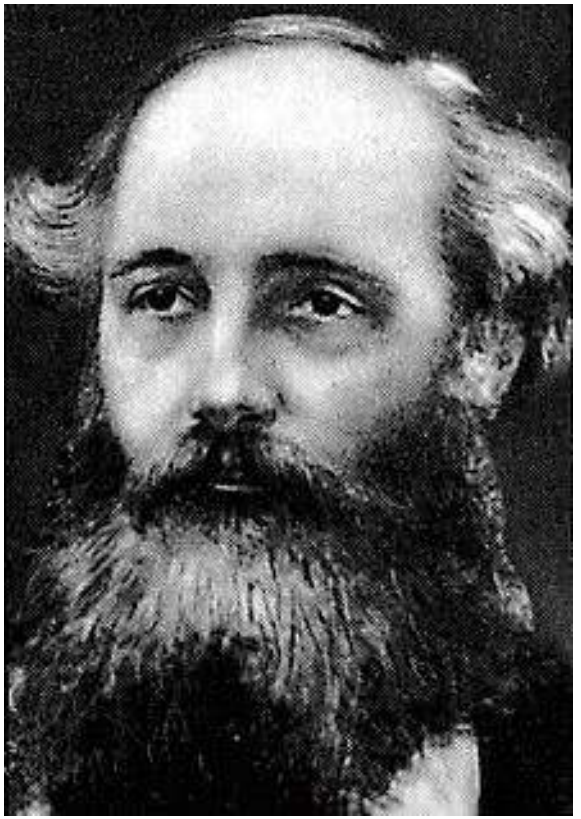
$$\bar{v} = \int_0^\infty v \cdot p(v)\, dv = \int_0^\infty 4\pi v^3 \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T} dv$$

- Making use of the integral $\int_0^\infty x^3 e^{-a x^2} = \frac{1}{2a^2}$

the average velocity is

$$\bar{v} = \left(\frac{8 k_B T}{\pi m} \right)$$

James Clerk Maxwell (1831-1879)

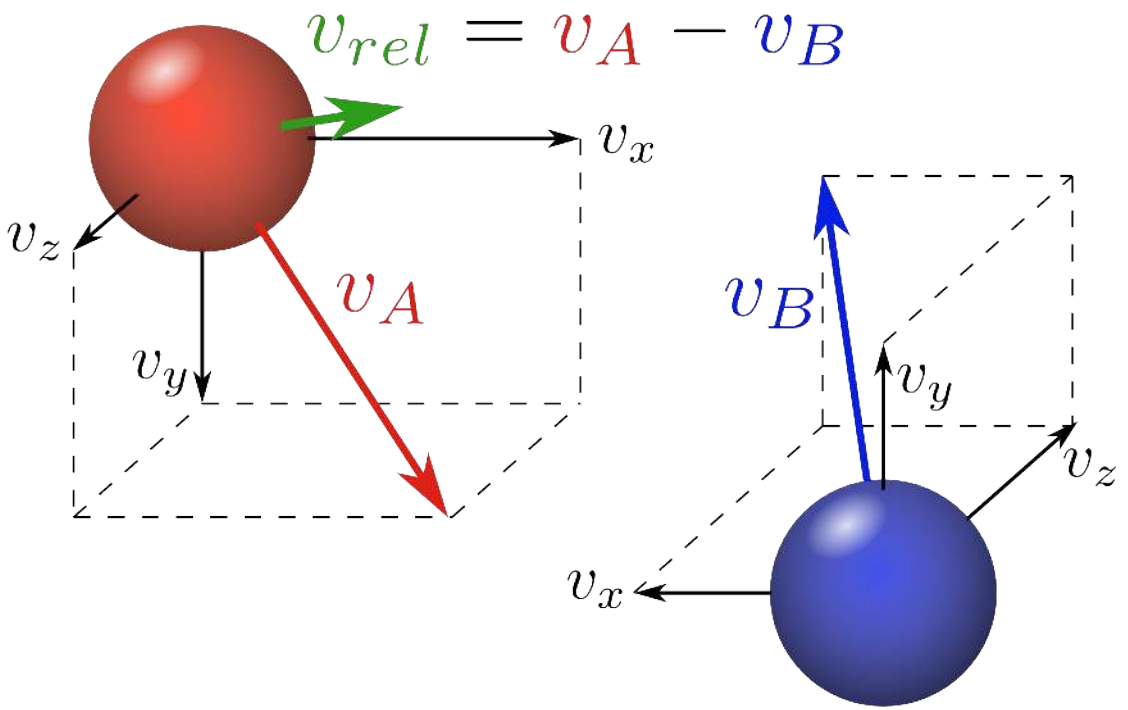


The collision theory

- Collision theory in pure form as described here applies only to gases
- Atoms or molecules are modelled by Newtonian rigid spheres
  - They are not compressible
  - Interaction between them occurs only when they touch each other
- They do not lose any kinetic energy during the collision

- Let us consider two atoms (spheres) A and B with radius r_A and r_B
- Let r_{eff} denote the effective radius $r_{eff}=r_A+r_B$
- Let v_A and v_B denote the velocity of the A and the B sphere, respectively
- To simplify calculations, let us consider the B sphere immobile and use the *relative velocity* $v=v_A-v_B$ rather than v_A and v_B

Relative velocity



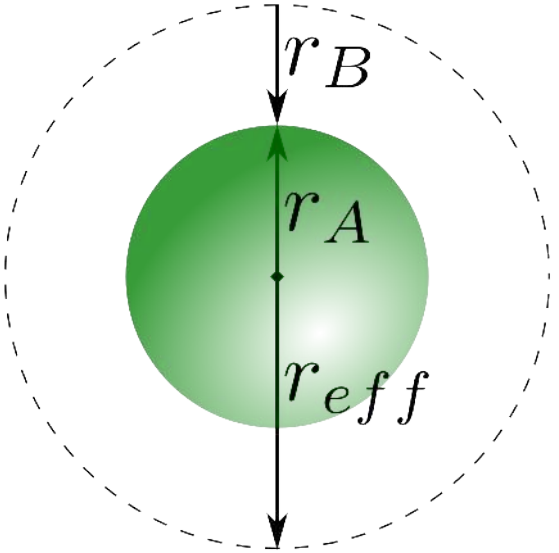
- Let *c* denote the *collision parameter* defined as the distance between straight paths of centres of spheres before collision
  - In the case of immobile sphere this is not a real path but a line which is parallel to the other path and go across the centre of the immobile sphere
- Collision occurs only if the collision parameter is smaller than the effective radius i.e.

$$c < r_{eff}$$

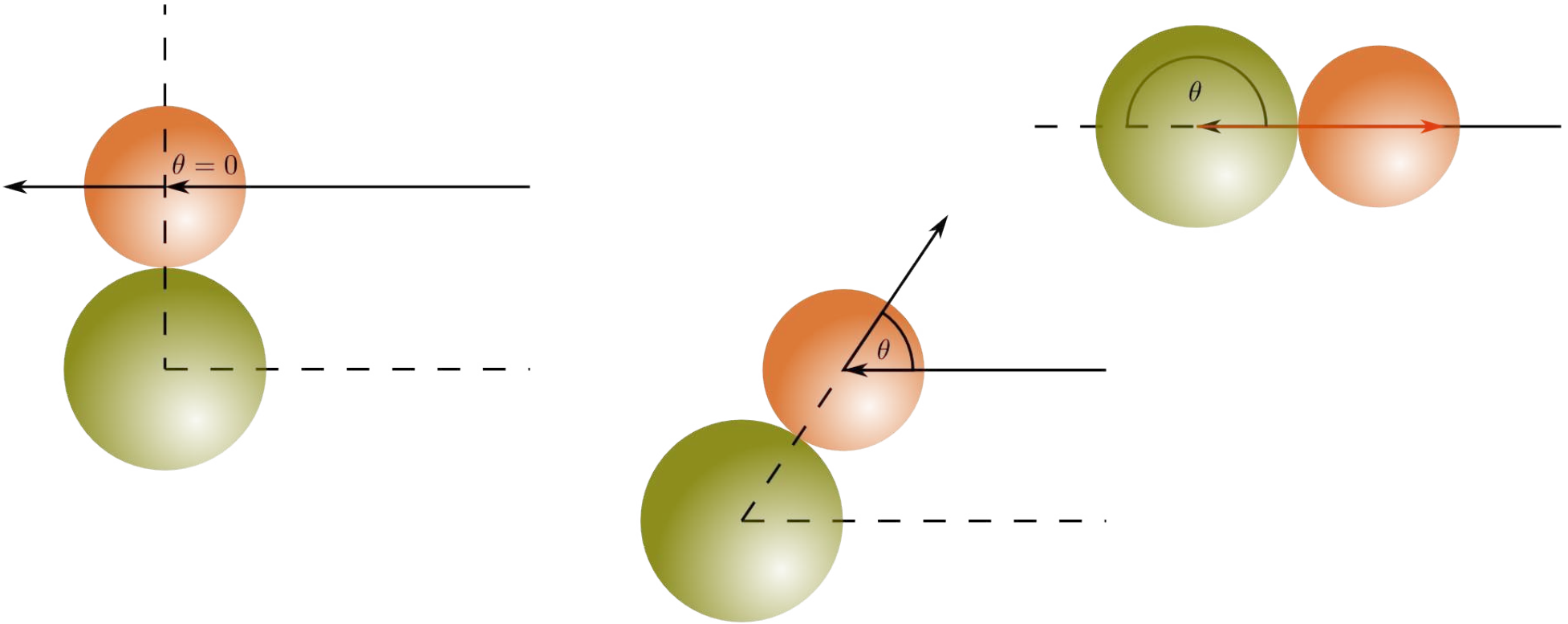
- In the case of $c=0$, the collision is frontal and if $c>r_{eff}$ a collision does not occur

- After collision the A atom is diverted by a θ angle which is a function of the collision parameter
- In the case of frontal collision $\theta=\pi$ and if $c>r_{eff}$ then $\theta=0$

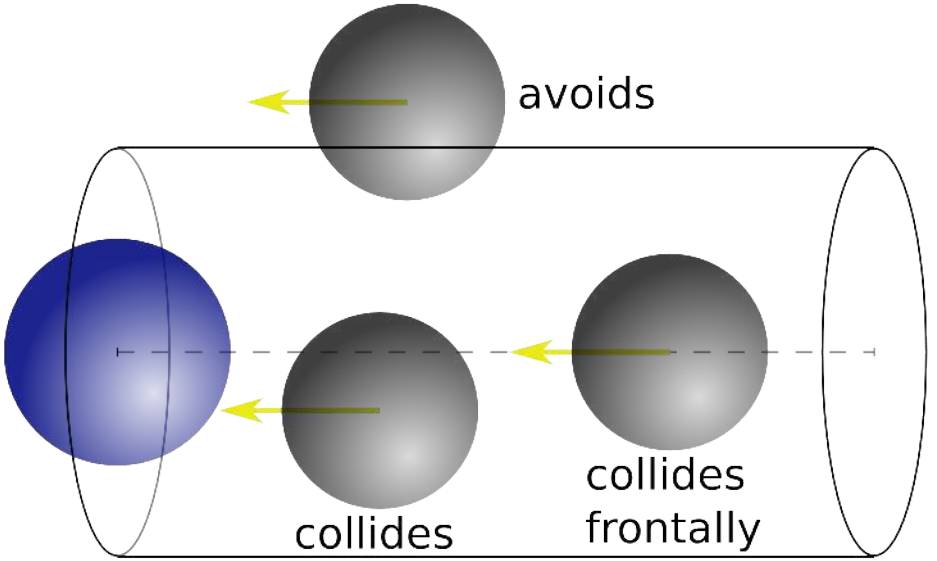
Reaction cross section



Direction of collisions



Collision cylinder



- Let us consider an A molecule traveling with velocity v in a unit volume within which there are N_B B molecules
- Collision occurs if the centre of a B molecule is in a circular $\pi \cdot r_{eff}^2$ area around the centre of A
- In unit time, an A molecule covers a distance v so it moves through a $\pi \cdot r_{eff}^2 \cdot v$ collision volume
- In a unit volume, there are N_A A molecules, so the number of collisions in unit volume and in unit time:

$$Z = N_A N_B \pi r_{eff}^2 v$$

- We are interested, however, not in collisions of one molecule but collisions of an ensemble of molecules
- Velocities of molecules are not the same but they follow the Maxwell-Boltzmann distribution as discussed earlier
- In the expression describing the number of collisions, we should substitute the velocity v of one molecule by the average velocity $\bar{v}$ of the ensemble of molecules

- According to the Maxwell-Boltzmann distribution, the average velocity $\bar{v}$ is

$$\bar{v} = \sqrt{\frac{8 k_B T}{m \pi}}$$

- Since we consider relative motions of molecules we should derive the average of relative velocities from the expression above

Two-body problem

- Let us consider two bodies with masses m_1 and m_2, respectively
- We are interested in only their relative motions and not in the motion of their centre of mass
- The kinetic energy of the whole system is

$$E_k = E_{k1} + E_{k2} = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2}$$

where p_1 and p_2 are the momentums, m_1 and m_2 are the masses of the bodies

- The position of the centre of mass is

$$x_{com} = \frac{m_1}{m} x_1 + \frac{m_2}{m} x_2$$

where

$$m = m_1 + m_2$$

and x_1 and x_2 are the positions of centres of mass of the first and second body, respectively

- The position difference vector of the two bodies

$$x = x_1 - x_2$$

- The positions of the bodies as a function of x_{com} and x are

$$x_1 = x_{com} + \left(\frac{m_2}{m}\right)x \qquad x_2 = x_{com} - \left(\frac{m_1}{m}\right)x$$

- Based on these expressions, we can define the momentums as a function of the centre of mass and the position difference of bodies

$$p_1 = m_1 \dot{x}_{com} + \left(\frac{m_1 m_2}{m}\right)\dot{x} \qquad p_2 = m_2 \dot{x}_{com} - \left(\frac{m_1 m_2}{m}\right)\dot{x}$$

- And the total kinetic energy as a function of x_{com} and x is

$$E_k = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} = \frac{m}{2}\dot{x}_{com}^2 + \frac{m_1 m_2}{2(m_1+m_2)}\dot{x}^2$$

where the dot on the top of letters denotes derivation with respect to time

- Let us introduce the reduced mass as

$$\mu = \frac{m_1 m_2}{m_1+m_2}$$

- Since we are interested in the motions influencing the relative positions of bodies, the distribution of relative velocities is calculated based on the kinetic energies of these relative motions
- In the expression of the average absolute velocity, the mass m of a single particle is substituted by the reduced mass μ of two particles:

$$\bar{v} = \frac{\sqrt{8\, k_B T}}{\mu\, \pi}$$

- Using the expression for the average relative velocity, we obtain that the total number of collisions in a unit volume and in unit time is

$$Z = N_A N_B \pi r_{eff}^2 \sqrt{\frac{8 k_B T}{\mu \pi}}$$

- For a reaction to occur, some rearrangement of valence electrons is required which is energetically expensive
- Thus, for a reaction to occur, a simple collision is not enough but it requires a collision with enough energy along the straight line connecting the centres of atoms
- We are interested in the proportion of collisions with enough energy

- According to the Maxwell Boltzmann distribution, the fraction of particles with relative velocity *v* is

$$p(v)\,dv = 4\pi \left(\frac{\mu}{2\pi k_B T} \right)^{3/2} v^2 e^{-\mu v^2 / 2 k_B T}\, dv$$

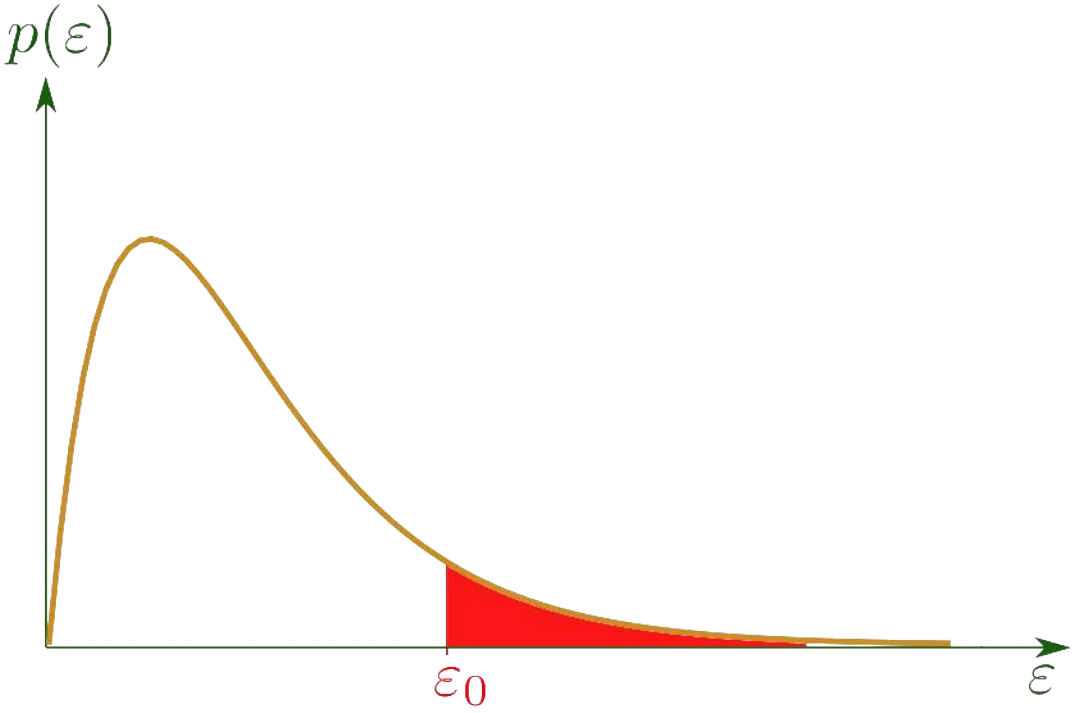
- The distribution of kinetic energies from the relative velocities is

$$p(\varepsilon)\,d\varepsilon = 4\pi\left(\frac{\mu}{2\pi\,k_B T}\right)^{3/2}\frac{2\varepsilon}{\mu}\,\frac{1}{\sqrt{2\,\mu\,\varepsilon}}\,e^{-\varepsilon/k_B T}\,d\varepsilon$$

taking into account that

$$v^2 = \frac{2\varepsilon}{\mu} \qquad \text{and} \qquad dv = \frac{d\varepsilon}{\sqrt{2\,\mu\,\varepsilon}}$$

Probability density function of collision energies

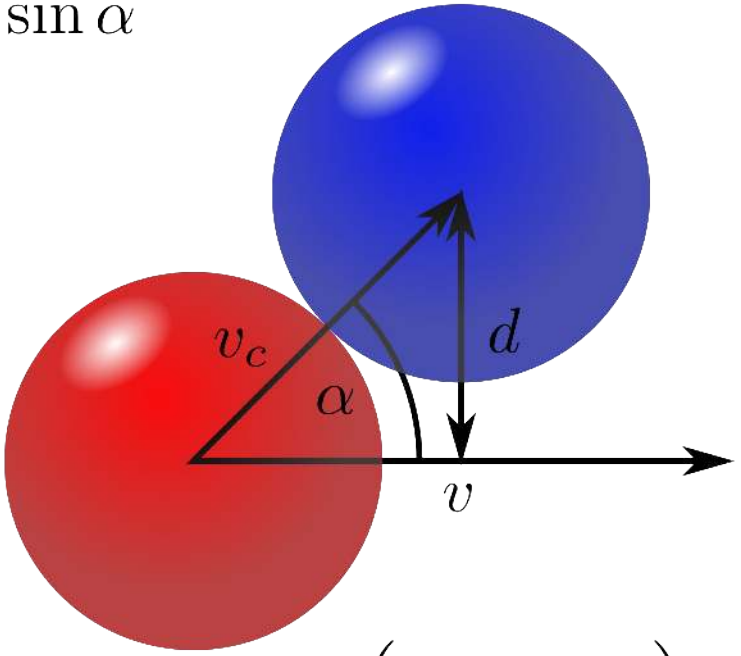


- In the case of a collision, only the kinetic energy due to the velocity component along the line connecting the centres of particles gets utilized
- We should determine this velocity based on the relative velocity
- The figure below helps us to understand it

Velocity component between centres

$$|v_c| = r_{eff}$$

$$d = r_{eff} \sin\alpha$$



$$v_c = v\cos\alpha = v\left(r_{eff}^2 - d^2\right)/r_{eff}^2$$

- Since

$$v_c = v_{rel}\left(r_{eff}^2 - d^2\right)/r_{eff}^2$$

the component of the kinetic energy we are interested in is

$$\varepsilon_c = \varepsilon\left(r_{eff}^2 - d^2\right)/r_{eff}^2$$

- Only those collisions lead to reaction where this component of kinetic energy is higher than a given limit energy

$$\varepsilon_c > \varepsilon_0$$

- Given the kinetic energy ε of relative velocity, we can define a maximum value of d where ε_c is exactly ε_0

$$\varepsilon_0 = \varepsilon_c = \varepsilon \left(r_{eff}^2 - d_{max}^2 \right) / r_{eff}^2$$

thus

$$d_{max}^2 = r_{eff}^2 \left(1 - \varepsilon_0 / \varepsilon \right)$$

- Since reaction occurs only when

$$d < d_{max}$$

we can define a modified effective reaction cross section

$$A_{eff} = \pi d_{max}^2$$

- The total number of collisions in unit time having enough energy for the reaction to occur, which is the rate of the reaction, is the integral over the distribution of relative kinetic energies from ε_0 to infinity

$$\nu = \int_{\varepsilon_0}^{\infty} v_{rel}\, p(\varepsilon)\, A_{eff}(\varepsilon)\, d\varepsilon\, N_A\, N_B$$

where ν is the rate of the reaction and v_{rel} is the relative velocity of molecules

- After substitution the equation is

$$\nu = \int_{\varepsilon_0}^{\infty} \sqrt{\frac{2\varepsilon}{\mu}} \sqrt{\frac{4}{\pi k_B^3 T^3}} \sqrt{\varepsilon}\, \pi r_{eff}^2 \left(1 - \frac{\varepsilon_0}{\varepsilon}\right) e^{-\varepsilon / k_B T} N_A N_B$$

- Integrating the equation we get

$$\nu = \sqrt{\frac{8 k_B T}{\pi \mu}}\, \pi r_{eff}^2\, e^{-\varepsilon_0 / k_B T} N_A N_B$$

- Since

$$v = k N_A N_B$$

based on the equation above, the rate constant is

$$k = \sqrt{\frac{8 k_B T}{\pi \mu}} \pi r_{eff}^2 e^{-\varepsilon_0 / k_B T}$$

- The relation between the gas constant and the Boltzmann constant is

$$R = k_B A_N$$

where $A_N = 6.022 \cdot 10^{23}$ mol^{-1} is the *Avogadro constant* which is the number of atoms or molecules in a mole

- Thus

$$E_0 / R = \varepsilon_0 / k_B$$

where E_0 relates to one mole material

Amedeo Avogadro (1776-1856)

- Based on the collision theory, we obtain a molecular description of both the exponential and the preexponential factor in the Arrhenius equation

$$A_{th} = \Phi_c = \sqrt{\frac{8 k_B T}{\pi \mu}} \pi r_{eff}^2$$

where *A* is the theoretically calculated preexponential factor and Φ_c is the collision frequency

- Based on the theory, predictions can be made and results calculated from the theory can be compared with the experimental data
- Unfortunately, most of the theoretical results are at most in a weak agreement with the experimental data

Comparison of theoretically and experimentally obtained reaction rates

Reaction	Collision frequency	Preexponential factor	Steric factor
$2ClNO \rightarrow 2Cl + 2NO$	$9.4 \cdot 10^{9}$	$5.9 \cdot 10^{10}$	0.16
$2ClO \rightarrow Cl_2 + O_2$	$6.3 \cdot 10^{7}$	$2.5 \cdot 10^{10}$	$2.3 \cdot 10^{-3}$
$H_2 + C_2H_4 \rightarrow C_2H_6$	$1.24 \cdot 10^{6}$	$7.3 \cdot 10^{11}$	$1.7 \cdot 10^{-6}$
$Br_2 + K \rightarrow Kbr + Br$	10^{12}	$2.1 \cdot 10^{11}$	4.3

- To improve the agreement between the results obtained by theory and experiments, a steric factor can be introduced which reflects the fact that the assumption of spherical particles causes serious inaccuracy and that the orientation of particles during the collision has a significant influence of whether a reaction occurs
- A considerable insufficiency of the collision theory is that we cannot calculate the steric factor in advance so the collision theory is unsuitable for predicting the rate constant

- This more accurate model of the reaction rate is the transition state theory proposed by *Henry Eyring* and *Michael Polanyi*
- In order to understand the transition state theory, we require some quantum mechanical introduction

Elementary quantum mechanics

- In the early 1900s it became apparent that experimental results can only be explained by assuming that energy is not continuous but it can adopt only discrete values
- These energy levels are predictable by the Schrödinger equation

$$\mathscr{H}\ \psi = E_i \psi$$

where $\mathscr{H}$ is the *Hamiltonian operator*, ψ is the *wave function* and E_i is the energy of a given energy level

William Rowan Hamilton (1805-1865)

- The wave function $\psi(x,y,z)$ does not have a easy-to-grasp meaning but its square ψ^2 is the probability density function of the location of the particle
- Hamiltonian operator describes the relevant forces acting on the particle studied
- To obtain the Hamiltonian operator for our problem, we can set out from two basic operators: the operator of momentum and the position coordinate

- The operator of the momentum is

$$\hat{p} = \frac{\hbar}{i}\frac{d}{dx}$$

where $\hat{p}$ is the momentum operator, i is the imaginary unit and

$$\hbar = \frac{h}{2\pi}$$

where $h = 6.626 \cdot 10^{-34}$ is the Planck constant

- The operator of the position coordinate is

$$\hat{x} = x\times$$

Where $\hat{x}$ is the operator of position and $x\times$ represents the multiplication by x

- Based on these operators, we can define the operator of kinetic energy

$$\hat{E} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

where $\hat{E}$ is the operator of the kinetic energy and m is the mass of the particle

Solution of the Schrödinger equation

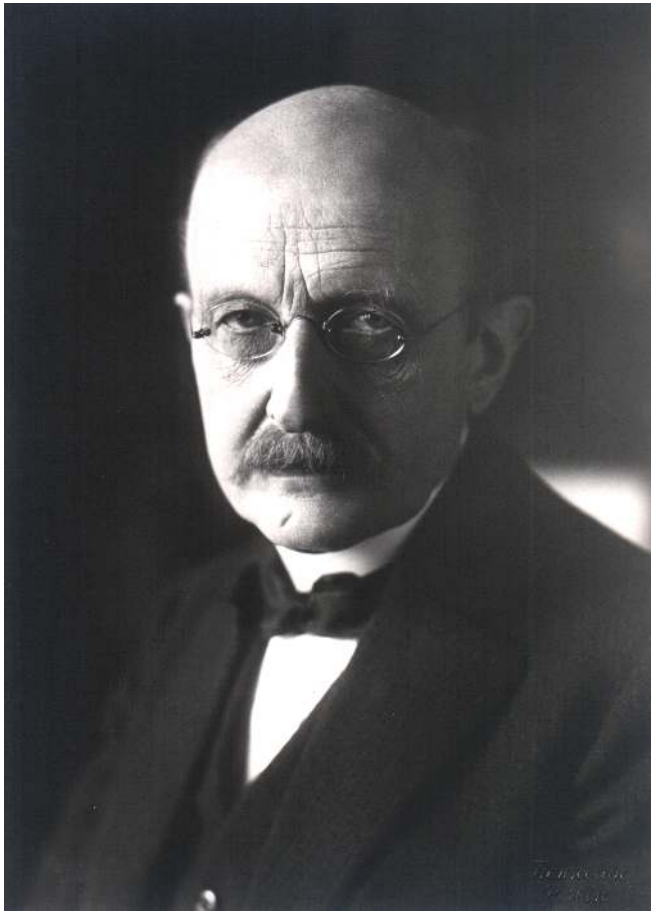
- To obtain the energies and the wave function, we can solve the Schrödinger equation
- For different problems, the Hamiltonian operator can adopt different forms, but generally it contains two terms corresponding to the kinetic and potential energy

$$\mathscr{H} = \hat{E} + \hat{V}(x)$$

Erwin Schrödinger (1887-1961)

Werner Heisenberg (1901-1976)

Max Planck (1858-1947)



Translational motion

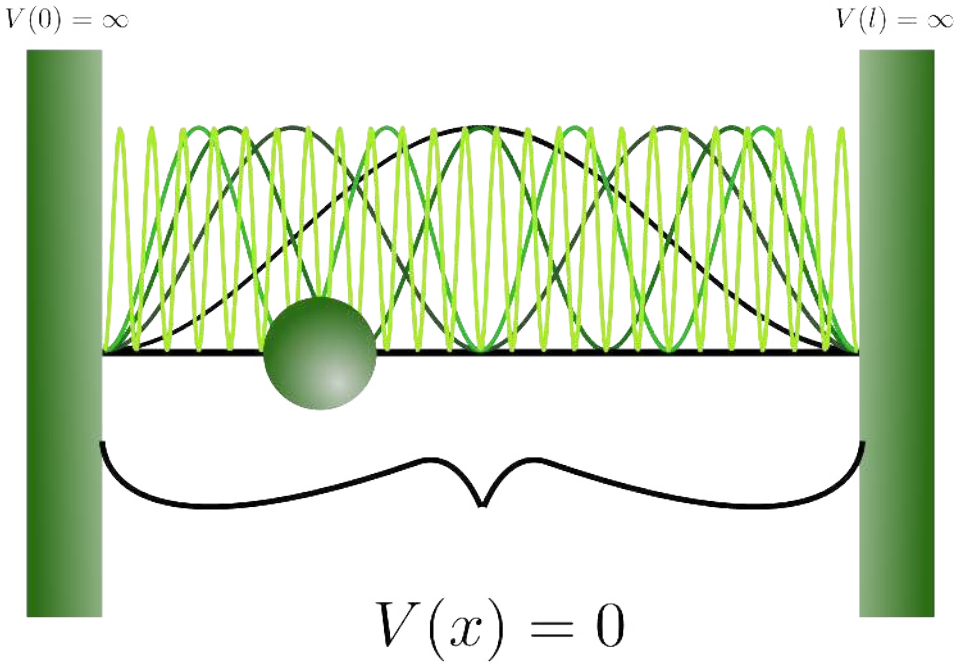
- Let us consider a particle in a box allowing only one-dimensional motion
- The walls of the box are represented mathematically by

$$V(0)=\infty \qquad \text{and} \qquad V(l)=\infty$$

where l is the length of the box and at any other 0<x<l position

$$V(x)=0$$

One-dimensional translational motion



- Thus the Hamiltonian operator for the one-dimensional translation is

$$\mathscr{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

and the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d\psi}{dx^2} = E\psi$$

- After rearranging the Schrödinger equation we obtain the

$$\frac{d^2\psi}{dx^2}+k^2\psi=0$$

second order differential equation where

$$k^2=\frac{2mE}{\hbar^2}$$

- The solution of the Schrödinger equation is

$$\psi(x) = A\sin kx + B\cos kx$$

where A and B are constant

- To get the value of A and B, we can utilize the constraint imposed by the potential energy at the walls, namely

$$V(0) = \infty \qquad \text{and} \qquad V(l) = \infty$$

- Because the potential energy at the walls is infinity, the probability that a particle stays there is zero, so

$$\psi^2(0)=0$$

and so

$$\psi(0)=0$$

- If x=0 then

$$A \sin kx = 0 \qquad \text{and} \qquad B \cos kx = 1$$

- Since Ψ(0) must be zero, B also must be zero
- So for Ψ(x) we obtain that

$$\psi(x) = A \sin kx$$

- The second boundary condition will help us to determine the value of A

$$\psi(l) = A \sin kl = 0$$

- Disregarding the trivial but uninteresting solution A=0 the equation above is satisfied only if

$$kl = n\pi$$

where

$$n = 1, 2, 3, \ldots$$

is a positive integer

- Setting out from the equation above we get

$$\sqrt{\frac{2mE_n}{\hbar^2}}l = n\pi$$

- And the energy values of different levels are

$$E_n = \frac{n^2\pi^2\hbar^2}{2ml^2} = \frac{n^2h^2}{8ml^2}$$

Energy levels for a particle in a box

$n = 4$ $E_4 = 16$

$n = 3$ $E_3 = 9$

$n = 2$ $E_2 = 4$

$n = 1$ $E_1 = 1$

- The wave function can be obtained by using the property of probability density functions that

$$\int_0^l \psi(x)^2 dx = 1$$

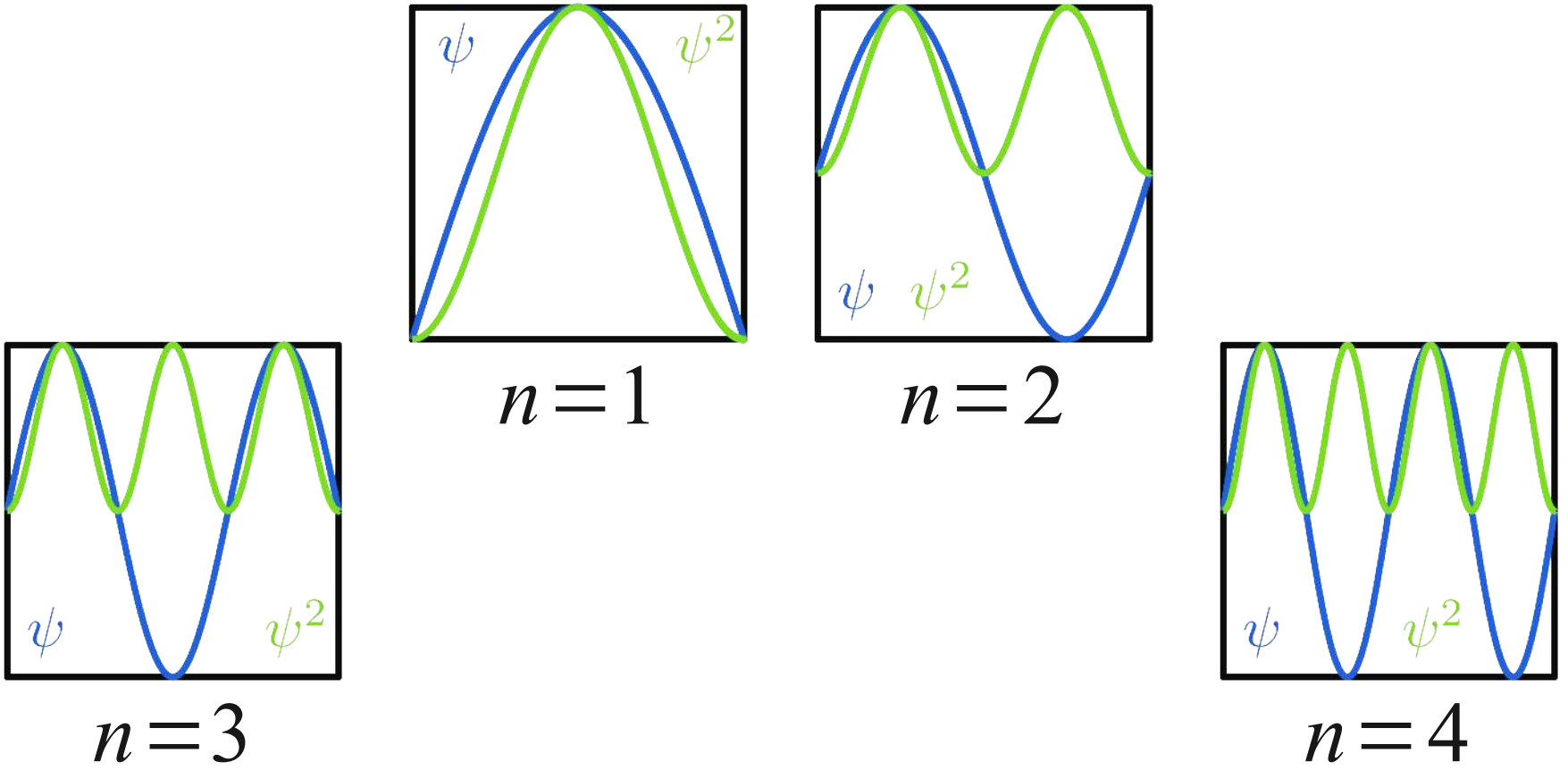
- Substituting the expression we got for Ψ(x)

$$A^2 \int_0^l \sin^2 kx \, dx = A^2 \frac{l}{2} = 1$$

- Thus the normalized *wave function* is

$$\psi_n(x) = \sqrt{\frac{2}{l}} \sin \frac{n \pi x}{l}$$

Wave functions and density functions for a particle in a box



- Let us generalize the problem to three dimensions
- The Schrödinger equation for a particle confined within a three dimensional box is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z)=E\,\psi(x,y,z)$$

- The equation can be separated and we get

$$\psi(x,y,z)=\psi(x)\psi(y)\psi(z)$$

and

$$E_n=E_x+E_y+E_z=\frac{h^2}{8m}\left(\frac{n_x^2}{l_x^2}+\frac{n_y^2}{l_y^2}+\frac{n_z^2}{l_z^2}\right)$$

where l_x, l_y and l_z are the length of the box in the x, y and z dimensions, respectively

Partition function for translation

- The general form of Boltzmann partition function is

$$Z = \sum_n e^{-E_n / kT}$$

- Substituting into the equation the energies we obtained by solving the Schrödinger equation, we get the partition function Z_t (t referring to translation)

$$z_t = \sum_n e^{-\frac{h^2}{8mkT}\left(\frac{n_x^2}{l_x^2}+\frac{n_y^2}{l_y^2}+\frac{n_z^2}{l_z^2}\right)}$$

- If the energy levels are sufficiently close to each other that so many energy levels are filled then the sum can be replaced by an integral

$$Z_t = \int_0^\infty e^{-\frac{h^2}{8mkT}\left(\frac{n_x^2}{l_x^2}+\frac{n_y^2}{l_y^2}+\frac{n_z^2}{l_z^2}\right)} dn$$

so

$$Z_t = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} l_x l_y l_z = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$$

where V is the volume

Harmonic oscillator

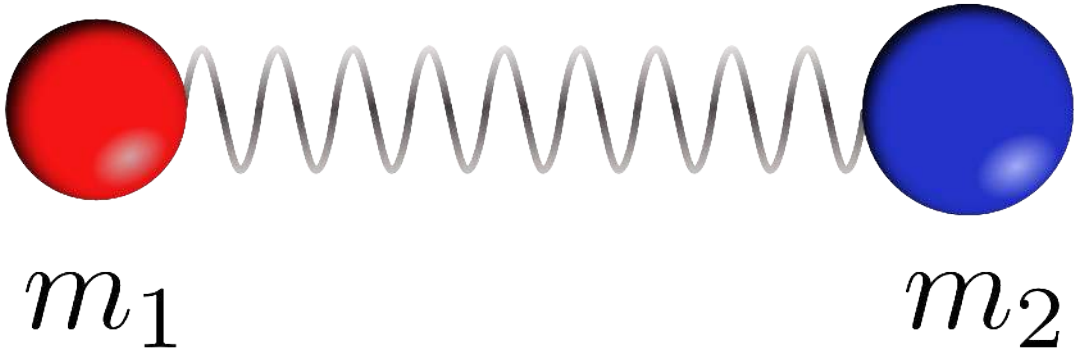
- For us, the most important motion is vibration which can be modelled as a harmonic oscillator
- Let us imagine our two-atom system as two bodies with mass *m* connected by a spring
- There is an equilibrium distance between the atoms where the potential energy is considered zero and which is at the x=0 place

- The potential energy as a function of the deviation from the equilibrium point is

$$V(x)=\frac{k_s x^2}{2}$$

where $V(x)$ is the potential energy and k_s is the spring constant which is characteristic of the given spring (or of the bond between the atoms in our case)

A model of harmonic oscillator



- Thus the total *Hamiltonian operator* for the vibration of a two-atom system is

$$\mathscr{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{k_s x^2}{2}$$

where μ is the reduced mass and the Schrödinger equation is

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi(x)}{dx^2} + \frac{k_s x^2}{2}\psi(x) = E\,\psi(x)$$

- After rearranging the equation we obtain a second-order differential equation for ψ

$$\frac{d^2\psi}{dx^2} - \frac{2\mu}{\hbar^2}\left(E - \frac{\mu\omega x^2}{2}\right)\psi = 0$$

where

$$\omega = 2\pi\nu = \sqrt{\frac{k_s}{\mu}}$$

is the angular frequency

- To obtain the wave functions, we apply a trick, namely we substitute

$$k=\frac{2E}{\hbar\omega} \qquad \text{and} \qquad \xi=\sqrt{\frac{\mu\omega}{\hbar}}x$$

into the equation above to get the simple form that

$$\frac{d^2\psi}{dx^2}+(k-\xi^2)\psi=0$$

- The solution can be written as

$$\psi = e^{-\frac{\xi^2}{2}} f(\xi)$$

where *f(ξ)* is some unknown function of ξ which we would like to determine

- Substituting this expression into the differential equation above we can write

$$\frac{d^2 f}{d\xi^2} - 2\xi \frac{df}{d\xi} + (k-1) f = 0$$

- Let us write f as a polynomial

$$f(\xi)=\sum_{i=0}^{n} c_i \xi^i$$

- It can be shown (derivation omitted) that since the polynomial has to be of finite length,

$$k=2n+1$$

- Polynomials *f(x)* satisfying the

$$\frac{d^2 f}{dx^2} - 2x\frac{df}{dx} + 2nf = 0$$

differential equation are called *Hermite polynomials* and denoted by $H_n(x)$

- Polynomials corresponding to the first seven (0-6) degrees are listed in the following table

Hermite polynomials

n	$H_n(x)$
0	1
1	$2x$
2	$4x^2-2$
3	$8x^3-12x$
4	$16x^4-48x^2+12$
5	$32x^5-160x^3+120x$
6	$64x^6-480x^4+720x^2-120$

Charles Hermite (1822-1901)

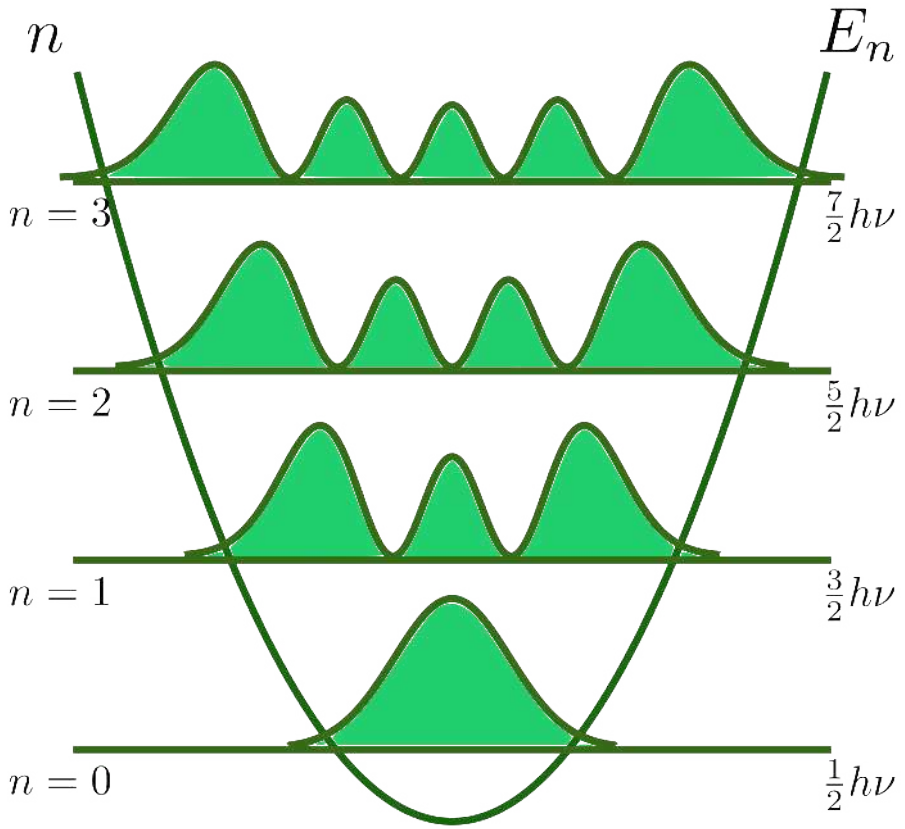
- Based on the equation $k=2n+1$, we obtain the energy levels:

$$E_n = \hbar\omega\left(n+\frac{1}{2}\right) = h\nu\left(n+\frac{1}{2}\right)$$

where n=0, 1, 2 ... is a non-negative integer

- It can be observed that even in the ground state ($n=0$) there is an oscillation with energy $E_n=h\nu/2$ which is called *zero-point energy*

Wave function and energy levels for a harmonic oscillator



Partition function of vibration

- Repeating the argument used in the case of translation, we get for the partition function of vibrational motion that

$$z_v = \sum_{n=0}^{\infty} e^{-(n+1/2)h\nu/kT} = e^{-h\nu/2kT}\left(1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + \ldots\right)$$

- Since the expression in the brackets in the equation above has the form

$$1 + x^2 + x^3 + \ldots$$

which is the series expansion of

$$(1 - x)^{-1}$$

the simple form of the partition function

$$z_v = \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}}$$

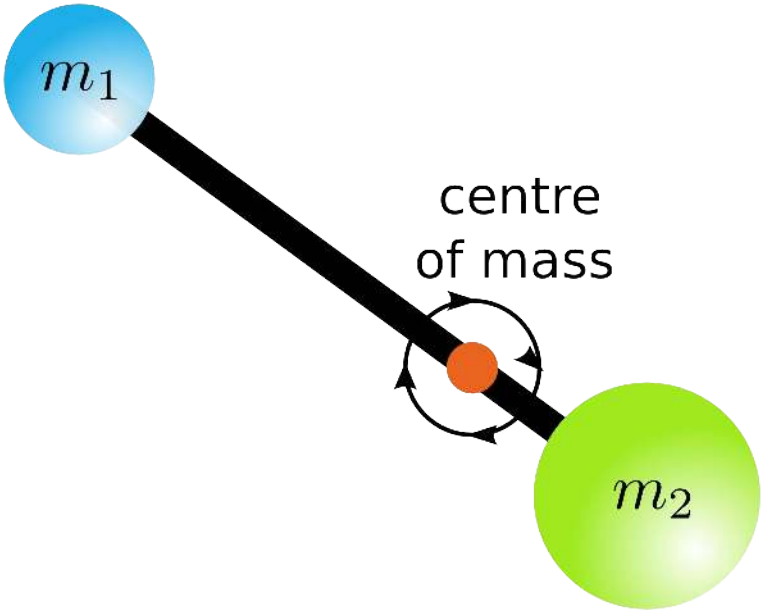
Rotation

- The third form of movement which contributes to the energy of a given particle is rotation
- The rotation of a molecule consisting of two atoms of masses m_1 and m_2 separated by a distance r can be modelled as a single particle with mass

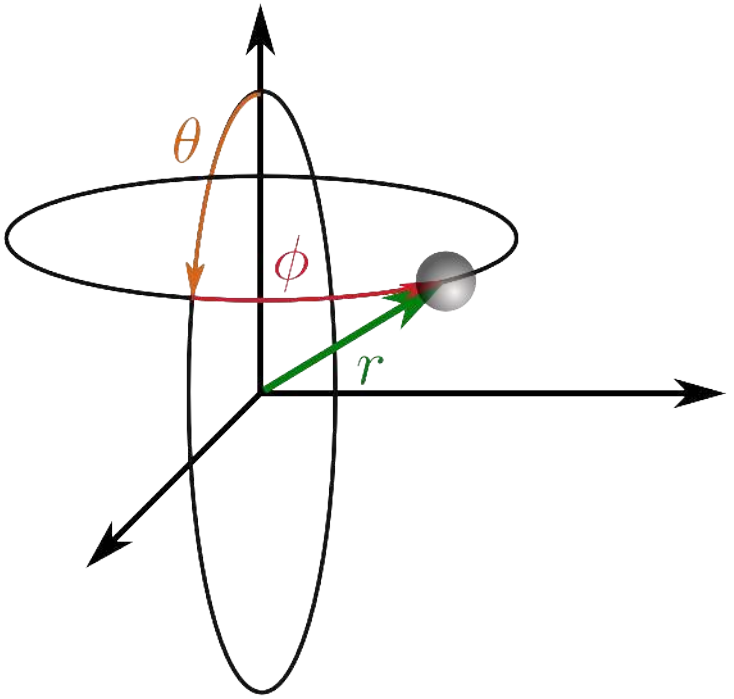
$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

orbiting at a distance r around a centre point

Rotation of a two-atomic molecule



Spherical polar coordinates of a particle



- The particle performing rotation has only kinetic energy so the Hamiltonian operator for it is

$$\mathscr{H} = -\frac{\hbar^2}{(2\mu)}\frac{d^2}{dx^2}$$

and thus the Schrödinger equation is

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi(x)}{dx^2} = E\,\psi(x)$$

- To make the calculations simpler, let us consider ψ as a function of r, θ and ϕ, where r is the radius of the orbit and θ and ϕ are polar angles
- Since r is constant we consider ψ as a function of only the two angles

- Thus the Hamiltonian operator expressed by θ and ϕ is

$$\mathscr{H} = -\frac{\hbar^2}{2\mu}\Delta$$

where Δ is

$$\Delta = \frac{1}{r^2}\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

the *Laplace* operator

Pierre Simon Laplace (1749-1827)

- After substitutions and rearrangement, the Schrödinger equation is

$$\frac{\partial^2\psi}{\partial\theta^2}+\cot\theta\frac{\partial\psi}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}=-\frac{2\mu r^2}{\hbar^2}E\psi$$

where the differential equation to be solved is

$$\frac{\partial^2\psi}{\partial\theta^2}+\cot\theta\frac{\partial\psi}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}+\frac{2I}{\hbar^2}E\psi=0$$

where $I=\mu r^2$ is the *moment of inertia*

- Omitting derivation again, the wave function is obtained as:

$$\psi_{\ell,m}(\theta,\phi)=\sin^{|m|}\theta\, P_{\ell,m}\cos\theta\, e^{im\phi}$$

which are called *spherical harmonics* and where $P_{\ell,m}$ is a *Legendre polynomial*, ℓ and m are quantum numbers

$$\ell=0,1,2\ldots \quad \text{and} \quad m=-\ell,-\ell+1\ldots 0,1\ldots \ell-1,\ell$$

Spherical harmonics

ℓ	m	$Y_{\ell,m}$
0	0	$(1/4\pi)^{1/2}$
1	0	$(3/4\pi)^{1/2} \cos\theta$
	±1	$(3/8\pi)^{1/2} \sin\theta\, e^{\pm i\Phi}$
2	0	$(5/16\pi)^{1/2} (3\cos^2\theta - 1)$
	±1	$(15/8\pi)^{1/2} \cos\theta \sin\theta\, e^{\pm i\Phi}$
	±2	$(15/32\pi)^{1/2} \sin\theta\, e^{\pm 2i\Phi}$
3	0	$(7/16\pi)^{1/2} (5\cos^3\theta - 3\cos\theta)$
	±1	$(21/8\pi)^{1/2} (5\cos^2\theta - 1) \sin\theta\, e^{\pm i\Phi}$
	±2	$(105/32\pi)^{1/2} \sin^2\theta \cos\theta\, e^{\pm 2i\Phi}$
	±3	$(35/64\pi)^{1/2} \sin^3\theta\, e^{\pm 3i\Phi}$

Adrien-Marie Legendre (1752-1833)

- The energy levels are

$$E_\ell = \frac{\ell(\ell+1)\hbar^2}{2I}$$

- It can be seen that the energy is the function of only the ℓ quantum number so states characterized by different m values but by the same ℓ have the same energy and this energy level is said to be *degenerate* and it has a degeneracy of $2\ell+1$

Partition function of rotation

- The corresponding partition function is

$$z_r = \sum_{\ell=0}^{\infty} (2\ell + 1) e^{-E_l / kT}$$

which can be approximated by an integral if

$$T \gg \frac{2 I k}{\hbar^2}$$

- Then

$$z_r = \frac{2 I k T}{\sigma \hbar^2}$$

where σ is a symmetry factor which is σ=1 for heteronuclear and σ=2 for homonuclear diatomic molecules

- For nonlinear molecules, there are three *moments of inertia* and the corresponding partition function is

$$z_{r,nonlinear} = \frac{\sqrt{\pi I_x I_y I_z}}{\sigma}\left(\frac{2kT}{\hbar^2}\right)^{3/2}$$

where I_x, I_y and I_z are the moments of inertia corresponding to the rotational degrees of freedom

Gibbs free energy as a function of the partition function

- We already know that the *Helmholtz free energy* expressed by the partition function is

$$F = -k_B T \ln Z$$

- Based on this the pressure is

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = k_B T \left(\frac{\partial \ln Z}{\partial V}\right)_T$$

- The *Gibbs free energy* is

$$G = F + pV$$

and so

$$G - G(0) = -k_B T \ln Z + k_B T V \left(\frac{\partial \ln Z}{\partial V} \right)_T$$

where G(0) is the Gibbs free energy at absolute zero temperature

- For an ideal gas where

$$pV = Nk_B T$$

the expression above becomes

$$G - G(0) = -k_B T \ln Z + N\, k_B T$$

- The partition function of the whole system for indistinguishable particles can be expressed by the partition functions of the individual particles

$$Z = \frac{z^N}{N!}$$

which can be approximated based on the Stirling formula

$$\ln Z = N \ln \frac{z}{N} + N$$

- Thus

$$G - G(0) = -Nk_B T \ln \frac{z}{N} - Nk_B T + Nk_B T$$

and after simplification

$$G - G(0) = -N k_B T \ln \frac{z}{N}$$

Relation of the equilibrium constant and the partition functions

- Now that we know the partition functions we can express the equilibrium constant *K* as a function of them
- Let us set out from the standard reaction free energy

$$\Delta_r G^0 = -RT \ln K$$

- Let us consider a simple bimolecular reaction

$$aA + bB \rightarrow cC + dD$$

where *a*, *b*, *c* and *d* are the stoichiometric coefficients of the *A*, *B*, *C* and *D* substances

- Let

$$\Delta_r G^\circ = c\, G^\circ_{C,m} + dG^\circ_{D,m} - aG^\circ_{A,m} - bG^\circ_{B,m}$$

be the standard reaction free energy of the reaction above

- Since

$$G^{\circ}_{X,m} = G^{\circ}_{X,m}(0) - k_B T \ln z^{\circ}_X$$

where z^0_X is the standard *partition function* of an X particle

- Thus, the standard reaction free energy, which regards to single molecules rather than a mole of molecules, is

$$\Delta_r G^\circ_m = cG^\circ_{C,m}(0) + dG^\circ_{D,m}(0) - aG^\circ_{A,m}(0) - bG^\circ_{B,m}(0) - k_B T\left(c\ln z^\circ_C + d\ln z^\circ_D - a\ln z^\circ_A - b\ln z^\circ_B\right)$$

- Since *G(0)=U(0),* the first part of the right hand side of the equation above is

$$\Delta_r \varepsilon_0 = cU^\circ_{C,m}(0) + dU^\circ_{D,m}(0) - aU^\circ_{A,m}(0) - bU^\circ_{B,m}(0)$$

the standard reaction internal energy per molecule, i.e. the difference between the molar ground state energy of the products and the reactants

- Since

$$\Delta_r G^\circ = -RT \ln K = A_N k_B T$$

thus

$$\ln K = -\frac{\Delta_r G^\circ}{A_N k_B T}$$

and thus

$$K = \frac{\left(z^\circ_{C,m}\right)^c \left(z^\circ_{D,m}\right)^d}{\left(z^\circ_{A,m}\right)^a \left(z^\circ_{B,m}\right)^b} e^{-\Delta_r \varepsilon_0 / RT}$$

Transition state theory

- The other approach to get the value of the rate constant of a reaction is the transition state or activated complex theory
- Transition state is the state with the highest energy along a given reaction coordinate
- The main advantage of transition state theory in contrast to the collision theory is that it does not require any intuitive, non-measurable and incalculable parameter such as the steric factor

- For simplicity and for easy understanding, let us investigate a simple bimolecular combination reaction with A and B as reactants
- We assume an activated complex which is close to or at the transition state

$$A + B \xrightarrow{k_1} C^{\ddagger} \xrightarrow{k^{\ddagger}} P$$

where A and B are reactants, P is the product and $C^{\ddagger}$ is the activated complex and k_1 and $k^{\ddagger}$ are the corresponding rate constants

- Transition state theory assumes that the conversion of the activated complex to product is the slow step of the reaction so it determines the velocity

$$v = k^{\ddagger}[C^{\ddagger}]$$

where v is the velocity and $k^{\ddagger}$ is the rate constant of the unimolecular transformation of the activated complex to the product, respectively

- The velocity of the reaction expressed by the rate constant of the whole reaction is

$$v = k_2[A][B]$$

where k_2 is the rate constant of the whole reaction, [A] and [B] are the concentrations of reactants A and B, respectively

- Since k_1 is fast, an equilibrium is established between the reactants and the activated complex

$$[C^{\ddagger}]=K^{\ddagger}[A][B]$$

where [C‡], [A] and [B] are the concentration of the activated complex, the A and the B reactant, respectively and K‡ is the equilibrium constant

- Thus

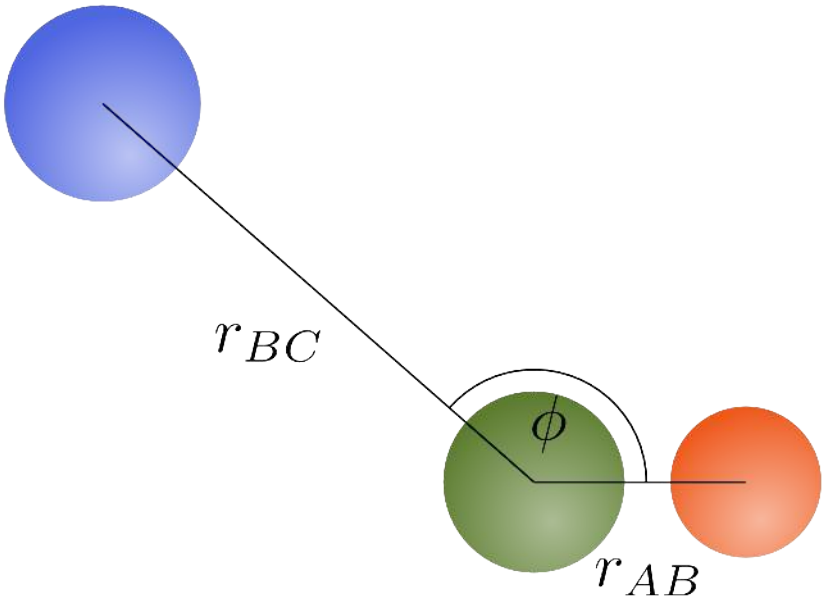
$$k_2=k^{\ddagger}K^{\ddagger}$$

- Now the task is for us to determine the value of $k^{\ddagger}$ and $K^{\ddagger}$
- To be able to continue we need the evaluation of the reaction coordinate and some skew to the area of statistical mechanics and quantum mechanics

Reaction coordinates

- Let us consider a concrete problem to get a picturesque image on the problem of the reaction coordinate
- Let the reaction be that an “A-B molecule and C atom” system converts to a “A atom B-C molecule” system
- The energy of the system can be described as a function of three degrees of freedom

Reaction coordinates

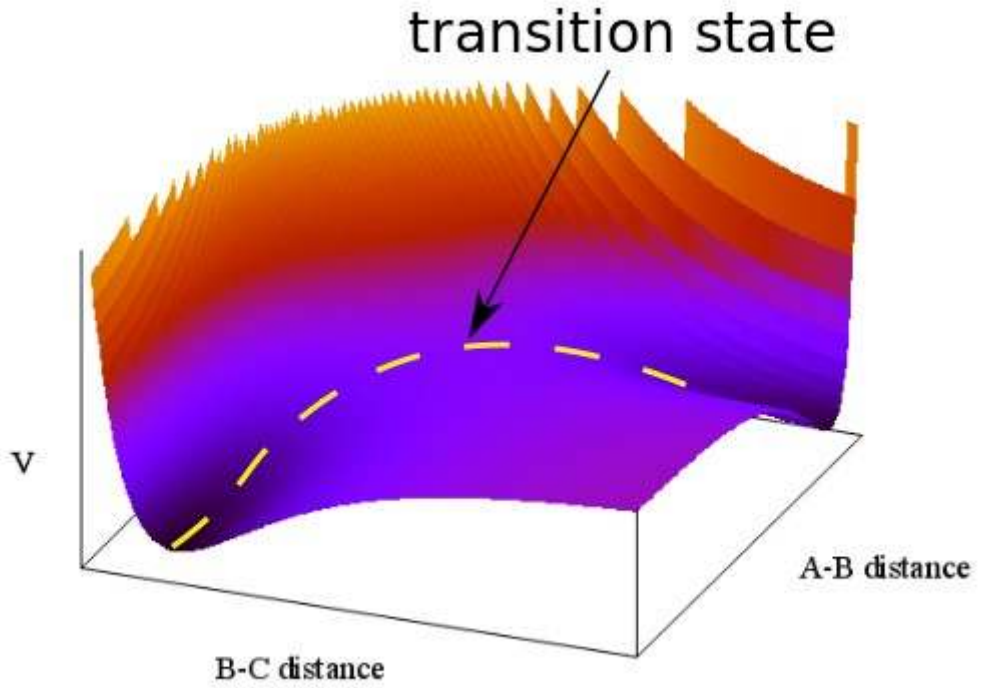


- The three reaction coordinates are: r_{AB} the distance between atoms A and B, r_{BC} the distance between B and C, and Φ the angle between the vector connecting A and B and the vector connecting B and C atoms
- If we want a picturesque image we have to reduce the number of reaction coordinates to two
- Let us set the value of Φ to 180 degrees and thus the potential energy will be the function of only two independent variables

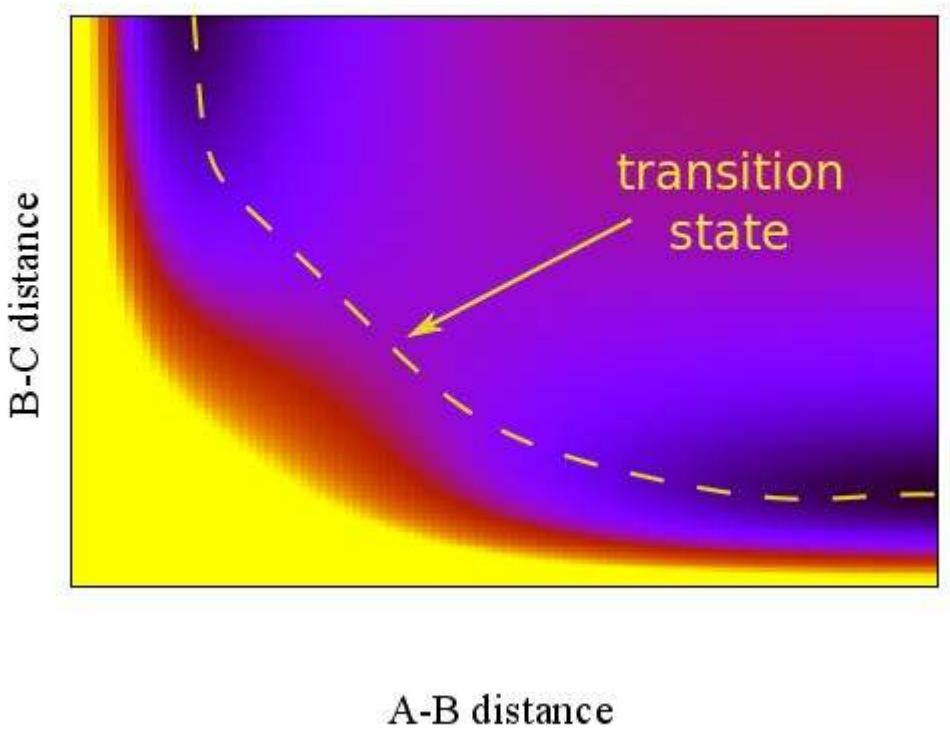
- Making use of these two reaction coordinates, we can depict a potential energy surface as a function of the distances between atoms
- Three locations on the potential energy surface are important:
  - A-B molecule and separated C atom
  - B-C molecule and separated A atom
  - Transition state
- There is a valley connecting the first and the second states (with broken yellow line in the figure below)

- The line running on the bottom of the valley corresponds to the reaction coordinate
- The highest point of the valley mentioned above is considered as the transition state
- In our case, transition state is when B is about halfway between A and C
- In a direction perpendicular to the line corresponding to the reaction coordinate, the transition state is at the bottom of a potential energy well, so it is a saddle point

Potential energy landscape



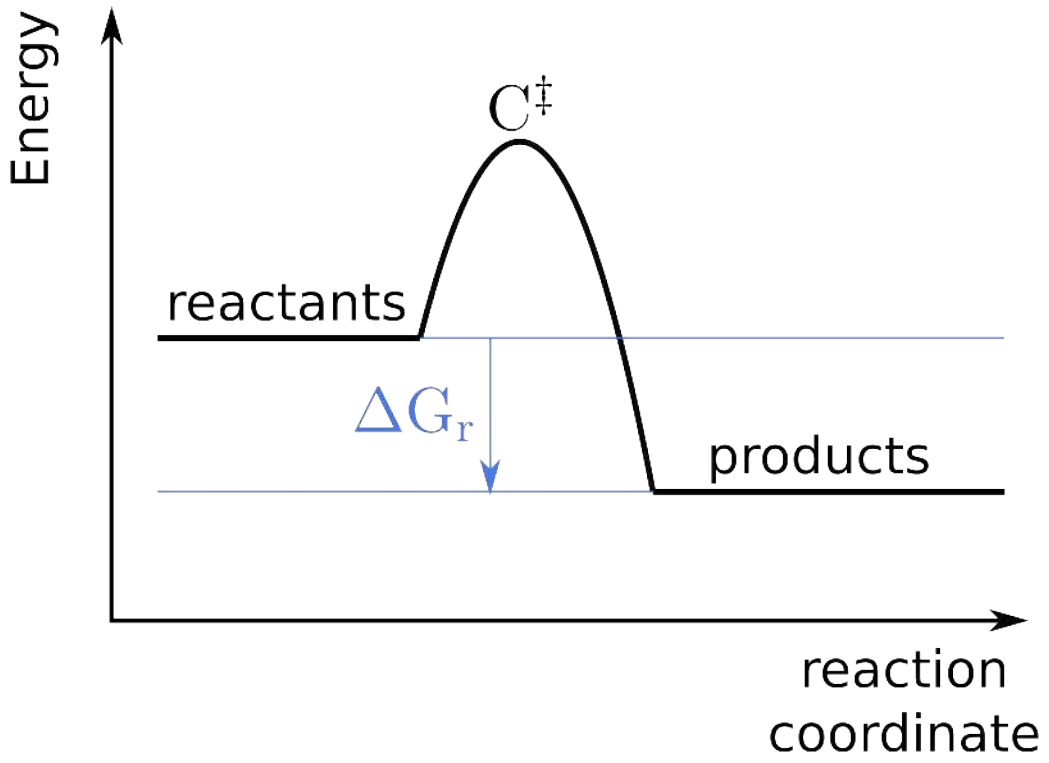
Potential energy surface in two dimensions



Reaction profile

- Let us get back to the reaction of the A and B atoms as reactants
- In this reaction, the potential energy can be considered as a function of the distance between A and B, so this distance may be chosen as reaction coordinate
- A reaction profile plots the potential energy against the reaction coordinate
- Transition state is at the top of the curve

Reaction profile



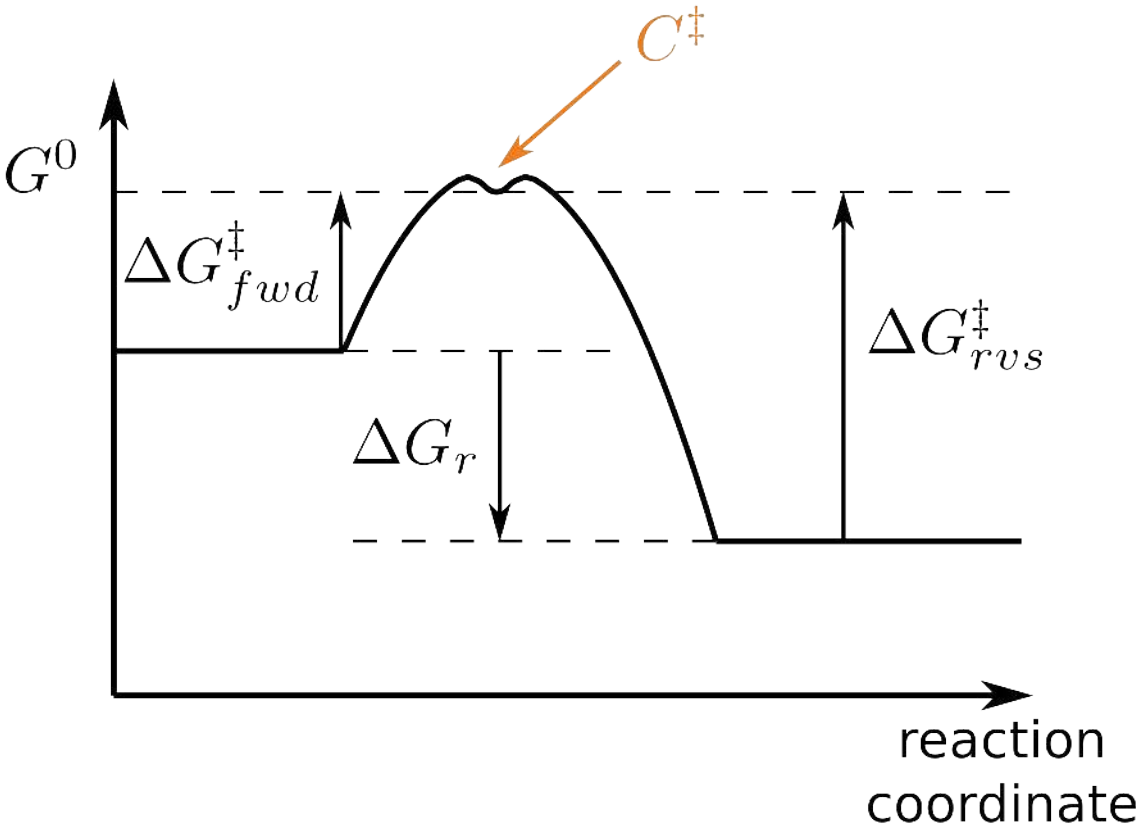
- Although products are lower in potential energy, a barrier has to be passed for the reaction to occur
- In the absence of significant entropy change during the reaction, potential energy can be substituted by the free energy
- The difference between free energy of products and reactants is the reaction free energy which is always negative if the reaction takes place spontaneously

$$\Delta G_r = G_{products} - G_{reactants}$$

The value of the rate constant $k^{\ddagger}$

- To transform to products, the system first has to pass the transition state
- We assume that around the transition state there is a shallow valley along the reaction coordinate in which the behaviour of the activated complex can be treated as a harmonic oscillator with frequency ν
- So the frequency by which the activated complex gets to and pass the transition state is also ν

Reaction profile proposed by Eyring



- Since not every oscillation leads to passing the transition state by the activated complex, it is only stated that $k^{\ddagger}$ is proportional to the frequency of vibration along the reaction coordinate

$$k^{\ddagger} = \kappa \nu$$

where ν is the frequency and κ is the *transmission factor* which often approaches 1

The value of the equilibrium constant $K^{\ddagger}$

- Since the activated complex occurs only transiently, practically its concentration is not measurable so the value of the equilibrium constant cannot be calculated based on concentrations
- Instead of using concentrations we can use the partition functions of the substances
- Let us get back to the reaction

$$A + B \rightarrow C^{\ddagger} \rightarrow P$$

- Combining transition state theory and the statistical mechanical derivation of the equilibrium constant, the rate constant for this reaction is obtained as:

$$k_2 = k^{\ddagger} K^{\ddagger} = k^{\ddagger} \frac{z^{\circ}_{C^{\ddagger},m}}{z^{\circ}_{A,m} \cdot z^{\circ}_{B,m}} e^{-\Delta_r \varepsilon_0 / RT}$$

where k_2 is the rate constant of the whole reaction, $k^{\ddagger}$ is the rate constant of the transformation of the activated complex to product and $K^{\ddagger}$ is the equilibrium constant of it

- Let us continue with the partition function of the activated complex
- Since we assume that the activated complex passes the transition state toward products by a vibrational motion, it is natural to separate the part of the partition function describing this vibrational mode from others

- The partition function of this oscillation – normalized by the zero point vibration – is

$$z' = \frac{1}{1 - e^{-h\nu / kT}}$$

where ν is the same frequency as we have already seen in the expression describing the rate constant $k^{\ddagger}$ of the *activated complex-product* transformation

- The expression can be approximated by

$$z' \approx \frac{k_B T}{h\nu}$$

since hν/kT << 1 and the exponential can be expanded as a series

- Thus the total partition function is

$$z_{C^\ddagger} \approx \frac{k_B T}{h\nu} \bar{z}_{C^\ddagger}$$

- The equilibrium constant $K^{\ddagger}$ is then

$$K^{\ddagger} = \frac{kT}{h\nu}\overline{K}$$

where $\overline{K}$ is the function of only $\overline{z}$ and independent of the vibration responsible for passing the transition state

- Thus we get the *Eyring equation* for the rate constant of the whole reaction

$$k_2 = \kappa \nu \frac{k_B T}{h \nu} \overline{K} = \kappa \frac{k_B T}{h} \overline{K}$$

- The partition functions can be obtained by spectroscopic measurements so we can calculate $\overline{K}$ and thus the rate constant of the total reaction k_2

Thermodynamic description of the transition state theory

- Having described the theory with the help of statistical and quantum mechanics, let us look at a purely thermodynamic analysis
- We can use the same expression as a starting point as in the statistical mechanical description, namely

$$K^{\ddagger} = \frac{[C^{\ddagger}]}{[A][B]}$$

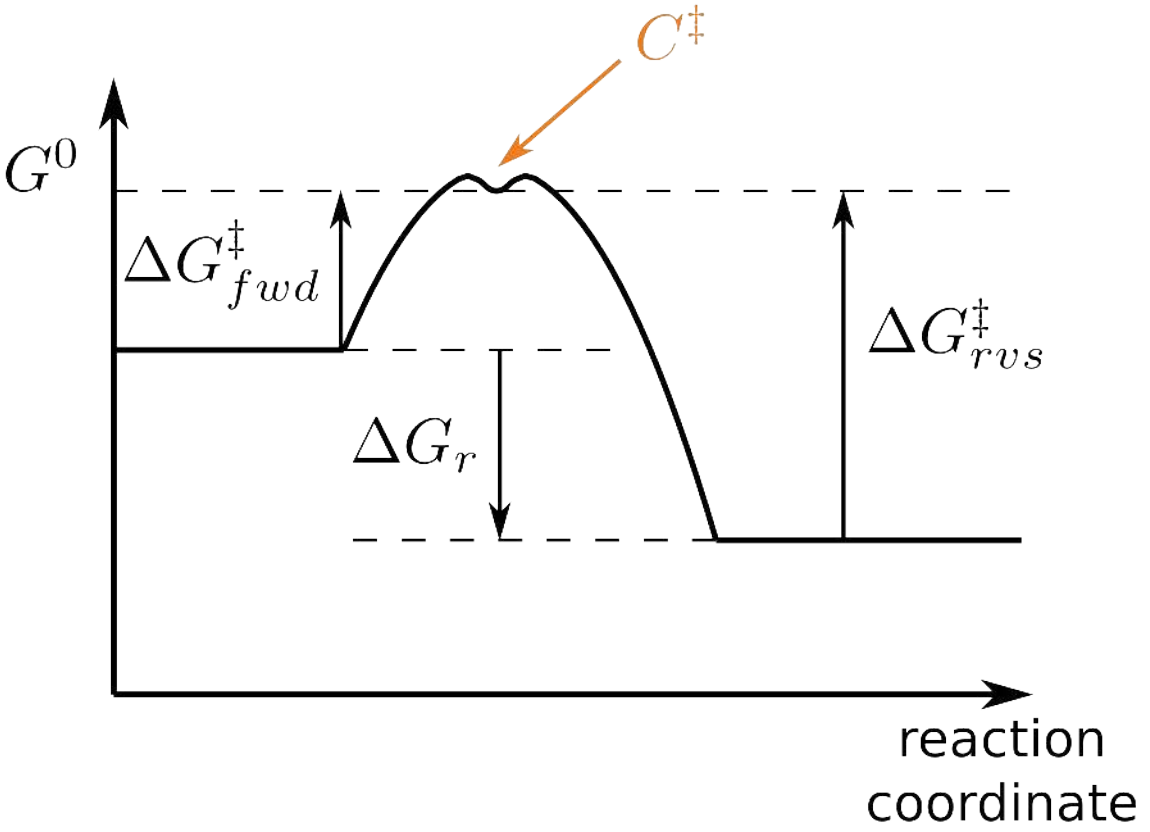
- We can talk about the *reaction free energy* $\Delta G^{\ddagger}$ for the formation of the activated complex $C^{\ddagger}$ at quasi-equilibrium

$$\Delta G^{\ddagger}_{fwd} = -RT \ln c^{\circ} \overline{K}$$

where the c° is the standard concentration which ensures that the free energy has the proper unit, and following from this

$$\overline{K} = \frac{1}{c^{\circ}} e^{-\Delta G^{\ddagger}_{fwd}/RT}$$

Modified reaction profile



- Thus for the rate constant $k^{\ddagger}$ we obtain

$$k_2 = \kappa \frac{k_B T}{h} \frac{1}{c^{\circ}} e^{-\Delta G^{\ddagger}_{fwd} / RT}$$

- Let us introduce the activation enthalpy $\Delta H^{\ddagger}$ and activation entropy $\Delta S^{\ddagger}$
- Expressing the activation free energy with them we get

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T \Delta S^{\ddagger}$$

- Substituting the expression above by that for the rate constant

$$k_2 = \kappa \frac{k_B T}{h} \frac{1}{c^\circ} e^{\Delta S^\ddagger / R} e^{-\Delta H^\ddagger / RT}$$

- To determine the relationship between activation enthalpy and activation energy, let us set out from the Arrhenius equation

$$k = Ae^{-E_A/RT}$$

- After rearrangements and derivation with respect to the temperature we obtain

$$E_A = RT^2 \frac{\partial \ln k}{\partial T}$$

- Since

$$\frac{\partial \ln k}{\partial T} = \frac{2}{T} + \frac{\Delta H^{\ddagger}}{RT^2}$$

the activation energy expressed with the activation enthalpy is

$$E_A = \Delta H^{\ddagger} + 2RT$$

- Substituting it to the equation expressing the total rate constant the equation will be

$$k_2 = e^2 \frac{kT}{h} \frac{RT}{p^0} e^{\Delta S^{\ddagger}/R} e^{-E_A/RT}$$

where

$$A = e^2 \frac{kT}{h} \frac{RT}{p^0} e^{\Delta S^{\ddagger}/R}$$

is the preexponential factor which appears in the Arrhenius equation