

## REACTION KINETICS AND REACTION MECHANISMS

Different levels of dealing with reaction rates:

- I. REACTION KINETICS  
macroscopic level – mathematical description
- II. REACTION MECHANISMS  
molecular level – interpretation
- III. THEORIES OF REACTION RATES  
Arrhenius equation, collision and activated complex theories

1

## III. THEORIES OF REACTION RATES AND RATE CONSTANTS

- Starting point: temperature dependence of  $k$
- Arrhenius theory** (Arrhenius, 189X)

$$k = A \cdot e^{-E_a/RT}$$

- Collision theory** (Arrhenius, McLewis, 1918)

$$k = p \cdot Z \cdot e^{-E_a/RT} = p \cdot \sigma \cdot \left( \frac{8k_B T}{\pi \mu} \right)^{1/2} N_A e^{-E_a/RT}$$

- collisions, steric factor, reactive collisions, harpoon mechanism (mainly **gas phase** reactions)

## III. THEORIES OF REACTION RATES AND RATE CONSTANTS

- Activated complex theory** (Eyring, Polányi, 193X), general, useful for **solution reactions**.

$$k = k^\ddagger \cdot K^\ddagger = \kappa \cdot \frac{k_B T}{h} \cdot \overline{K} = \kappa \cdot \frac{k_B T}{h} \cdot e^{\Delta S^\ddagger/R} \cdot e^{-\Delta H^\ddagger/RT}$$

- thermodynamic approach (entropy, enthalpy and free energy of activation)
- quantum mechanical approach (potential surfaces, trajectories)
- statistical mechanical approach
- The three different approaches complement each other.

## Temperature dependence of rate constants

- General** (but not infallible) **guideline**: an increase in  $T$  causes an increase in  $v$  (both for exothermic and endothermic reactions).

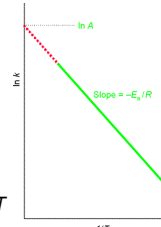
- Thermostating is important!

- Semiquantitative**:

a factor of 2-3x for each 10°C

- Fully quantitative**: the T dependence of  $k$ :

- $k = A \exp(-B/T)$ .
- Logarithmic form:  $\ln k = \ln A - B/T$



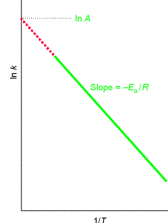
## Temperature dependence of rate constants

- The **Arrhenius plot** often gives a straight line:

- slope:  $-E_a/R$
- intercept (extrapolation to  $1/T = 0$ ):  $\ln A$
- $A$ : pre-exponential factor (Later terminology: collision constant)

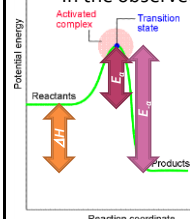
- Occasionally:

- a) curvature or break point: **multistep reaction**;
- b) negative  $T$ -dependence: **exothermic pre-equilibrium**.



## Arrhenius equation:

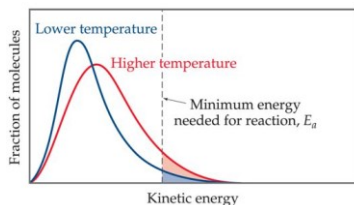
- $E_a$  activation energy: the excess energy needed for a reactive collision vs. an average collision.
- No interpretation for the pre-exponential factor  $A$ .
- In the observed  $k = A e^{-B/T}$  equation,  $B = E_a/R$



- $E_a$  is visualized on a reaction profile as shown in the figure.
- $E_a$  is important to understand the temperature dependence of  $k$  and to classify the reaction intermediates.

## Arrhenius equation:

- Interpretation: **Maxwell–Boltzmann energy distribution:**



- At a higher temperature  $T_2$ , more particles have a kinetic energy greater than the  $E_a$  energy of activation.

## Arrhenius equation:

- Theoretical objectives:** to derive the experimentally observed equation from the model and find a way to obtain the parameters from more fundamental properties.
  - Activation energy  $E_a$  was a characteristic reaction parameter that could not be calculated in any theoretical way.
  - $A$  was not interpreted by Arrhenius originally.
- Importance:** Svante Arrhenius started the development of reaction rate theories. (He was awarded the Nobel prize for the theory of electrolytic dissociation.) The core idea is still considered to be valid.

## Collision theory (gas phase reactions):

- (more modern terminology than originally used)
- For the  $A + B \rightarrow P$  reaction,  $v = k_2[A][B]$
- Core idea:** the reaction rate is the product of a collision ( $z_{AB}$ ) and a probability ( $f$ ) factor:  $\frac{dN_A}{dt} = -z_{AB} \cdot f$ 
  - The probability factor  $f$  is a Boltzmann factor (or **energy factor**):  $f = e^{-E_a/RT}$
  - The **collision factor**  $z_{AB}$  is borrowed from the statistical model (kinetic theory) of gases:  $z_{AB} = \sigma \left( \frac{8k_B T}{\pi \mu} \right)^{1/2} N_A^2 [A][B]$

## Collision theory (gas phase reactions):

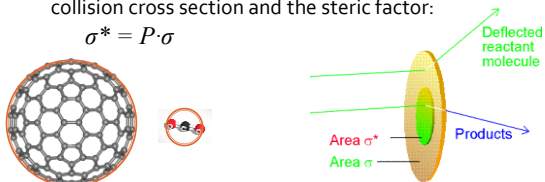
- The rate equation of the process then:

$$\frac{d[A]}{dt} = \sigma \left( \frac{8k_B T}{\pi \mu} \right)^{1/2} N_A e^{-E_a/RT} [A][B]$$

- $A$  is interpreted by molecular parameters, but  $E_a$  remained experimental only.
- The first calculations for the  $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$  reaction gave excellent agreement. In other processes, deviations were seen. Usual strategy: keep the core idea and introduce corrections:
  - $\mu$  (reduced mass) unique, cannot be corrected,
  - $\sigma$  (collision cross section) is less strict, a correction of a factor of about 2 may be reasonable.

## Collision theory (gas phase reactions):

- $\sigma$  (collision cross section) is less strict, a correction of a factor of about 2 may be reasonable:
- A possible explanation is the use of the **P steric factor**:  $1 - 10^{-3}(10^{-4})$  may be acceptable.
- The  **$\sigma^*$  reactive cross section** is the product of the collision cross section and the steric factor:  $\sigma^* = P \cdot \sigma$



## Collision theory (reactions in solution):

- In solution, there are characteristic molecular motions and „environmental“ factors:
  - at 0.02 M concentration, the average reactant distance is  $\sim 10 \cdot d_A$
  - at 1 atm in a gas, the mean free path is  $\sim 10 \cdot d_A$
- no difference in the kinetics.
- For a reaction to occur, a collision and transformation of the reactants are needed:
  - collisions because of diffusion,
  - excess energy needed for a reactive collision.

### Collision theory (reactions in solution):

- Based on elementary processes, there are:
  - diffusion limited and  $E_a \sim 0$
  - energy limited reactions.  $E_a \gg 0$

### Collision theory (reactions in solution):

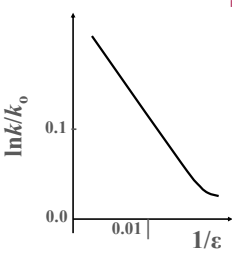
- The rate constant of diffusion limited bimolecular elementary reactions can be calculated based on the diffusion model.
- A molecules are stationary, B molecules move. The  $J$  matter flux on the  $4\pi r^2$  surface around A:
 
$$J = 4\pi r^2 J_1$$
 where  $J$  is the flux (Fick's first law):
 
$$J = 4\pi r^2 D_B d[B]/dr$$
- Integration until  $R^*$  critical radius, introducing  $D = D_A + D_B$  and allowing for the diffusion of A gives:
 
$$k_d = 4\pi R^* D N_A$$

### Collision theory (reactions in solution):

- In most energy limited reactions the rate determining aspect is chemical activation. The exponential  $E_a$  term appears in the rate constant  $k$ , and diffusion does not limit the rate any more (there are a lot of collision, few of which lead to reaction).
  - There is no theoretical minimum for bimolecular rate constants.
  - In practice, very slow reactions are not quite useful.
  - Acceleration:  $T$ ,  $c$  and catalyst(s).
- No theory for calculating  $E_a$ .
- For this, some of the properties of the solutions are necessary to know:

### Collision theory (reactions in solution):

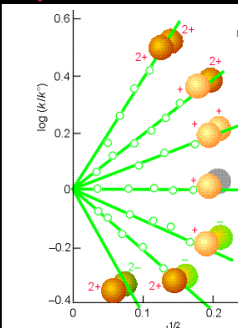
- Effect of solvent permittivity on  $k$  in solution:
  - reactions of ions (dipoles),
  - influences the electrostatic interaction.



$$\ln k = \ln k_0 - \frac{z_A z_B e^2}{\epsilon d_{AB} k_B T}$$

### Collision theory (reactions in solution):

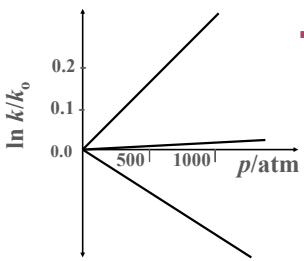
- Effect of ionic strength on  $k$  in solution:
  - unavoidable in ionic reactions: the reactants themselves cause some ionic strength.



$$\lg k = \lg k_0 + 1,02 z_A z_B I^{1/2}$$

### Collision theory (reactions in solution):

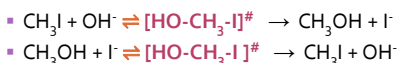
- The effect of pressure on  $k$  in solution:
  - pressures higher than  $10^2 - 10^3$  atm have measurable effects.
  - Experimental observation:



$$\ln k = \ln k_0 - (\Delta V^\ddagger / RT) p$$

## Activated complex<sup>#‡</sup> theory:

- The starting point is the interaction between the reactant and not their collisions: in a primary interaction, and „activated complex“ is formed, for which the formalism of **equilibrium** is still applicable – even though it reacts very rapidly so its lifetimes is very short (**transition state**).

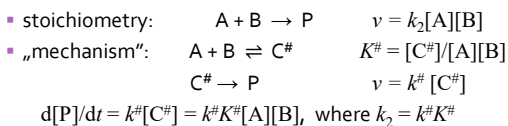


## Activated complex<sup>#‡</sup> theory:

- Every elementary reaction has its own activated complex!
- The reverse reaction (always!) occurs through the same activated complex.
- In a multistep reaction, each step has its characteristic activated complex.
- The activated complex is formed from the reactants that appear in the rate equation and the orders of reaction give the composition.
- The solvent may participate in the activated complex, but this information is not available from experiments.
- The geometry of the activated complex is unique.

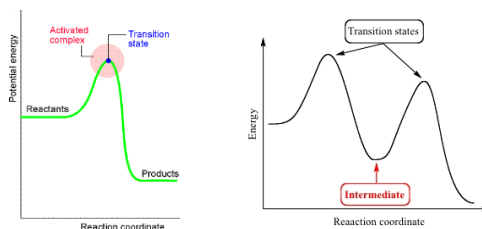
## Activated complex<sup>#‡</sup> theory:

- Core idea:** in the elementary reaction A + B



## Activated complex<sup>#‡</sup> theory:

- The **activated complex** is a maximum in energy along the reaction coordinate, the „easily“ detectable *steady state* or *pre-equilibrium intermediate(s)* represent minima.



## Activated complex<sup>#‡</sup> theory: thermodynamic approach

- If the activated complex is written as an equilibrium, thermodynamic formalism can be used:

- $(\Delta G = -RT \ln K, \text{ so } K^\ddagger = \frac{RT}{p^0} \times K)$

- In this case:

- $\Delta^\ddagger G = -RT \ln K = -RT \ln(p^0/RT)K^\ddagger$ .

- Therefore, the  $k_2$  rate constant:

$$k_2 = k^\ddagger K^\ddagger = \frac{k_B T}{h} \cdot \frac{RT}{p^0} \cdot e^{-\Delta^\ddagger G/RT}$$

## Activated complex<sup>#‡</sup> theory: thermodynamic approach

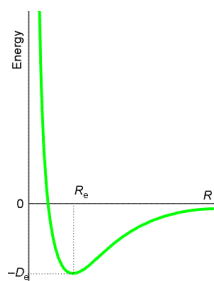
- As  $\Delta^\ddagger G = \Delta^\ddagger H - T\Delta^\ddagger S$  is valid:

$$k_2 = \frac{k_B T}{h} \cdot \frac{RT}{p^0} \cdot e^{\Delta^\ddagger S/R} \cdot e^{-\Delta^\ddagger H/RT} \quad \begin{array}{l} \Delta^\ddagger G: \text{ free energy of activation} \\ \Delta^\ddagger H: \text{ enthalpy of activation} \\ \Delta^\ddagger S: \text{ entropy of activation} \end{array}$$

- These are thermodynamic functions associated with 1 mol of activated complex.

## Activated complex<sup>#‡</sup> theory: quantum mechanical approach

- The energy of two atoms as a function of their distance (as the only variable of the equation) can be described by a potential energy curve:



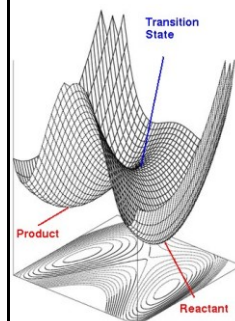
## Activated complex<sup>#‡</sup> theory: quantum mechanical approach

- For three atoms, the reaction depends on three distances (or two distances and an angle).
- In this case, potential energy surfaces (hypersurfaces) must be calculated and plotted.
- Thus, 1 parameter is fixed: the angle is  $180^\circ$ , which means that the reactants are always in a single line. The reaction:
 
$$A-B + C \rightarrow [A-B-C]^\ddagger \rightarrow A + B-C$$
- (Specifically the  $H_2(\alpha\beta) + H(\gamma) \rightleftharpoons H(\alpha) + H_2(\beta\gamma)$  exchange reaction.)
- Axes: nuclear distances  $R_{AB}$ ,  $R_{BC}$ ; the energy of the activated complex ( $E_{pot}$ ) is plotted as a function of these distances.
- The calculation is carried out by complicated quantum chemical methods. The results are shown graphically:

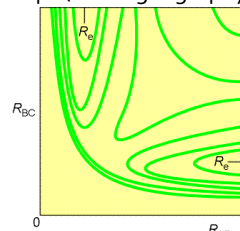
## Activated complex<sup>#‡</sup> theory: quantum mechanical approach

- A verbal description of the potential energy surface (PES):
  - The two „valleys“ rise and meet in a saddle point, which is a local maximum in one direction and simultaneously a local minimum in the other (perpendicular) direction.
  - The maximum (along a given trajectory) corresponds to the maximum  $E_a$  along the reaction coordinate.
  - The saddle point represents the activated complex.
  - The potential surface is only symmetric for an exchange reaction of the type  $H_2(\alpha\beta) + H(\gamma) \rightleftharpoons H_2(\alpha\gamma) + H(\beta)$ .

## Activated complex<sup>#‡</sup> theory: quantum mechanical approach



- Common and didactic view of surfaces: contour maps (like in geography).



## Activated complex<sup>#‡</sup> theory: quantum mechanical approach

- A verbal description of the reaction path:
  - Reactant C is far away, bond distance  $R_{AB}$  did not change.
  - C approaches B (along the AB line),  $R_{BC}$  decreases and  $R_{AB}$  increases.
  - Simultaneously, the potential energy  $E_{pot}$  of the system increases as it approaches the saddle point.
  - In the saddle point, which represent the activated complex,  $R_{AB}$  and  $R_{BC}$  are nearly the same,  $E_{pot}$  reaches its maximum.
  - After the saddle point,  $E_{pot}$  decreases,  $R_{BC}$  also decreases (strengthening of the new bond),  $R_{AB}$  increases and the old bond breaks entirely.
  - In the final state, only products A and BC exist.

## Activated complex<sup>#‡</sup> theory:

- Experimental detection of the activated complex
  - C<sup>#</sup> was a rational assumption for a long time as it has an extremely short life time ( $10^{-15}$  s, femtosecond, fs).
  - Detection in a few simple gas reactions was achieved in the late 20<sup>th</sup> century:
  - Ahmed Zewail (1999, Nobel prize).



### Activated complex<sup>‡</sup> theory: statistical mechanical approach

- As seen earlier:  $k_2 = k^\ddagger K^\ddagger$
- The values of  $k^\ddagger$  and  $K^\ddagger$  must be computed.
  - $k^\ddagger$ : the activated complex passes through the energy barrier and „oscillates away“ with frequency  $\nu$  into the products.
  - $k^\ddagger = \kappa \nu$
  - $\kappa$ : transmission coefficient ( $\sim 1$ ), a measure of the possibilities of other transformations of the activated complex (e.g. „rotating away“).

### Activated complex<sup>‡</sup> theory: statistical mechanical approach

- The value of  $K^\ddagger$  can be expressed by **q partition function q** [q, standard molar partition function in statistical thermodynamics, MSc course].
 
$$q = \frac{1}{1 - e^{-h\nu/k_B T}}$$

$$K = \frac{(p_{C^\ddagger} / p^0)}{(p_A / p^0)(p_B / p^0)} = \frac{p_{C^\ddagger}}{(p_A / p_B) p^0}$$

$$K^\ddagger = \frac{RT}{p^0} \times K = \frac{k_B T}{h\nu} \times \bar{K}$$

where  $K = \left( \frac{N_A q_{C^\ddagger}^0}{q_A^0 q_B^0} \right) e^{-\Delta E_0 / RT}$  and  $\bar{K} = \left( \frac{RT}{p^0} \right) \left( \frac{N_A q_{C^\ddagger}^0}{q_A^0 q_B^0} \right) e^{-\Delta E_0 / RT}$

### Activated complex<sup>‡</sup> theory: Eyring plot

- Graphical determination of  $\Delta^\ddagger G$ ,  $\Delta^\ddagger H$  and  $\Delta^\ddagger S$ :
  - we saw that  $k = \kappa \cdot \frac{k_B T}{h} \cdot \bar{K}$ ,
  - $\kappa \cdot \bar{K} = e^{-\Delta^\ddagger G / RT}$  and
  - $\Delta^\ddagger G = \Delta^\ddagger H - T\Delta^\ddagger S$ ,
  - so:  $k = \frac{k_B T}{h} \cdot e^{\Delta^\ddagger S / R} \cdot e^{-\Delta^\ddagger H / RT}$
  - After rearrangement:  $\frac{k}{T} = \frac{k_B}{h} \cdot e^{\Delta^\ddagger S / R} \cdot e^{-\Delta^\ddagger H / RT}$
  - Logarithmic form:  

$$\ln \frac{k}{T} = \ln \frac{k_B}{h} + \frac{\Delta^\ddagger S}{R} - \frac{\Delta^\ddagger H}{RT}$$
 for first-order rate constant

### Activated complex<sup>‡</sup> theory: Eyring plot

The following Eyring plot describes the temperature dependence of the rate constant for formation, in solution, of InP nanocrystals from In- and P-containing molecular precursors. Determine approximate values for  $\Delta^\ddagger H$  and  $\Delta^\ddagger S$  for the rate-determining step.

**Arrhenius plot**  
(slide 4-5)

$$\ln \frac{k}{T} = \ln \frac{k_B}{h} + \frac{\Delta^\ddagger S}{R} - \frac{\Delta^\ddagger H}{RT}$$