

## 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

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## II. REACTION MECHANISMS

- **kinetics** – **mechanisms**:
- observed fact – postulate
- unique – often multiple possibilities
- „trade“ – „art“
- **Mechanism** and its role: elementary reaction that interpret
  - a) the net stoichiometry of the process (observed intermediates if there are any) and
  - b) kinetic observations (the rate equation).
- rate equation  $\leftrightarrow$  mechanism

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## Concept and properties of elementary reactions:

- **Elementary reaction**: consumption of a few reactant molecules, the dissociation and formation of maximum 1–2 bonds through a single activated complex. Elementary reactions are reversible!
- types of elementary reactions and their rate equations:
  - unimolecular  
 $A \rightarrow \text{product(s)}$
  - bimolecular (most common)  
 $A + B \rightarrow \text{product(s)}$  or  $2A \rightarrow \text{product(s)}$
  - termolecular (rare)  
 $A + B + C$  or  $A + 2B$  or  $3A \rightarrow \text{product(s)}$ .
- **Order of reaction and molecularity are the same!**

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## Law of kinetic mass action:

- For elementary reactions, the rate equation can be deduced from the stoichiometry. For example:
  - $A \rightarrow \text{product(s)}$  –  $d[A]/dt = k_1[A]$
  - $A \rightleftharpoons B$  –  $d[A]/dt = k_1[A] - k_{-1}[B]$
  - $A + B \rightarrow \text{product(s)}$  –  $d[A]/dt = k_2[A][B]$
  - $2A \rightarrow \text{product(s)}$  –  $d[A]/dt = k_2[A]^2$
  - $A + B + C \rightarrow \text{product(s)}$  –  $d[A]/dt = k_3[A][B][C]$
  - $A + 2B \rightarrow \text{product(s)}$  –  $d[A]/dt = k_3[A][B]^2$
- An elementary reaction is always reversible, but the rate of the reverse reaction is often negligible.

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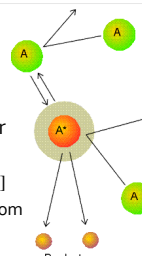
## Unimolecular processes:

- There is a single reactant, this is transformed into product(s) through decay, isomerization, inversion (cyclopropane  $\rightarrow$  propene,  $N_2O_5 \rightarrow N_2O_3 + O_2 \dots$ )
- **Stoichiometry**:  $A \rightarrow P$
- **Rate equation**:  $d[P]/dt = k_{\text{exp}}[A]$ 
  - $k_{\text{exp}}$ : experimental rate constant
- **Mechanism**: bimolecular collisions are often assumed (but not *a priori* necessary). How can bimolecular collisions lead to first order?

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## Unimolecular processes:

- **Lindemann–Hinshelwood mechanism**:
  - $A + A \rightleftharpoons A^* + A$   $k_1$  and  $k_{-1}$
  - $A^* \rightarrow P$   $k_2$
- The mechanism should lead to the experimentally observed rate equation for the production of P.
  - The rate of product formation:  $d[P]/dt = k_2[A^*]$
  - $[A^*]$  is not measurable, but can be obtained from the mechanism:  
 $d[A^*]/dt = k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*]$
  - The **steady state** approximation is used:  $[A^*]$  is low and constant, therefore  $d[A^*]/dt = 0$ .

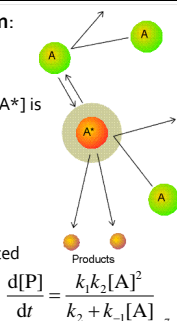


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## Unimolecular processes:

### Lindemann–Hinshelwood mechanism:

- $A + A \rightleftharpoons A^* + A$   $k_1$  and  $k_{-1}$
- $A^* \rightarrow P$   $k_2$
- The **steady state** approximation is used:  $[A^*]$  is low and constant, therefore  $d[A^*]/dt = 0$ .
- The previous two points together:  
 $k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*] = 0$
- A differential equation is turned into an algebraic equation!
- $[A^*]$  can be derived from this and substituted into the equation characterizing the production of P:



## Termolecular (third order?) reactions:

- Stoichiometry:  $2 \text{NO}(g) + \text{O}_2(g) = 2 \text{NO}_2(g)$
- Kinetics:  $d[\text{NO}_2]/dt = k_{\text{exp}}[\text{NO}]^2[\text{O}_2]$
- Mechanism:
  - Three-body collision.** Feasible? If not:
  - Two bimolecular steps:**
    - a rapid pre-equilibrium:  $2 \text{NO} \rightleftharpoons \text{N}_2\text{O}_2$ ,  $K_1 = [\text{N}_2\text{O}_2]/[\text{NO}]^2$
    - rate determining second step:  $\text{N}_2\text{O}_2 + \text{O}_2 \rightarrow 2 \text{NO}_2$
- The rate of product formation:  $\frac{1}{2} d[\text{NO}_2]/dt = k_2[\text{N}_2\text{O}_2][\text{O}_2]$ .  
 $[\text{N}_2\text{O}_2]$  is obtained from the equilibrium and substituted into the previous equation:  $d[\text{NO}_2]/dt = 2 k_2 K_1 [\text{NO}]^2 [\text{O}_2]$ .
- The product  $k_{\text{exp}} = 2k_2 K_1$  separated kinetically!
- $K_1$  can only be measured in independent measurements.

## Termolecular (third order?) reactions:

### Other, equivalent mechanisms can also be postulated to interpret the same rate equation:

- $\text{NO} + \text{O}_2 \rightleftharpoons \text{NO} \cdot \text{O}_2$   $K' = [\text{NO} \cdot \text{O}_2]/[\text{NO}][\text{O}_2]$   
 $\text{NO} \cdot \text{O}_2 + \text{NO} \rightarrow 2 \text{NO}_2$ 
    - After a derivation similar to the previous one:  
 $\frac{1}{2} d[\text{NO}_2]/dt = k_2 [\text{NO} \cdot \text{O}_2][\text{NO}]$
    - $[\text{NO} \cdot \text{O}_2]$  can be given from the equilibria:  
 $d[\text{NO}_2]/dt = k_2 K' [\text{NO}]^2 [\text{O}_2]$ . This (also) agrees with the experimental rate equation.
- There is no way of distinguishing **b)** from **c)** kinetically.
  - Detection of the intermediate –  $\text{N}_2\text{O}_2$  or  $\text{NO} \cdot \text{O}_2$  – may be decisive (e.g. spectrophotometrically).

## Interpretation of higher reaction orders:

- Second (or third) order with respect to  $\text{H}^+$  is common, e.g.  
 $v = k_{\text{exp}}[\text{A}][\text{B}][\text{H}^+]^2$  A:  $\text{BrO}_3^-$ ; B:  $\text{I}^-$
- a) Four-body collisions are completely unfeasible.
- b) A possible mechanism:
 

$\text{A} + \text{H}^+ \rightleftharpoons \text{AH}^+$	rapid protonation pre-equilibrium
$\text{AH}^+ + \text{H}^+ \rightleftharpoons \text{AH}_2^{2+}$	another rapid pre-equilibrium
$\text{B} + \text{AH}_2^{2+} \rightarrow \text{product}$	slow rate determining step

  - $[\text{AH}_2^{2+}]$  can be expressed from the two pre-equilibria:  
 $v = k_3 K_1 K_2 [\text{A}][\text{B}][\text{H}^+]^2$
- The product  $k_{\text{exp}} = k_3 K_1 K_2$  cannot be separated kinetically.

## Negative reaction order and its rationalization:

- $\ominus$  second (or third) order with respect to  $\text{H}^+$ , for example:  
 $v = k'_{\text{exp}} [\text{AH}_2][\text{B}][\text{H}^+]^{-2}$   $\text{AH}_2$ : oxalic acid
- a) Possible mechanism: twice deprotonated reactant is involved in the rate determining step.
 

$\text{AH}_2 \rightleftharpoons \text{AH}^- + \text{H}^+$	rapid deprotonation pre-equilibrium
$\text{AH}^- \rightleftharpoons \text{A}^{2-} + \text{H}^+$	another rapid pre-equilibrium
$\text{B} + \text{A}^{2-} \rightarrow \text{products}$	(slow) rate determining step

  - $[\text{A}^{2-}]$  can be derived from the two pre-equilibria:  
 $v = k'_3 K'_1 K'_2 [\text{A}][\text{B}][\text{H}^+]^{-2}$
- The product  $k'_{\text{exp}} = k'_3 K'_1 K'_2$  cannot be separated kinetically.

## Zeroth order and its rationalization:

- A reactant does not appear in the rate determining step.
  - Rationalization: this reactant only enters the mechanism after the rate determining step in a relatively fast process.
  - E.g. halogenation of acetone:  $\text{A} + \text{X}_2 \rightleftharpoons \text{AX} + \text{HX}$
  - Kinetics:  $v = k[\text{A}][\text{H}^+]$
- a) Mechanism:
  - first step: acid catalyzed enolization; slow step:  
 $\text{CH}_3\text{CO}-\text{CH}_3 + \text{H}^+ \rightleftharpoons \text{CH}_3\text{COH}=\text{CH}_2 + \text{H}^+$
  - second step: halogenation of the enol form; fast step:  
 $\text{CH}_3\text{COH}=\text{CH}_2 + \text{X}_2 \rightarrow \text{CH}_3\text{CO}-\text{CH}_2\text{X} + \text{HX}$
- Message:** kinetic data give very little information for processes after the rate determining step.

### Kinetics of enzyme catalysis and the Michaelis–Menten equation:

- Enzymes: efficient, specific biocatalysts
- Stoichiometry:**  $S \xrightarrow{E} P$
- Kinetics:** initial rates are measured (because...):

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### Kinetics of enzyme catalysis and the Michaelis–Menten equation:

- Two more observations:
  - Maximum in the  $T$ -dependence. **Arrhenius equation** and denaturing.

- The pH-dependence also often shows a maximum. Amphoteric amino acids!

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### Kinetics of enzyme catalysis and the Michaelis–Menten equation:

- Description of  $v$ - $[S]$  curves:  $v = \frac{a}{\frac{b}{[S]} + 1}$  or  $v = \frac{a[S]}{b + [S]}$
- Constants  $a$  and  $b$  have chemical meaning:
  - $a$ : as  $[S]$  increases,  $v$  saturates so that a further increase in  $[S]$  does not accelerate the product formation any more. In this case  $[S] \gg b$ , i.e.  $a = v_{max}$ .
  - $b$ : when  $b = [S]$ ,  $v = v_{max}/2$  holds, so  $[S]_{1/2} = b$ .
  - Leonor Michaelis and Maud Leonora Menten (1912).

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### Kinetics of enzyme catalysis and the Michaelis–Menten equation:

- The equation is interpreted by the **Briggs-Haldane mechanism:**
  - $E + S \rightleftharpoons ES$   $k_1$  and  $k_{-1}$
  - $ES \rightarrow P + E$   $k_2$ , rate determining step

- Product formation:  $d[P]/dt = k_2[ES]$ . What is  $[ES]$ ?
- Both the rapid pre-equilibrium and steady-state approximations can be applied.
- Important: the overall enzyme concentration  $[E]_0$  is distributed between free enzyme  $[E]$  and enzyme-substrate  $[ES]$  forms, so  $[E]_0 = [E] + [ES]$  should be considered as a mass balance equation.

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### Kinetics of enzyme catalysis and the Michaelis–Menten equation:

a) **steady state approximation:**

- $d[ES]/dt = k_1 \cdot [E] \cdot [S] - k_{-1} \cdot [ES] - k_2 \cdot [ES] = 0$
- So:  $[ES] = \frac{k_1[E][S]}{k_{-1} + k_2} = \frac{k_1([E]_0 - [ES])[S]}{k_{-1} + k_2}$
- $v = \frac{d[P]}{dt} = k_2 \cdot [ES] = \frac{k_2 \cdot [S] \cdot [E]_0}{K_M + [S]}$
- $K_M$  is the Michaelis constant:  $K_M = \frac{k_{-1} + k_2}{k_1}$
- The equation obtained agrees with the experiments.
  - $[S] \gg K_M$  at large  $[S]$  and therefore  $v_{max} = k_2 \cdot [E]_0$
  - So:  $v = \frac{[S] \cdot v_{max}}{K_M + [S]}$

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### Kinetics of enzyme catalysis and the Michaelis–Menten equation:

b) **rapid pre-equilibrium:**

- $K_1 = \frac{[ES]}{[E][S]}$
- Sol:  $[ES] = \frac{k_1[E]_0[S]}{k_{-1} + k_1[S]}$
- $v = \frac{d[P]}{dt} = k_2 \cdot [ES] = \frac{k_2 \cdot [S] \cdot [E]_0}{K_1 + [S]}$
- $K_1$  is the kinetic constant:  $K_1 = \frac{k_{-1}}{k_1}$
- The equation derived agrees with the observations.
  - For large  $[S]$ ,  $[S] \gg K_1$ , and  $v_{max} = k_2 \cdot [E]_0$
  - In addition:  $v = \frac{[S] \cdot v_{max}}{K_1 + [S]}$

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### Kinetics of enzyme catalysis and the Michaelis–Menten equation:

- A common evaluation method:
  - Experimental rate equation — **Lineweaver–Burk plot**

$$v = \frac{d[P]}{dt} = \frac{k_2[S][E]}{K_M + [S]} \quad \frac{1}{v} = \frac{1}{k_2[E]} + \frac{K_M}{k_2[E][S]}$$

**modern** **outdated**

### Kinetics of enzyme catalysis and the Michaelis–Menten equation:

- Summary:** both approximations are OK, but the „compositions“ of the  $K_1$  and  $K_M$  constants differ.
- Studies of the slow  $S \rightarrow P$  enzymatic reaction must be complemented by kinetic studies on the „pre steady state“ phase of the  $E+S \rightleftharpoons ES$  equilibrium (in order to resolve  $k_1$  and  $k_{-1}$ ) – usually a fast technique is needed (stopped flow, T-jump etc.)
- The  $[P]-t$  kinetic traces of the  $S \rightarrow P$  are also useful.
- Enzymatic reactions can show diverse stoichiometric and kinetic properties – see biochemistry.

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### Gas phase formation of hydrogen halides: HBr

- It is quite instructive to compare the formation of **HBr** and other **HX**. The same stoichiometry, but ...
- HBr formation:
  - measurements:** Bodenstein, Lind (1907)
  - explanation:** Christiansen, Herzfeld, Polányi (1919)
- a classic example used in reaction kinetics
- Stoichiometry:  $H_2 + Br_2 \rightleftharpoons 2 HBr$
- Kinetics:  $v = \frac{k[H_2][Br_2]^{3/2}}{[Br_2] + k'[HBr]} = \frac{k[H_2][Br_2]^{1/2}}{1 + \frac{k'[HBr]}{[Br_2]}}$
- A suitable mechanism was necessary. Finding it took a decade!

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### Gas phase formation of hydrogen halides: HBr

- Mechanism: five (irreversible) elementary steps.
 

$Br_2 \rightarrow 2 Br\cdot$	$v_a = k_a[Br_2]$
$Br\cdot + H_2 \rightarrow HBr + H\cdot$	$v_b = k_b[Br\cdot][H_2]$
$H\cdot + Br_2 \rightarrow HBr + Br\cdot$	$v_c = k_c[H\cdot][Br_2]$
$H\cdot + HBr \rightarrow Br\cdot + H_2$	$v_d = k_d[H\cdot][HBr]$
$2 Br\cdot + M \rightarrow Br_2 + M$	$v_e = k_e[Br\cdot]^2$

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### Gas phase formation of hydrogen halides: HBr

- Mechanism: five (irreversible) elementary steps.
 

$Br_2 \rightarrow 2 Br\cdot$	$v_a = k_a[Br_2]$
$Br\cdot + H_2 \rightarrow HBr + H\cdot$	$v_b = k_b[Br\cdot][H_2]$
$H\cdot + Br_2 \rightarrow HBr + Br\cdot$	$v_c = k_c[H\cdot][Br_2]$
$H\cdot + HBr \rightarrow Br\cdot + H_2$	$v_d = k_d[H\cdot][HBr]$
$2 Br\cdot + M \rightarrow Br_2 + M$	$v_e = k_e[Br\cdot]^2$
- Notice:
 

$Br_2 \rightleftharpoons 2 Br\cdot$	reversible
$Br\cdot + H_2 \rightleftharpoons HBr + H\cdot$	reversible
$H\cdot + Br_2 \rightarrow HBr + Br\cdot$	irreversible
- A **typical chain reaction**: a reaction of a reactive intermediate produces another reactive intermediate and these form a chain (cycle).

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### Gas phase formation of hydrogen halides: HBr

- Visualization of the mechanism for the chain reaction:
- Chain length = number of products / chain initiation

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### Gas phase formation of hydrogen halides: HBr

- Types of step in chain reactions:
  - initiation: generation of a **chain carrier** (radical)
  - propagation: 1 radical → product + 1 radical
  - branching: 1 radical → several radicals
  - retardation: product + radical → „anything“ + radical
  - termination: radical recombination or inhibition (e.g. on the wall, reaction with M)
- Reactive intermediate (often a radical, R·):
  - unpaired electron (paramagnetic)
  - very reactive: reacts rapidly (some are stable!)
  - its concentration is very low and  $d[R]/dt \sim 0$
  - detectable by ESR or using a radical scavenger

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### Gas phase formation of hydrogen halides: HBr

- Kinetics of HBr formation:
 

$Br_2 \rightarrow 2 Br\cdot$ $Br\cdot + H_2 \rightarrow HBr + H\cdot$ $H\cdot + Br_2 \rightarrow HBr + Br\cdot$ $H\cdot + HBr \rightarrow Br\cdot + H_2$ $2 Br\cdot + M \rightarrow Br_2 + M$	$v_a = k_d[Br_2]$ $v_b = k_1[Br\cdot][H_2]$ $v_c = k_2[H\cdot][Br_2]$ $v_d = k_3[H\cdot][HBr]$ $v_e = k_4[Br\cdot]^2$
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- $$\frac{d[HBr]}{dt} = k_1[Br\cdot][H_2] + k_2[H\cdot][Br_2] - k_3[H\cdot][HBr] \quad (\text{HBr formation})$$

$$\frac{d[H\cdot]}{dt} = k_1[Br\cdot][H_2] - k_2[H\cdot][Br_2] - k_3[H\cdot][HBr] = 0 \quad (\text{steady state})$$

$$\frac{d[Br\cdot]}{dt} = 2k_d[Br_2] - k_1[Br\cdot][H_2] + k_2[H\cdot][Br_2] + k_3[H\cdot][HBr] - 2k_4[Br\cdot]^2 = 0 \quad (\text{steady state})$$

$$[Br\cdot] = \left(\frac{k_d[Br_2]}{k_e}\right)^{1/2} \quad [H\cdot] = \frac{k_1(k_d/k_e)^{1/2}[H_2][Br_2]^{3/2}}{k_2[Br_2] + k_3[HBr]}$$

$$\frac{d[HBr]}{dt} = \frac{2k_1k_d(k_e/k_e)^{1/2}[H_2][Br_2]^{3/2}}{[Br_2] + (k_3/k_2)[HBr]}$$
- Comparison with experiments: agreement

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### Gas phase formation of hydrogen halides: HBr

- Kinetics of HBr formation:
 

$Br_2 \rightarrow 2 Br\cdot$ $Br\cdot + H_2 \rightarrow HBr + H\cdot$ $H\cdot + Br_2 \rightarrow HBr + Br\cdot$ $H\cdot + HBr \rightarrow Br\cdot + H_2$ $2 Br\cdot + M \rightarrow Br_2 + M$	$v_a = k_d[Br_2]$ $v_b = k_1[Br\cdot][H_2]$ $v_c = k_2[H\cdot][Br_2]$ $v_d = k_3[H\cdot][HBr]$ $v_e = k_4[Br\cdot]^2$
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- Results from numerical integration:

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### Gas phase formation of hydrogen halides: HI

- Stoichiometry:  $H_2 + I_2 \rightleftharpoons 2 HI$
- Kinetics:  $v = k_2[H_2][I_2] - k_{-2}[HI]^2$
- Mechanism:
  - if  $H_2 + I_2 \rightleftharpoons 2 HI$  is an elementary reaction, kinetic mass action gives:  $v = k_2[H_2][I_2] - k_{-2}[HI]^2$ 
    - this agrees with the experimental rate equation.
    - Note: the  $H_2 + I_2 \rightarrow 2 HI$  reaction played an important role in setting up the collision theory.

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### Gas phase formation of hydrogen halides: HI

- Stoichiometry:  $H_2 + I_2 \rightleftharpoons 2 HI$
- Kinetics:  $v = k_2[H_2][I_2] - k_{-2}[HI]^2$
- Mechanism:
  - chain reaction possible. Steps of the mechanism:
 
$$I_2 \rightleftharpoons 2 I\cdot$$

$$I\cdot + H_2 \rightleftharpoons HI + H\cdot$$

$$H\cdot + I_2 \rightleftharpoons HI + I\cdot$$

$$\frac{d[HI]}{dt} = k_2[I\cdot][H_2] - k_{-2}[HI][I_2] + k_3[H\cdot][I_2] - k_{-3}[HI][I\cdot]$$
    - After simplifications:  $v = k_{exp}[H_2][I_2]$
- Both mechanism play a role – in a ratio that depends on T (because of the effect of temperature on the dissociation of  $I_2$ )

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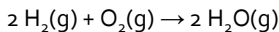
### Branching chain reactions: explosions

- Explosion:** a rapid exothermic reaction that causes large pressure increase (pressure wave + detonation).
- Two types:
  - Thermal explosion: increase in T, therefore in k and v
  - Chain explosion: branching in a chain reaction
- Flame:** a „standing wave“ of explosion (reaction propagation = reactant input)
- Kinetics in a particular system:**

$$2 H_2(g) + O_2(g) \rightarrow 2 H_2O(g)$$

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## Branching chain reactions: explosions



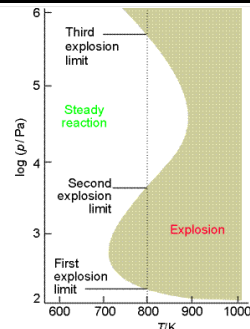
- There are pressure ranges where the rate of the reaction is well-measurable and – depending on  $T$  – there are **explosion limits**:
  - lower (1<sup>st</sup>),
  - upper (2<sup>nd</sup>) and
  - thermal (3<sup>rd</sup>) explosion limits.
- The three explosion limits are in the 700-900 °C range. They can be measured and plotted on a graph.

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## Branching chain reactions: explosions

### Summary of the explosion limits:

- lower (1<sup>st</sup>),
- upper (2<sup>nd</sup>) and
- thermal (3<sup>rd</sup>) explosion limit.



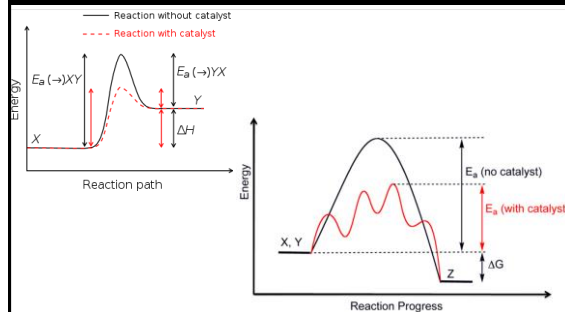
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## Catalysis, autocatalysis and oscillation

- Properties of catalytic phenomena:
  - a catalyst accelerates a reaction by reacting and then re-producing (no apparent consumption),
  - a catalyst is often written on both sides of the stoichiometric equation, but its order of reaction is positive,
  - a catalyst opens a new path for the reaction: the rate of this catalyzed process is typically larger than the rate of the reaction without the catalyst,
  - a catalyst never influences the position of the equilibrium (thermodynamic neutrality), it accelerates both the forward and reverse reactions.

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## Catalysis, autocatalysis and oscillation



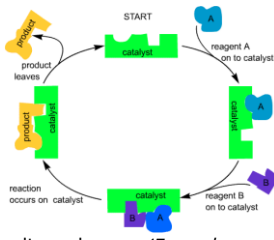
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## Catalysis, autocatalysis and oscillation



Kinetics:

$$v_0 = k_0[\text{A}]_0 + k_k[\text{A}]_0[\text{K}]_0$$



- There are much more complicated cases. (From the chemical point of view, we will talk about it later.)

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## Catalysis, autocatalysis and oscillation

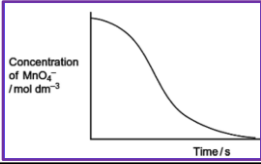
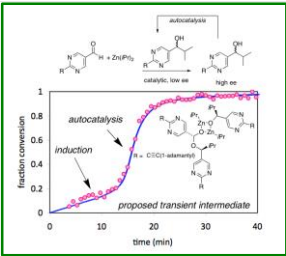
- Autocatalysis:
  - Stoichiometry:  $\text{A} \rightarrow \text{P}$
  - Kinetics:  $v = k_0[\text{A}] + k_{ak}[\text{A}][\text{P}]$

Typical autocatalytic trace:

- S-shaped
- induction period
- point of inflection:  $v_{max}$
- E.g.:  $\text{MnO}_4^-$  + oxalate ( $\text{Mn}^{2+}$  catalysis)
  - <https://www.youtube.com/watch?v=Ijijy38sExPE>
- Soai reaction (chiral autocatalysis)

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### Catalysis, autocatalysis and oscillation

### Catalysis, autocatalysis and oscillation

- Autocatalysis and chemical oscillation.
- Lotka–Volterra-mechanism:**

$$|A| + X \rightarrow 2X \quad d[X]/dt = k_a[A][X]$$

$$X + Y \rightarrow 2Y \quad d[Y]/dt = k_b[X][Y]$$

$$Y \rightarrow B \quad d[Y]/dt = -k_c[Y]$$
- Solution: numerical integration.
- Only the concentrations of X and Y oscillate (not A and B!)
- The Lotka–Volterra model predicts a *steady state* but **non-equilibrium** system. This is not  $d[X]/dt = 0$  type *steady state*!

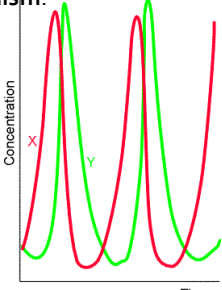
### Catalysis, autocatalysis and oscillation

- Lotka–Volterra-mechanism:**

$$|A| + X \rightarrow 2X$$

$$X + Y \rightarrow 2Y$$

$$Y \rightarrow B$$



<https://www.youtube.com/watch?v=WasYuiOk5xQ>