

GENIE OF CATALYSIS



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Outline

1. Introduction—Genie of Catalysis
2. Catalysis—Basic Ideas
3. How a Catalyst Works
4. Application of Catalysis
5. Outlook

1. Introduction—Genie of Catalysis





1. Introduction—Genie of Catalysis

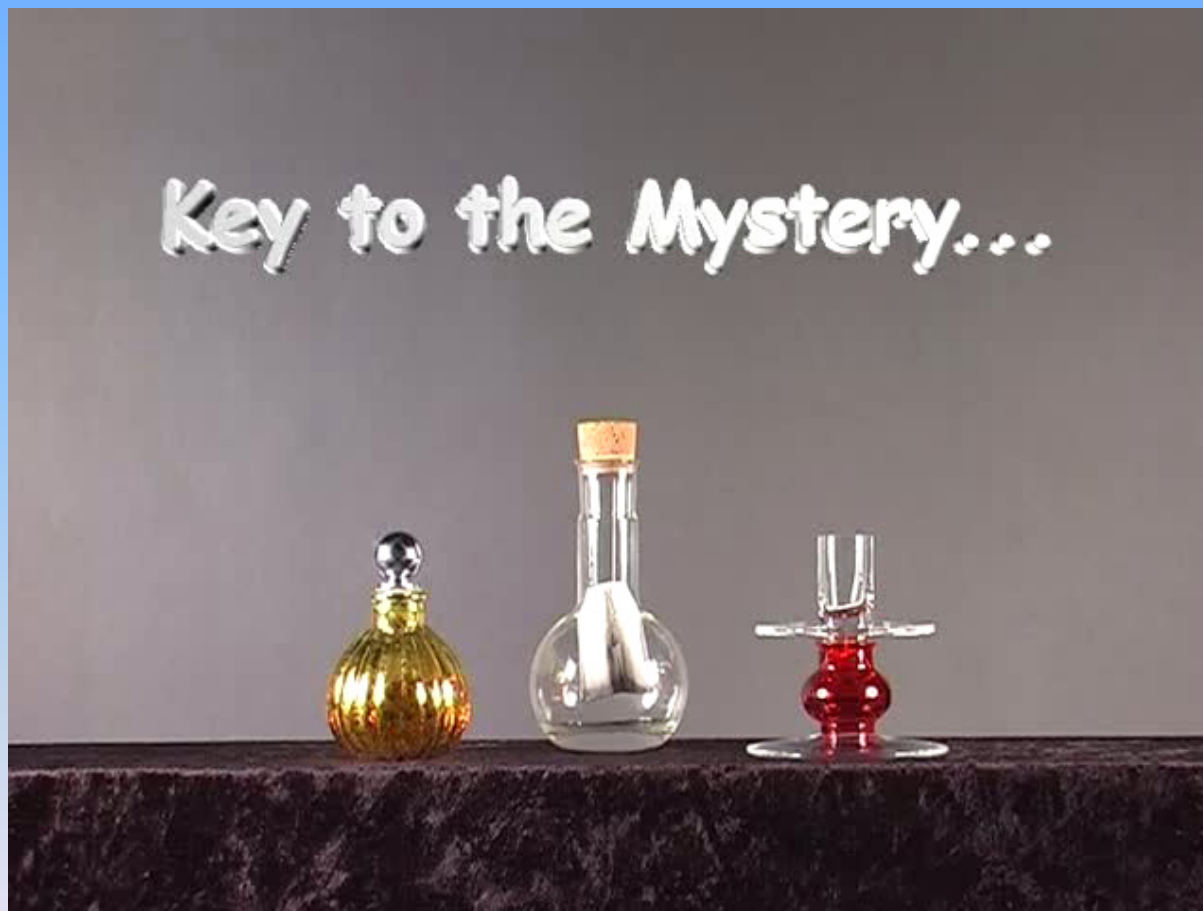




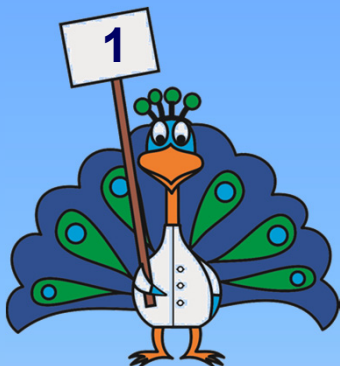
1. Introduction—Genie of Catalysis



Key to the Mystery...



Key to the “Mystery”



Procedure:

MnO₂ in a tea bag is held in place above a H₂O₂ solution in a Florence flask by means of a stopper. When the stopper is removed the tea bag drops into the solution.

Observation:

The “genie of catalysis” emerges from the flask ...



Explanation:

Hydrogen peroxide in aqueous solution exhibits a strong tendency to decompose into water and oxygen (disproportionation):



The decomposition rate at room temperature is, however, immeasurably small. But the rate can be appreciably increased by the addition of a ***catalyst*** such as manganese dioxide.

2. Catalysis—Basic Ideas





Definition and First Basic Terms

catalysis: acceleration of a chemical reaction by means of small amounts of a substance, called ***catalyst***, that itself is not consumed by the overall reaction

We can differentiate between

- ***heterogeneous catalysis***: phase of the catalyst different from that of the reaction mixture; example: decomposition of hydrogen peroxide by manganese dioxide
- ***homogeneous catalysis***: catalyst in the same phase as the reaction mixture
- ***enzymatic catalysis***: intermediate position, because enzymes, the biocatalysts in living organisms, are proteins, i.e. macromolecules with diameters between 10 and 100 nm, that are colloiddally dispersed in solution and mostly much bigger than the substrate molecules

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Decomposition of H_2O_2 by Homogeneous Catalysis

Procedure:

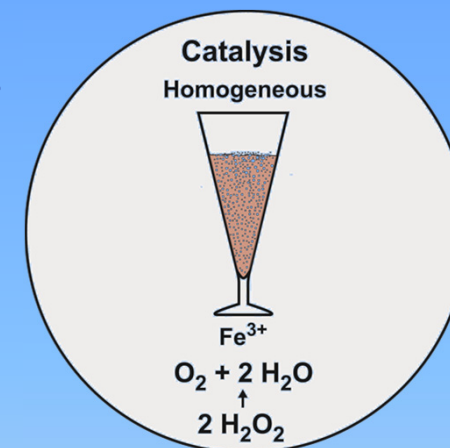
A solution of hydrogen peroxide is filled into a goblet. Subsequently, iron(III) chloride solution is added.

Observation:

The solution's color changes from pale yellow to brownish orange. In addition, a noticeable formation of gas can be observed after a while. The pale yellow color returns together with the end of bubbling.

Explanation:

Fe^{3+} ions are an example for a *homogeneous catalyst*. The catalytic decomposition of hydrogen peroxide can be essentially explained by two different mechanisms based on the mutual redox transition Fe(III)/Fe(V) (KREMER-STEIN mechanism) and Fe(III)/Fe(II) (HABER-WEISS mechanism), respectively.



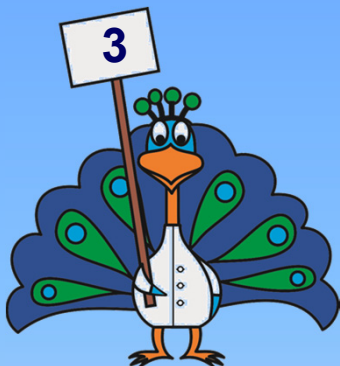
“Dancing Absinthe”



“Dancing Absinthe”



“Dancing Absinthe”



Procedure:

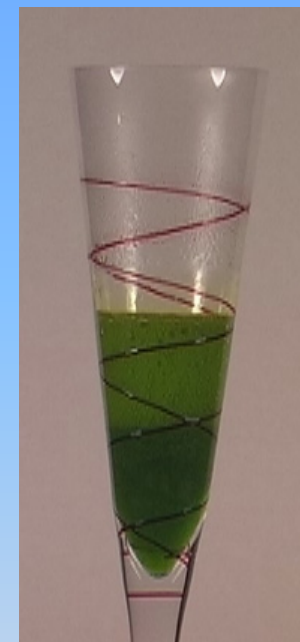
Hydrogen peroxide solution is added to a strongly acidified green copper(II) chloride solution.

Observation:

After a while, an evolution of gas starts which becomes more and more intense whereby a foam head is formed. In the following, the strength of foam formation changes in rhythmical intervals.

Explanation:

The oscillating reaction is based on the decomposition of H_2O_2 catalyzed by copper(II) chloride. Only if the solution is supersaturated with O_2 , larger amounts of gas are released. Thereby, more O_2 is released as can be reproduced by the catalytic reaction. Only if the solution is again supersaturated, the next strong gas evolution can take place.



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Decomposition of H_2O_2 by Enzymatic Catalysis

Procedure:

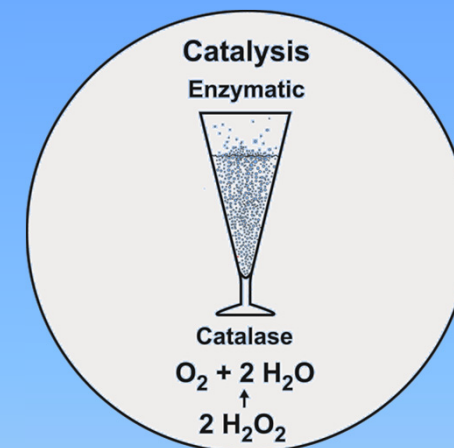
A solution of hydrogen peroxide is filled into a goblet. Subsequently, a solution of the enzyme catalase is added.

Observation:

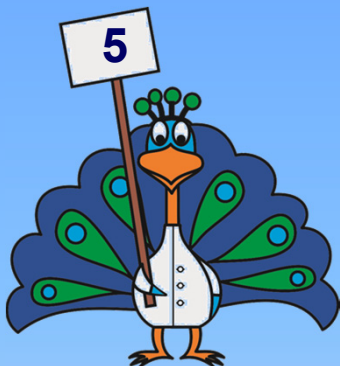
A strong evolution of gas takes place and the goblet gets warm.

Explanation:

The cytotoxin hydrogen peroxide is one of the by-products of many cellular reactions. Aerobic cells protect themselves against peroxide by the action of the enzyme catalase. Therefore, catalase is nearly ubiquitous among animal organisms, especially it is found in liver and red blood cells. But catalase also occurs in plant tissues, and is especially abundant in plant storage organs such as potato tubers, corms, and in the fleshy parts of fruits.



Strawberry Ice Cream



Procedure:

Dishwashing liquid, egg white, red food dye and catalase solution are thoroughly mixed in the glass cup. Subsequently, hydrogen peroxide solution is added.

Observation:

A foamy red and white substance rises in the glass cup which looks like a strawberry sundae.



Explanation:

The oxygen generated by the decomposition of hydrogen peroxide creates bubbles in the soapy liquid thereby turning it into foam. A glowing splint can be used to test that the gas produced is oxygen.

More Basic Terms (I)



inhibitor: decreases the rate of a catalyzed reaction or sometimes even stops the reaction completely
substance is used up in the process—in contrast to a catalyst

everyday example: poisoning of the exhaust gas catalytic converter in motor vehicles by the heavy metal lead; this is why lead-free fuels must always be used



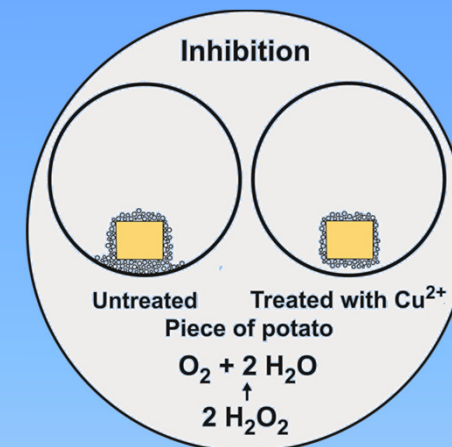
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Inhibition of the Enzyme Catalase

Procedure:

One of two potato pieces is put in CuCl_2 solution, the other one in water. The two pieces are then added to hydrogen peroxide solution in two Petri dishes.



Observation:

An intense formation of foam can be observed immediately around the untreated potato piece. Around the potato piece treated with CuCl_2 solution, however, the formation of gas takes place more slowly.

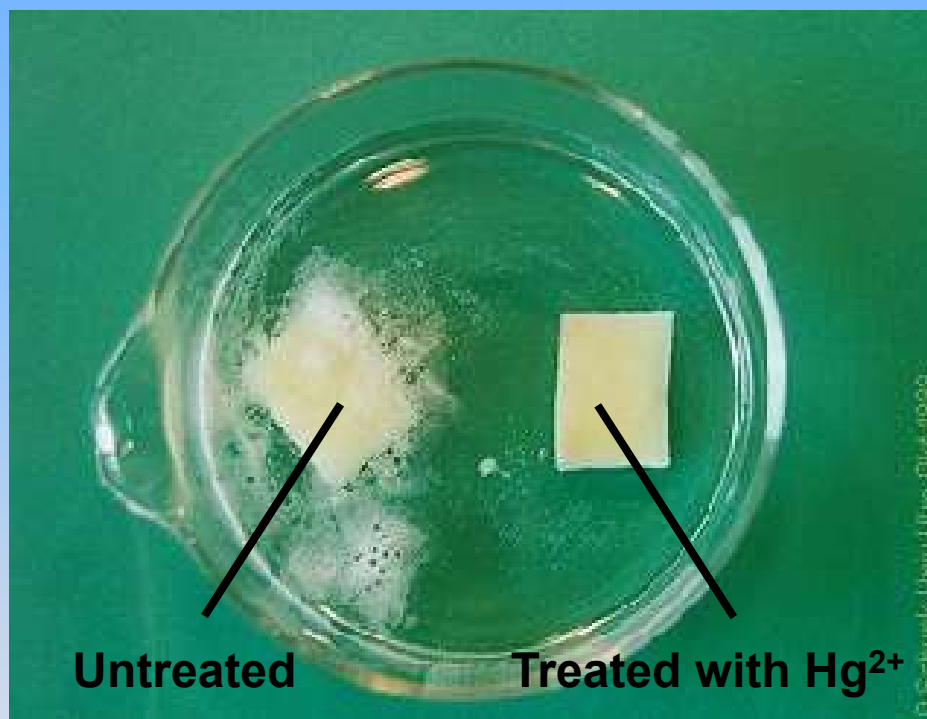
Explanation:

The structure of enzymes is often stabilized by disulfide bridges between cystine chains. Heavy metal ions exhibit a high affinity for sulfur. Therefore, such ions may modify the structure of the enzyme thereby reducing or even destroying its catalytic properties.

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Inhibition of the Enzyme Catalase



Obviously, highly toxic Hg^{2+} ions are considerably more efficient as inhibitors (precisely because they are highly toxic).

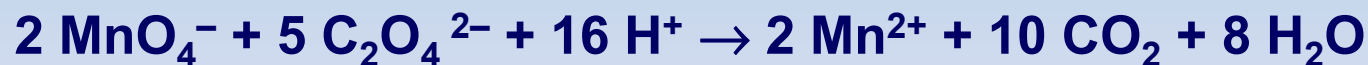
More Basic Terms (II)



autocatalysis: catalyst is formed only during the reaction

at the beginning of the reaction, the concentration of the catalyst and therefore the reaction rate are both extremely small
as the formation of catalyst proceeds, the reaction rate also increases until consumption of the reactant overcompensates for the increase of the catalyst concentration

example: reduction of permanganate by oxalic acid



catalyzed by the Mn^{2+} ions formed during the reaction

role of the Mn^{2+} ions can be easily demonstrated by adding them right at the beginning of the reaction

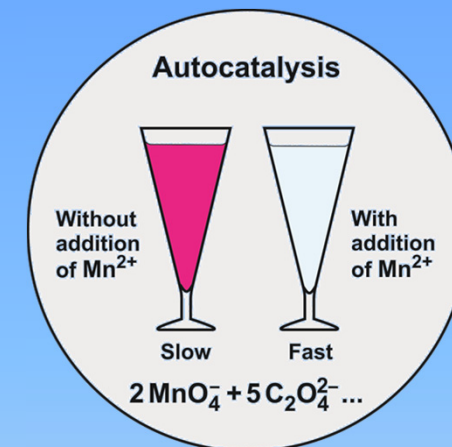
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Autocatalysis

Procedure:

Purple permanganate solution is poured together with pure water into one of two goblets already containing acidified oxalic acid solution. Subsequently, permanganate solution together with water enriched with Mn^{2+} ions is added to the second goblet.

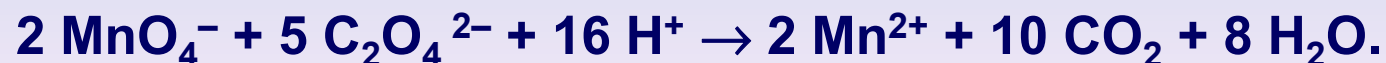


Observation:

The decolorization begins immediately when Mn^{2+} ions are added.

Explanation:

The permanganate ions are reduced by the oxalate ions to colorless Mn^{2+} ions while the oxalate ions are oxidized to gaseous CO_2 :



As has been demonstrated, the Mn^{2+} ions act in fact as catalyst.

3. How a Catalyst Works



Short Repetition of Basic Principles of Kinetics

rate of a general chemical reaction



given by the conversion rate

$$\omega = \frac{1}{v_i} \frac{dn_i}{dt}$$

or in a homogeneous environment by the rate density r

$$r = \frac{\omega}{V} = \frac{1}{v_i} \frac{dc_i}{dt}$$



But which factors affect the reaction rate?

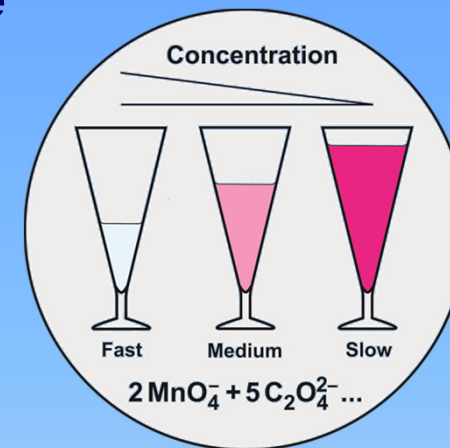
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Concentration Dependence of the Reaction Rate

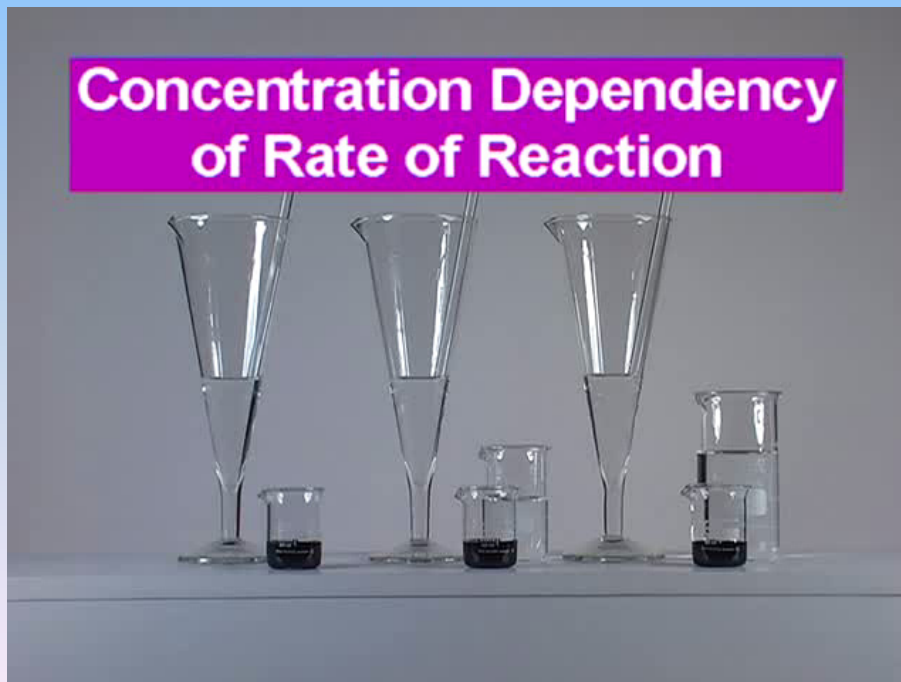


Procedure:

Acidified oxalic acid solution is mixed with differently diluted solutions of potassium permanganate.



Concentration Dependency of Rate of Reaction



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Concentration Dependence of the Reaction Rate

Procedure:

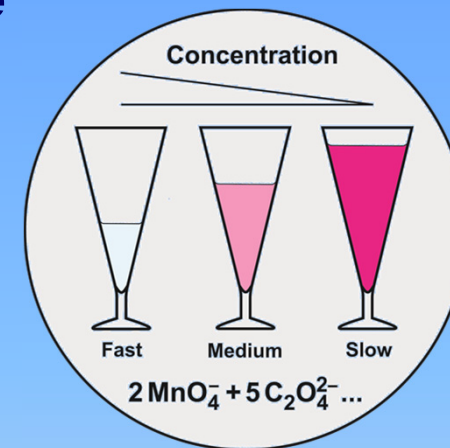
Acidified oxalic acid solution is mixed with differently diluted solutions of potassium permanganate.

Observation:

The decolorizing process appears first in the most concentrated solution.

Explanation:

The higher the dilution, meaning the lower the concentration of the reactants, the more slowly the reaction proceeds.



Rate Law

rate density r obviously dependent on

- the concentrations of the reactants A, B, ...,

but also on

- the temperature,
- the presence of substances not appearing in the conversion formula (catalysts, inhibitors)



analytical description by the *rate law*

$$r = k(T) \cdot c_A^a \cdot c_B^b \dots$$

k : rate coefficientⁿ

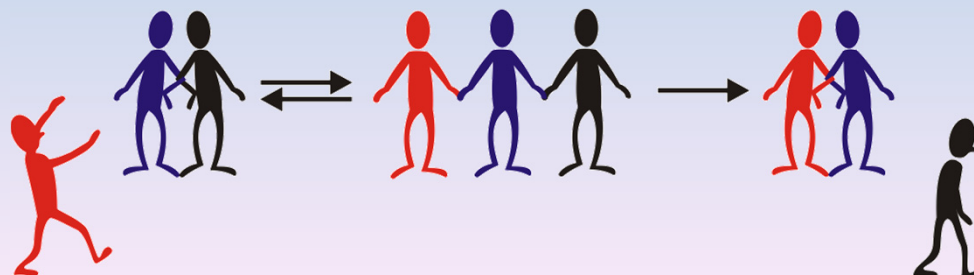
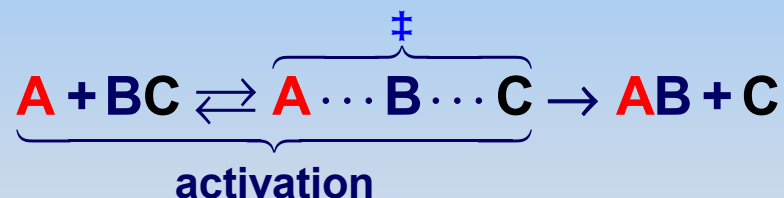
$n = a + b + \dots$: reaction order

Transition State Theory

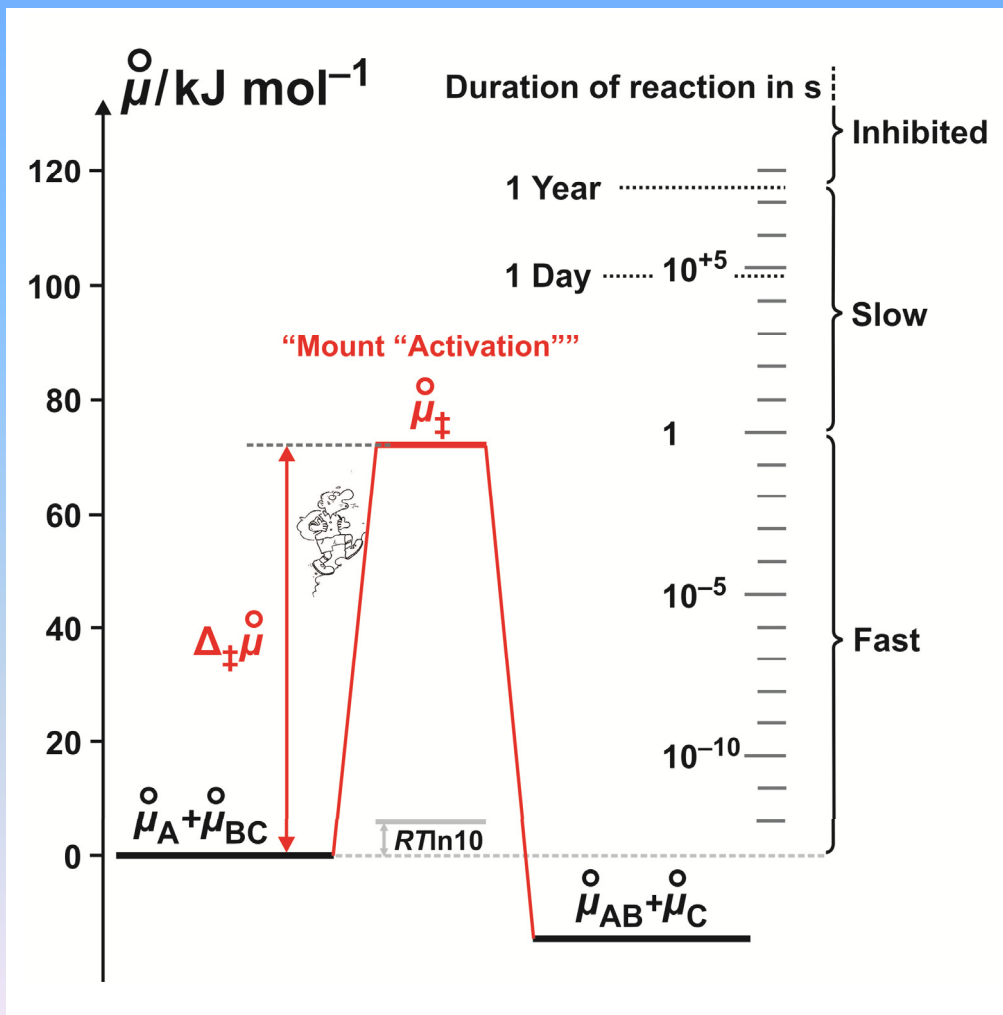
one of the theories explaining the temperature dependence of reaction rate

subdivision of a single-stage reaction into two smaller steps, i.e.

- formation of a “*transition complex*,” in which the rearrangement of all atoms involved takes place; this *activation reaction* requires energy input
- decomposition of the transition complex into the products



Activation Threshold



difference in the rate of various reactions solely determined by the height $\Delta_{\ddagger} \mu^{\circ}$ of the step-like potential threshold between the chemical potentials of the starting substances and that of the transition complex

The higher the activation threshold is, the lower the rate coefficient and the slower the reaction.

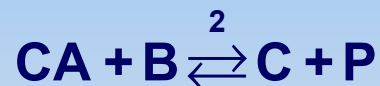
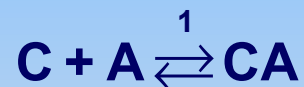
How a Catalyst Works

by bonding to a catalyst, intermediate substances are produced that subsequently decompose, thereby regenerating the catalyst, i.e.

a simple chemical reaction such as



can therefore be “redirected” by the catalyst C:



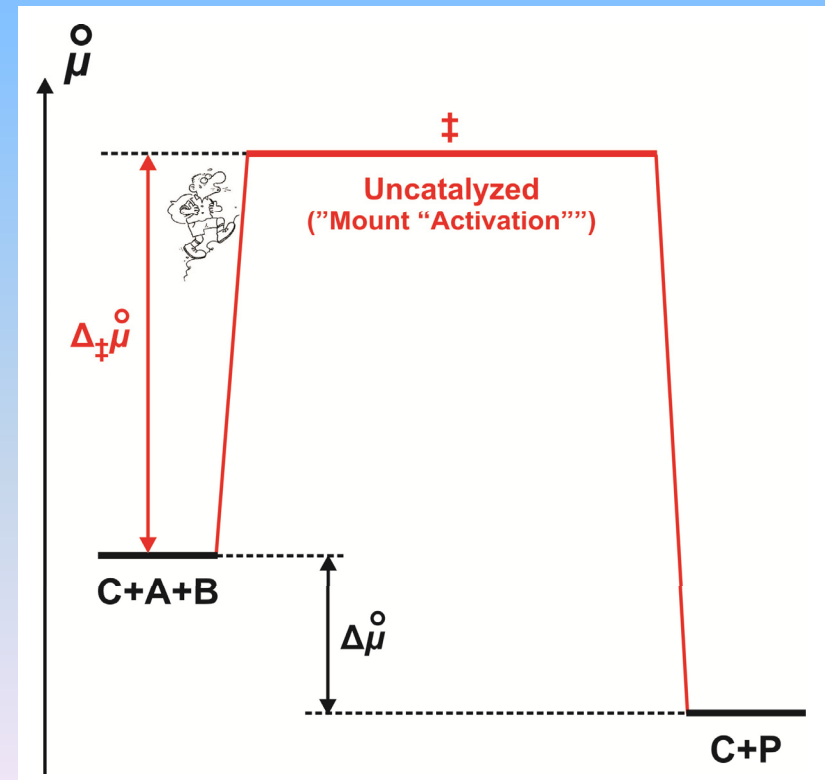
But why can the addition of a catalyst (that results in an alternative reaction mechanism) accelerate a reaction?

How a Catalyst Works

rate coefficient k of the *uncatalyzed* reaction which proceeds via a transition state complex \ddagger ,

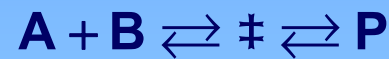


only determined by the activation threshold $\Delta_{\ddagger} \overset{\circ}{\mu}$



How a Catalyst Works

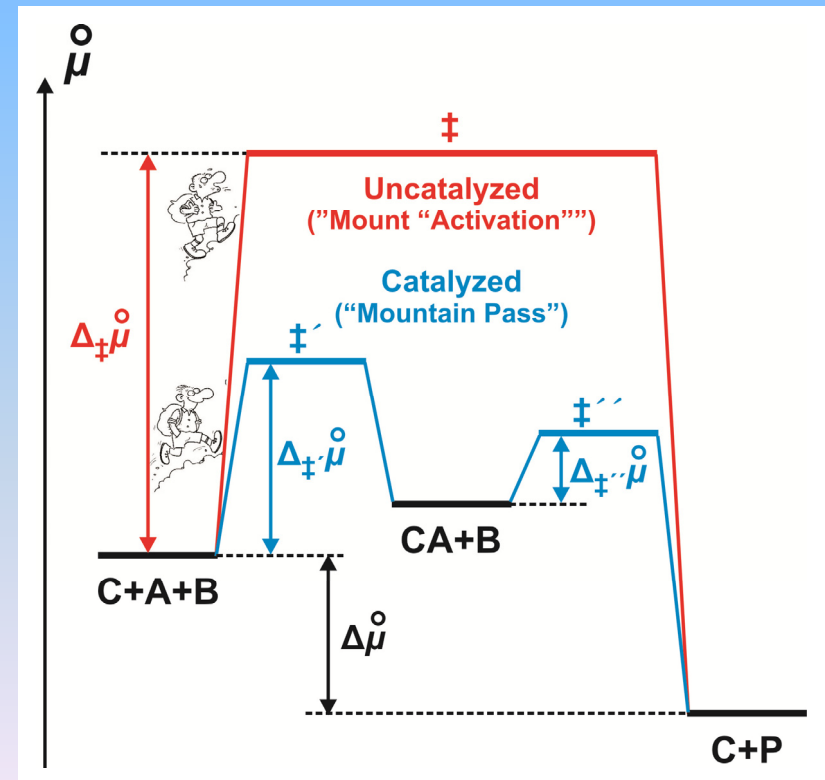
rate coefficient k of the *uncatalyzed* reaction which proceeds via a transition state complex \ddagger ,



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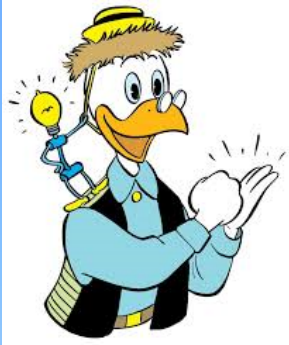
increased formation and decomposition rate of the intermediate CA in the *catalyzed* reaction can only be explained by lower activation thresholds:



4. Application of Catalysis



“Nothing is too hard for an engineer”



most common example in technical application is a solid used as *heterogenous catalyst* (in this context also called *contact catalyst*):

the catalyst provides a surface on which the reaction can take place

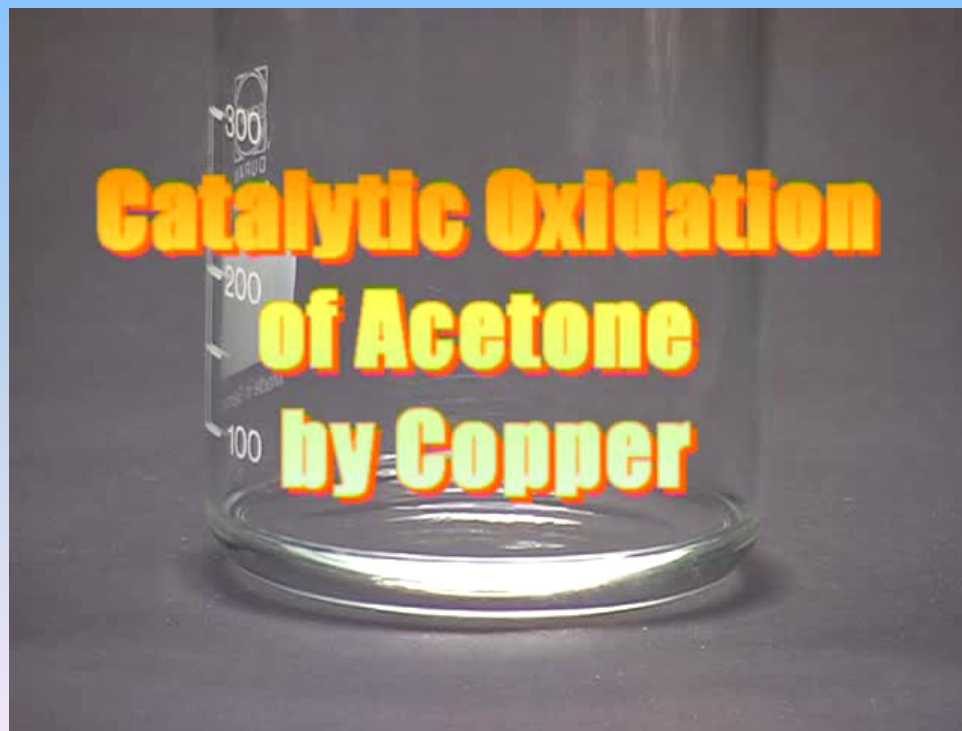
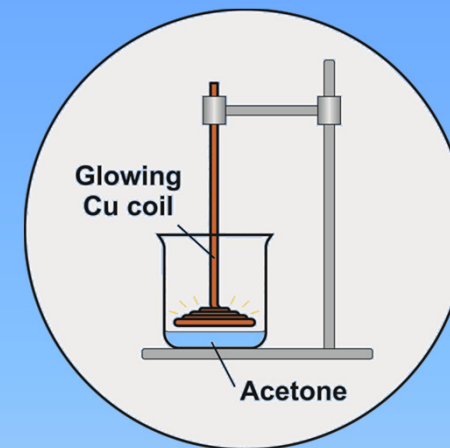
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Catalytic Oxidation of Acetone

Procedure:

A red-hot copper coil is fixed over acetone in a beaker.



9



Catalytic Oxidation of Acetone

Procedure:

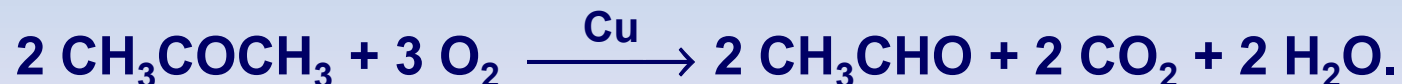
A red-hot copper coil is fixed over acetone in a beaker.

Observation:

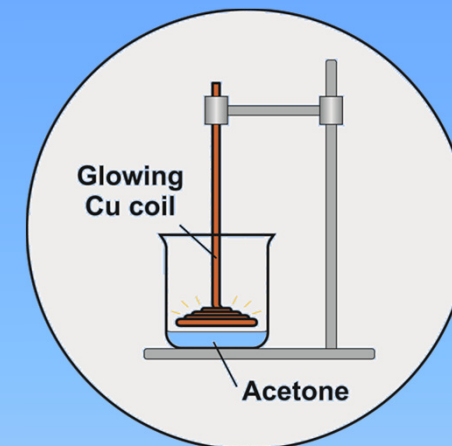
The coil glows with fluctuating intensity and in changing colors from black to light orange. There is also the typical pungent fruity smell of aldehyde.

Explanation:

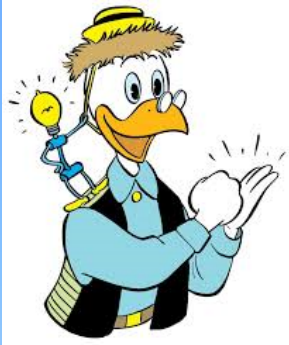
Acetone is oxidized to acetaldehyde, carbon dioxide and water,



The reaction is *heterogeneously* catalyzed by copper. The catalytic surface processes are visible by the fluctuating glowing and the changing colors of the copper coil.



“Nothing is too hard for an engineer”



surface should be as large as possible and therefore a high degree of dispersion of the catalyst is desirable

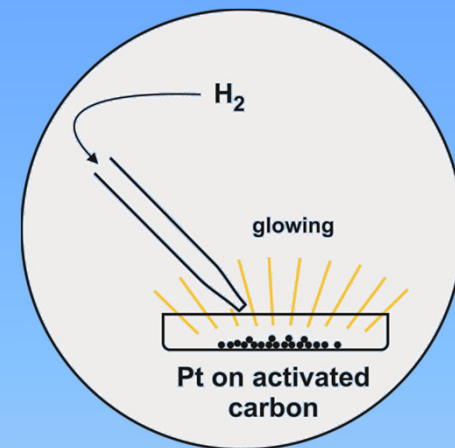
⇒ *supported high-area catalyst*: very small particles of catalytically active material such as platinum or rhodium are applied for stability to highly porous carrier materials (aluminum oxide, silicon dioxide, activated carbon, as well as zeolites)

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Catalyzed Gas Ignition

Procedure:

Hydrogen gas is passed over a small heap of platinized activated carbon in a porcelain dish.



10



Catalyzed Gas Ignition

Procedure:

Hydrogen gas is passed over a small heap of platinized activated carbon in a porcelain dish.

Observation:

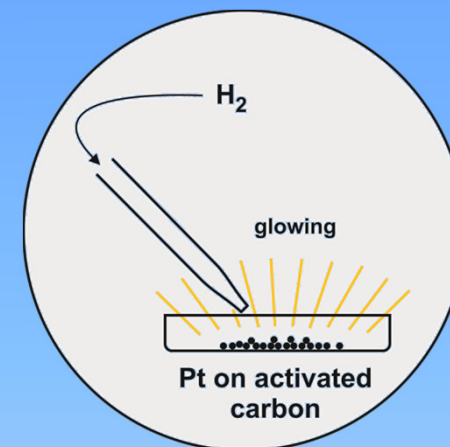
After a short time, the catalyst begins to glow and the gas ignites with a gentle bang.

Explanation:

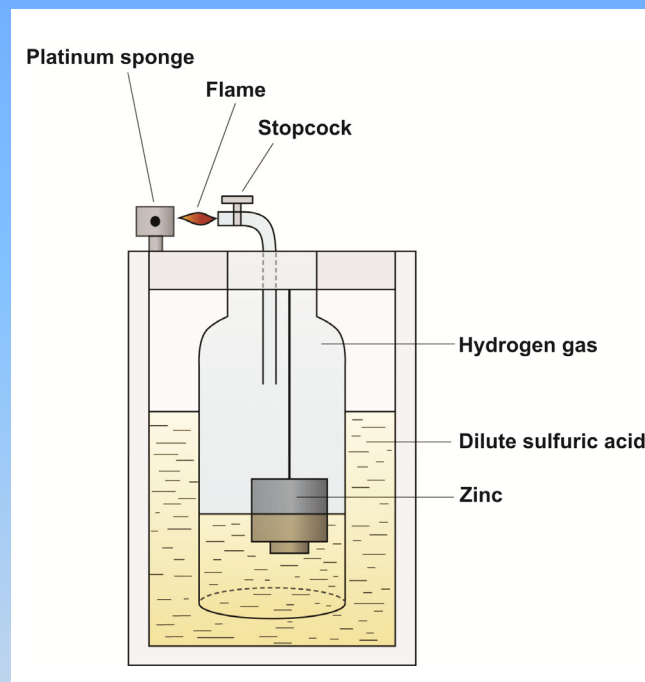
Hydrogen gas exhibits a strong tendency to “burn” to water:



The reaction rate at room temperature is, however, immeasurably small. But the rate can be appreciably increased by finely dispersed platinum as catalyst.



DÖBEREINER'S Lighter



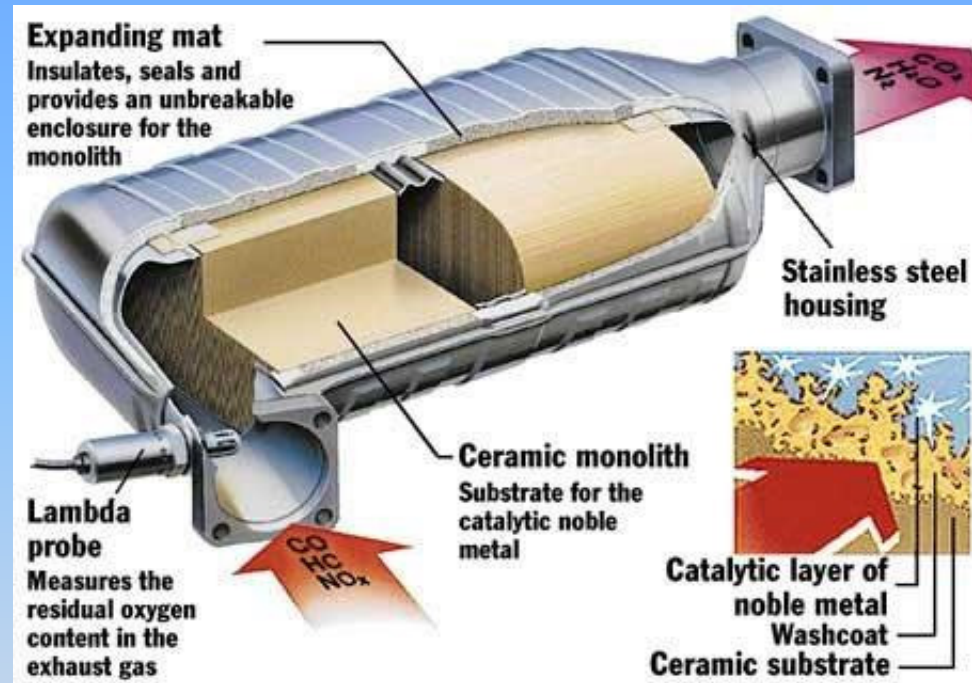
Explanation:

Zinc reacts with sulfuric acid, generating hydrogen gas,



When the stopcock is opened, the hydrogen stream is directed onto a bit of platinum sponge and the gas ignites.

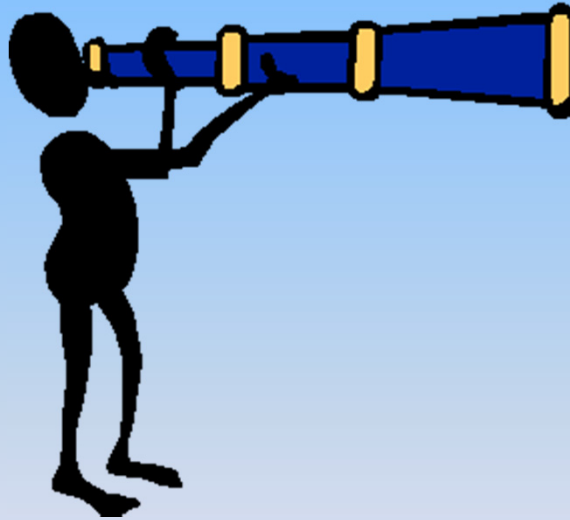
Exhaust-Gas Catalytic Converter

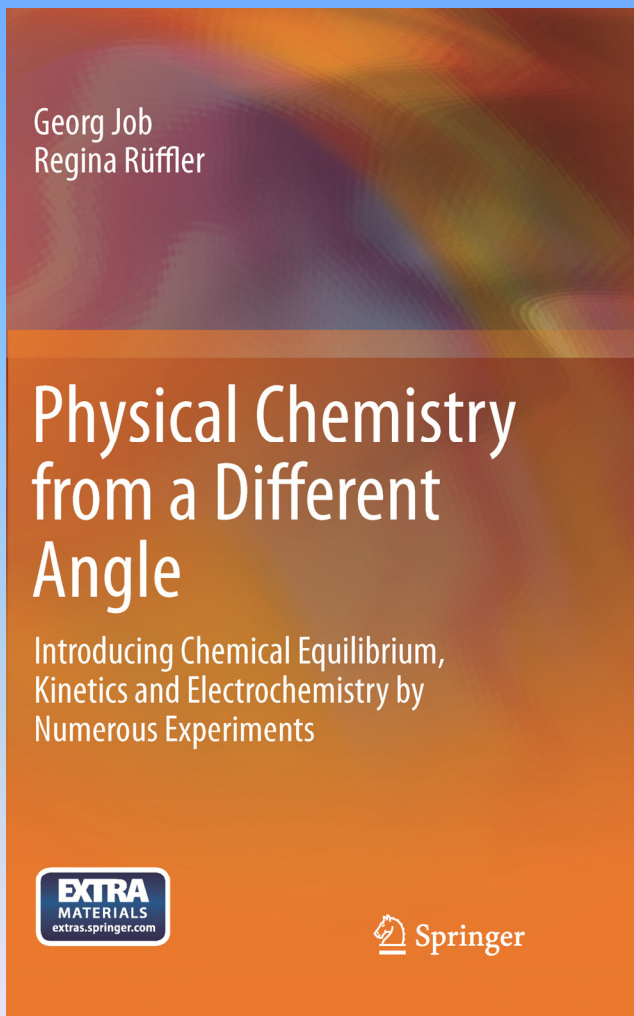


elimination of combustion pollutants by use of catalysis

catalytically active substance: alloy of platinum group metals, mostly platinum and rhodium, which is dispersed finely over a fine-pored ceramic honeycomb body acting as the carrier

5. Outlook





Georg Job, Regina Rüffler
**Physical Chemistry
From a Different Angle**

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Kinetics and Electrochemistry by
Numerous Experiments**

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