

Demonstration experiments



to the poster presentation

“Chemical Potential in Kinetics”

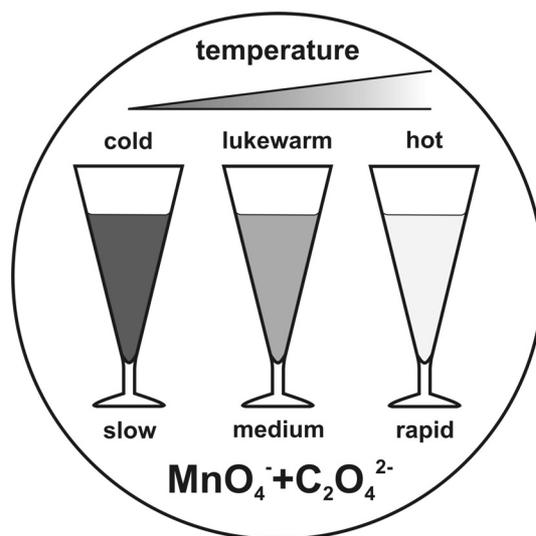
Regina Rüffler, Georg Job

**41st IUPAC World Chemistry Congress
Turin, August 2007**



**Further informations on the homepage:
www.job-foundation.org**

Temperature Dependence of Reaction Rate



Equipment:

3 goblets
3 beakers (250 mL)
3 beakers (100 mL)
3 glass rods
measuring cylinders
Dewar vessel or plastic bowl
laboratory heating plate

Chemicals:

potassium permanganate solution (0.2 M)
oxalic acid solution (0.5 M)
sulphuric acid (4 M)
deionised water
crushed ice

Safety:

potassium permanganate (KMnO_4): O, Xn, N R8-22-50/53 S2-60/61
oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$): Xn R21/22 S2-24/25
sulfuric acid (H_2SO_4): C R35 S1/2-26-30-45



O



Xn



N



C

It is necessary to wear safety glasses and protective gloves, because every contact with eyes or skin should be avoided.

Procedure:

Preparation: 15 mL oxalic acid solution, 30 mL sulphuric acid and 60 mL deionised water are filled in each of the three 250-mL beakers, 15 mL potassium permanganate solution in each of the 100-mL beakers. One 250-mL and one 100-mL beaker are cooled down to approx. 0°C in an ice bath, a second pair of beakers is heated to approx. 50°C in a water bath on the laboratory heating plate, the last pair of beakers remains at room temperature.

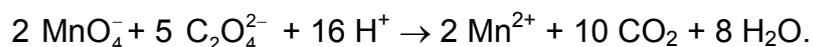
Procedure: The acidified oxalic acid solutions with different temperatures are filled into the goblets. Subsequently, the ice cold, then the lukewarm and finally the hot potassium permanganate solution is added rapidly to the corresponding oxalic acid solution and the solutions are stirred up.

Observation:

The solutions change their colour from purple to claret-red and tawny and finally to colourless; simultaneously, a slight effervescence can be observed. The decolourisation of the hot solution is completed after approx. 0.5 min, that of the lukewarm solution after approx. 2.5 min and that of the ice cold solution after approx. 15 min.

Explanation:

Purple permanganate ions are reduced in acidic solution by oxalate ions to the nearly colourless manganese(II) ions, whereas the oxalate ions are oxidised to gaseous carbon dioxide:



The reaction rate depends obviously on the temperature. An increase in temperature normally results in an acceleration of the reaction. An old rule of thumb used by chemists says that the rate of a reaction roughly doubles with each ten-degree temperature increase (the factor varies in fact between 1.5 and 4). A more detailed theoretical treatment requires the consideration of the so-called ARRHENIUS equation of the rate constant, that was the starting point for the two most important theories of the reaction rate, the collision theory and the transition state theory.

Disposal:

The solutions are poured in the container for heavy-metal waste.

Decomposition of Hydrogen Peroxide by Various Catalysts

Equipment:

3 goblets
measuring cylinders
spatula
(food grater
200-mL Erlenmeyer flask
cheese cloth or cotton tea filter
beaker)

Chemicals:

hydrogen peroxide solution (6%)
iron(III) chloride solution (0.1 M)
manganese dioxide powder
catalase solution (1%) or crude potato extract
(peeled raw potato
deionised water
crushed ice)

Safety:

hydrogen peroxide solution (H_2O_2): Xn R22-41 S26-39
manganese dioxide (MnO_2): Xn R20/22 S25
iron(III) chloride (FeCl_3): Xn R22-38-41 S26-39



Xn

It is necessary to wear safety glasses and protective gloves, because every contact with eyes or skin should be avoided.

Procedure:

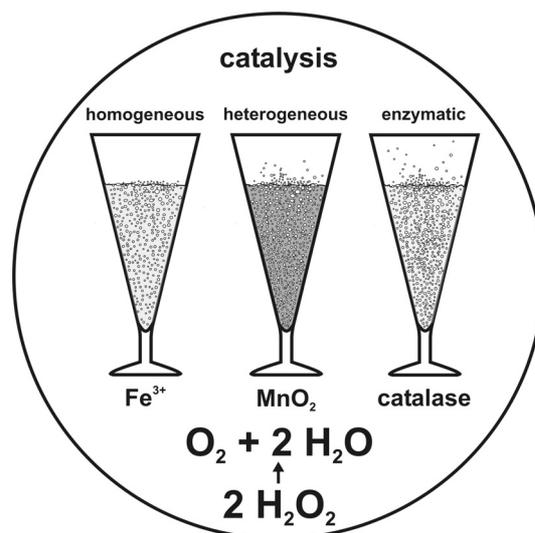
Preparation of crude potato extract: Approx. 20 g of peeled raw potato are finely grated by means of a food grater. The paste is scraped into a 200-mL Erlenmeyer flask and 25 mL ice-cooled deionized water are added. The flask is swirled in intervals for about 15 min. Subsequently, the suspension is filtered through a sheet of cheese cloth or a cotton tea filter into a chilled beaker.

Procedure: 20 mL hydrogen peroxide solution are filled into each of the three goblets.

Homogeneous catalysis: 2 mL iron(III) chloride solution are added to the first goblet.

Heterogeneous catalysis: A spatula-tipfull of powdered manganese dioxide is added to the second goblet.

Enzymatic catalysis: 1 mL catalase solution or alternatively 2 mL of the filtered clear potato extract are added to the third goblet.



Observation:

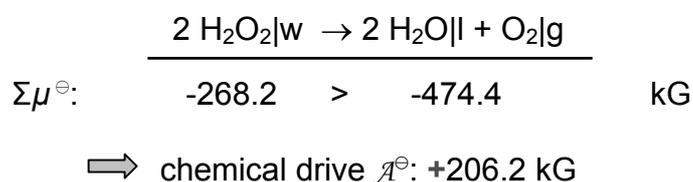
Homogeneous catalysis: The colour of the solution changes from pale yellow to brownish orange. Additionally, a noticeable formation of gas can be observed after a while. The pale yellow colour returns together with the end of bubbling.

Heterogeneous catalysis: A strong effervescence combined with the formation of fog can be observed (therefore, the experiment is also known as "genie in a bottle"). The liquid gets dark because of the finely dispersed black manganese dioxide and the goblet warms up considerably.

Enzymatic catalysis: In the case of the catalase solution a strong evolution of gas takes places and the goblet gets warm. The reaction catalyzed by the catalase from potato extract is weaker and a distinct foam layer is formed.

Explication:

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



Necessary chemical potentials ($T = 298 \text{ K}$, $p = 101.3 \text{ kPa}$):

Substance	Chemical potential μ^\ominus [kG]
$\text{H}_2\text{O}_2 \text{w}$	-134.1
$\text{H}_2\text{O} \text{l}$	-237.2
$\text{O}_2 \text{g}$	0

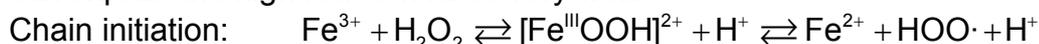
The decomposition rate at room temperature is, however, immeasurably small. But the rate can be appreciably increased by the addition of a catalyst.

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

According to the mechanism proposed by KREMER and STEIN an intermediate oxygen complex of iron with oxidation number +V is primarily formed by the reaction of Fe^{3+} with H_2O_2 . This complex reacts with another H_2O_2 molecule to water and oxygen thereby re-forming Fe^{3+} .



According to the mechanism proposed by HABER and WEISS the Fe^{3+} ions initiate a radical reaction, after which the chain reactions consume the hydrogen peroxide. This mechanism can explain the high reaction rates very well.





Manganese dioxide is an example for a *heterogeneous catalyst*, i.e. the phase of the catalyst is different from that of the reaction mixture. The surface of solid manganese dioxide provides a particularly favourable environment to catalyze the decomposition, though the mechanism is not understood very well. For increasing the surface area available for contact with the hydrogen peroxide solution a finely graded powder is used. The observed fog (the "genie") is caused by condensing water vapour mixed with oxygen gas.

Enzymatic catalysis takes an intermediate position, because enzymes 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. The cytotoxic 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.

The detailed structure of catalase differs from one organism to another, but the general quaternary structure is analogous to hemoglobin in that catalase is tetrameric and each polypeptide chain, composed of more than 500 amino acids, contains an iron-centered porphyrin ring. However, in contrast to hemoglobin, catalase utilizes Fe(III). This iron can formally be oxidized to Fe(V) in the oxidation-reduction cycle, but the processes at the active site of the enzyme are not understood very well. But the incorporation of the iron ions in the porphyrin and in the enzyme protein improves apparently their catalytic activity because the effect of catalase is much stronger than that of the iron ions in solution.

Disposal:

Hydrogen peroxide solutions can be disposed of down the drain with running water. Manganese dioxide can be reused after drying.

Inhibition of the Enzyme Catalase by Hg^{2+} Ions

Equipment:

2 small beakers
2 Petri dishes
tweezers

Chemicals:

peeled raw potato
hydrogen peroxide solution (6%)
mercury(II) chloride (0.1%)

Safety:

hydrogen peroxide solution (H_2O_2): Xn R22-41 S26-39
mercury(II) chloride (HgCl_2): T+, N R28-34-48/24/25-50/53 S1/2-36/37/39-45-60-61



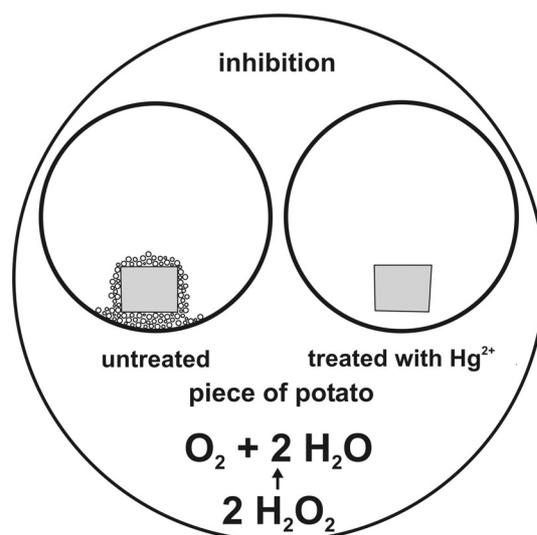
Xn



T(+)



N



Mercury(II) chloride is highly toxic! It can also be absorbed through the skin. The substance causes severe eye irritation and possible burns.

It is necessary to wear safety glasses and protective gloves, because every contact with eyes or skin should be avoided. An adequate ventilation has to be provided.

Procedure:

Preparation: Two pieces of approximately equal size are cut out of the potato. 20 mL mercury(II) chloride solution are filled in the first and 20 mL water in the second beaker. Subsequently, a potato piece is put in each of the beakers for approx. 1 min. The two Petri dishes are filled with hydrogen peroxide solution.

Procedure: The potato pieces are taken with tweezers out of the beakers and added to the hydrogen peroxide solution in the Petri dishes.

Observation:

An intense formation of foam caused by the escape of a gas can be observed immediately around the untreated potato piece. Around the potato piece treated with HgCl_2 solution, however, nearly no formation of gas takes place.

Explanation:

The disproportionation of hydrogen peroxide in aqueous solution to oxygen and water according to



is highly accelerated by the reaction-specific enzyme catalase contained for example in potatoes.

The tertiary and quaternary structure of proteins and therefore also of enzymes is often stabilized by disulphide bridges between cystine chains. Heavy-metal ions, especially highly poisonous Hg^{2+} ions, exhibit a high affinity for (anionic) sulphur. Therefore, such ions may disrupt the disulphide bonds and modify the structure of the protein. This modification has an influence on the "active site;" the enzyme loses its catalytic properties irreversibly ("enzyme poisoning").

Disposal:

The solution containing mercury has to be disposed of as specially hazardous heavy-metal waste.

Catalytic Oxidation of Acetone

Equipment:

400-mL beaker
ring stand, clamp
coil made of copper wire (thickness: 2 mm)
laboratory burner
crucible tongs

Chemicals:

acetone

Safety:

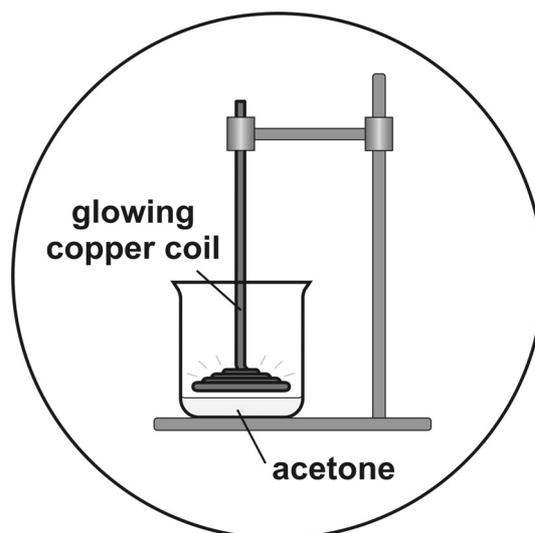
acetone (CH₃COCH₃): F, Xi R11-36-66-67 S9-16-26



F



Xi



Both the liquid and the vapour are highly flammable. Acetone has a relatively high vapour pressure and should be handled only with adequate ventilation. It is also necessary to wear safety glasses and protective gloves.

Procedure:

Preparation: Approx. 30 mL acetone are filled in the beaker. The clamp with the copper coil is fitted at the stand in an adequate height so that the coil is about 1 cm above the liquid acetone.

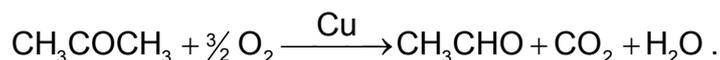
Procedure: After removing from the beaker the copper coil is heated in the burner flame until it glows red. Subsequently, it is returned quickly to the beaker in the former position.

Observation:

The coil glows with fluctuating intensity and in changing colours from black to light orange. The pungent fruity odour of aldehyde can be noticed.

Explanation:

Acetone is oxidized to acetaldehyde, carbon dioxide and water,



The reaction is catalyzed by copper. Primarily, the copper itself is oxidized to copper oxide and subsequently it transfers this oxygen to acetone thereby returning to the metallic form. The catalytic surface processes are visible by the fluctuating glow and the changing colours of the copper coil. The covering with oxygen is responsible for the dark colour of the surface (formation of copper oxide). By the subsequent reaction with acetone the copper surface becomes bright again because of the transfer of the oxygen and begins to glow because of the released reaction energy.

Disposal:

The remaining acetone is collected in a container for halogen-free organic solvents or alternatively, it can be redistilled.

Catalytic Gas Lighter

Equipment:

pressure-reducing valve
glass tube with tapered end
flexible tube
tweezers
Petri dish
(50-mL beaker
glass rod)

Chemicals:

hydrogen (gas cylinder)
platinized quartz wool or
platinized activated charcoal
(quartz wool
sodium hexachloroplatinate(IV) hexahydrate
ascorbic acid solution (5 wt.-%)
deionised water)

Safety:

hydrogen (H₂): F+ R12 S9-16-33

sodium hexachloroplatinate(IV) hexahydrate (Na₂PtCl₆·6 H₂O): T R25-41-42/43 S22-26-36/39-45

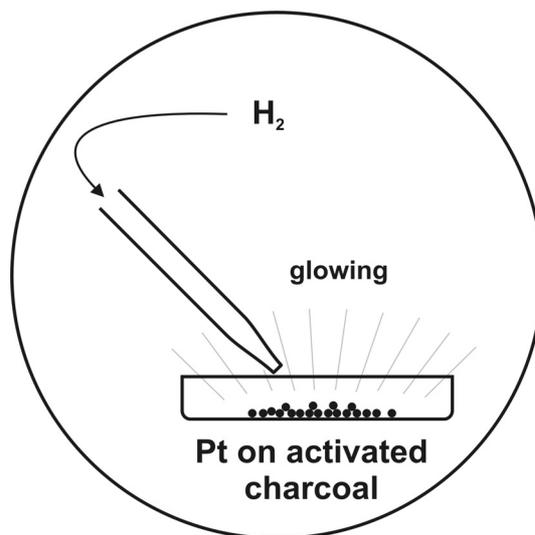
ascorbic acid (C₆H₈O₆): S24/25



F(+)



T



Hydrogen is extremely flammable and forms explosive mixtures with air (explosive limits in air: 4-75 % per volume).

It is necessary to wear safety glasses and recommended to wear work gloves. Because of the escaping hydrogen an adequate ventilation has to be provided.

Procedure:

Preparation of platinized quartz wool: 10 mg sodium hexachloroplatinate(IV) hexahydrate are dissolved in 20 mL deionised water. The quartz wool is washed with acetone for removal of disturbing residues on the surface and then well dried. The hexachloroplatinate solution and 10 mL ascorbic acid solution are poured into the beaker and the mixture is stirred up well. Subsequently, a “flake” of cleaned quartz wool (approx. 0.5-0.6 g) is added to the solution. After a few hours the solution gets dark because platinum precipitates. The mixture should be allowed to stand *at least overnight* in the covered beaker. Thereby, the quartz wool should always be covered by liquid. Subsequently, the quartz wool that looks grey now is taken out of the solution, washed with deionised water and dried. Before use, the platinized quartz wool has to be heated thoroughly for a few seconds to activate it.

Procedure: Hydrogen out of a gas cylinder is directed through a glass tube onto platinized quartz wool held by tweezers or on a small heap of platinized activated charcoal in a Petri

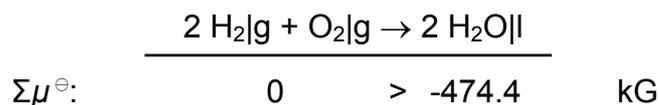
dish (a little bit of glass wool should be filled in the tapered end of the tube for avoiding backlash).

Observation:

After a little while, the catalyst begins to glow, and the gas jet ignites spontaneously with a gentle bang. The gas burns with a hot but nearly colourless flame.

Explanation:

Hydrogen “burns” to water according to



⇒ chemical drive \mathcal{A}^\ominus : +474.4 kG

The drive of the reaction is positive, i.e. the reaction should take place spontaneously.

Necessary chemical potentials ($T = 298 \text{ K}$, $p = 101.3 \text{ kPa}$):

Substance	Chemical potential μ^\ominus [kG]
H ₂ g	0
O ₂	0
H ₂ O l	-237.2

The reaction rate at room temperature is, however, immeasurably small because the “potential barrier” on the path from the reactants to the products is too high. But this “barrier” can be overcome by the flame of a lighted taper or match (“hydrogen-oxygen reaction”). By contrast, finely dispersed platinum as catalyst provides an alternative path with a lower “barrier.” The hydrogen gas ignites without initiating flame, the catalyzed reaction can be used quite the contrary as source for fire lighting. Based on this effect Johann Wolfgang Döbereiner constructed in 1823 a pneumatic gas lighter, the famous “Döbereiner’s lighter.”

Platinum as catalyst provides a surface on which the reaction can take place. It seems that both H₂ and O₂ undergo “dissociative chemisorption” on the platinum surface. By stepwise reaction of the chemisorbed atoms (firstly, a H atom diffuses to an adsorbed O atom, forming a surface-coordinated hydroxyl group, and subsequently, this species reacts with a second H atom) water is formed. Because the surface atoms of the catalyst are responsible for the acceleration of the reaction a surface as large as possible and therefore a high degree of dispersion of the platinum is desirable. The very small particles of the active phase are deposited on a support material for stabilisation, in our experiment on quartz wool or activated charcoal.

Disposal:

The catalyst can be reused many times. Otherwise, the platinum has to be treated as heavy metal waste.