

Course 10240 Design Build 2 - Rational catalyst design
Georg Kastlunger & Ole Trinhammer, DTU Physics, June 2024

H_2O_2 decomposition

Sabatier's principle illustrated by Catalytic decomposition of hydrogen peroxide

First a word of caution:

H_2O_2 is strongly oxidizing,
It is used for disinfection, including water sanitation
(but highly diluted!)

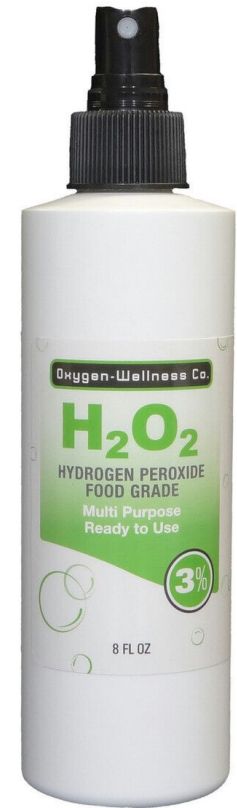
If H_2O_2 or NaOH solution get in your eyes:

Flush your eyes: Immediately rinse your eyes with lukewarm water for at least 15 minutes.

Tell TA

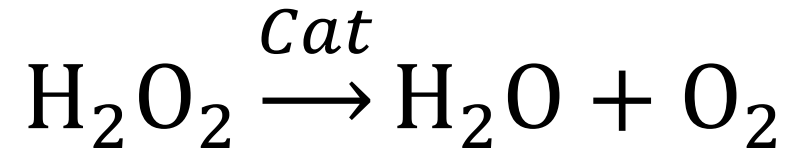
Avoid rubbing your eyes: Rubbing your eyes can cause further irritation and spread the hydrogen peroxide.

Remove contact lenses: If you wear contact lenses and hydrogen peroxide gets into your eyes, remove your lenses as soon as possible.



Sabatier's principle illustrated by Catalytic decomposition of hydrogen peroxide

Measure activity of different catalysts by monitoring oxygen evolution



Sabatier's principle:

Activity is maximum at intermediate binding energy for key process step
Capture reactants (high binding required), release products (low binding required)
i. e. **compromise gives optimum**

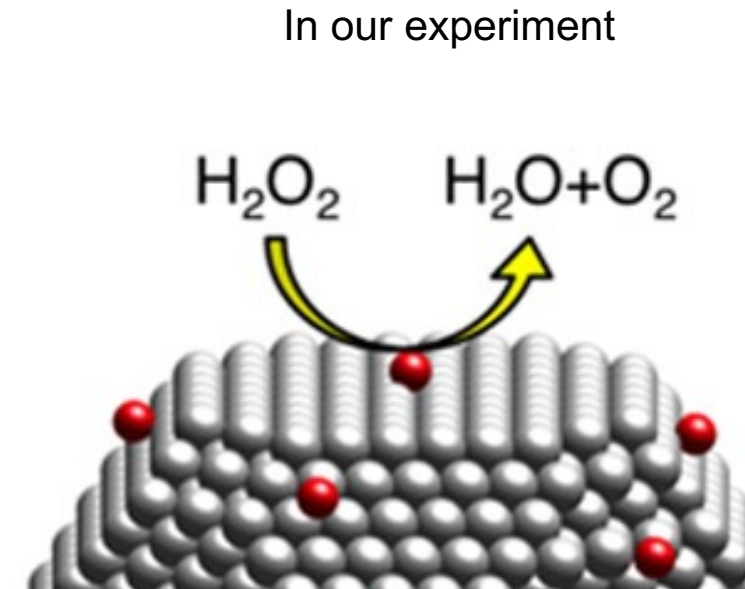
Heterogeneous catalysis

The catalyst is in a different phase (**solid**, liquid, gas) than reactants

A catalyst speeds up reactions, but does not influence the overall energy released or consumed

Industrial catalytic processes:

Process	Reactants, Product/s (not balanced)	Catalyst	Comment
Sulfuric acid synthesis (Contact process)	$\text{SO}_2 + \text{O}_2, \text{SO}_3$	vanadium oxides	Hydration of SO_3 gives H_2SO_4
Ammonia synthesis (Haber-Bosch process)	$\text{N}_2 + \text{H}_2, \text{NH}_3$	iron oxides on alumina (Al_2O_3)	Consumes 1% of world's industrial energy budget ^[2]
Nitric acid synthesis (Ostwald process)	$\text{NH}_3 + \text{O}_2, \text{HNO}_3$	unsupported Pt-Rh gauze	Direct routes from N_2 are uneconomical
Hydrogen production by Steam reforming	$\text{CH}_4 + \text{H}_2\text{O}, \text{H}_2 + \text{CO}_2$	Nickel or K_2O	Greener routes to H_2 by water splitting actively sought
Ethylene oxide synthesis	$\text{C}_2\text{H}_4 + \text{O}_2, \text{C}_2\text{H}_4\text{O}$	silver on alumina, with many promoters	Poorly applicable to other alkenes
Hydrogen cyanide synthesis (Andrussov oxidation)	$\text{NH}_3 + \text{O}_2 + \text{CH}_4, \text{HCN}$	Pt-Rh	Related ammoxidation process converts hydrocarbons to nitriles
Olefin polymerization Ziegler-Natta polymerization	propylene, polypropylene	TiCl_3 on MgCl_2	Many variations exist, including some homogeneous examples
Desulfurization of petroleum (hydrodesulfurization)	$\text{H}_2 + \text{R}_2\text{S}$ (idealized organosulfur impurity), $\text{RH} + \text{H}_2\text{S}$	Mo-Co on alumina	Produces low-sulfur hydrocarbons, sulfur recovered via the Claus process



https://en.wikipedia.org/wiki/Heterogeneous_catalysis

H₂O₂ decomposition – the overall reaction



3 minute discussion with neighbor:

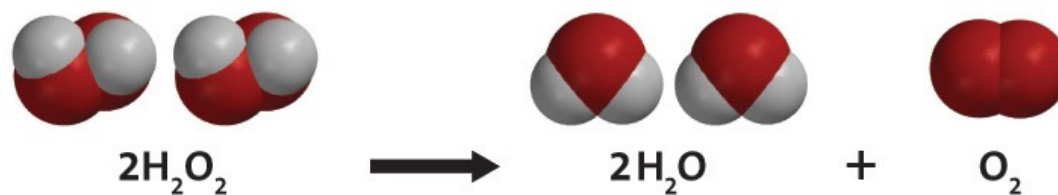
How can you balance the reaction so the same number of
H and O are on both sides?

H₂O₂ decomposition – the overall reaction

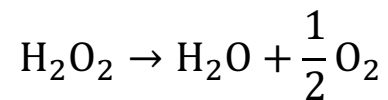


3 minute discussion with neighbor:

How can you balance the reaction so the same number of H and O are on both sides?



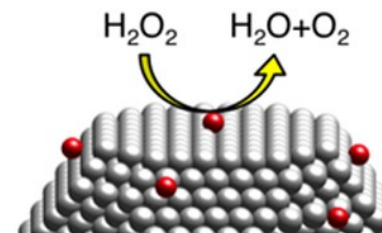
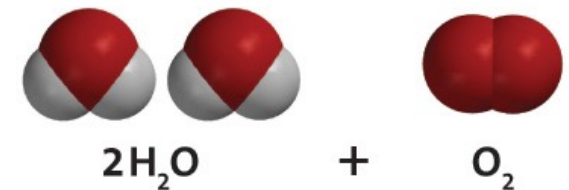
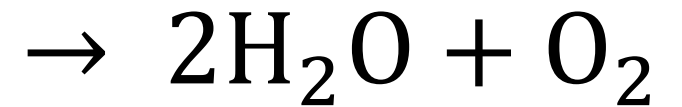
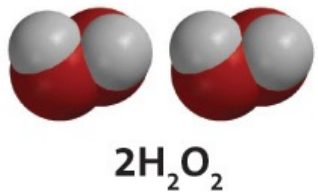
OR:



Reaction steps

5 minute discussion with neighbor:

What could be relevant intermediate steps and how could a catalyst help?



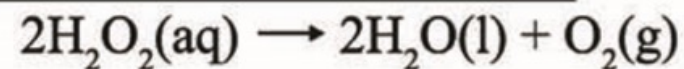
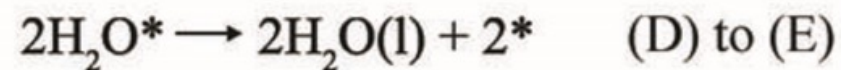
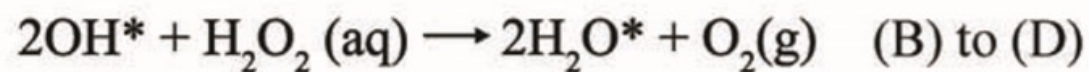
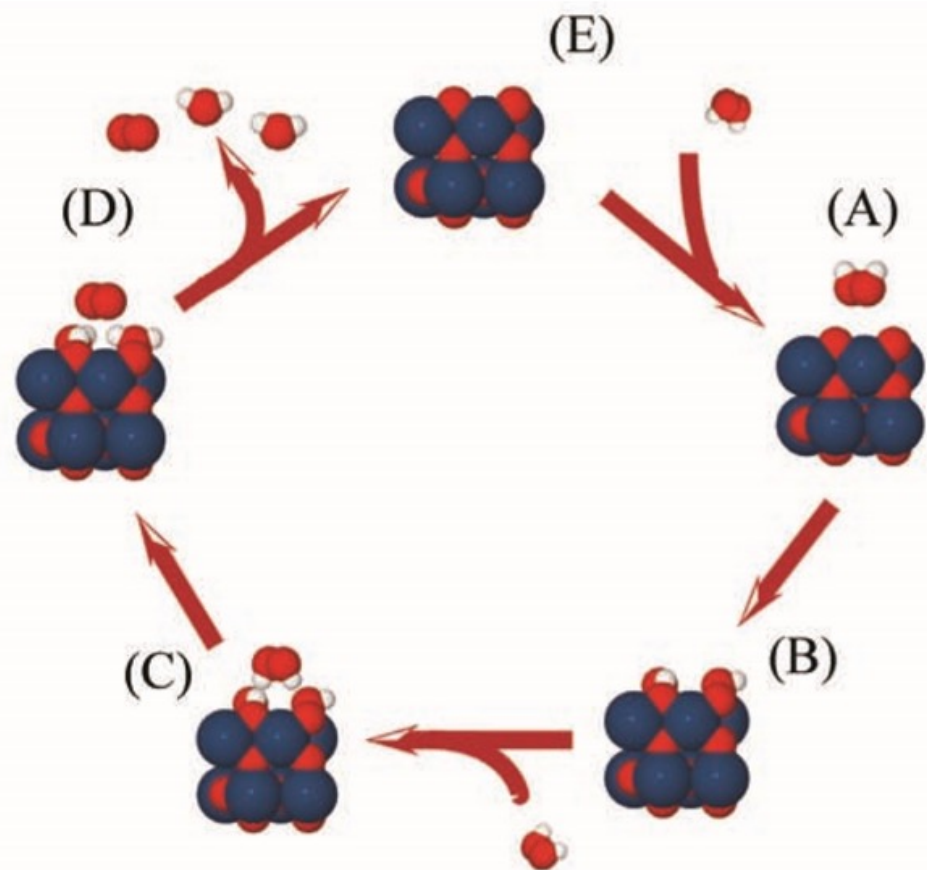
Reaction steps

Anders B. Laursen, Isabela Costinela Man, Ole L. Trinhammer, Jan Rossmeisl, and Søren Dahl
The Sabatier Principle Illustrated by Catalytic H_2O_2 Decomposition on Metal Surfaces
 dx.doi.org/10.1021/ed101010x, J. Chem. Educ. 2011, **88**, 1711–1715

Trinhammer, Laursen, Man, Rossmeisl and Dahl

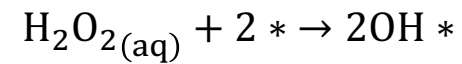
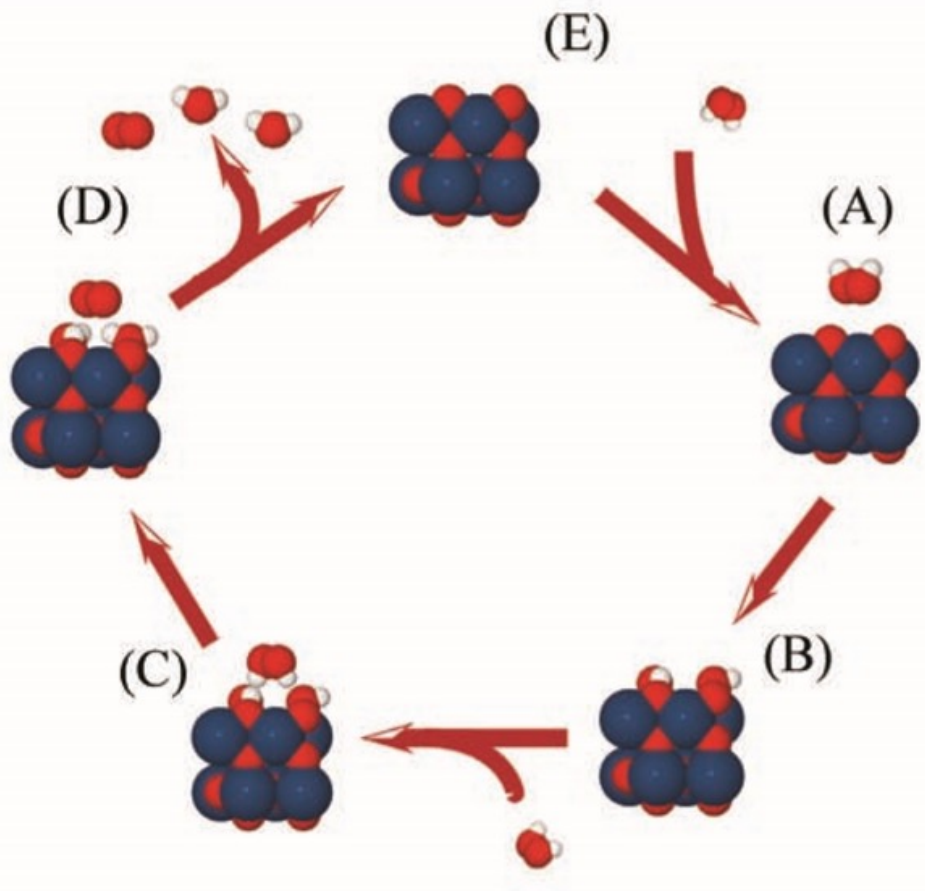
Vulkanplot – Sabatiers princip i heterogen katalyse

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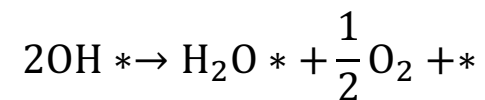


We can simplify it though!

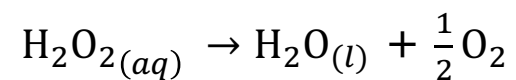
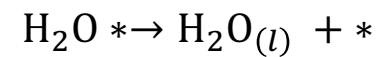
Reaction steps



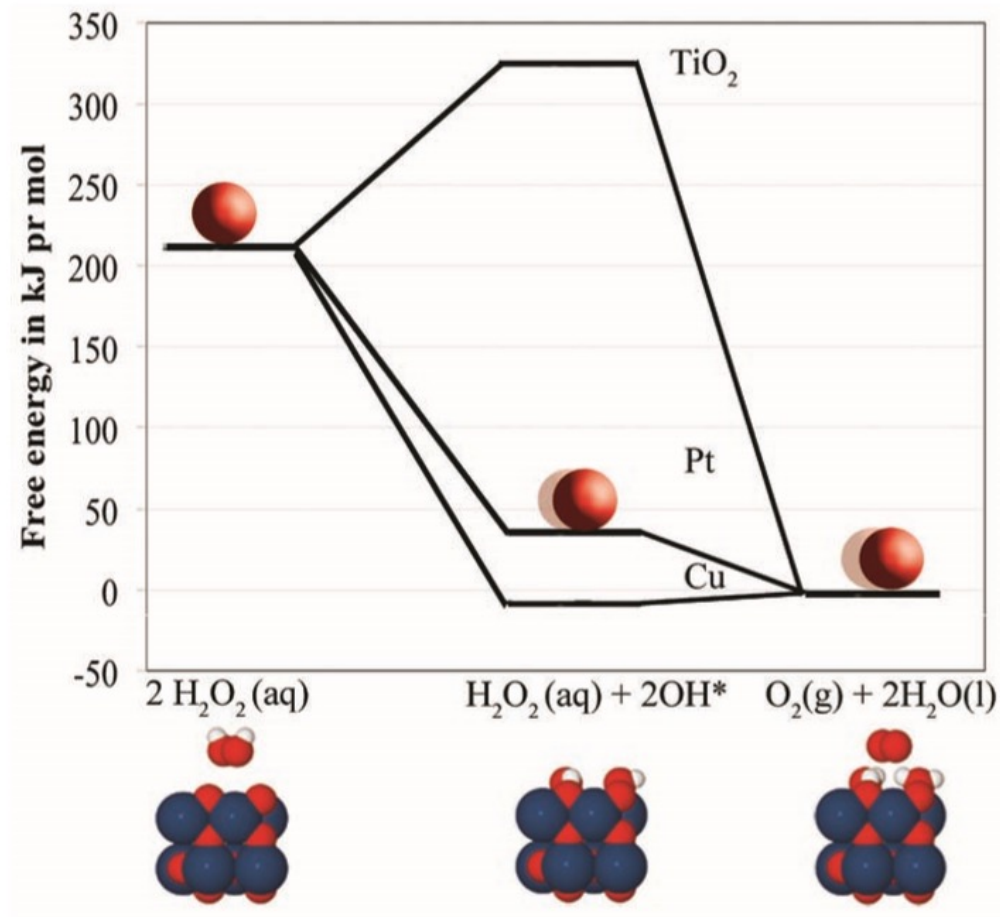
(slow, rate limiting step)



(fast, equilibrated steps)



Key intermediate: OH binding on catalyst surface



Reaction kinetics – the rate limiting step



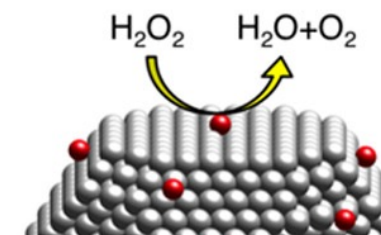
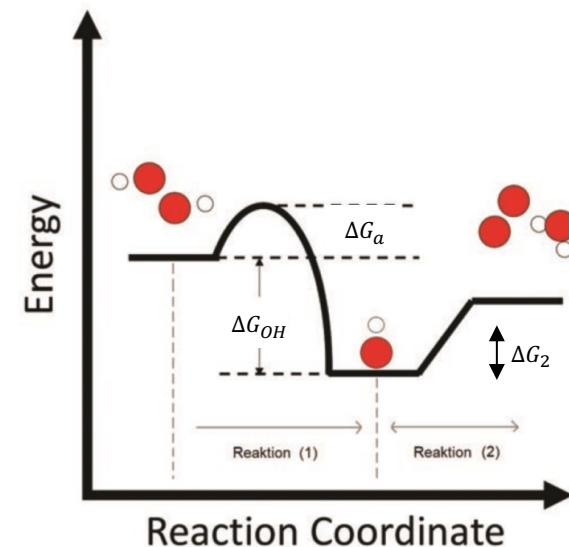
reaction rate, $r = k_1 c_{\text{H}_2\text{O}_2} \theta_*^2$
 (θ_* = fraction of free catalyst sites)

$$k_1 = \frac{kT}{h} e^{-\frac{\Delta G_a}{kT}}$$

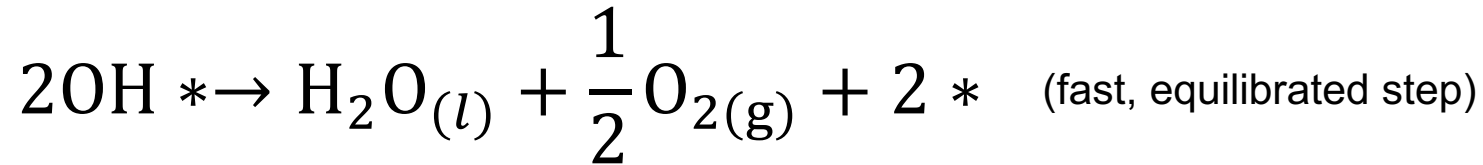
Final reaction rate:

$$r = \frac{kT}{h} e^{-\frac{\Delta G_a}{kT}} c_{\text{H}_2\text{O}_2} \theta_*^2$$

What is the value of θ_* and G_a ?



Reaction kinetics – How to get θ_*



$$K = \frac{a_{\text{H}_2\text{O}} a_{\text{O}_2}^{0.5} \theta_*^2}{\theta_{\text{OH}}^2} = \text{equilibrium constant}$$

a =activity, mostly pressure for gases and concentration for dissolved species, unitless, a of H_2O is generally set to 1

$$\theta_{\text{OH}} = 1 - \theta_* = \text{fraction of surface covered in } ^*\text{OH}$$

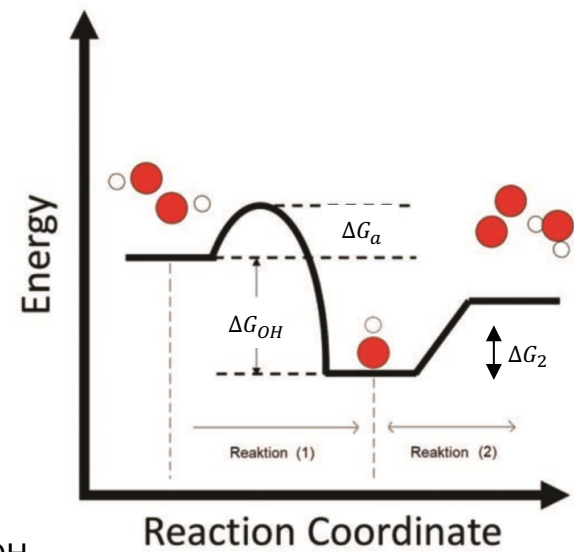
$$K(1 - \theta_*)^2 = p_{\text{O}_2}^{0.5} \theta_*^2$$

$$\theta_* = \frac{1}{1 + \sqrt{\frac{p_{\text{O}_2}^{0.5}}{K}}}$$

Can we estimate K ?

Yes, from the Gibbs free energy of the reaction: $K = e^{-\frac{\Delta G_2}{k_B T}}$

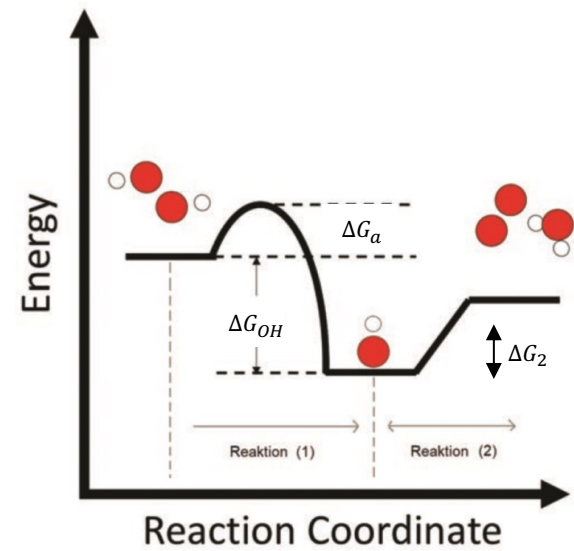
$$\Delta G_2 = \Delta G_{\text{H}_2\text{O}} + \frac{1}{2}\Delta G_{\text{O}_2} - 2\Delta G_{\text{OH}}$$



Reaction kinetics – How to get ΔG_a

$$r = \frac{kT}{h} e^{-\frac{\Delta G_a}{kT}} c_{\text{H}_2\text{O}_2} \theta_*^2$$

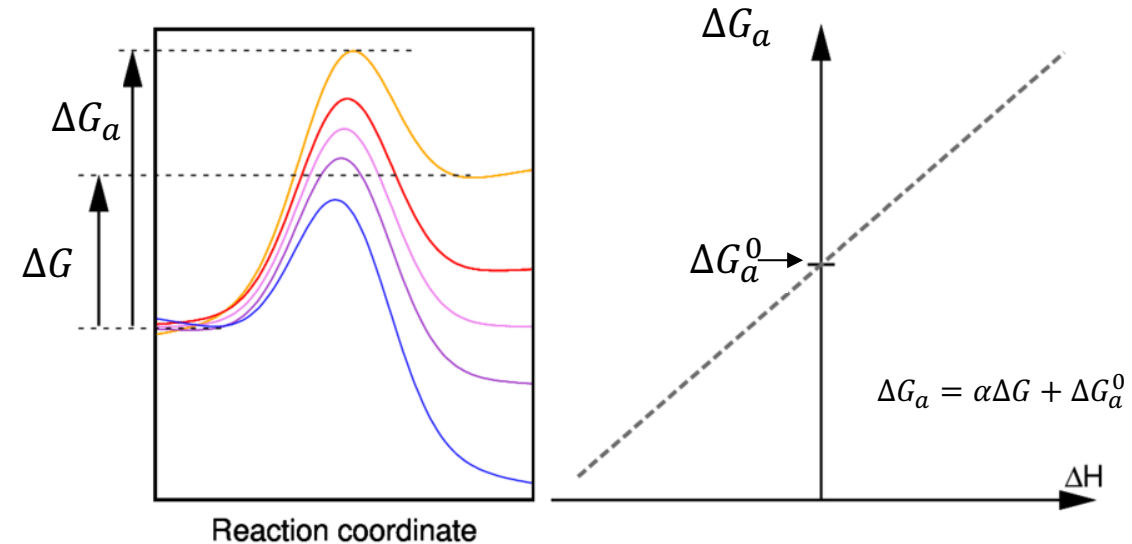
1. Calculate it with density functional theory – calculating transition states is tedious
2. Perform experiments at varying temperature - $(\ln(r) = \ln\left(\frac{kT}{h} c_{\text{H}_2\text{O}_2} \theta_*^2\right) - \frac{\Delta G_a}{kT})$, Arrhenius plot)
3. Find a simpler quantity that correlates with ΔG_a - **Bell–Evans–Polanyi principle (BEP)**



$$\Delta G_a = \alpha \Delta G_{\text{OH}} + \beta, \quad \alpha > 0$$

How can we get α and β ?

Calculate several ΔG_{OH} and ΔG_a explicitly and fit.



Reaction kinetics – Summary & Sabatier principle

$$\Delta G_a = \alpha \Delta G_{OH} + \beta$$

$$\theta_* = \frac{1}{1 + \sqrt{\frac{p_{O_2}^{0.5}}{K}}}$$

$$K = e^{-\frac{\Delta G_{H_2O} + \frac{1}{2}\Delta G_{O_2} - 2\Delta G_{OH}}{k_B T}}$$

$$r = \frac{kT}{h} e^{-\frac{\Delta G_a}{kT}} c_{H_2O_2} \theta_*^2$$

DIY in the theory exercise

Limit cases:

Weak binding:

$\Delta G_{OH} \rightarrow \infty, K \rightarrow \infty, \theta_* \rightarrow 1 = 100\%$ (empty surface)

$$r \sim k_1 c_{H_2O_2} \theta_*^2 = k_1 c_{H_2O_2} = \frac{kT}{h} e^{-\frac{\Delta G_a}{kT}} c_{H_2O_2} \sim e^{-\frac{\alpha \Delta G_{OH}}{kT}} \rightarrow 0$$

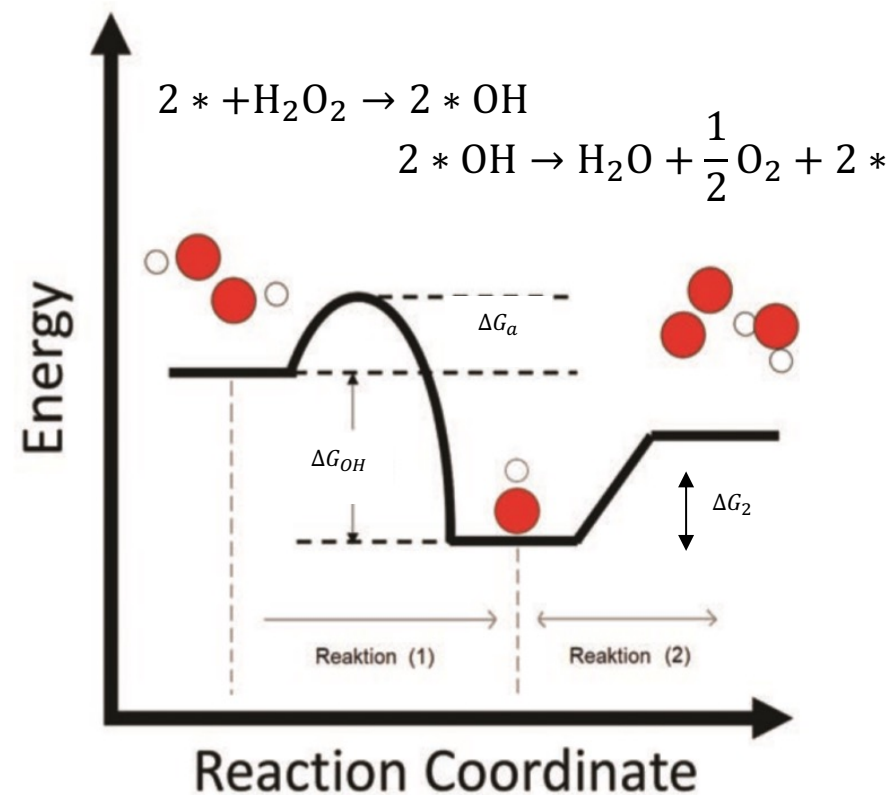
Adsorbing reactant is limiting the process!

Strong binding:

$\Delta G_{OH} \rightarrow -\infty, K \rightarrow 0, \theta_*^2 = \frac{K}{p_{O_2}^{0.5}} \sim e^{\frac{2\Delta G_{OH}}{kT}}$

$$r \sim e^{-\frac{\Delta G_a}{kT}} e^{\frac{2\Delta G_{OH}}{kT}} \sim e^{\frac{(2-\alpha)\Delta G_{OH}}{kT}} \rightarrow 0$$

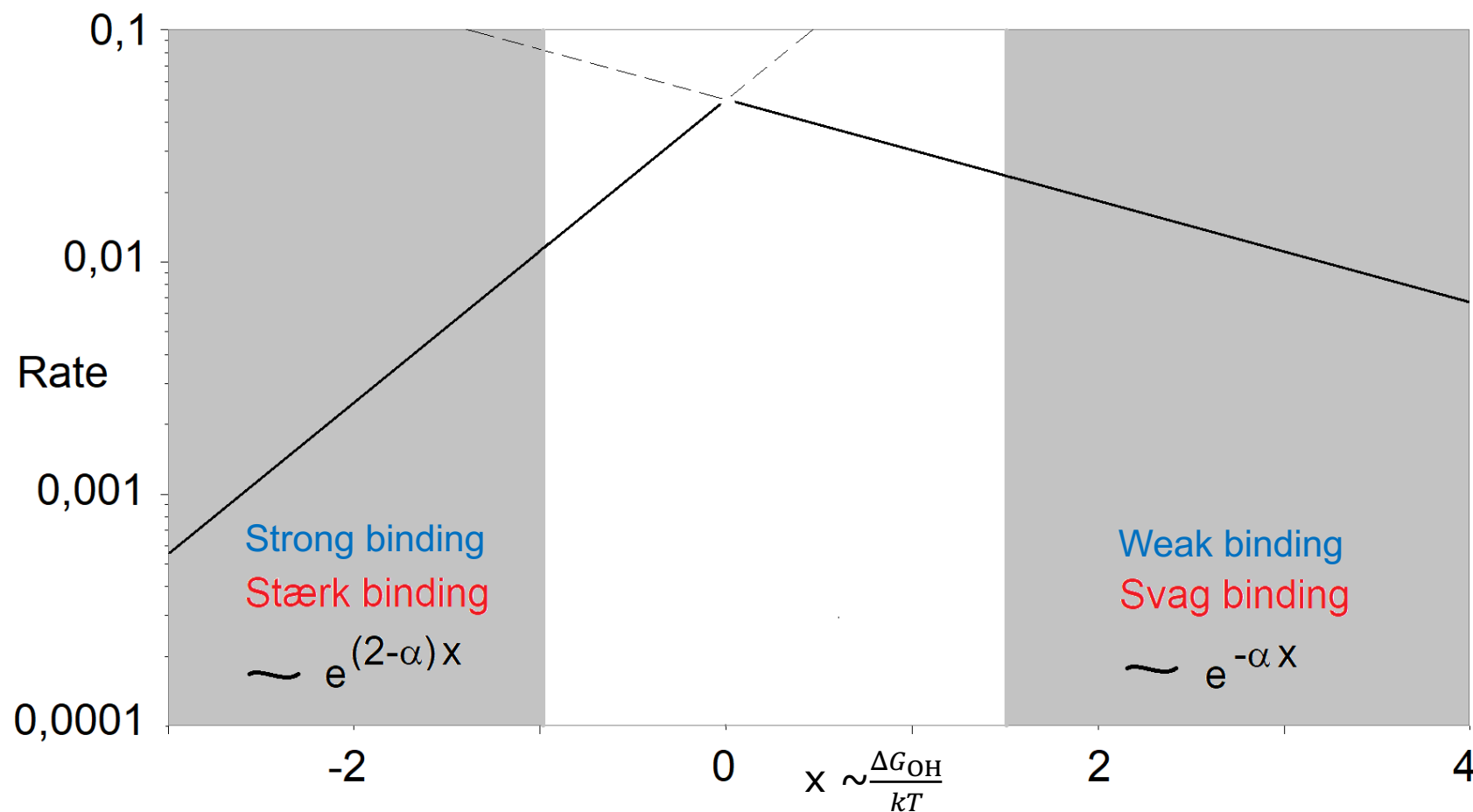
Desorbing the product is limiting the process!



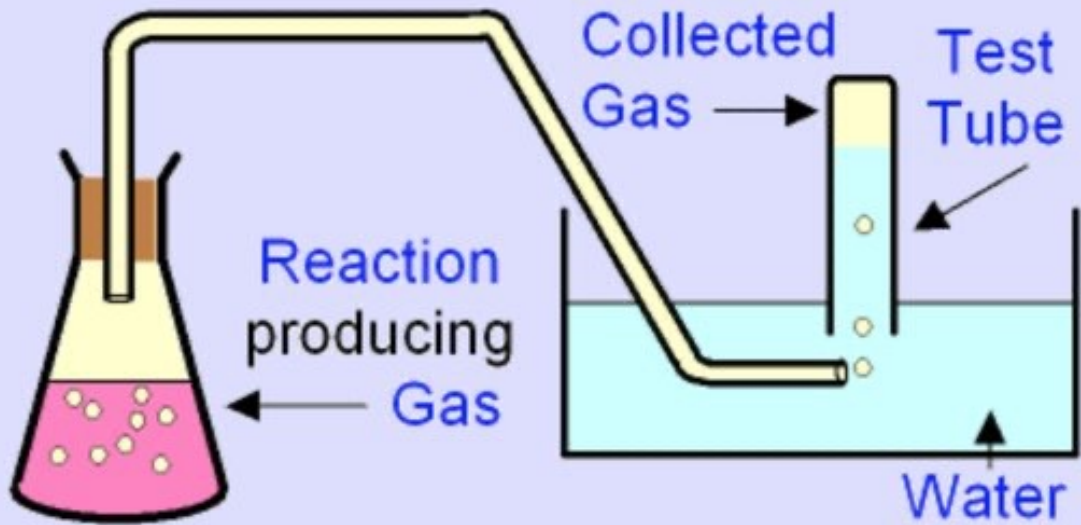
Sabatier's principle



Volcano plot



Experimental setup (Manual on Learn)



Experimental data (example for powder catalyst)

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	
1	Catalysis of oxygen evolution from hydrogenperoxid							Catalyst:	MnO2		Date	sep-19	2010		
2											Department of Physics, DTU, Ole Trinhammer				
3	Measurements in green fields						Area	mass	0,132 g						
4							parameters:	specific area	0,8867 m^2/g						
5															
6	Volume		Time		Time	Volume									
7	Scale reading					increase									
8	mL		hh:mm:ss		sec	mL									
9	120		16:11:10		0	0			Temp (ambient)						
10	140		16:11:30		20	20			20 oC						
11	160		16:11:50		40	40			The temperature is used for the molar volume						
12	180		16:12:20		70	60			to calculate the activity.						
13	200		16:12:49		99	80									
14	220		16:13:16		126	100			If you forgot to read of the temperature						
15	240		16:13:44		154	120			your result will still be rather accurate						
16									if it was done at room temperature						
17															
18															
19															

Uncertainties are ± 1 on last digit if nothing else is stated

Example: wire surface area (cylinder)

$$A = 2\pi r h + 2\pi r^2 = \pi d h + \frac{1}{2} \pi d^2$$

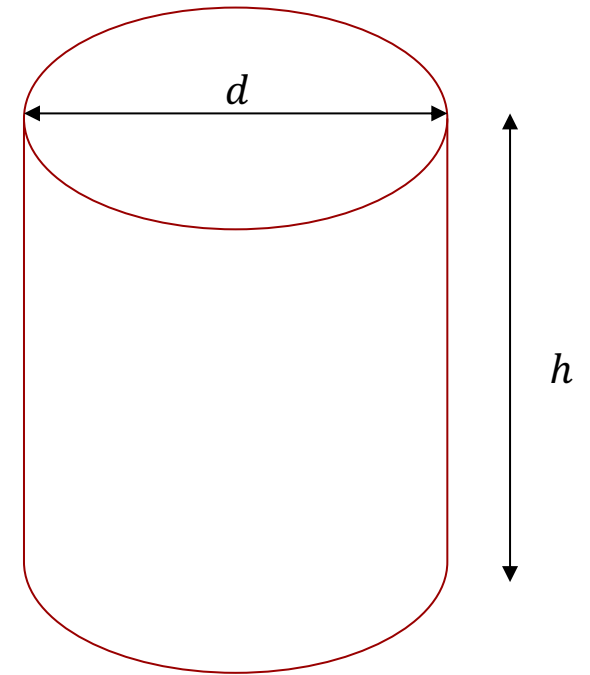
Given *absolute* uncertainties δd and δh

What is the absolute uncertainty δA and what is the *relative* uncertainty

$$\frac{\delta A}{A} = ?$$

Estimate by *error propagation* (better uncertainty propagation) – general case

$$f = f(x, y, z, \dots)$$
$$\delta f^2 = \left(\frac{\partial f}{\partial x}\right)^2 \delta x^2 + \left(\frac{\partial f}{\partial y}\right)^2 \delta y^2 + \left(\frac{\partial f}{\partial z}\right)^2 \delta z^2 + \dots$$



Uncertainty – why the derivatives?

Example

We have measured a certain angle:

$$\theta = 73.5^\circ \pm 0.5^\circ = 1.283 \pm 0.009$$

The relative uncertainty is:

$$\frac{\delta\theta}{\theta} = \frac{0.5^\circ}{73.5^\circ} = 0.0068 = 0.7\%$$

Uncertainty – why the derivatives?

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$$f = \sin \theta = \sin 73.5^\circ = 0.9588 \dots$$

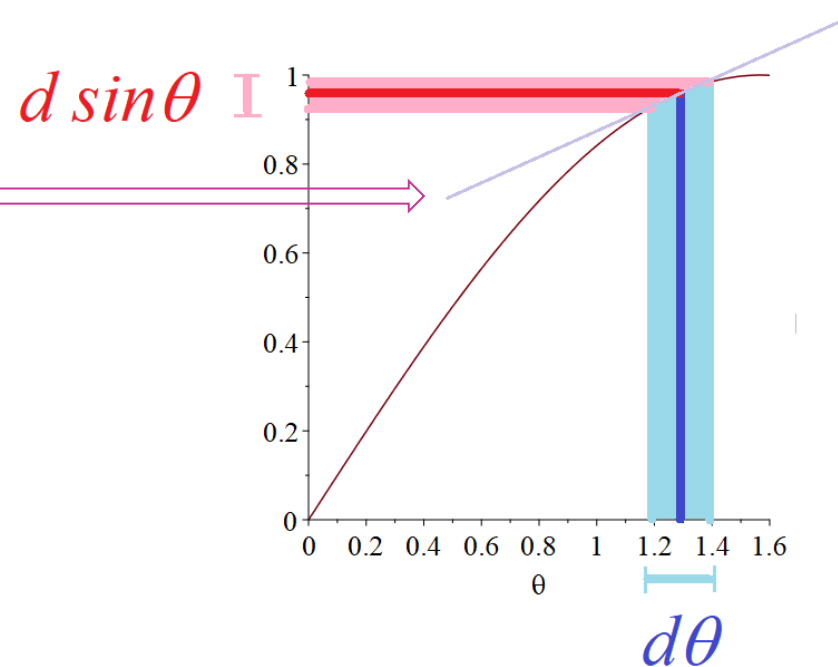
$$\frac{\partial f}{\partial \theta} = \cos \theta$$

$$\delta f \approx \frac{\partial f}{\partial \theta} \cdot \delta \theta$$

$$\delta \sin \theta = \cos(1.283) \cdot 0.0087 \dots = 0.002478 \dots$$

$$\frac{\delta f}{f} = \left(\frac{\delta \sin \theta}{\sin \theta} \right) = \frac{0.002478 \dots}{0.9588 \dots} = 0.00258 \dots = \mathbf{0.3\%}$$

SLOPE !



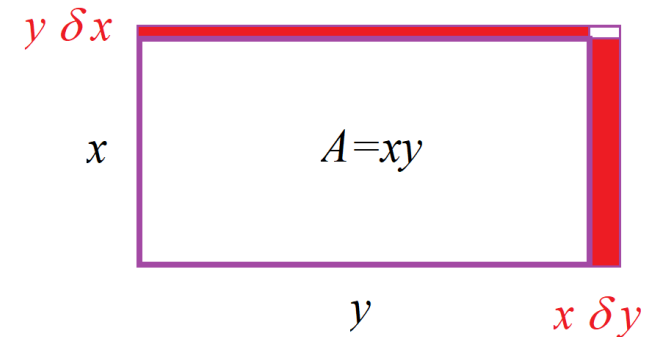
Uncertainty – why the Pythagorean sum?

Because we assume the variables x, y, z, \dots in $f(x, y, z, \dots)$ are independent
The uncertainties contribute term by term

Worst case:

$$A = xy \rightarrow \delta A = (x + \delta x)(y + \delta y) - xy \approx x \delta y + y \delta x$$

$$\delta A = \frac{\partial A}{\partial x} \delta x + \frac{\partial A}{\partial y} \delta y$$



Independent variation

$$\delta A \approx \sqrt{\left(\frac{\partial A}{\partial x}\right)^2 \delta x^2 + \left(\frac{\partial A}{\partial y}\right)^2 \delta y^2}$$

Uncertainty – Gaussian products

$$X(x) = \frac{1}{\sigma_X \sqrt{2\pi}} e^{-\frac{1}{2} \left(\frac{x - \mu_X}{\sigma_X} \right)^2}$$

$$Y(y) = \frac{1}{\sigma_Y \sqrt{2\pi}} e^{-\frac{1}{2} \left(\frac{y - \mu_Y}{\sigma_Y} \right)^2}$$

$e^{-x^2} \cdot e^{-y^2} = e^{-(x^2+y^2)} \rightarrow$
 circular contours \sim
 Pythagorean error
 propagation

