

3 Related Factors

Kinetics:

How fast a reaction will occur

Equilibrium:

How much of reaction will occur

Thermodynamics:

If a reaction will occur

14. Chemical Kinetics

Reactions rates

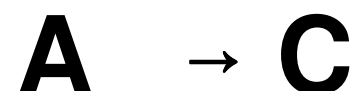
**Change in quantity of reactant
or product over time**

Rates can be low or high

**Must be able to measure rates to
determine how to control them
with concentration or temperature**

Chemical Kinetics

Reactions rates



$$\mathbf{Rate} = \frac{\Delta[\mathbf{C}]}{\Delta t} = - \frac{\Delta[\mathbf{A}]}{\Delta t}$$

C is product: $\Delta[\mathbf{C}] = \mathbf{C}_{\text{final}} - \mathbf{C}_{\text{initial}}$

$\Rightarrow \Delta[\mathbf{C}]$ always +

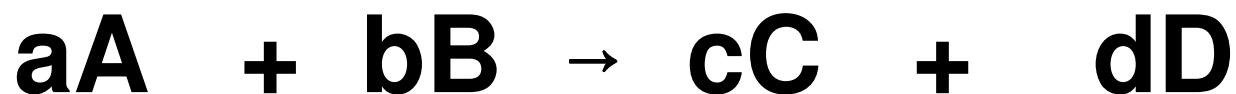
A is reactant: $\Delta[\mathbf{A}] = \mathbf{A}_{\text{final}} - \mathbf{A}_{\text{initial}}$

$\Rightarrow \Delta[\mathbf{A}]$ always -

Chemical Kinetics

Reactions rates

In general



$$rate = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t}$$

Chemical Kinetics

Reactions rates



$$\text{rate} = -\frac{1}{2} \frac{\Delta [\text{H}_2\text{O}_2]}{\Delta t}$$

rates usually decrease during a reaction

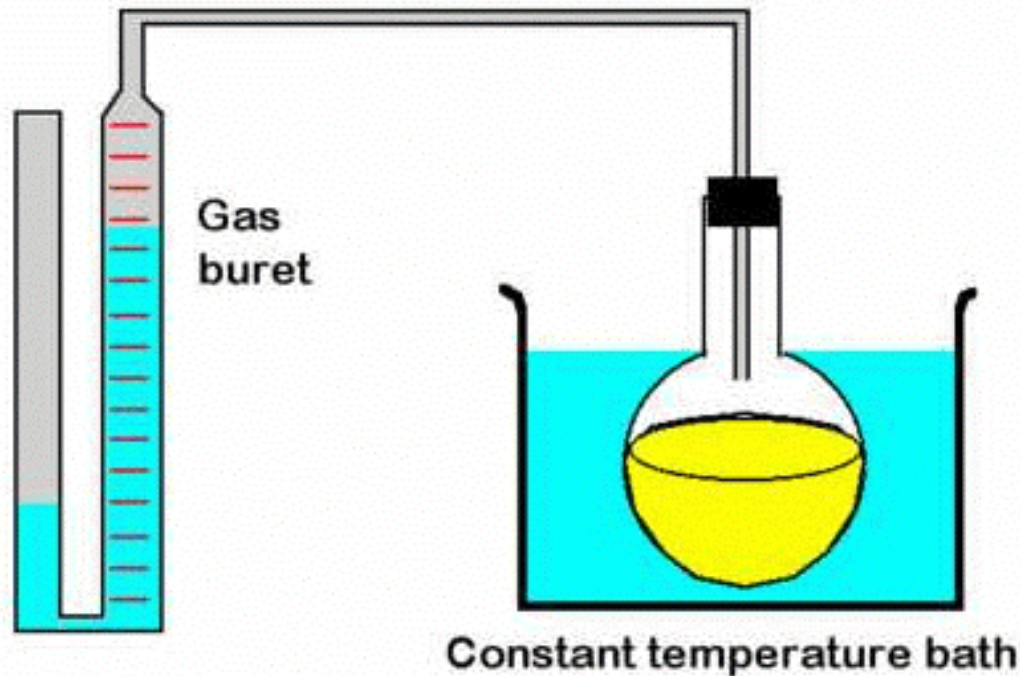
This is the **average rate**

Units: mol/L.sec

Could measure vol increase of O_2

Chemical Kinetics

Reactions rates



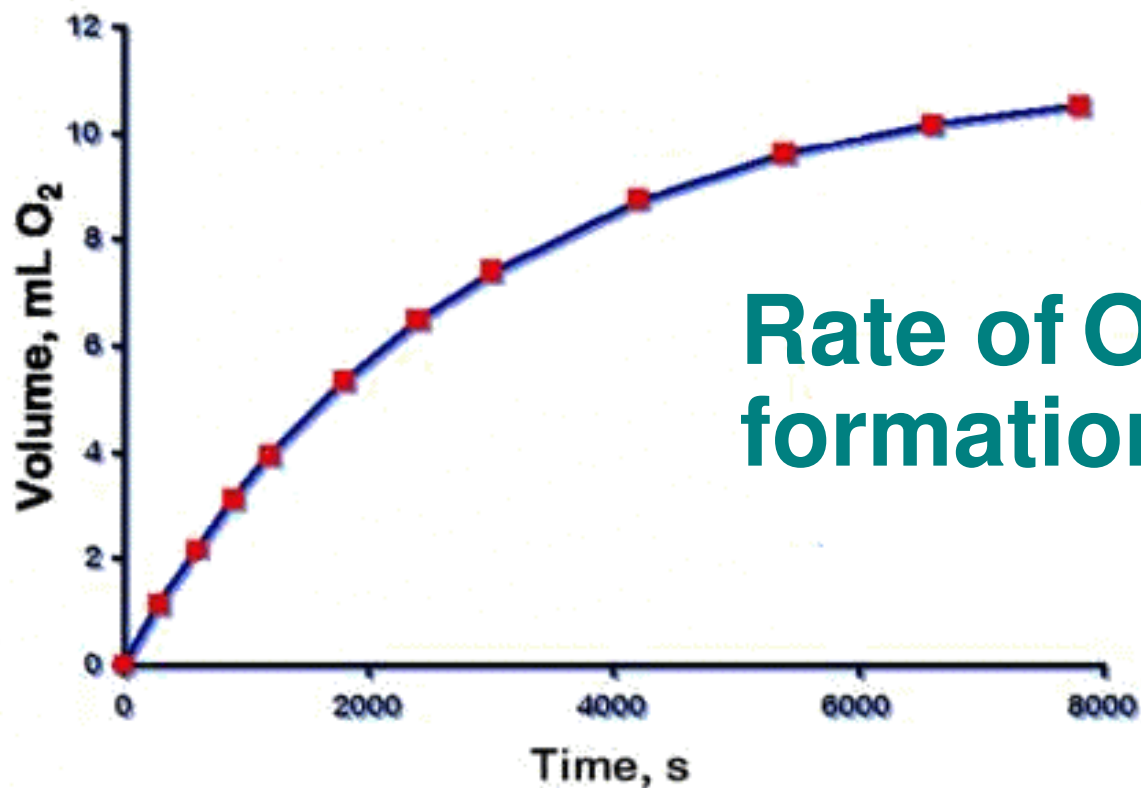
Data for an experiment



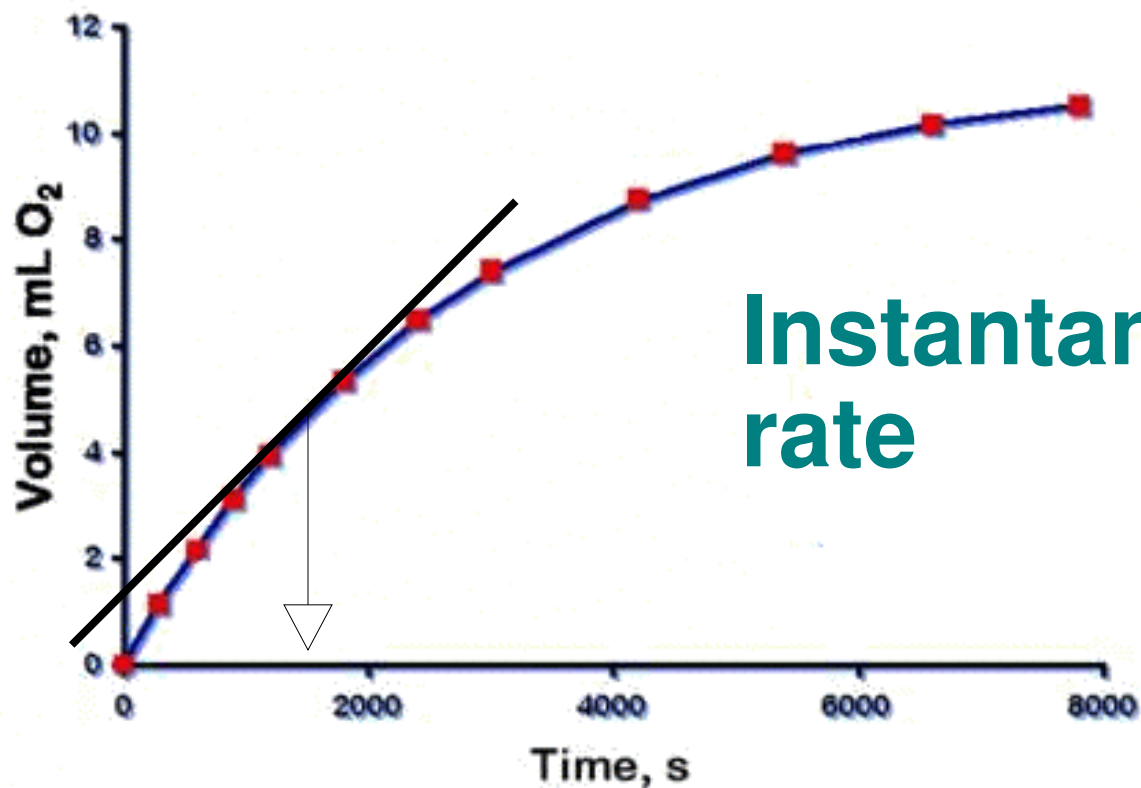
<u>Time (s)</u>	<u>Volume STP O₂, mL</u>
0	0
300	1.15
600	2.18
900	3.11
1200	3.95
1800	5.36
2400	6.50
3000	7.42
4200	8.75
5400	9.62
6600	10.17
7800	10.53

Plot graph of vol O₂ verses time

Data for an experiment



Data for an experiment



What affects reaction rates?

1. Nature of reactants



Chemical reactivity: K vrs. Fe

2. State of subdivision

For reaction between two phases

More surface area →

faster reaction

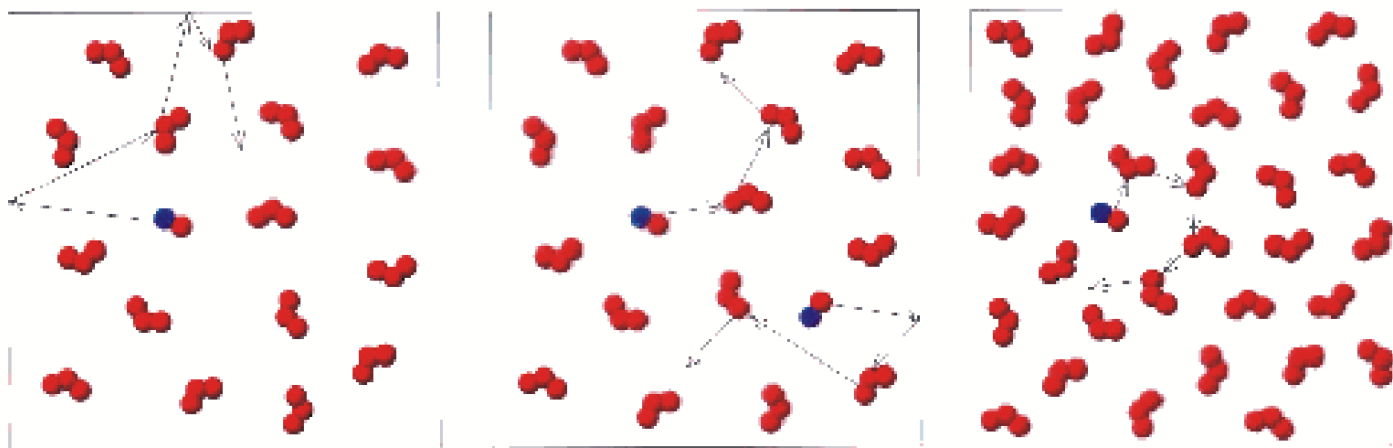
What affects reaction rates?

3. Temperature

High $T \rightarrow$ faster reaction

4. Reactant concentration

High concentrations \rightarrow
faster reaction



What affects reaction rates?

5. Catalyst

Enhances rate,
not used up during reaction

Rate laws

$$v = d/t$$

$$d = t \times v$$

$$d \propto v$$

If t is constant: $d = kv$

Rate laws



$$\text{rate} = k [A]^m [B]^n [C]^p$$

**k,m,n,p determined by
experiment**

Rate laws

k = rate constant

**Varies with temperature;
units vary**

**Magnitude of k → whether fast
or slow**

**For $2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2$
rate = $k[\text{H}_2\text{O}_2]$ $k \approx 10^{-5}$**

Rate laws



$$\text{rate} = k[\text{H}^+][\text{OH}^-]$$

$$k = 10^{11}$$

Determining rate laws

Repeat reaction several times
vary [reactant]
measure rate

See how varying
[reactant] affects rate

Determining rate laws

Find rate law for



$$\text{rate} = k[\text{NO}]^x[\text{O}_2]^y$$

Exp	[NO]	[O₂]	Rate
A	1 x 10⁻³	1 x 10⁻³	7 x 10⁻⁶
B	1 x 10⁻³	2 x 10⁻³	14 x 10⁻⁶
C	1 x 10⁻³	3 x 10⁻³	21 x 10⁻⁶
D	2 x 10⁻³	3 x 10⁻³	84 x 10⁻⁶
E	3 x 10⁻³	3 x 10⁻³	189 x 10⁻⁶

How is rate affected by changing [NO]

$$\text{rate} = k[\text{NO}]^2[\text{O}_2]^1$$

$$k = 7 \times 10^3 \text{ L}^2/\text{mol}^2.\text{sec}$$

Reaction Order

Sum of individual orders



NO is second order

O₂ is first order

Overall reaction is third order

Can have zero order

Half life

Time for 50% of
reactant to be used up

1st order: $\ln \left\{ \frac{[A_t]}{[A_o]} \right\} = -kt$

$$t_{1/2} = \frac{0.693}{k}$$

Half life

2nd order:
$$\frac{1}{[A_t]} = \frac{1}{[A_0]} + kt$$

$$t_{1/2} = \frac{1}{k[A_0]}$$

See worked examples: 14.3 -14.5

Collision Theory

How do atoms/molecules/ions react ?

Fast reactions: high k

Slower reactions: low k

Collision Theory

How do atoms/molecules/ions react ?

For reaction during collision:

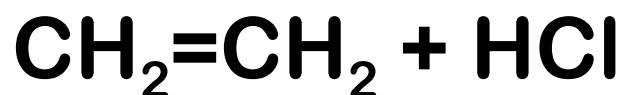
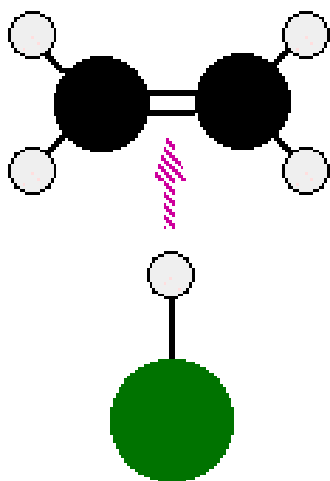
1. molecules must be correctly oriented
2. sufficient energy for valence shells to penetrate

Intermediate

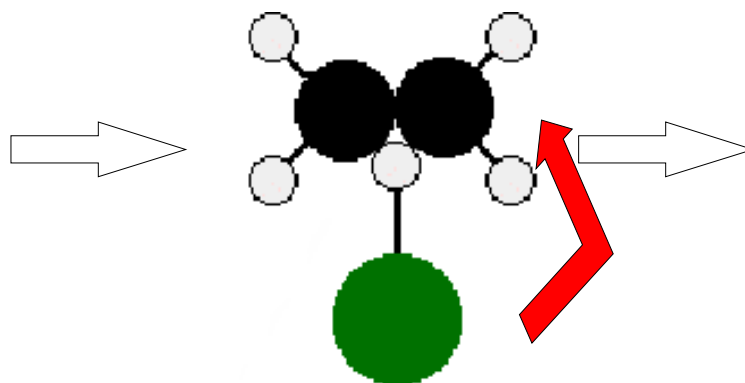
transition state or activated complex

Collision Theory

Reactants

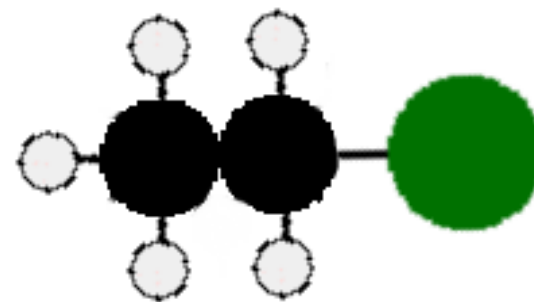


Intermediate



OR

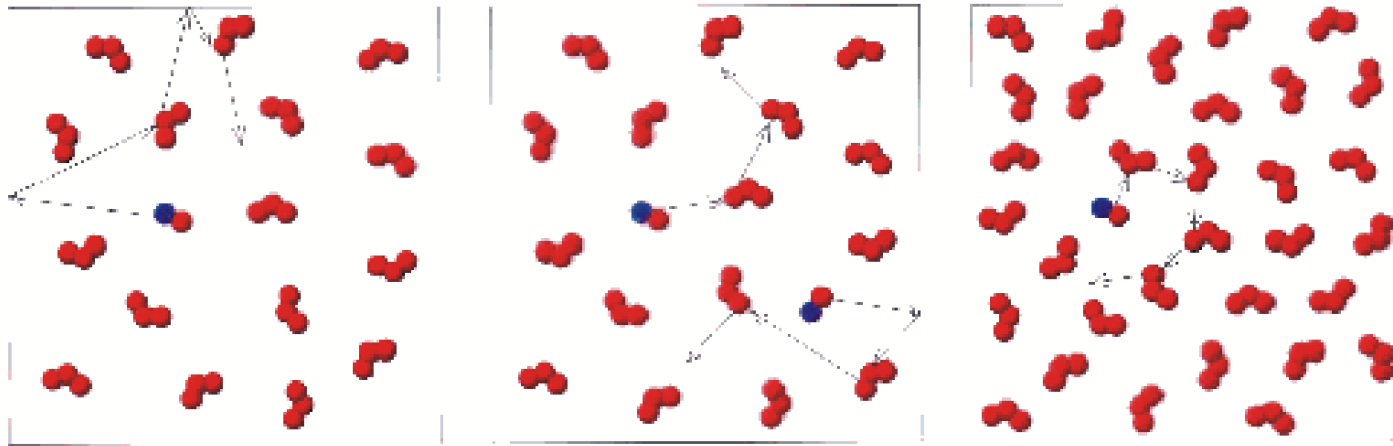
Product



transition state or activated complex

Collision Theory

Collision theory explains why increasing [reactant] causes increase in reaction rate



Activation Energy (E_a)

Energy needed to form activated complex

Slow reaction → **high E_a**

Fast reaction → **low E_a**

**E_a an energy barrier,
related to k & T**

Arrhenius equation

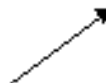


$$k = Ae^{\frac{-E_a}{RT}}$$

Arrhenius equation

- Rate Constant, $k = A e^{-E_a / RT}$

Frequency Factor



Energy of
Activation



Absolute
Temperature



Gas Constant



$R = 8.31 \text{ J/mol.K}$

T in Kelvin

E_a in J/mol or kJ/mol

A = frequency factor constant & related to frequency & orientation of colliding species

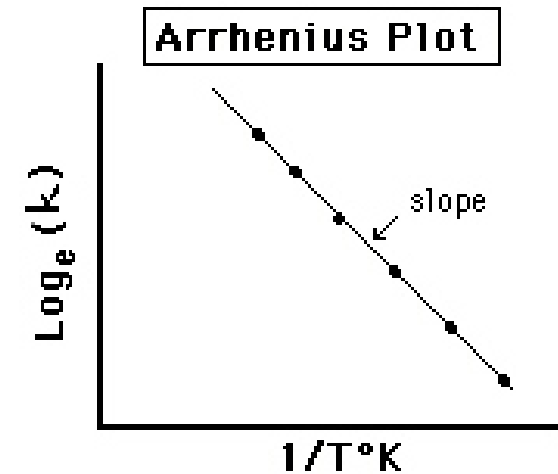
Arrhenius equation

Arrhenius Plot

Rearrange the Arrhenius Equation

$$\blacklozenge \ln(k) = \ln(A) - Ea/R (1/T)$$

Y axis \nearrow Intercept \nearrow Slope \uparrow X axis



$$\ln(k) = - Ea/R (1/T) + \ln(A)$$

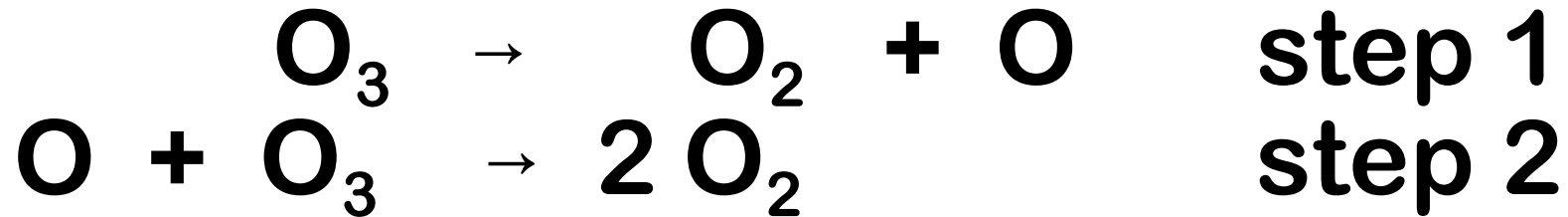
$$y = ax + b$$

Elementary Reactions

Chemical equations show overall process

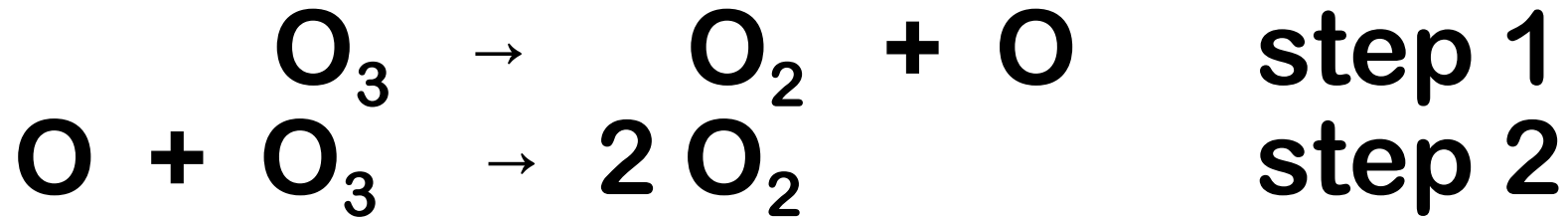
Usually composed of several steps which show reaction mechanism or path

Elementary Reactions



**Add two steps to give overall
reaction O is intermediate**

Elementary Reactions



**Each step is elementary reaction
Cannot be broken into simpler steps**

Elementary Reactions

3 types

1. Unimolecular

1 reactant → products

A → products

rate = $k[A]$

Elementary Reactions

3 types

2. Bimolecular

2 reactants collide → products

A + B → products rate = k[A][B]

Elementary Reactions

3 types

3. Termolecular

3 reactants collide → products



$$\mathbf{\text{rate} = k[A][B][C]}$$

Reaction mechanisms

Kinetics gives mechanism of reaction

Most reactions not simple

Made up of several elementary reaction steps

Each elementary step has a rate law

Rate-determining step:
slow step in mechanism

Reaction mechanisms

Rate law for each step can be determined from each elementary equation

But overall rate law not derived from overall equation

**If first step is rate-determining
first step rate law = overall rate law**

Each elementary step has a rate law

Reaction mechanisms



Rate law for each step can be determined from each equation

$$\text{Overall rate} = k[\text{O}_3]$$

If rate-determining step not 1st step
rate law complex

Catalysts

1. Homogeneous: same phase
2. Heterogeneous: different phase
industrially important:
catalytic converters;
 NH_3 , H_2SO_4

Catalysts

Effect of catalysts on E_a

