CHEM465-665
Chemical Kinetics Summary

☺

Final summary

Thermodynamics

Relationship between macroscopic properties of a system.

Kinetics

Chemical kinetics, is the study of rates of chemical processes.

Quantum mechanics

Quantum mechanics deals with phenomena and objects of nanoscopic size. In principle, quantum mechanics provides a mathematical description of close to everything.

Summary or
Primer on PChem class room kinetics

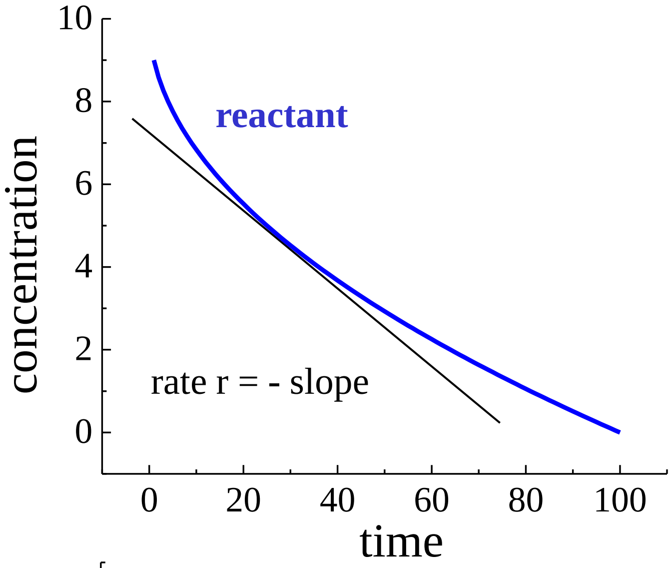
- Conversion rates
- Reaction rates
- Rate laws
- Reaction order
- Half time
- Arrhenius Eq.

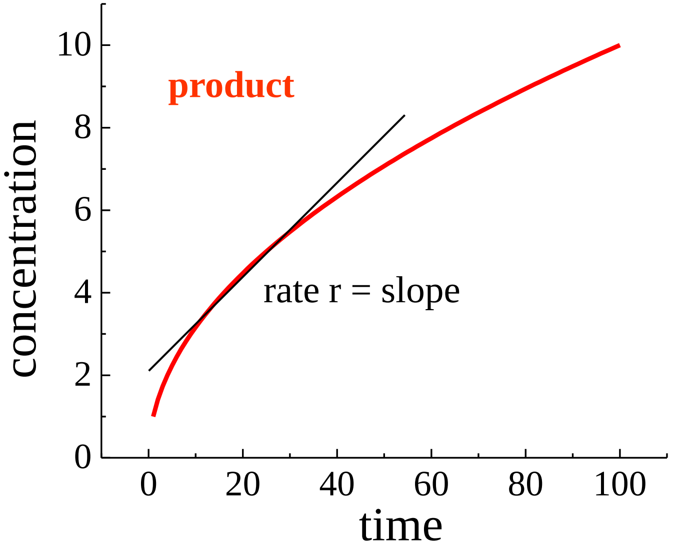
Please note that this is not a complete summary.
Write your own summary to prepare for the finals as well as look in the study guide.

http://www.uweburghaus.us/classes/summary_drafts.html

Chemical kinetics - definitions

Chemical kinetics, is the study of rates of chemical processes.





$$aA \rightarrow bB$$

A, B: molecules
[A],[B]: concentrations
a, b: stoichiometric factors
n_a, n_b: particle numbers
V: volume

Rate of conversion

$$J = -\frac{1}{a}\frac{dn_A}{dt} = \frac{1}{b}\frac{dn_B}{dt}$$

Rate of reaction

$$r = \frac{J}{V} = -\frac{1}{a}\frac{d[A]}{dt}$$

Rate laws

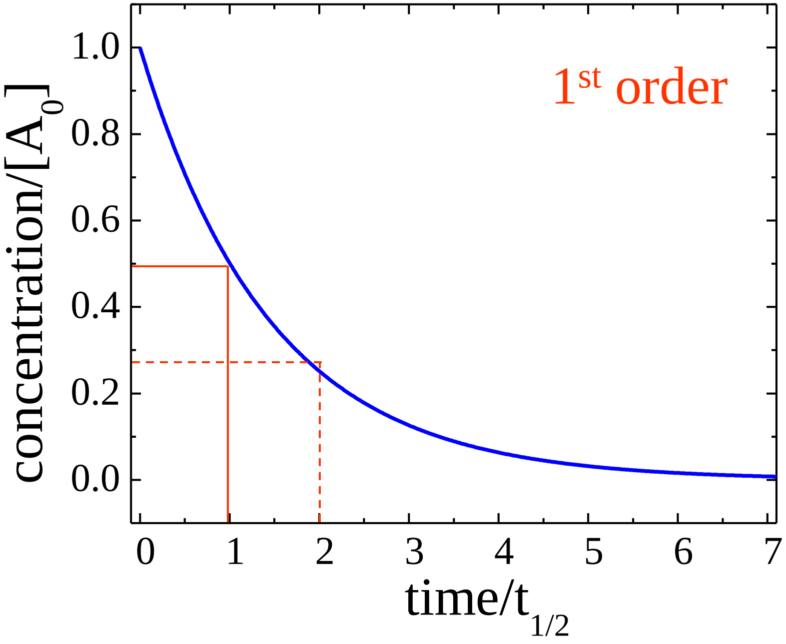
$$r = k[A]^{\alpha}[B]^{\beta}....$$

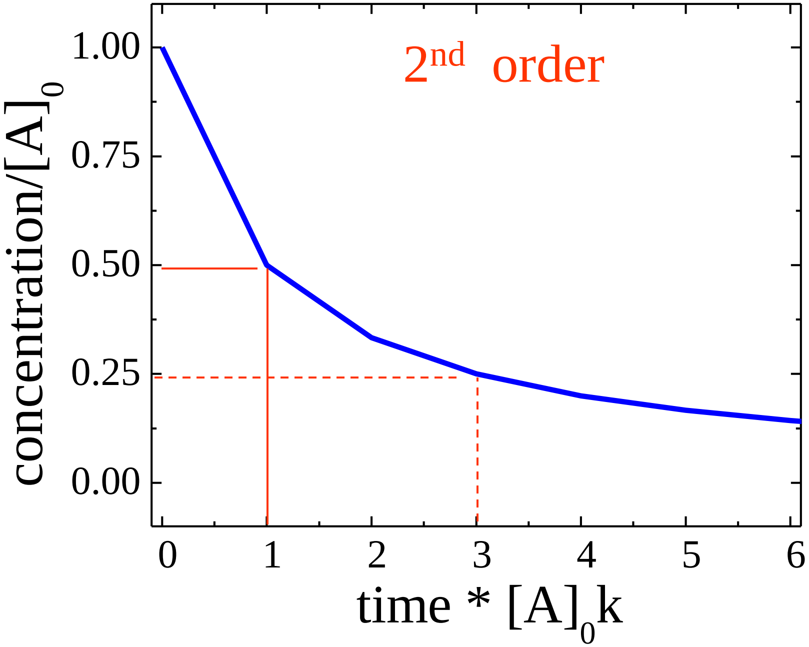
r: reaction rate = number of particles formed in a given time
k: reaction rate coefficient
α, β: partial reaction orders
$\alpha+\beta+...$: total reaction order

Examples: 1st and 2nd order kinetics

	1st order	2nd order
gas phase	$2N_2O_5\,(g) \rightarrow 4NO_2(g) + O_2(g)$	$2I \rightarrow I_2$ $2NOBr \rightarrow 2NO + Br$ $2NO_2 \rightarrow 2\,NO + O_2$
gas-surface	$O_2\,(gas) \rightarrow 2O_{ad}$, k $r = kO_2(gas)$	$CO_{ad}+O_{ad} \rightarrow CO_2\,(gas)$, k_r $CO_{ad} \leftrightarrow CO(gas)$, k_d $r = k_r CO_{ad} O_{ad}$
liquid phase	$H_2O_2(l) \rightarrow H_2O(l) + 1/2O_2(g)$	$H^+ + OH^- \rightarrow H_2O$

Summary – 1st and 2nd order kinetics





$$t_{1/2} = \frac{\ln(2)}{k}$$

$$[A](t) = [A]_0 e^{-kt}$$

$$r = k[A]^1$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

$$[A](t) = \frac{[A]_0}{1 + kt[A]_0}$$

$$r = k[A]^2$$

Reaction types we looked at:

$$r = \frac{d[A]}{dt} = k$$

0th order kinetics

$$r = \frac{d[A]}{dt} = k[A]$$

1st order kinetics

$$r = \frac{d[A]}{dt} = k[A]^2$$

2nd order kinetics

$$t_{1/2} = \frac{1}{k[A]_0}$$

$$\left.\begin{aligned} r &= \frac{d[A]}{dt} = \frac{d[B]}{dt} \\ r &= k[A][B] \end{aligned}\right\} \text{2nd order kinetics}$$

$T_{1/2}$– 1st and 2nd order kinetics

Reaction Order	$t_{½}$
0	$\frac{[A_0]}{2k}$
1	$\frac{\ln(2)}{k}$
2	$\frac{1}{k[A_0]}$

Summary – 1st and 2nd order kinetics

$$\dim(r) = \frac{concentration}{time}$$

$$\dim(k) = \frac{concentration^{1-n}}{time}$$

1st order

$$\dim(k) = \frac{1}{\sec}$$

2nd order

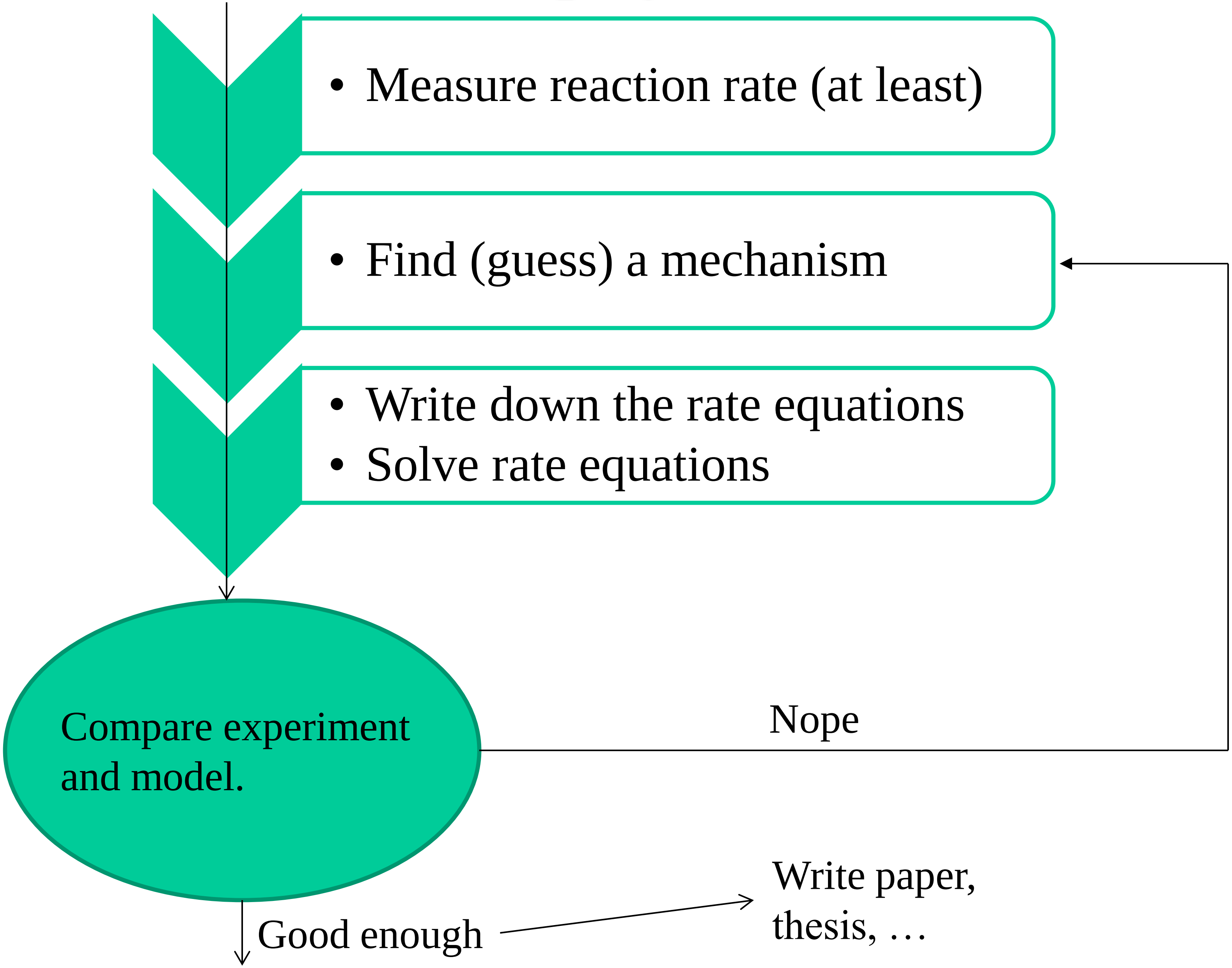
$$\dim(k) = \frac{1}{\frac{cm^3}{mol}\sec} = \frac{mol}{cm^3 \sec}$$

in theory papers:

$$\dim(\tilde{k}) = \frac{1}{\sec}$$

$$\tilde{r} = [A]r$$

Typical outline of a kinetics project:



- Measure reaction rate (at least)
- Find (guess) a mechanism
- Write down the rate equations
- Solve rate equations

Compare experiment and model.

Nope

Good enough

Write paper, thesis, …

Kinetics is ...?

Understand T

What is T?

Kinetics is understanding temperature dependence.

Arrhenius

Svante August Arrhenius (born 1859)

- his ancestors were farmers
- his uncle was Professor of Botany
- 1876 he entered University of Uppsala to study mathematics, chemistry and physics.
- thesis in 1884 about electro chemistry
- 1903 nobel prize in chemistry

$$r = k[A]^n \ldots.$$

$$k = \nu e^{-E/RT}$$

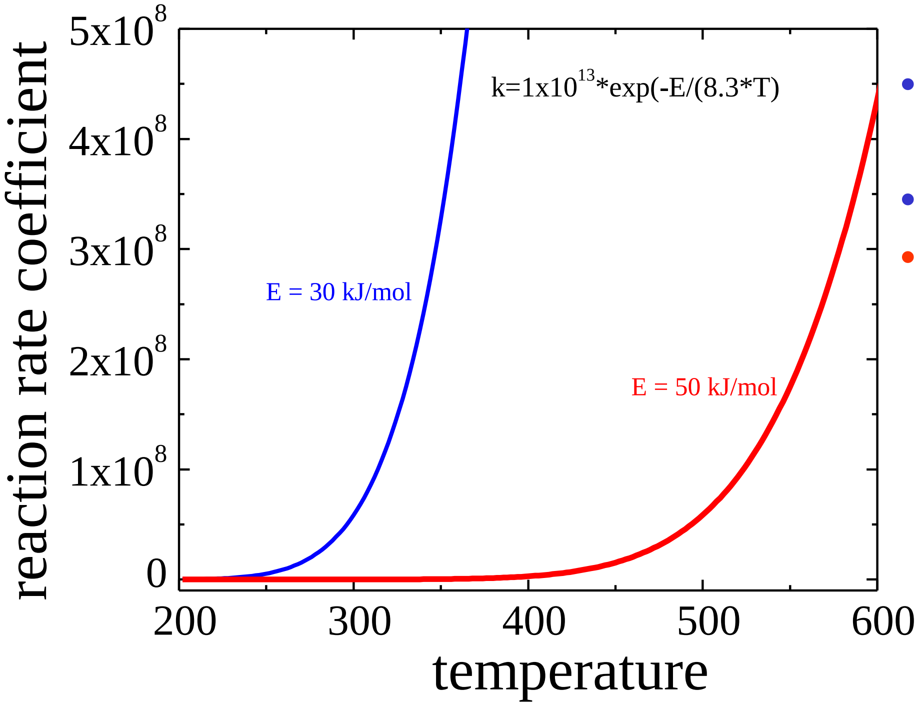
ν: pre-exponential factor
E: activation energy
R: gas constant
T: temperature

http://nobelprize.org/nobel_prizes/chemistry/laureates/1903/arrhenius-bio.html

Arrhenius equation – this is very important → therefore more details here

important

Arrhenius equation – this is very important → more details here



- The larger T the "faster" the reactions
- Small E → "fast" reaction
- Large E → "slow" reaction

Let me use kiddy terms here.

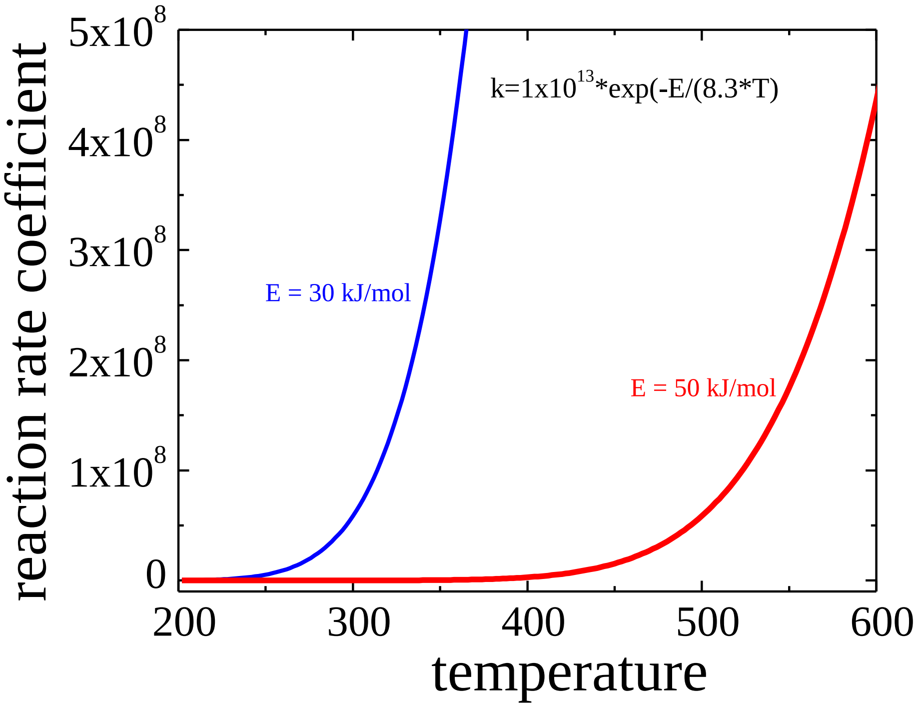
Arrhenius

$$r = k[A]^n \ldots .$$

$$k = \nu e^{-E/RT}$$

ν: pre-exponential factor
E: activation energy
R: gas constant
T: temperature

Branching ratios, apparent activation energies



- The larger T the "faster" the reactions

Really ?

Be aware of "pitfalls" …

Example:
CO oxidation on silver and gold catalysts is "faster" at lower temperatures than at large T.

How is this possible?

$$CO_{ad} \xleftrightarrow[Flux,E_d]{} CO_{gas}$$

$$CO_{ad} + O_{ad} \xrightarrow[k_r]{} CO_{2,gas}$$

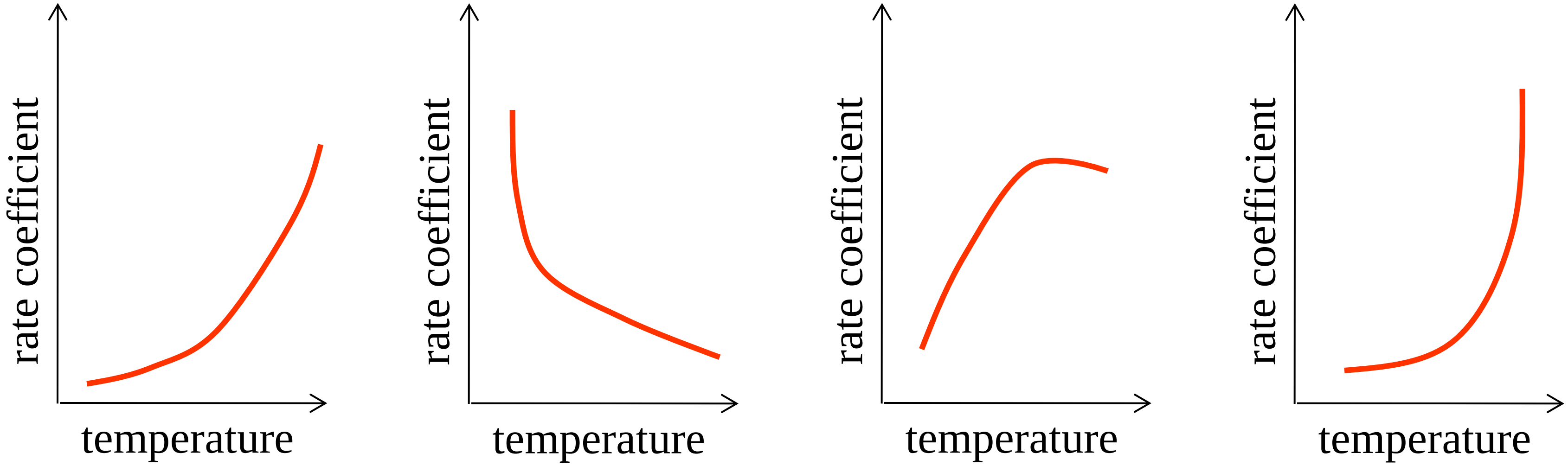
$$k_{CO_2} = \frac{k_d}{k_r} \approx e^{\{-\underbrace{(E_d - E_r)}_{\text{apparent activation energy}}/RT\}}$$

$E_d - E_r < 0$ Ag, Au

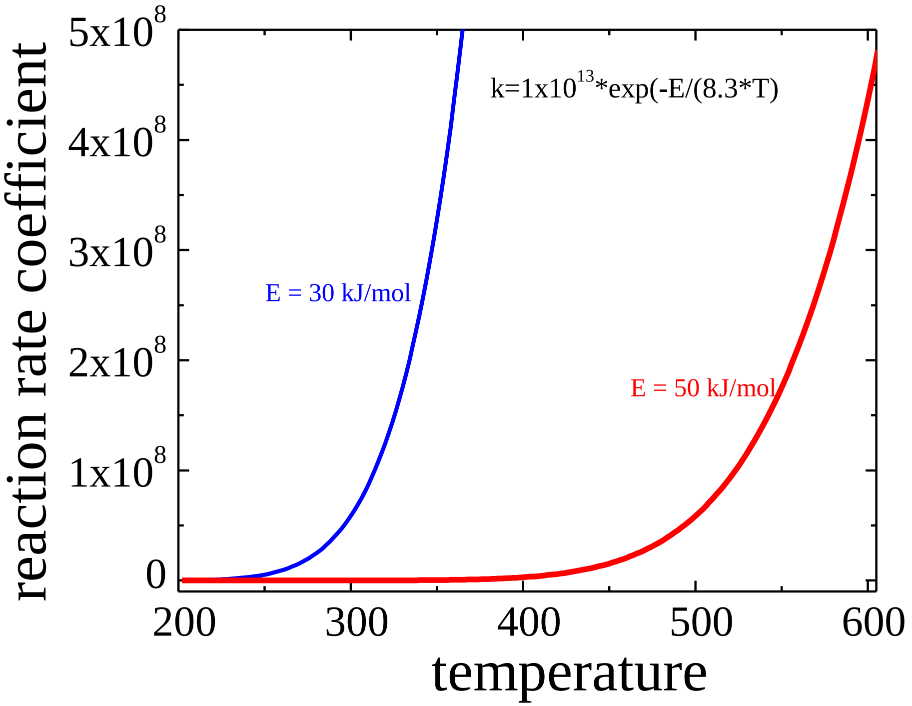
$E_d - E_r = 0$ "no" temperature dependence

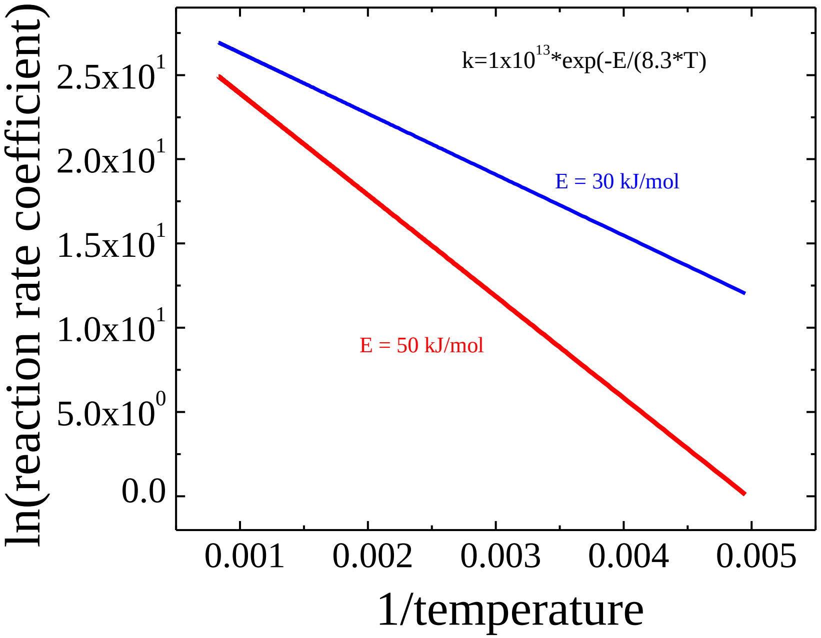
$E_d - E_r > 0$ Pt, Pd

Possible temperature dependence of reaction rate coefficients



Linearization of the Arrhenius Eq.





$$k = \nu e^{-E_a/RT}$$

Arrhenius Eq.

$$\ln(k) = \ln(\nu) - \frac{E_a}{R}\frac{1}{T}$$

$$\text{slope} = \frac{E_a}{R}$$

$$\text{intercept} = \ln(\nu)$$

Arrhenius equation – analogy with Van’t Hoff equation

$$\frac{d\ \ln(K_p^0)}{dT} = \frac{\Delta H^0}{RT^2}$$

Van’t Hoff Eq.

$$\frac{d\ \ln(k)}{dT} = \frac{E_a}{RT^2}$$

Arrhenius idea

analogy

interation

$$\frac{d\ln(k)}{dT} = \frac{E_a}{RT^2}$$

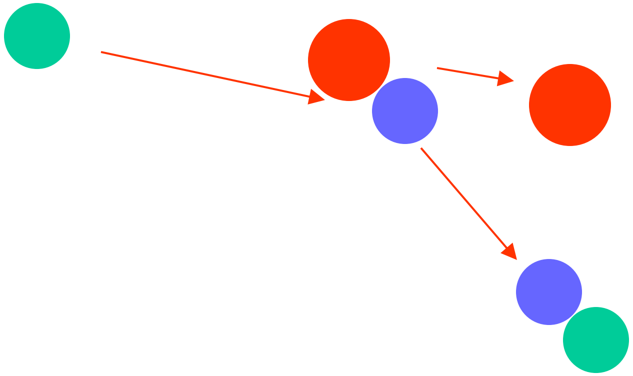
$$\int d(\ln(k)) = \int \frac{E_a}{RT^2}\,dT$$

$$\ln(k) = -\frac{E_a}{R}\frac{1}{T}$$

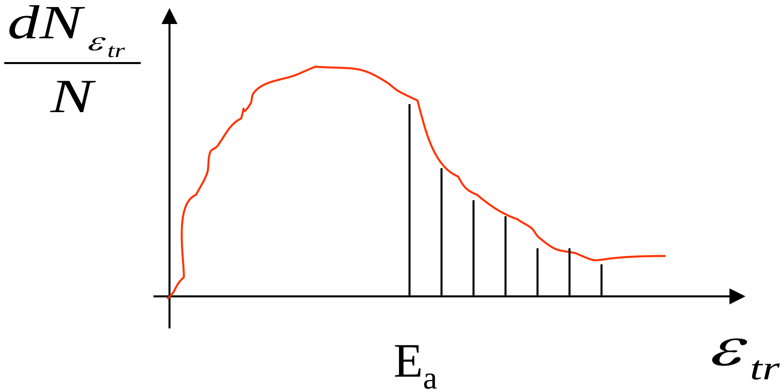
$$k = e^{-E_a/RT}$$

Arrhenius equation: Where is the activation energy, E_a, coming from?

Just giving you an idea…

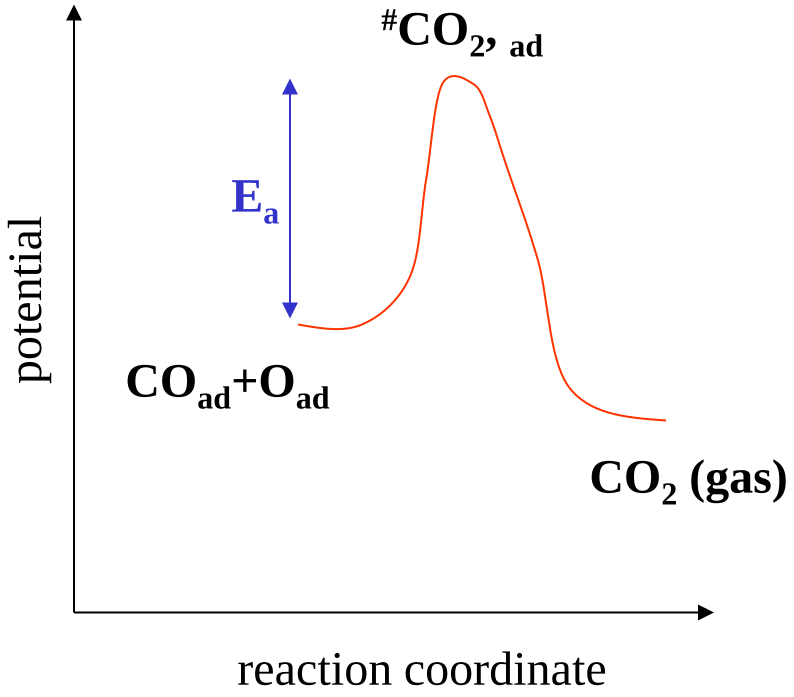


Threshold for bond breaking
bond making?



$$\frac{dN_{\varepsilon_{tr}}}{N} = g e^{-\frac{\varepsilon_{tr}}{kT}}$$

Arrhenius equation – where is the preexponential coming from? Just giving you an idea:

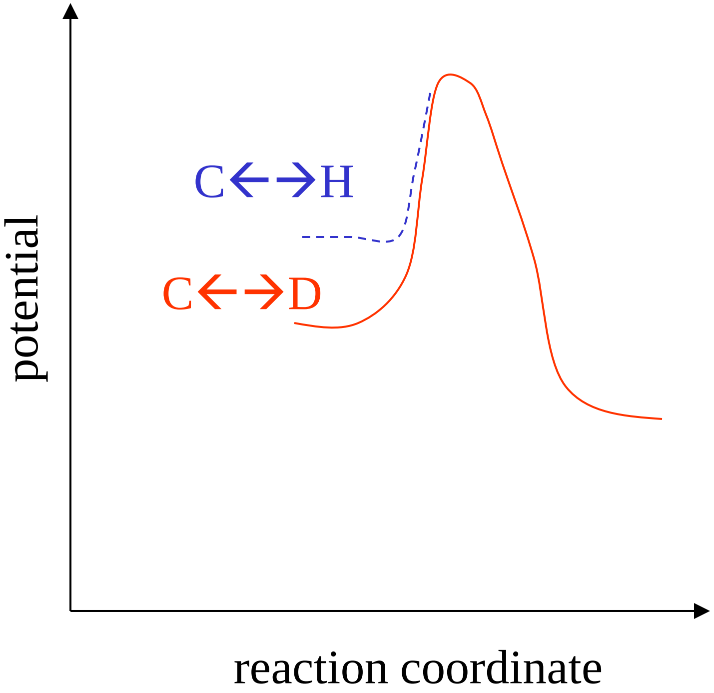


ν ~ probability for going over the “hill”

ν: molecular vibrations
$\nu \sim 10^{13}$/sec

transition state theory → more details later

Kinetic isotope effects



Consider a reaction that includes a

C←→H
C←→D

bond breaking.

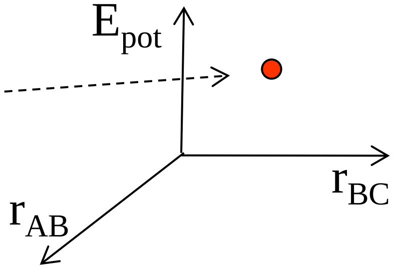
The difference in the zero point energies leads to different activation energies.

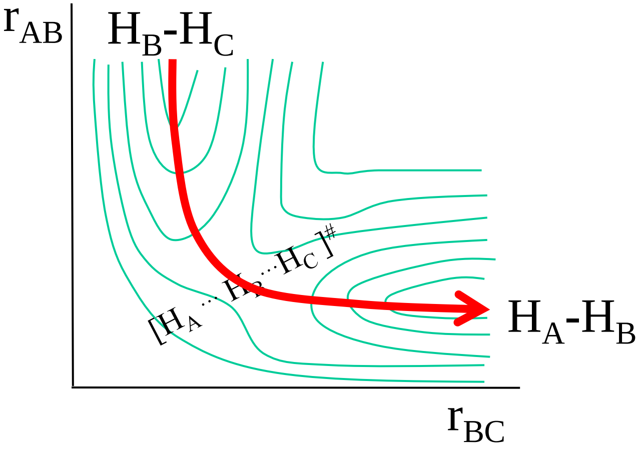
Primer – potential energy surface for a chemical reaction **in the gas-phase**

$$\underbrace{H_A + H_B}_{r_{AB}}\text{-}H_C \rightarrow [H_A \cdots H_B \cdots H_C]^\# \rightarrow H_A\text{-}H_B + H_C$$

r_{BC}

$\Rightarrow$ $E_{pot}(r_{AB}, r_{BC})$



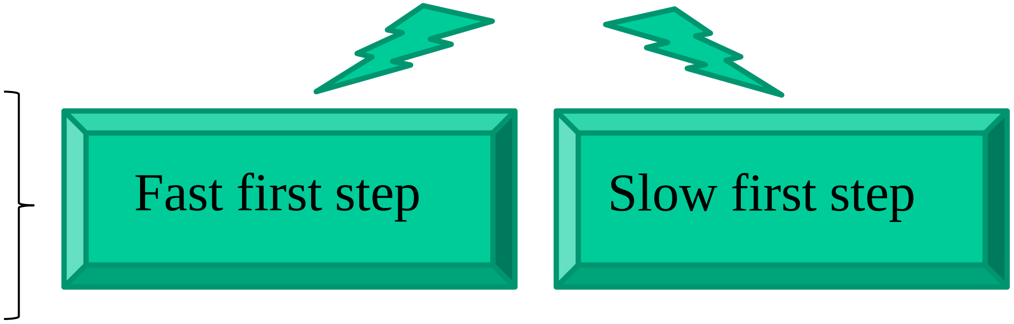


e.g. W.H. Miller, Annu. Rev. Phys. Chem. Vol. 41, 1990

"tricks"

Pre-equilibrium approximation
vs.
Steady-state approximation

What should I use and when?



Reaction mechanism

What step determines the product formation?

Fast first step

Slow first step

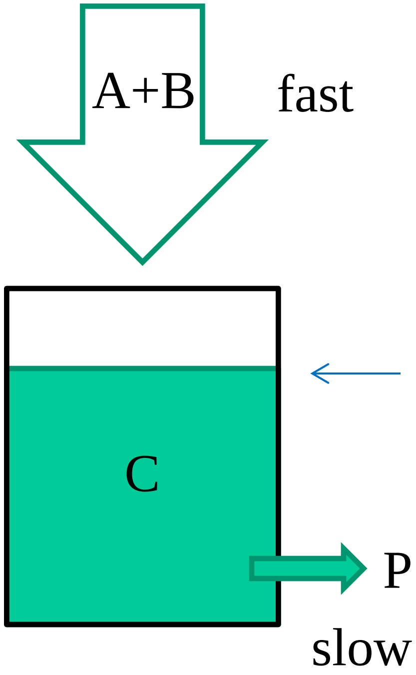
Pre-equilibrium approximation

Steady-state approximation

http://chemwiki.ucdavis.edu/Physical_Chemistry/Kinetics/Rate_Laws/Reaction_Mechanisms/Pre-equilibrium_approximation

Pre-equilibrium approximation

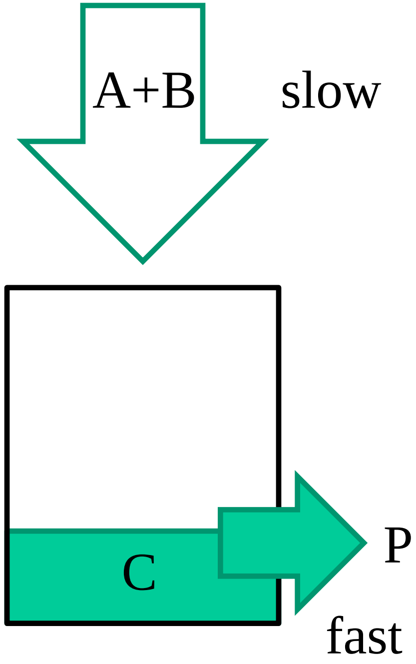
$$A+B \underset{fast}{\longleftrightarrow} C \xrightarrow{slow} P$$



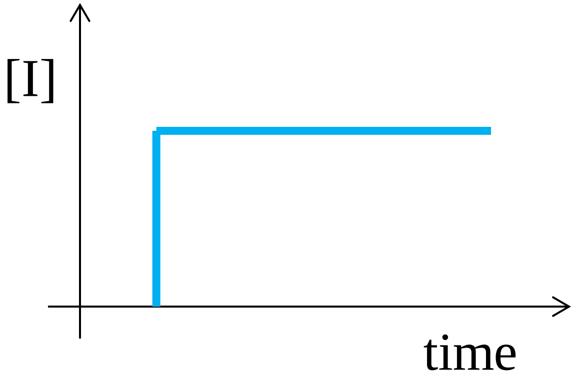
Constant and high level,
“at equilibrium”

Rate determining step approximation

$$A+B \underset{slow}{\longleftrightarrow} C \xrightarrow{fast} P$$



Steady-state approximation



R → I → P

$$\frac{d[I]}{dt} \approx 0$$

steady state approximations

Mathematical condition.

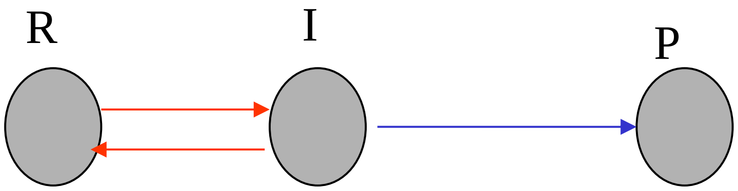
Example $A \rightarrow B \rightarrow C, k_1, k_2$

Stead-state obeyed for: **$k_2/k_1 > 10$**

2nd reaction much faster than the first.
Intermediate forms slowly, but reacts fast.
→ Intermediate concentration stays low.
→ Relative concentration change is small.

Interpretation.

Summary / Recipes



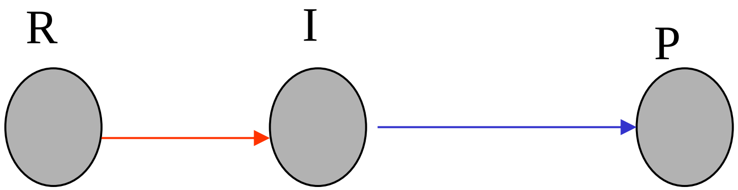
Fast
Establish
equilibrium

slow

Rate determining step

Use pre-equilibrium formalism

May not always work.
Always think.

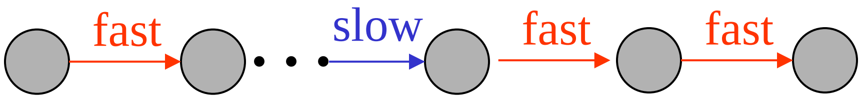


slow

Rate determining step

fast

Use steady-state approximation



Rate determining step

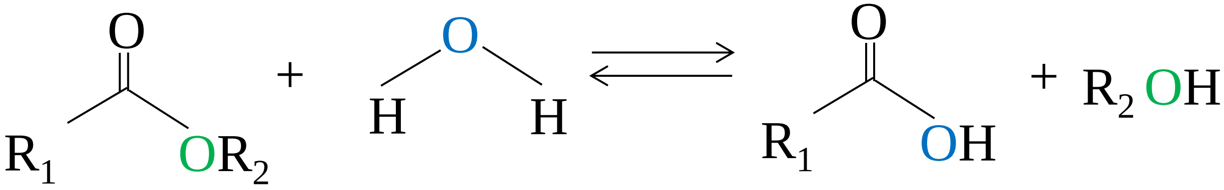
R: reactants
I: intermediate
P: products

Pseudo 1st order kinetics

For example: concentration of one reactant much larger than for all other reactants.

▷ Majority component becomes a constant eliminating a variable.

Pseudo 1st order kinetics - example



Hydrolysis: the cleavage of chemical bonds by adding water.

$$A + B \rightleftharpoons C + D$$

2nd order

$$B >> A$$

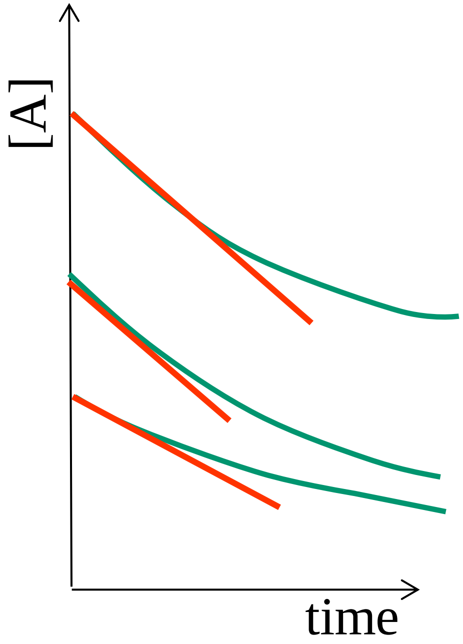
$$A \overset{B}{\rightleftharpoons} C + D$$

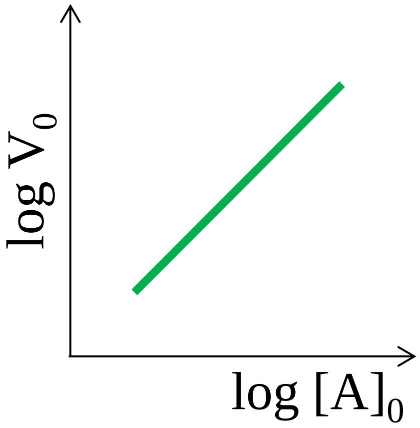
Pseudo 1st order

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

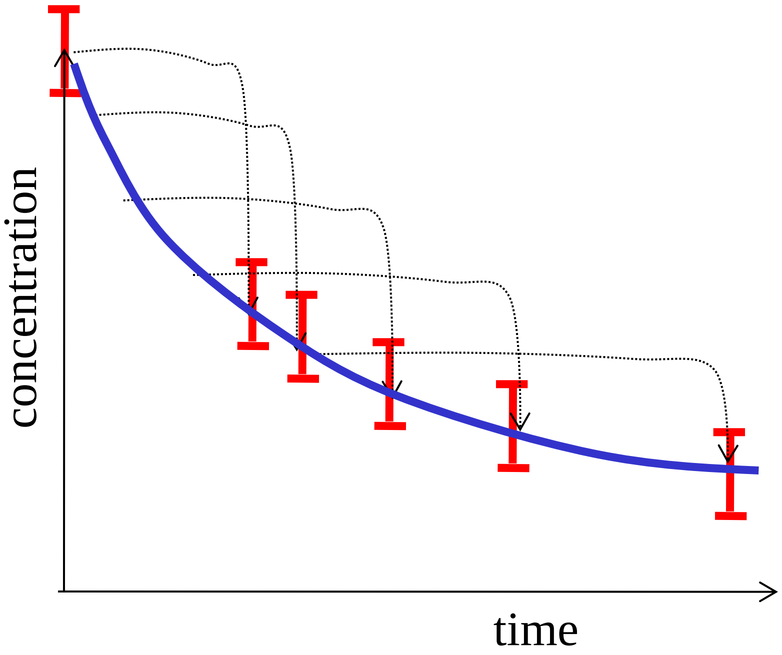
van’t Hoff Method

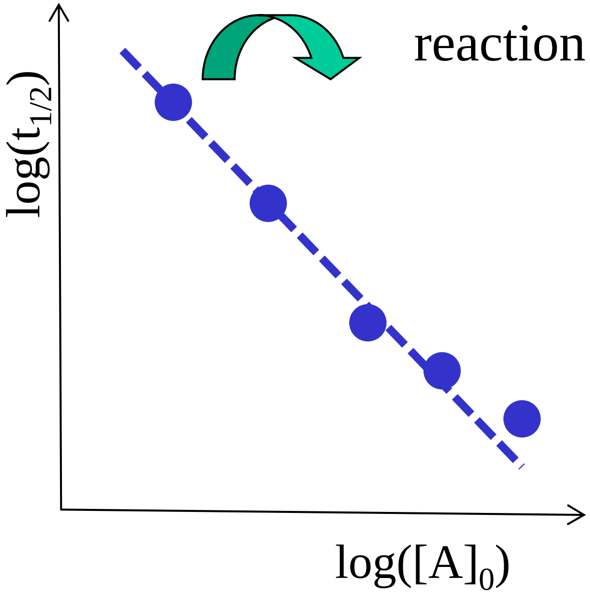
Analyze initial reaction rate





Half-life method (e.g. determining the reaction order)





reaction order

$$r = k[A]^n$$

$$t_{1/2} = \frac{2^{n-1}-1}{(n-1)[A]^{n-1}k} \;\curvearrowright\; \log(t_{1/2}) = \log\left(\frac{2^{n-1}-1}{(n-1)k}\right) - (n-1)\log([A]_0)$$

Problem: experimental uncertainty

Strategies

"tricks"

Lots of “tricks” have been developed ….

1) Use some kind of approximation to decouple the differential equations in order to integrate them analytically.

2) Linearize the result in order to obtain kinetics parameters from simple data plots.

However, this is hopeless in most cases considering realistic problems.

Carl David Tolmé Runge (1856 – 1927) was a German mathematician, physicist, and spectroscopist.

Martin Wilhelm Kutta (1867 – 1944) was a German mathematician.

http://en.wikipedia.org/wiki/Runge-Kutta

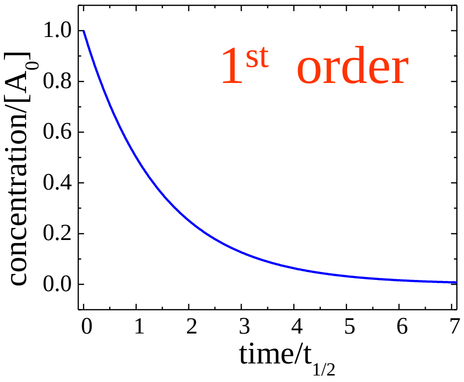
Use special techniques for stiff differential equations

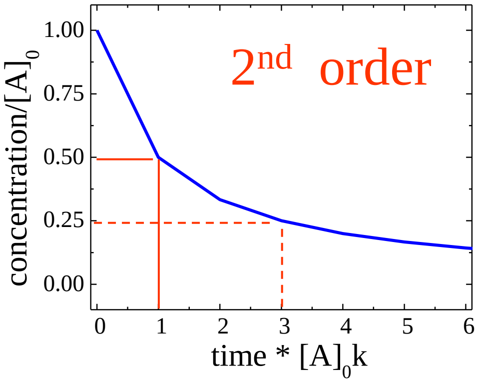
Summary of the kinetics primer

$$aA \rightarrow bB$$

Rate of reaction

$$r = \frac{J}{V} = -\frac{1}{a}\frac{d[A]}{dt}$$





$$\boxed{\begin{aligned} r &= k[A]^n\ldots. \\ k &= \nu e^{-E/RT} \end{aligned}}$$

ν: pre-exponential factor
E: activation energy
R: gas constant
T: temperature

Branching ratios
Steady state approximation
Rate determining step
Pre-equilibrium

In addition you should be familiar with

0th order reaction
Determining reaction rates and reaction orders
Sequential reactions
Rate determining step approximation
Pre-equilibrium
Nth order reactions
Parallel reactions
Reversible reactions
Lindemann
Catalysis idea