CHEM763
Chemical Kinetics

Class
17

☺

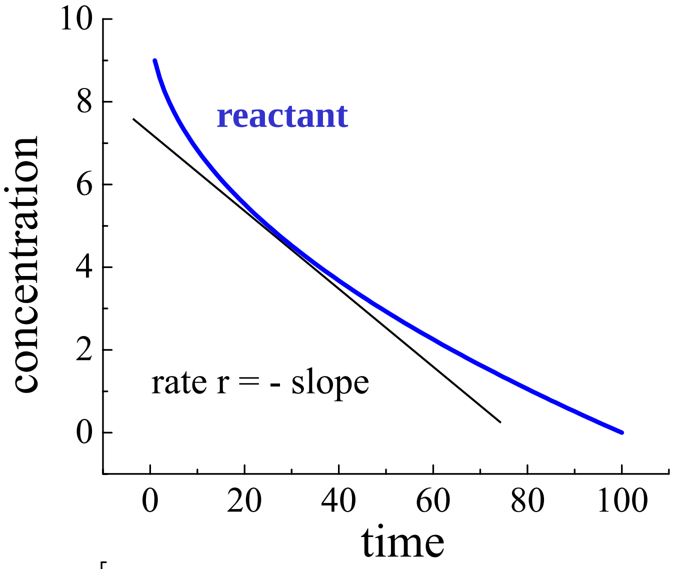
Final summary

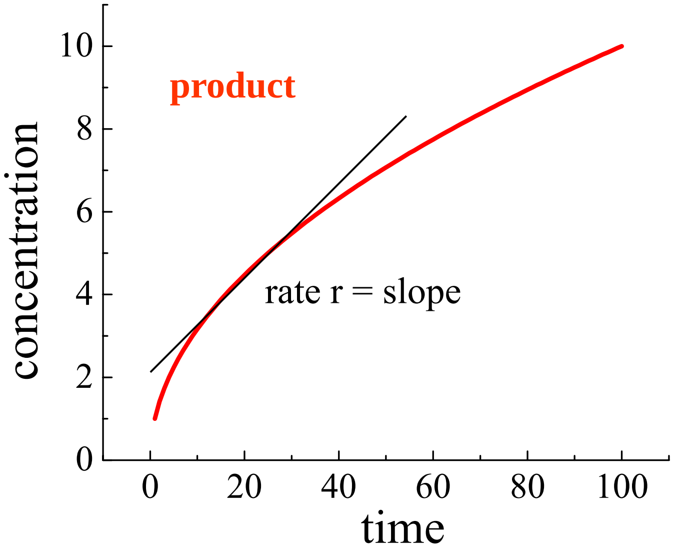
Summary or
Primer on PChem class room kinetics

- 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.

Chemical kinetics - definitions





$$aA \rightarrow bB$$

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

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

Common mistakes – use correct & precise wording

r: is the rate of a process and not a velocity (we are not discussing cars on a highway)

k: is a reaction rate coefficient and not a speed constant or something … *k is not even constant it depends on the temperature*

ν: is the preexponential coefficient and not a frequency factor, *only for 1st order processes equals the dimension of ν 1/s and even in that case it is not a frequency*

You are a scientist use the correct wording and not kiddy bla bla….

Rate laws

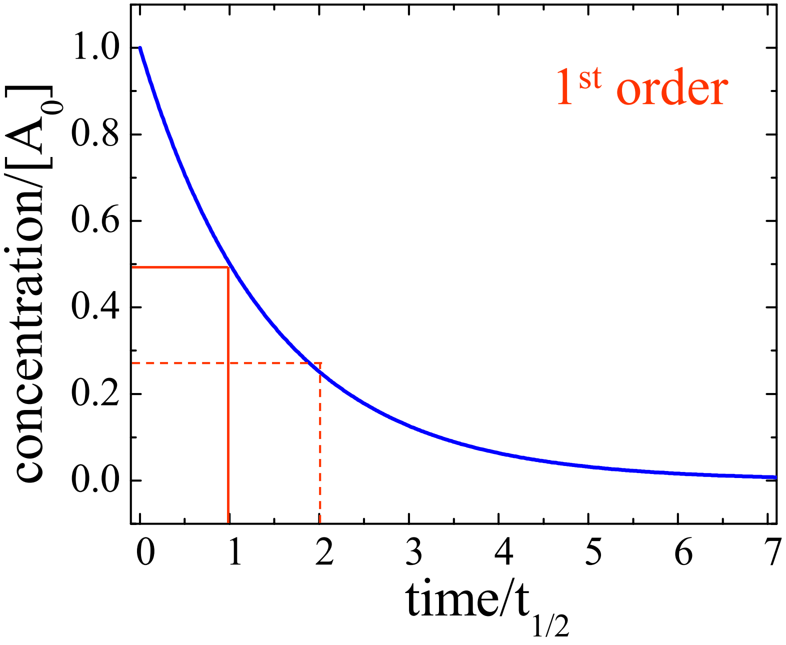
$$r = k[A]^{\alpha}[B]^{\beta}....$$

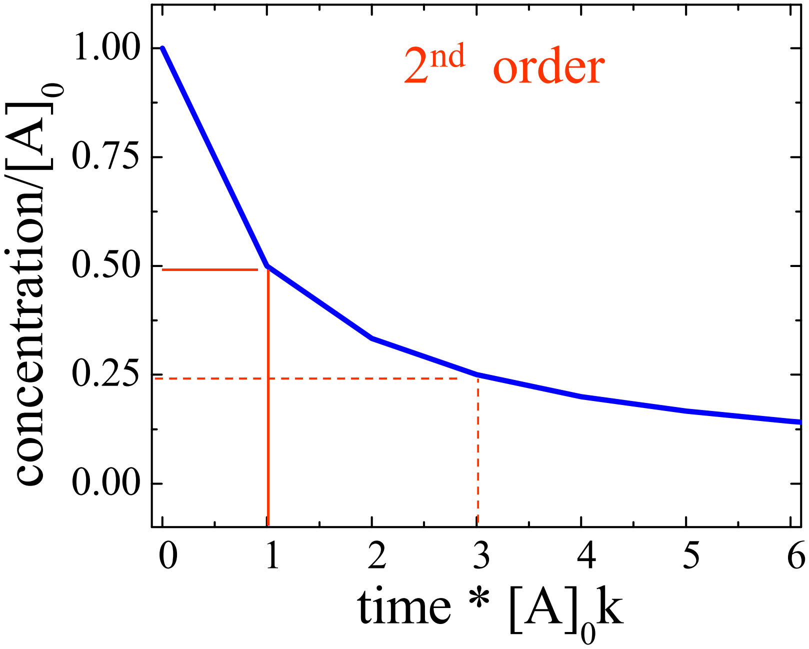
r: reaction rate = number of particles formed in a given time
k: reaction rate coefficient
α, β: partial reaction orders
α+β+...: total reaction order

Examples: 1st and 2nd order kinetics

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

Summary – 1st and 2nd order kinetics





$$t_{½} = \frac{\ln(2)}{k}$$

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

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

$$t_{½} = \frac{1}{k[A]_0}$$

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

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

Summary – 1st and 2nd order kinetics

Reaction Order	$t_{1/2}$
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	2nd order
$\dim(k) = \frac{1}{\sec}$	$\dim(k) = \frac{1}{\frac{cm^3}{mol}\sec} = \frac{mol}{cm^3\sec}$ **in theory papers:** $\dim(\tilde{k}) = \frac{1}{\sec}$ $\tilde{r} = [A]r$

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

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

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

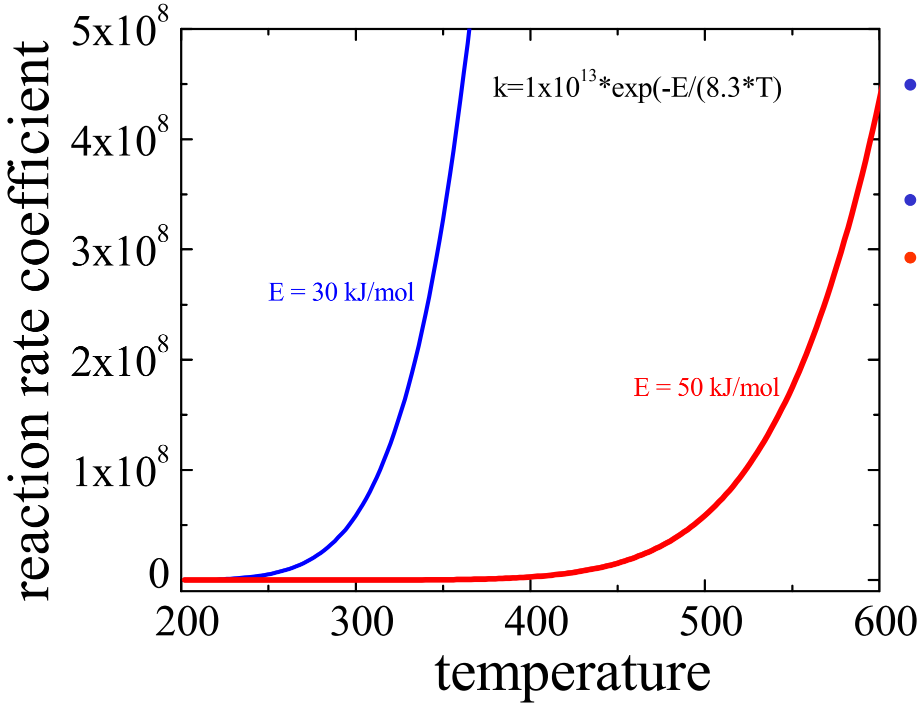
ν: pre-exponential factor
E: activation energy
R: gas constant
T: temperature

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.

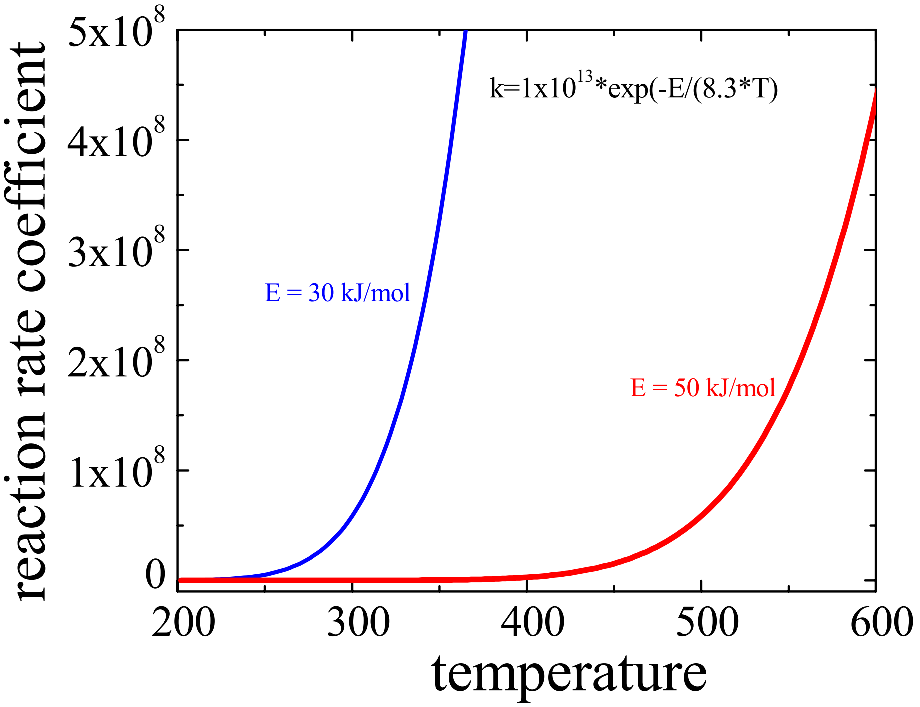
Arrhenius

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

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

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?

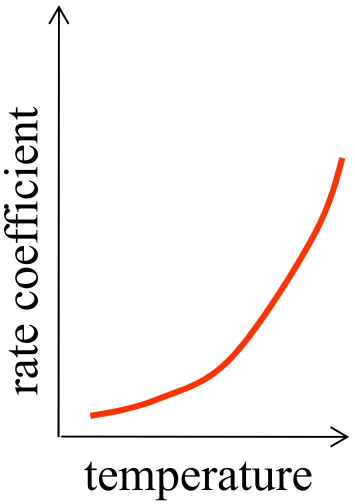
$$CO_{ad} \xleftrightarrow[Flux, E_d]{} CO_{gas}$$

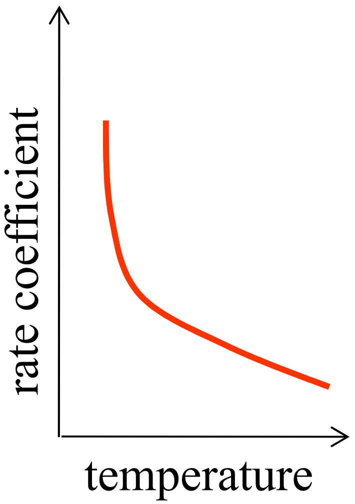
$$CO_{ad} + O_{ad} \xrightarrow[k_r]{} CO_{2,gas}$$

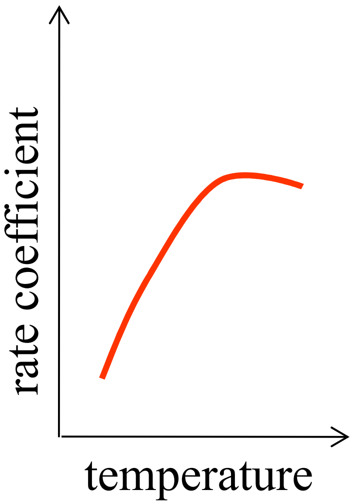
$$k_{CO_2} = \frac{k_d}{k_r} \approx e^{\{-\underbrace{(E_d - E_r)}_{\text{apparent activation energy}}/RT\}}$$

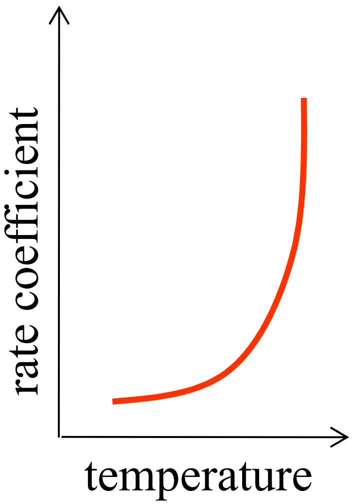
$E_d - E_r < 0$	Ag, Au
$E_d - E_r = 0$	"no" temperature dependence
$E_d - E_r > 0$	Pt, Pd

Possible temperature dependence of reaction rate coefficients

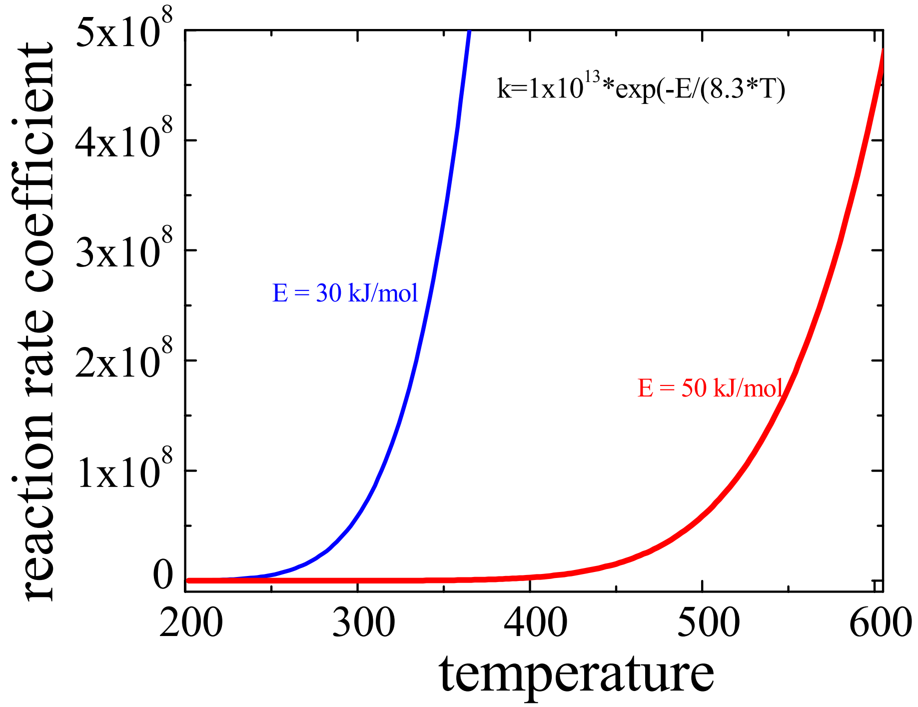


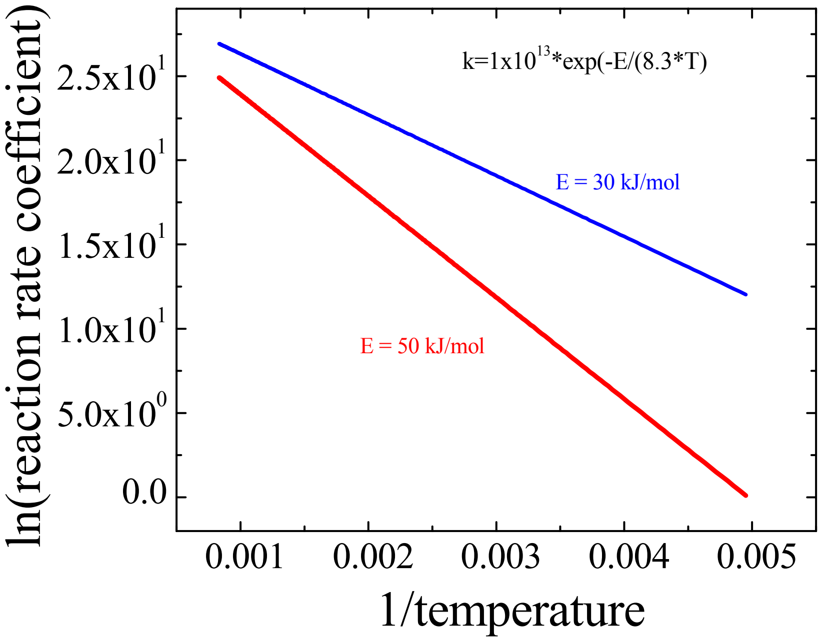






Linearization of the Arrhenius Eq.





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

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

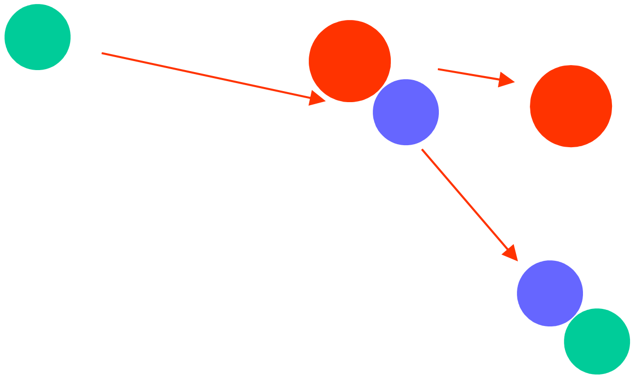
$$\frac{d\ \ln(k)}{dT} = \frac{E_a}{RT^2} \qquad / *"dT"$$

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

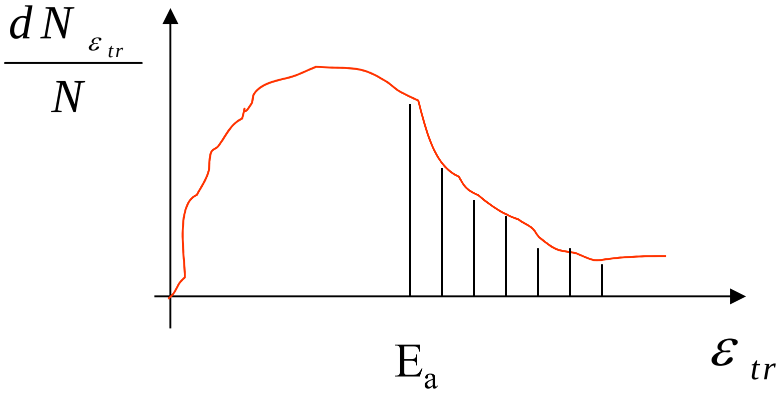
$$\ln(k) = -\frac{E_a}{R}\frac{1}{T}$$

$$k = e^{-E_a/RT}$$ Arrhenius Eq.

Arrhenius equation: Where is the activation energy, E$_a$, coming from? Just giving you an idea…

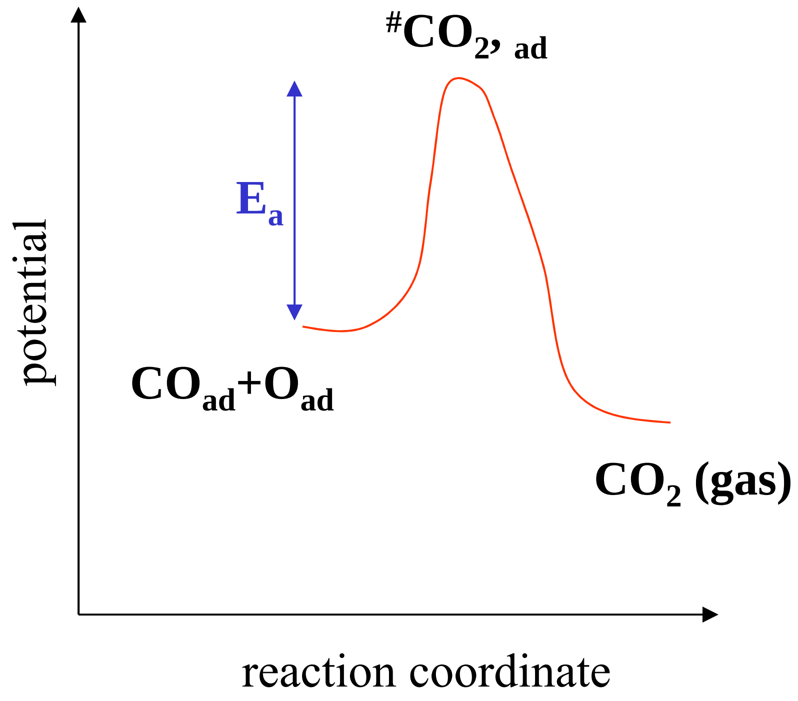


Threshold for bond breaking
bond making?



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

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



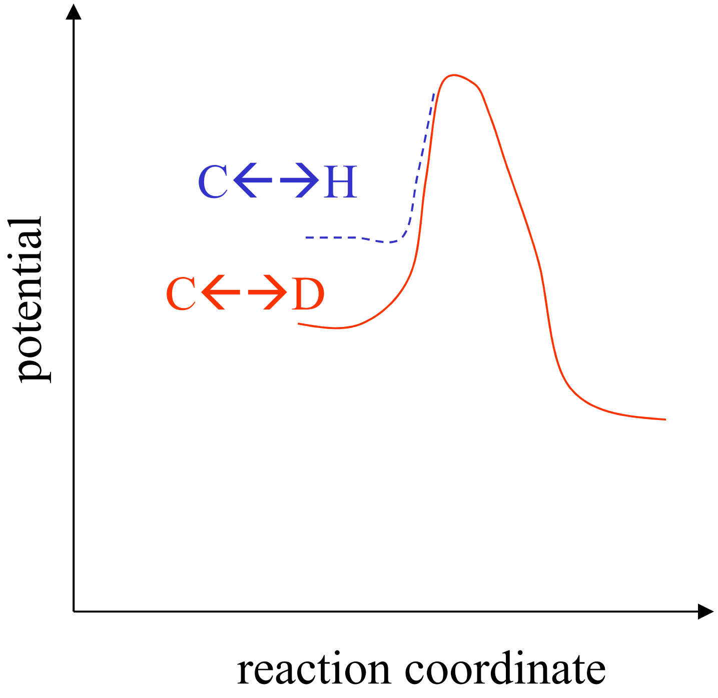
ν ~ probability for going over the "hill"

ν: molecular vibrations

ν ~ 10^{13}/sec

transition state theory → more details later

Kinetic isotope effects



Consider a reaction that includes a

C←→H

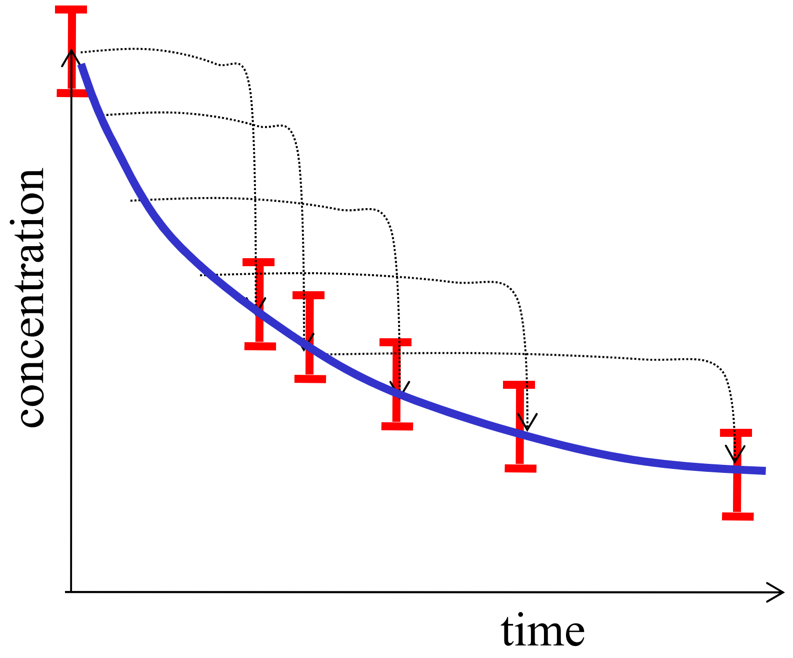
C←→D

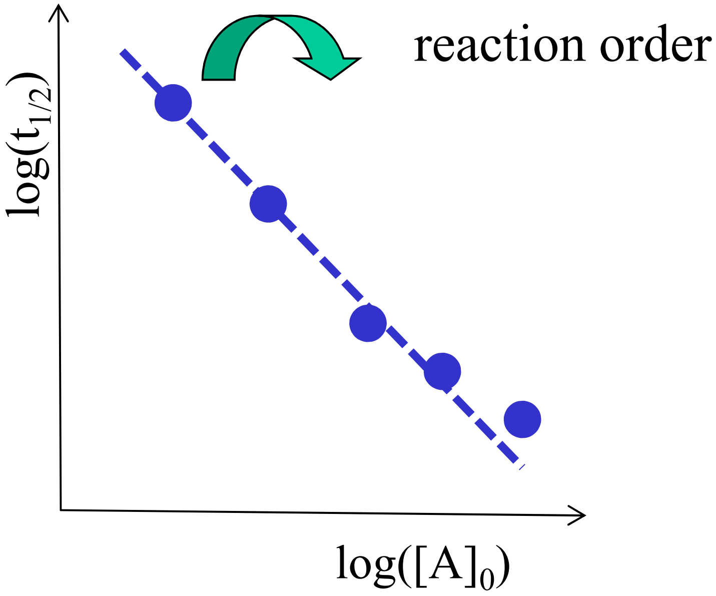
bond breaking.

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

"tricks"

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





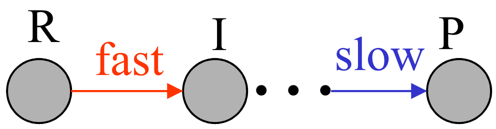
$$r = k[A]^n$$

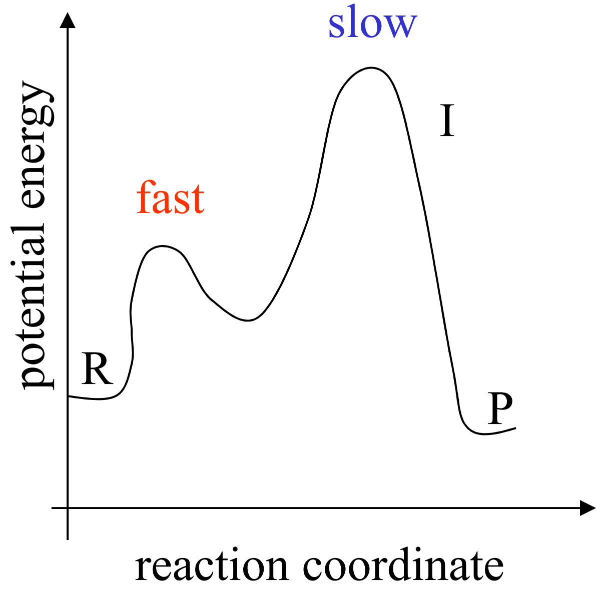
$$t_{1/2} = \frac{2^{n-1}-1}{(n-1)[A]^{n-1}k} \curvearrowright \log(t_{1/2}) = \log\left(\frac{2^{n-1}-1}{(n-1)k}\right) - (n-1)\log([A]_0)$$

Problem: experimental uncertainty

Steady state approximation
Rate determining step approximation
Pre-equilibrium

not exactly the same but related ideas: briefly



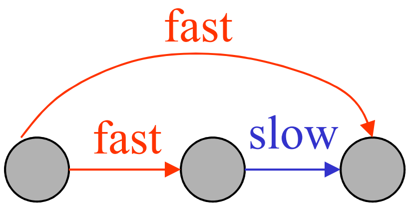


$$R \rightarrow I \rightarrow P$$

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

steady state approximations

Another example:



R: reactants
I: intermediate
P: products

"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

Computational / numerical integration of rate equations

Kinetics leads typically to coupled first order differential equations such as:

$$\frac{dy}{dt} = y(t) - y(t)z(t)$$

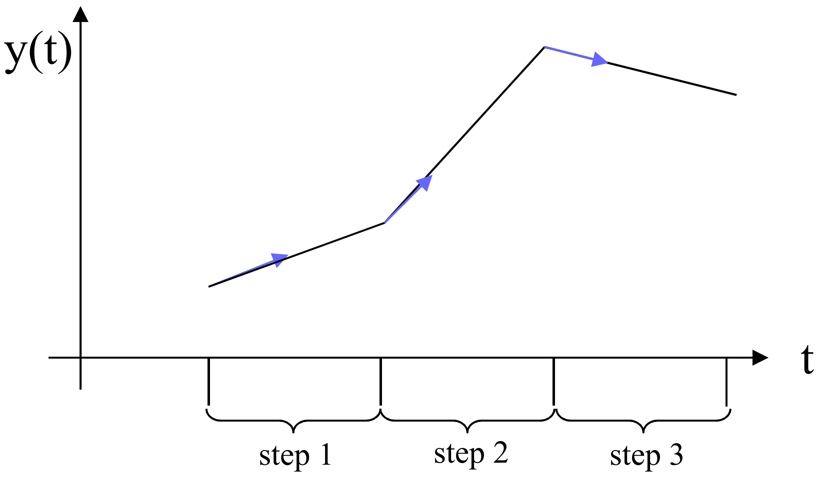
$$\frac{dz}{dt} = -z(t)$$

or $$\frac{dy_i(t)}{dt} = f_i'(t, y_1, \ldots, y_n)$$

$f_i'(t, y_1, \ldots, y_n)$ are known functions.

How can we find y(t), z(t) which obeys these equations (for a simple initial value problem e.g. y(t=0)=1.5, z(t=0)=0)?

Just giving you an idea how this works:



Euler method

$$y_{n+1} = y_n + \Delta n f'(x_n, y_n)$$

Midpoint method:

Do a trial step to the middle of the interval Δn use this information to compute the direction for the full step.

Runge-Kutta method ☺

This one consists basically of four Euler steps.

It is one of the most often used workhorses.

Computational / numerical integration of rate equations

Runge-Kutta is great ☺

but most rate equations are
“stiff” differential equations. ☹

$$\frac{d[CO]}{dt} = F - \underset{\substack{\uparrow \\ 1\text{x}10^{13}}}{k_d}[CO] - \underset{\substack{\uparrow \\ 1\text{x}10^{-2}}}{k_r}[CO][O]$$

Runge-Kutta and other standard methods work here only with very very small step sizes over small intervals. I learned this the hard way…

Look in numeric books, computational chemistry techniques outlines, etc..
The program you can down load from our web site applies the Rosenbrock algorithm which can handle stiff equations.

W.H. Press, B.P. Flannery, S.A. Teukolsky, and W.T. Vetterling,
Numerical recipes, 3rd edition, Cambridge University Press.

Computational / numerical integration of rate equations

Explicit methods

$$y_{n+1} = y_n + \Delta n f'(x_n, y_n)$$

The new value y_{n+1} is given explicitly from the old (y_n) one.

This is not a very stable scheme.

If f ‘ is doing strange things the scheme does not converge.

Implicit methods

$$y_{n+1} = \frac{y_n}{1+n*h}$$

have a better stability.

For example:
h→ ∞ then y_{n+1} → 0

want more..?..

W.H. Press, B.P. Flannery, S.A. Teukolsky, and W.T. Vetterling, *Numerical recipes*, 3rd edition, Cambridge University Press.

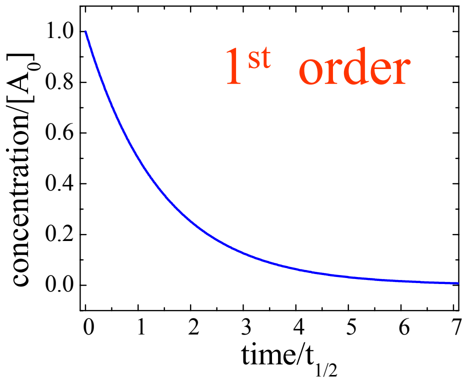
http://en.wikipedia.org/wiki/Spock

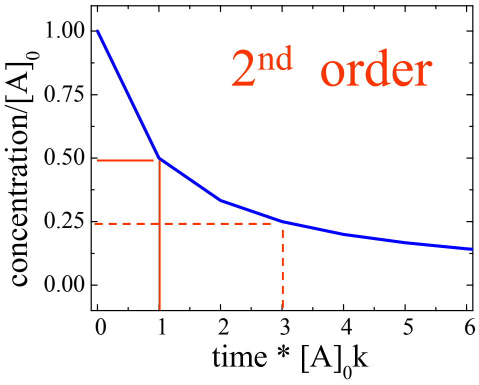
Summary of the kinetics primer

$$aA \rightarrow bB$$

Rate of reaction

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





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

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

Branching ratios
Steady state approximation
Rate determining step
Pre-equilibrium

Computational / numerical integration of rate equations

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
Perturbation-relaxation methods
Diffusion controlled reactions
Lindemann
Catalysis idea
Radical chain reactions
Polymerization
Explosions