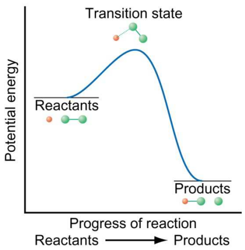

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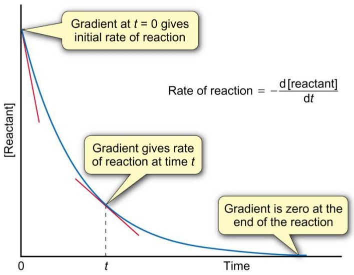
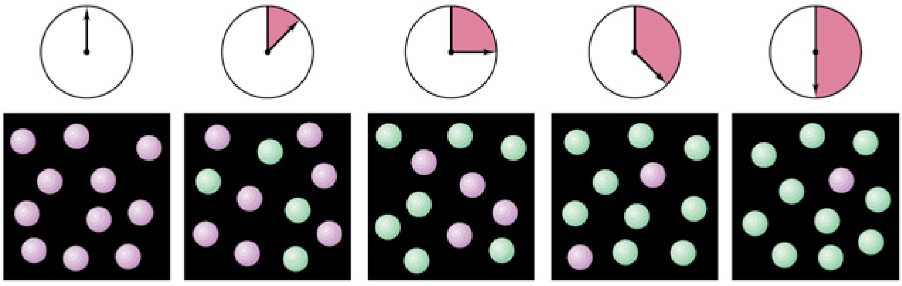
Chemistry^3 Chapter 8, pp.339-403
Kotz, Chapter 15, pp.670-723.



Lecture 10-11

Chemical Kinetics: Integrated rate equations

Chemical Kinetics : time course of chemical transformation



Thermodynamics tells us whether a chemical reaction is possible or not.
Chemical kinetics tells us how fast a particular chemical reaction will proceed.
Chemical kinetics deals with the rate of change of chemical transformations i.e. how quickly reactant molecules transform to products.

Chemically relevant questions.

- What can we say about chemical reactions?
  - Reactants mix and products form.
  - A balanced equation is essential quantitative tool for calculating product yields from reaction amounts.
- What about the dynamics of chemical reactions?
- Useful questions that require answers include:
  - Will the reaction proceed by itself and release energy, or will it require energy to proceed?
    - Thermodynamics (free energy) and thermochemistry.
  - What will the reactant and product concentrations be when the reaction is complete
    - Thermodynamics and chemical equilibrium.
  - How fast is the chemical reaction proceeding at a given moment?
    - Chemical kinetics.
- An essential concept in chemical kinetics is that of chemical reaction rate. This is defined in terms of the change in species concentration (amount per unit volume, i.e. mol/L) with respect to time (s).

Timescales in Chemical Kinetics

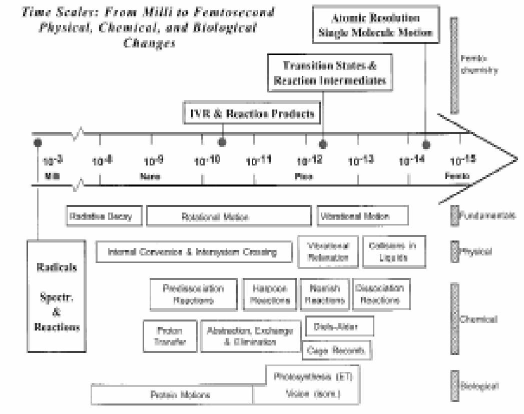


Fig. 1 Timescales. The relevance to physical, chemical, and biological changes. The fundamental limit of the vibrational motion defines the regime for femtochemistry. Examples are given for each change and scale.

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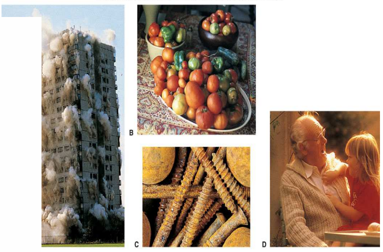

Experimental timescales range from
minutes (typical JF/SF kinetics experiments)
down to femtoseconds.
1 femtosecond (fs) = 10^{-15} s

Sometimes chemical reactions proceed too quickly!

Adidas Dublin City Marathon 2004
25th Anniversary.

Why is chemical kinetics useful?
The ozone layer hole and atmospheric kinetics

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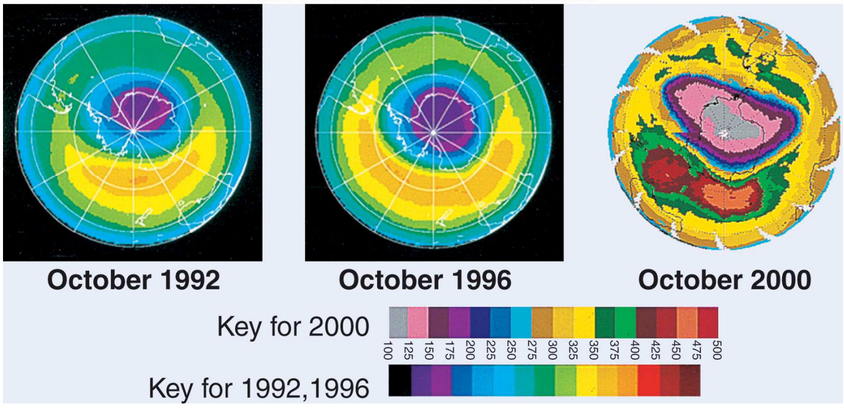


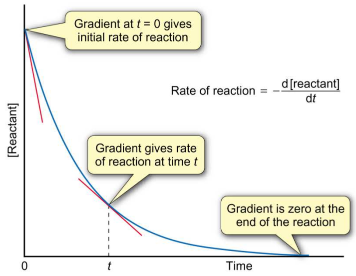
The increasing size of the Antarctic ozone hole.

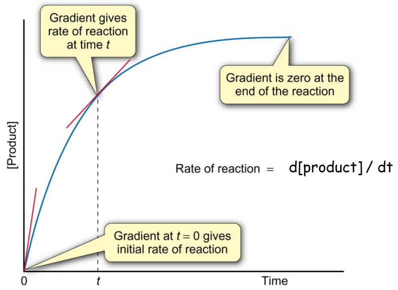
Basic ideas in reaction kinetics.

- Chemical reaction kinetics deals with the rate of velocity of chemical reactions.
- We wish to quantify
  - The velocity at which reactants are transformed to products
  - The detailed molecular pathway by which a reaction proceeds (the reaction mechanism).
- These objectives are accomplished using experimental measurements.
- We are also interested in developing theoretical models by which the underlying basis of chemical reactions can be understood at a microscopic molecular level.
- Chemical reactions are said to be activated processes : energy (usually thermal (heat) energy) must be introduced into the system so that chemical transformation can occur. Hence chemical reactions occur more rapidly when the temperature of the system is increased.
- In simple terms an activation energy barrier must be overcome before reactants can be transformed into products.

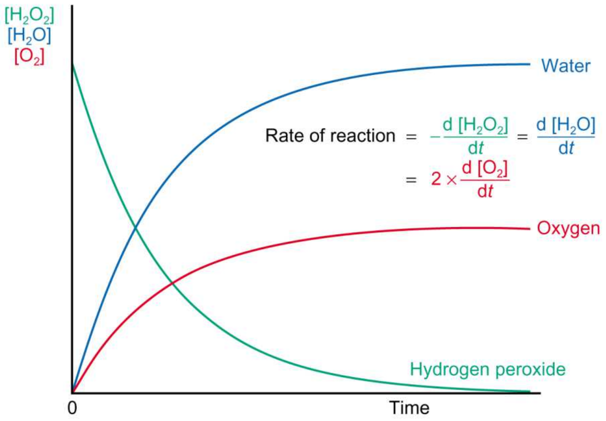
Reaction rate : definition

- What do we mean by the term reaction rate?
  - The term rate implies that something changes with respect to something else.
- How may reaction rates be determined ?
  - The reaction rate is quantified in terms of the change in concentration of a reactant or product species with respect to time.
  - This requires an experimental measurement of the manner in which the concentration changes with time of reaction. We can monitor either the concentration change directly, or monitor changes in some physical quantity which is directly proportional to the concentration.
- The reactant concentration decreases with increasing time, and the product concentration increases with increasing time.
- The rate of a chemical reaction depends on the concentration of each of the participating reactant species.
- The manner in which the rate changes in magnitude with changes in the magnitude of each of the participating reactants is termed the reaction order.





$$\boxed{2H_2O_2(aq) \rightarrow 2H_2O(\ell) + O_2(g)}$$

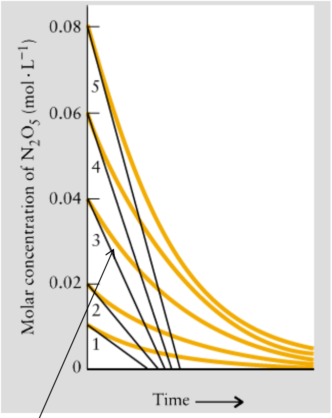


Reaction rate can be quantified by monitoring changes in either reactant concentration or product concentration as a function of time.

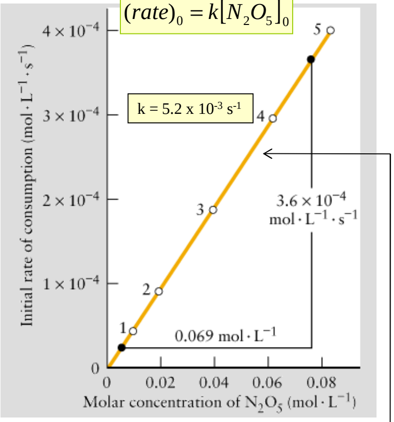
Working out a rate equation.

$$\boxed{2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)}$$

$$(rate)_0 \propto [N_2O_5]_0$$
$$(rate)_0 = k[N_2O_5]_0$$



Initial rate determined by evaluating tangent to concentration versus time curve at a given time t_0.



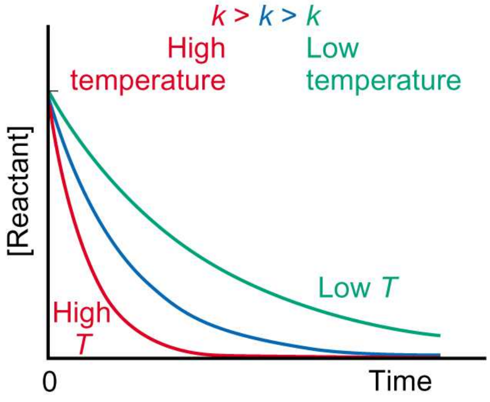
Initial rate is proportional to initial concentration of reactant.

Rate Equation.

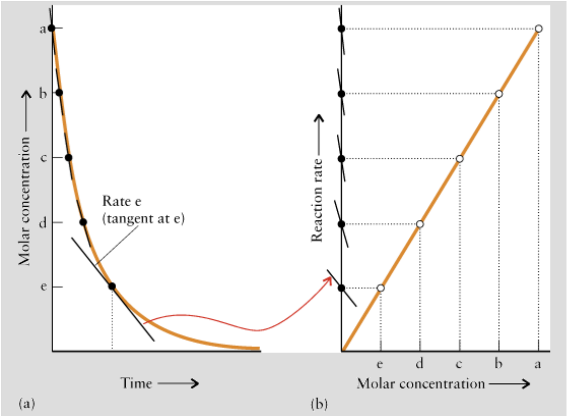
$$rate = -\frac{d[N_2O_5]}{dt} = k[N_2O_5]$$

k = rate constant

Reaction rate varies with extent of reaction.
Rate constant k stays constant over duration of reaction.
Value depends on temperature of reaction medium only.
Rate constant k is a good indicator of reaction velocity.



First order kinetics



- The rate equation must be integrated to obtain an expression for the reactant concentration as a function of time.
- To do this we need an initial condition which tells us the reactant concentration at zero time.

$$-\frac{dc}{dt} = kc$$

$$t = 0 \quad c = c_0$$

First order differential rate equation.

For a first order reaction the following relationship between rate and concentration is valid for any time t.

$$R_t \propto [A]_t = c_t$$

$$R_t = -\frac{d[A]_t}{dt} = k[A]_t = kc_t$$

First order kinetics:
Reaction rate is directly proportional to the reactant concentration.

Rate equation

- The reaction rate (reaction velocity) R is quantified in terms of changes in concentration [J] of reactant or product species J with respect to changes in time.
- The magnitude of the reaction rate changes as the reaction proceeds.
- Rate of reaction is often found to be proportional to the molar concentration of the reactants raised to a simple power (which need not be integral). This relationship is called the ***rate equation***.
- The manner in which the reaction rate changes in magnitude with changes in the magnitude of the concentration of each participating reactant species is called the ***reaction order***.
- The components of the rate equation:
  - rate
  - rate constant
  - reactant reaction order

  must always be determined experimentally.
- An experimental approach to finding the components is:
  - Use concentration vs time measurements to find the initial rate.
  - Use initial rates from several experiments to determine the reaction orders for each participating reactant species.
  - Use this data to calculate the rate constant.

$$aA + bB \xrightarrow{k} pP + qQ$$

$$Rate = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{p}\frac{d[P]}{dt} = \frac{1}{q}\frac{d[Q]}{dt}$$

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

k = rate constant
α,β = reaction orders

Reaction Order :
the reaction order is a measure of the sensitivity of the reaction rate to changes in the concentration of the reactants.

Note : Units of rate :- concentration/time , hence R_J has units mol dm^{-3}s^{-1} .
υ_J denotes the ***stoichiometric coefficient*** of species J. If J is a reactant υ_J is negative and it will be positive if J is a product species.

$$R_J = \frac{1}{\upsilon_J}\lim_{\Delta t \to 0}\frac{\Delta[J]}{\Delta t} = \frac{1}{\upsilon_J}\frac{d[J]}{dt}$$

Kinetics of oxidation of iodide ion by peroxydisulfate ion.

- In this lab experiment you are asked to determine the rate equation, reaction order and rate constant for this electron transfer or redox reaction.
- Reaction is thermodynamically favoured (ΔG^0 = -285 kJmol^{-1}), but occurs slowly, so that the kinetics can be readily measured.
- We measure the initial rate. Here we make a rate measurement under conditions where the reactant concentrations have hardly changed from their initial values.
- We use a very sensitive method to measure the time Δt taken for a fixed quantity of iodine (I_2) to be generated, and hence by stoichiometry, for a fixed quantity ($\Delta[S_2O_8^{2-}]$ of peroxydisulfate ion to be lost. Hence the rate R can be calculated.
- This is done by adding to the reaction mixture a fixed quantity of thiosulfate which reacts very quickly with any iodine molecules generated. We also add some starch indicator to the reaction mixture.
- When all thiosulfate ions are consumed the starch will react quickly with further iodine molecules generated in the oxidation reaction and the solution will become blue.
- The time Δt taken between the mixing of the reactants and the appearance of the blue colour corresponds to the time taken for all the known amount of added thiosulfate ion to be consumed. By stoichiometry we can then calculate the corresponding quantity of peroxydisulfate consumed during this period.
- Reaction orders x and y obtained by measuring initial reaction rate for various initial concentrations of iodide and peroxydisulfate ions. We show that x = 1 and y = 1.

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

$$Rate\ R = -\frac{d[S_2O_8^{2-}]}{dt} = \frac{d[I_2]}{dt}$$
$$= k[S_2O_8^{2-}]^x[I^-]^y$$

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

$$2\ mol\ S_2O_3^{2-} = 1\ mol\ I_2$$
$$1\ mol\ I_2 = 1\ mol\ S_2O_8^{2-}$$
$$1\ mol\ S_2O_3^{2-} = \frac{1}{2}\ mol\ S_2O_8^{2-}$$

$$Initial\ rate\ R_0 = -\frac{\Delta[S_2O_8^{2-}]}{\Delta t} = \frac{2.5\times10^{-4}}{\Delta t}$$

$$k = \frac{R_0}{[S_2O_8^{2-}]_0^x[I^-]_0^y} = \frac{2.5\times10^{-4}/\Delta t}{[S_2O_8^{2-}]_0^x[I^-]_0^y}$$

Determination of reaction order via the initial rate method.

Experiment	$[O_2]_0$	$[NO]_0$	Initial rate Mol $L^{-1}s^{-1}$
1	1.1×10^{-2}	1.3×10^{-2}	3.21×10^{-3}
2	2.2×10^{-2}	1.3×10^{-2}	6.40×10^{-3}
3	1.1×10^{-2}	2.6×10^{-2}	12.80×10^{-3}
4	3.3×10^{-2}	1.3×10^{-2}	9.60×10^{-3}
5	1.1×10^{-2}	3.9×10^{-2}	28.80×10^{-3}

$$O_2(g) + 2NO(g) \rightarrow 2NO_2(g)$$

$$R = k[O_2]^{\alpha}[NO]^{\beta}$$

We want to evaluate the reaction orders α and β from the initial rate data.

Experiment 1 & 2.

$$[NO]_1 = [NO]_2$$

$$\frac{R_2}{R_1} = \frac{k[O_2]_2^{\alpha}[NO]_2^{\beta}}{k[O_2]_1^{\alpha}[NO]_1^{\beta}} = \frac{[O_2]_2^{\alpha}}{[O_2]_1^{\alpha}} = \left\{\frac{[O_2]_2}{[O_2]_1}\right\}^{\alpha}$$

$$\frac{6.4\times10^{-3}}{3.21\times10^{-3}} = \left\{\frac{2.2\times10^{-2}}{1.1\times10^{-2}}\right\}^{\alpha}$$

$$1.99 = 2^{\alpha}$$

$$\log(1.99) = \alpha\log(2)$$

$$\alpha = \frac{\log(1.99)}{\log(2)} \cong \frac{\log 2}{\log 2} = 1$$

Hence reaction is first order wrt O_2.
When $[O_2]$ doubles, the rate doubles.

Experiment 3 & 1.

$$[O_2]_3 = [O_2]_1$$

$$\frac{R_3}{R_1} = \frac{k[O_2]_3^{\alpha}[NO]_3^{\beta}}{k[O_2]_1^{\alpha}[NO]_1^{\beta}} = \left\{\frac{[NO]_3}{[NO]_1}\right\}^{\beta}$$

$$\frac{12.8\times10^{-3}}{3.21\times10^{-3}} = \left\{\frac{2.60\times10^{-2}}{1.30\times10^{-2}}\right\}^{\beta}$$

$$3.99 = 2^{\beta}$$

$$\log 4 = \beta\log 2$$

$$\beta = \frac{\log 4}{\log 2} = 2$$

Hence reaction is second order wrt NO.
When [NO] doubles the rate quadruples.

We conclude that the rate law is given by the expression outlined across.

$$R = k[O_2][NO]^2$$

$$xA + yB \xrightarrow{k} \text{Products}$$

stoichiometric coefficients

empirical **rate equation** (obtained from experiment)

rate constant k

$$R = -\frac{1}{x}\frac{d[A]}{dt} = -\frac{1}{y}\frac{d[B]}{dt} = k[A]^{\alpha}[B]^{\beta}$$

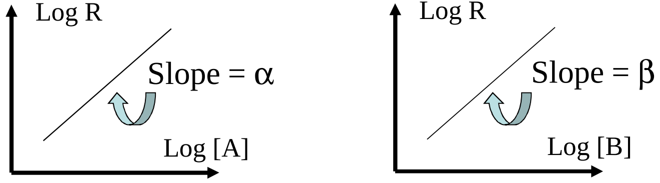
*α, β = **reaction orders** for the reactants (got experimentally)*

Reaction order determination.

Vary [A] , keeping [B] constant and measure rate R.
Vary [B] , keeping [A] constant and measure rate R.

Rate equation can not in general be inferred from the stoichiometric equation for the reaction.

Reaction orders obtained from Slope of log/log plots.



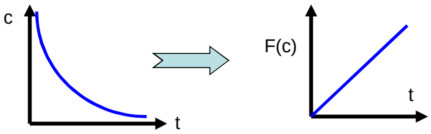
The bottom line.
A rationale and procedure for the study of chemical kinetics.

- Get the concentration versus time data.
- Figure out what mathematical expression the data fit.
- Deduce the rate law.
- Evaluate the rate constant.
- Work out a mechanism consistent with the rate law.
- Do something useful : speed up, slow down or control the reaction.

Chemistry ^{3} Chapter 8, pp.339-398.
Atkins de Paula 5th edition,Chapter 10, pp.219-240.

Quantitative Chemical Kinetics

- The kinetics of a chemical reaction are quantified by determining the rate constant k.
- This is usually done by measuring changes in the reactant or product concentration (or some physical quantity such as optical absorbance or conductivity proportional to concentration) as a function of time.
- The rate equation is formulated from the experimental data.
- If the rate equation (which relates reaction rate to reactant concentration) can be cast into one of a number of standard types, then it can be analytically integrated using suitable methods to obtain a mathematical expression for the concentration as a function of time.
- This concentration/time relationship can then be manipulated to generate a linear equation which can be graphed. The rate constant is then obtained from the graph.
- We shall look at a number of simple examples of chemical reactions which may be subjected to quantitative mathematical analysis. There are many more of course. As the reaction gets more complex the degree of complexity involved in integrating the rate equation increases.
- It is important to note that the rate constant must be measured at a constant temperature, since it will only be constant under such conditions.
- Also the time scale involved in the chemical reaction (can vary from 10^{-15}s to minutes) will determine the type and sophistication of the experimental technique used to measure the rate constant. The shorter the timescale probed, the more sophisticated (and expensive) is the experimental methodology employed.



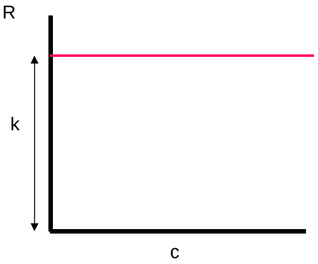
Zero Order Kinetics : Integrated rate equation.

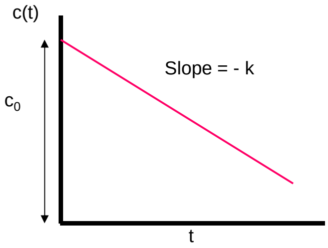
Chemistry^3
Box 8.6. p.369.

- Applicable to chemical reactions on surfaces.
- Reaction proceeds at the same rate regardless of reactant concentration.
- Hence rate is independent of concentration.

$$\boxed{c = c_0 \quad t = 0}$$

$$\boxed{\begin{aligned} R &= -\frac{dc}{dt} = k \\ c(t) &= -kt + c_0 \end{aligned}}$$



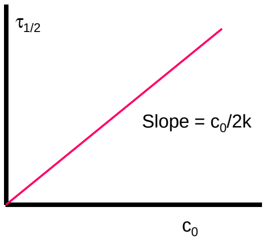


Zero order kinetics: half life.

- Half life $\tau_{1/2}$:
  - Time taken for concentration of reactant to fall to 50% of its initial value.
  - Half life will always be inversely proportional to the rate constant since a large rate constant will always imply a short half life and vice versa.
  - The half life is directly proportional to the initial reactant concentration for a reaction exhibiting zero order kinetics.

$$\boxed{t = \tau_{1/2} \quad \text{when} \quad c(t) = c_0/2}$$

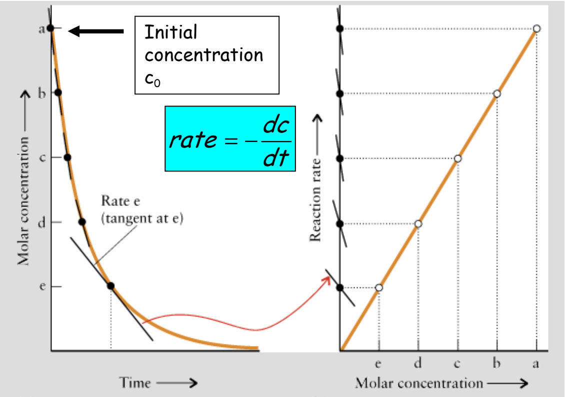
$$\boxed{\begin{aligned} c(t) &= -kt + c_0 \\ c_0/2 &= -k\tau_{1/2} + c_0 \\ \tau_{1/2} &= \frac{c_0}{2k} \end{aligned}}$$



First order kinetics: Integrated rate equation

$$\boxed{A \xrightarrow{k} \text{Products}}$$

Chemistry ^{3} Box 8.1
p. 350 Derivation.



First order differential rate equation.

$$\boxed{-\frac{dc}{dt} = kc}$$

Initial condition

$$\boxed{t = 0 \quad c = c_0}$$

Solve differential equation

Separation of variables

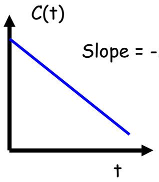
$$\boxed{c(t) = c_0 e^{-kt} = c_0 \exp\left[-kt\right]}$$

Reactant concentration as function of time.

k = first order rate constant, units: s^{-1}

$$\boxed{\ln c(t) = -kt + \ln c_0}$$

$$y = mx + b$$

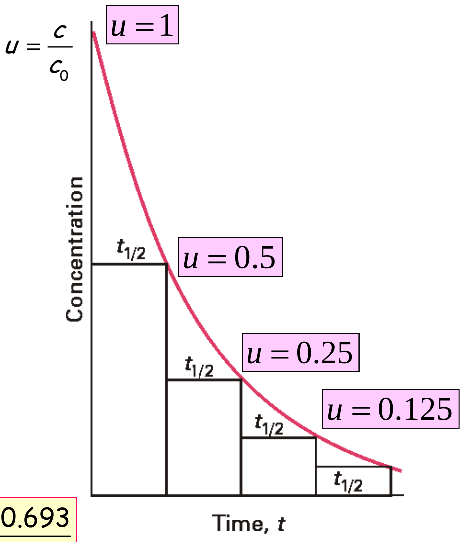


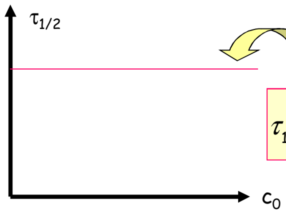
A plot of ln c(t) as function of time t is diagnostic of 1st order kinetics.

First order kinetics : half life

$$t = \tau_{1/2} \qquad c = c_0 / 2$$

In each successive period of duration $\tau_{1/2}$ the concentration of a reactant in a first order reaction decays to half its value at the start of that period. After n such periods, the concentration is $(1/2)^n$ of its initial value.





$$\tau_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

half life independent of initial reactant concentration

Second Order Kinetics: Equal reactant concentrations.

Chemistry ^{3} Box 8.2, p.351
Derivation.

$$2A \xrightarrow{k} P$$

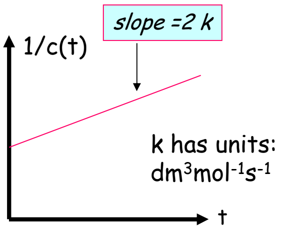
Rate equation

$$-\frac{da}{dt} = 2kc^2$$
$$t = 0 \qquad c = c_0$$

separate variables
integrate

$$\frac{1}{c} = 2kt + \frac{1}{c_0}$$

$$c(t) = \frac{c_0}{1 + 2kc_0 t}$$

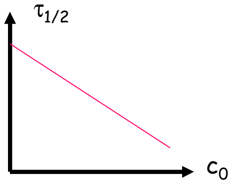


k has units:
$dm^3 mol^{-1} s^{-1}$

half life

$$t = \tau_{1/2} \qquad c = \frac{c_0}{2}$$

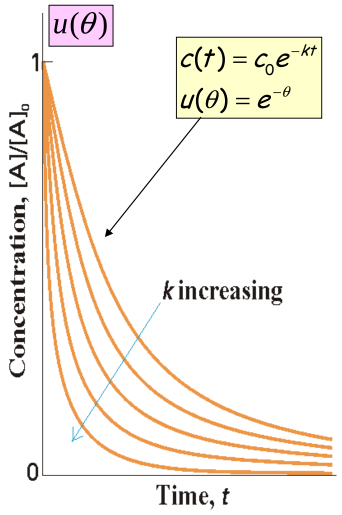
$$\tau_{1/2} = \frac{1}{2kc_0}$$
$$\tau_{1/2} \propto \frac{1}{c_0}$$
$$\tau_{1/2} \downarrow \quad as \quad c_0 \uparrow$$



rate varies as square of reactant concentration

Half life inversely proportional to initial reactant concentration.

1st order kinetics

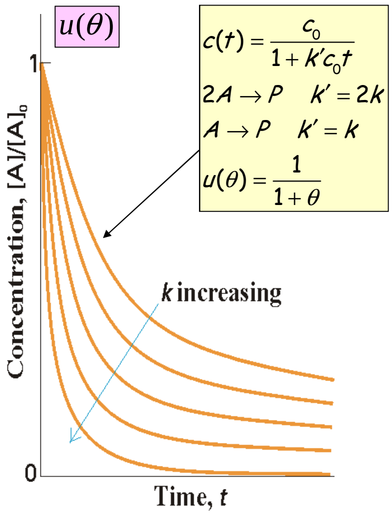


$c(t) = c_0 e^{-kt}$

$u(\theta) = e^{-\theta}$

$\theta = kt$

2nd order kinetics



$c(t) = \dfrac{c_0}{1 + k' c_0 t}$

$2A \rightarrow P \quad k' = 2k$

$A \rightarrow P \quad k' = k$

$u(\theta) = \dfrac{1}{1+\theta}$

$\theta = k' c_0 t$

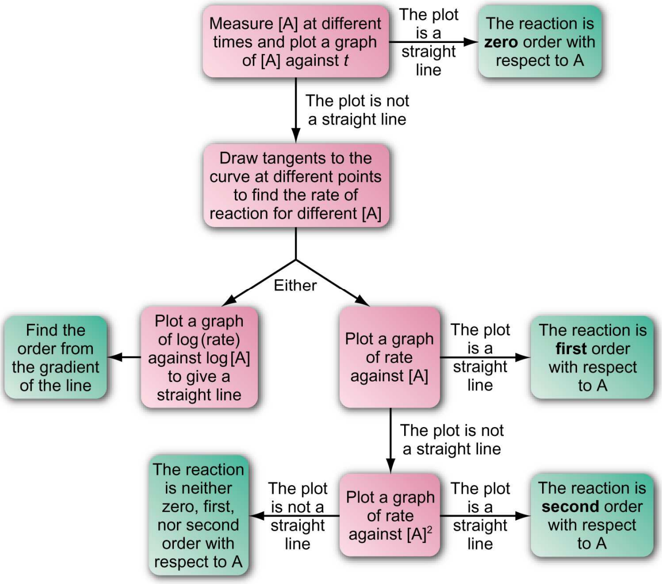
Table 8.2 A summary of equations for elementary reactions

Type of reaction	Order of reaction	Differential rate equation	Integrated rate equation	Half life, $t_{1/2}$
A → products	First order	$-\dfrac{d[A]}{dt} = k[A]$	$\ln [A]_t = \ln [A]_0 - kt$	$\dfrac{\ln 2}{k}$
A + A → products	Second order	$-\dfrac{d[A]}{dt} = 2k[A]^2$	$\dfrac{1}{[A]_t} = \dfrac{1}{[A]_0} + 2kt$	$\dfrac{1}{2k[A]_0}$
A + B → products where $[A] \ll [B]$	Pseudo-first order	$-\dfrac{d[A]}{dt} = k'[A]$ where $k' = k[B]_0$	$\ln [A]_t = \ln [A]_0 - k't$ $= \ln [A]_0 - kt[B]_0$	$\dfrac{\ln 2}{k'} = \dfrac{\ln 2}{k[B]_0}$

Table 8.3 Using integrated rate equations to study complex reactions

	Order		
	0	1	2
Rate equation	Rate $= k'$	Rate $= k'[A]$	Rate $= k'[A]^2$
Integrated rate equation	$[A]_t = [A]_0 - k't$	$\ln [A]_t = \ln [A]_0 - k't$	$\dfrac{1}{[A]_t} = \dfrac{1}{[A]_0} + 2k't$ *
Plot of [A] vs t	**Straight line**	Curve	Curve
Plot of ln [A] vs t	Curve	**Straight line**	Curve
Plot of $\dfrac{1}{[A]_0}$ vs t	Curve	Curve	**Straight line**
Half life, $t_{1/2}$	Not constant	**Constant**	Not constant

* The multiplication factor before k' depends on the stoichiometry of the reaction.



Measure [A] at different times and plot a graph of [A] against *t*

The plot is a straight line → The reaction is **zero** order with respect to A

The plot is not a straight line ↓

Draw tangents to the curve at different points to find the rate of reaction for different [A]

Either

Plot a graph of log (rate) against log [A] to give a straight line → Find the order from the gradient of the line

Plot a graph of rate against [A]

The plot is a straight line → The reaction is **first** order with respect to A

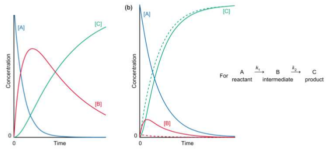
The plot is not a straight line ↓

Plot a graph of rate against $[A]^2$

The plot is a straight line → The reaction is **second** order with respect to A

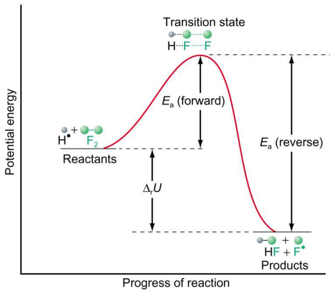
The plot is not a straight line → The reaction is neither zero, first, nor second order with respect to A

COLÁISTE NA TRÍONÓIDE, BAILE ÁTHA CLIATH | TRINITY COLLEGE DUBLIN
Ollscoil Átha Cliath | The University of Dublin



For A (reactant) $\xrightarrow{k_1}$ B (intermediate) $\xrightarrow{k_2}$ C (product)

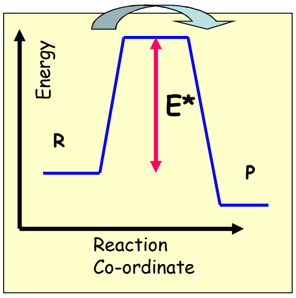
Lecture 12



Chemical Kinetics (II):
Effect of temperature on reaction rate
& Reaction Mechanisms

Chemical reactions are activated processes.

- We can picture the progress of a chemical reaction in terms of a plot of energy versus reaction co-ordinate (this is a quantity which is a measure of the progress of the reaction along the most energetically facile pathway).
- The reactants R have to climb an uphill energy barrier of height E* in order to transform into products P.
- The height of this energy barrier can be related to the experimentally determined activation energy E_A.
- The greater the quantity of thermal energy supplied, the more easily the energy barrier is surmounted.

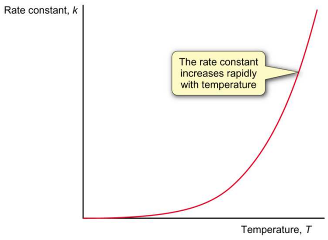


Chemistry ^{3} section 8.7, pp.383-389.

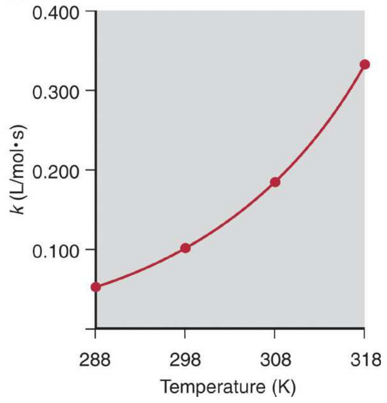
Dependence of the rate constant on temperature

Ester hydrolysis: Reactant concentrations held constant and temperature is varied. As temperature increases the rate and rate constant increases. Note that k nearly doubles with each temperature rise of 10 K.

Exp't	[Ester]	[H_2O]	T (K)	Rate (mol/L•s)	k (L/mol•s)
1	0.100	0.200	288	1.04×10^{-3}	0.0521
2	0.100	0.200	298	2.02×10^{-3}	0.101
3	0.100	0.200	308	3.68×10^{-3}	0.184
4	0.100	0.200	318	6.64×10^{-3}	0.332



Can we quantitatively predict the manner in which the rate constant varies with temperature ?



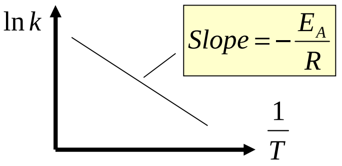
Temperature effects in chemical kinetics.

- Chemical reactions are activated processes : they require an energy input in order to occur.
- Many chemical reactions are activated via thermal means.
- The relationship between rate constant k and temperature T is given by the empirical **Arrhenius equation**.
- The activation energy E_A is determined from experiment, by measuring the rate constant k at a number of different temperatures. The Arrhenius equation is used to construct an Arrhenius plot of ln k versus 1/T. The activation energy is determined from the slope of this plot.

$$\boxed{k = A\exp\left[-\frac{E_A}{RT}\right]}$$

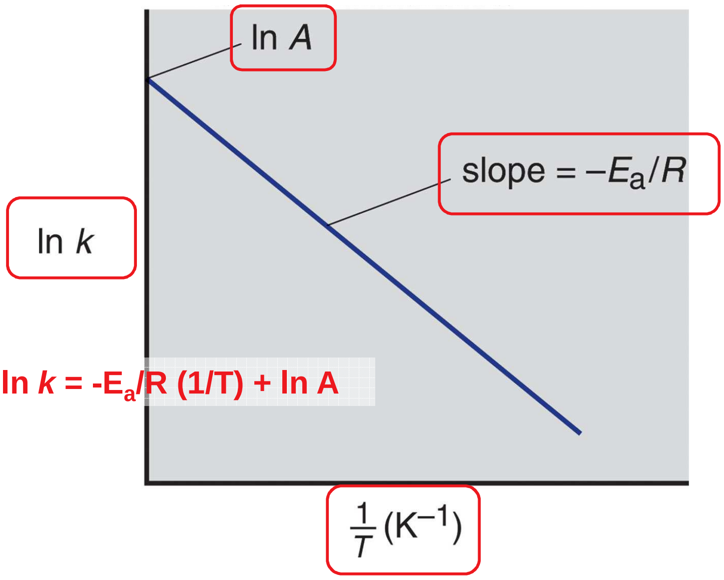
Pre-exponential factor

$$\boxed{E_A = -R\left(\frac{d\ln k}{d(1/T)}\right) = RT^2\left(\frac{d\ln k}{dT}\right)}$$



$$\boxed{Slope = -\frac{E_A}{R}}$$

Figure 16.11 **Graphical determination of the activation energy**



ln *k* = $-E_a$/R (1/T) + ln A

Using the Arrhenius equation to predict rate constants.

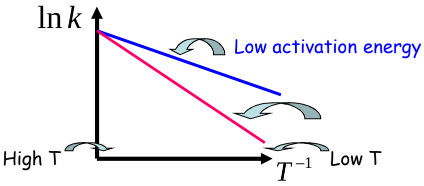
- We can use the Arrhenius equation to predict a rate constant at one temperature, given its value at another temperature if we know the value of the activation energy E_A for the reaction.
- If $k = k_1$ at temperature T_1 and $k = k_2$ at temperature T_2 and if $T_2 > T_1$ then we can show that

$$\boxed{\ln\left\{\frac{k_2}{k_1}\right\} = \frac{E_A}{R}\left\{\frac{1}{T_1} - \frac{1}{T_2}\right\}}$$

- We can also use this expression to obtain the activation energy E_A if the rate constants at two different temperatures are known.

$$\boxed{E_A = \frac{R\ln\left\{\frac{k_2}{k_1}\right\}}{\left\{\frac{1}{T_1} - \frac{1}{T_2}\right\}}}$$

A large activation energy signifies a high sensitivity of the reaction rate to changes in temperature.



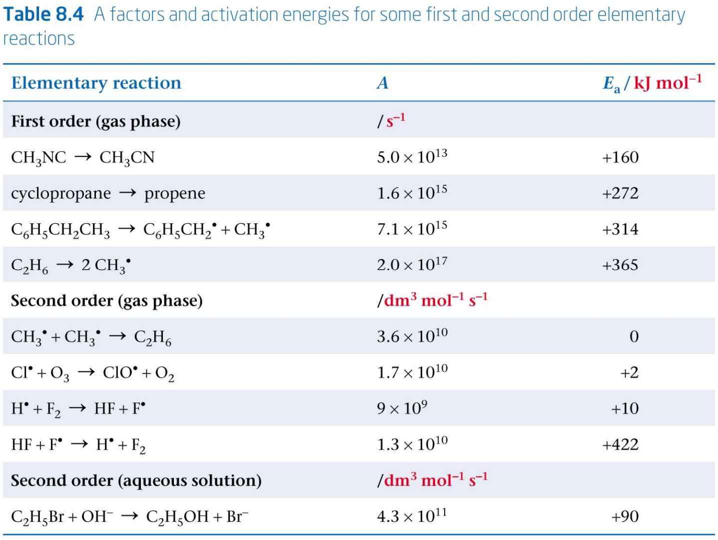


Table 8.4 A factors and activation energies for some first and second order elementary reactions

Elementary reaction	A	E_a / kJ mol^{-1}
First order (gas phase)	/ s^{-1}	
$CH_3NC \rightarrow CH_3CN$	5.0×10^{13}	+160
cyclopropane → propene	1.6×10^{15}	+272
$C_6H_5CH_2CH_3 \rightarrow C_6H_5CH_2^\bullet + CH_3^\bullet$	7.1×10^{15}	+314
$C_2H_6 \rightarrow 2\,CH_3^\bullet$	2.0×10^{17}	+365
Second order (gas phase)	/dm^3 mol^{-1} s^{-1}	
$CH_3^\bullet + CH_3^\bullet \rightarrow C_2H_6$	3.6×10^{10}	0
$Cl^\bullet + O_3 \rightarrow ClO^\bullet + O_2$	1.7×10^{10}	+2
$H^\bullet + F_2 \rightarrow HF + F^\bullet$	9×10^{9}	+10
$HF + F^\bullet \rightarrow H^\bullet + F_2$	1.3×10^{10}	+422
Second order (aqueous solution)	/dm^3 mol^{-1} s^{-1}	
$C_2H_5Br + OH^- \rightarrow C_2H_5OH + Br^-$	4.3×10^{11}	+90

Determining the Energy of Activation

PROBLEM: The decomposition of hydrogen iodide,

$$2HI(g) \longrightarrow H_2(g) + I_2(g)$$

has rate constants of $9.51\text{x}10^{-9}$ L $mol^{-1}s^{-1}$ at 500. K and $1.10\text{x}10^{-5}$ $Lmol^{-1}$ s^{-1} at 600. K. Find the activation energy E_a.

PLAN: Use the modification of the Arrhenius equation to find E_a.

SOLUTION:

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad E_a = -R \ln \frac{k_2}{k_1}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)^{-1}$$

$$E_a = -(8.314\text{J/mol*K})\left(\ln \frac{1.10\text{x}10^{-5}\text{L/mol*s}}{9.51\text{x}10^{-9}\text{L/mol*s}}\right)\left(\frac{1}{600\text{K}} - \frac{1}{500\text{K}}\right)$$

$E_a = 1.76\text{x}10^5$J/mol = 176kJ/mol

Collision theory of bimolecular gas phase reactions.

- We focus attention on gas phase reactions and assume that chemical reactivity is due to collisions between molecules.
- The theoretical approach is based on the kinetic theory of gases.
- Molecules are assumed to be hard structureless spheres. Hence the model neglects the discrete chemical structure of an individual molecule. This assumption is unrealistic.
- We also assume that no interaction between molecules until contact.
- Molecular spheres maintain size and shape on collision. Hence the centres cannot come closer than a distance δ given by the sum of the molecular radii.
- One must have an A,B (or an A,A) encounter over a sufficiently short distance to allow reaction to occur.
- Colliding molecules must have sufficient energy of the correct type to overcome the energy barrier for reaction. A threshold energy E* is required.
- The reaction rate will depend on two factors :
  - the number of collisions per unit time (the collision frequency)
  - the fraction of collisions having an energy greater than a certain threshold energy E*.

Chemistry^3 p.391 Collision Theory.

SCT : Chemical reactivity related to collisions between reacting molecules.

Very simplistic
Approach.

Experiment:
Arrhenius
equation

$$\boxed{k = A\exp\left[-\frac{E_A}{RT}\right]}$$

SCT final results (Chem^3 p.391)

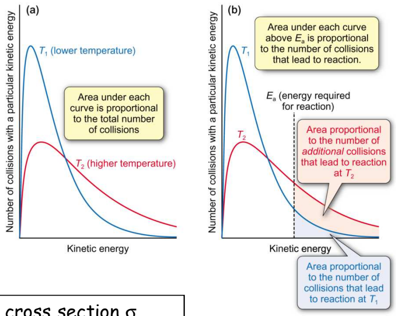
$$k = N_A\sigma\left\{\frac{8k_BT}{\pi\mu}\right\}^{1/2}\exp\left[-\frac{E^*}{RT}\right] = z_{AB}\exp\left[-\frac{E^*}{RT}\right]$$

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

$$k = 2N_A\sigma\left\{\frac{k_BT}{\pi m}\right\}^{1/2}\exp\left[-\frac{E^*}{RT}\right] = z_{AA}\exp\left[-\frac{E^*}{RT}\right]$$

Pre-exponential factor A related to
collisions per unit time

Exponential factor related
to fraction of
collisions which result in reaction

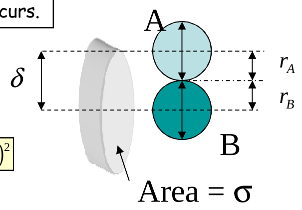


The collision cross section σ
defines where a collision occurs.

Effective collision
diameter

$$\delta = r_A + r_B$$

$$\sigma = \pi\delta^2 = \pi(r_A + r_B)^2$$



The ***collision cross section*** for two molecules can be regarded to be the area within which the center of the projectile molecule A must enter around the target molecule B in order for a collision to occur.

We compare the results of SCT with the empirical Arrhenius eqn. in order to obtain an interpretation of the activation energy and pre-exponential factor.

$$k = A_{obs}\exp\left[-\frac{E_A}{RT}\right]$$

A,B encounters

$$k = N_A\sigma\left\{\frac{8k_BT}{\pi\mu}\right\}^{1/2}\exp\left[-\frac{E^*}{RT}\right] = z_{AB}\exp\left[-\frac{E^*}{RT}\right]$$

$$A_{obs} = z_{AB} = A'\sqrt{T}A$$

$$A' = N_A\sigma\sqrt{\frac{8k_B}{\pi\mu}}$$

Pre-exponential factor

$$k = 2N_A\sigma\left\{\frac{k_BT}{\pi m}\right\}^{1/2}\exp\left[-\frac{E^*}{RT}\right] = z_{AA}\exp\left[-\frac{E^*}{RT}\right]$$

A,A encounters

$$A_{obs} = z_{AA} = A''\sqrt{T}A$$

$$A'' = 2N_A\sigma\sqrt{\frac{8k_B}{\pi m}}$$

- SCT predicts that the pre-exponential factor should depend on temperature.
- The threshold energy and the activation energy can also be compared.
- Activation energy exhibits a weak T dependence.

$$\frac{d\ln k}{dT} = \frac{E_A}{RT^2}$$

Arrhenius

SCT

$$\frac{d\ln k}{dT} = \frac{E^* + RT/2}{RT^2}$$

$$E_A = E^* + \frac{RT}{2}$$

$$E_A \cong E^*$$

SCT : a summary.

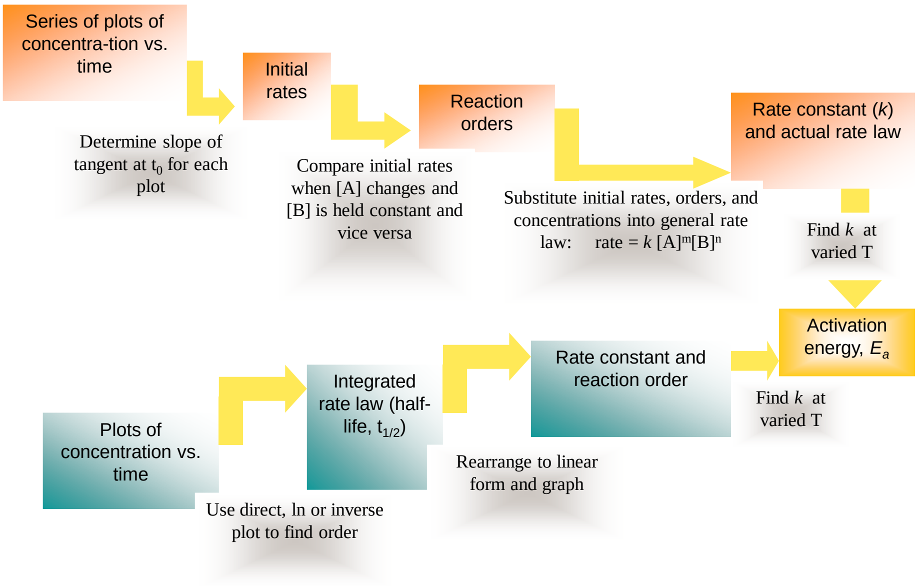
- The major problem with SCT is that the threshold energy E* is very difficult to evaluate from first principles.
- The predictions of the collision theory can be critically evaluated by comparing the experimental pre-exponential factor with that computed using SCT.
- We define the **steric factor** P as the ratio between the experimental and calculated A factors.
- We can incorporate P into the SCT expression for the rate constant.
- For many gas phase reactions P is considerably less than unity.
- Typically SCT will predict that A_{calc} will be in the region 10^{10}-10^{11} $\mathrm{L mol^{-1} s^{-1}}$ regardless of the chemical nature of the reactants and products.
- What has gone wrong? The SCT assumption of hard sphere collision neglects the important fact that **molecules possess an internal structure**. It also neglects the fact that the relative orientation of the colliding molecules will be important in determining whether a collision will lead to reaction.
- We need a better theory that takes molecular structure into account. The **activated complex theory** does just that .

$$P = A_{\exp} / A_{calc}$$

$$k = P z_{AB} \exp\left[-\frac{E^*}{RT}\right]$$

$$k = P z_{AA} \exp\left[-\frac{E^*}{RT}\right]$$

Information sequence to determine the kinetic and activation parameters of a reaction.



Series of plots of concentra-tion vs. time

Determine slope of tangent at t_0 for each plot

Initial rates

Compare initial rates when [A] changes and [B] is held constant and vice versa

Reaction orders

Substitute initial rates, orders, and concentrations into general rate law: rate = $k\,[A]^m[B]^n$

Rate constant (*k*) and actual rate law

Find *k* at varied T

Activation energy, E_a

Plots of concentration vs. time

Use direct, ln or inverse plot to find order

Integrated rate law (half-life, $t_{1/2}$)

Rearrange to linear form and graph

Rate constant and reaction order

Find *k* at varied T

Consecutive Reactions .

$$A \xrightarrow{k_1} X \xrightarrow{k_2} P$$

- Mother / daughter radioactive decay.

$$^{218}Po \rightarrow {}^{214}Pb \rightarrow {}^{214}Bi$$

$$k_1 = 5\times10^{-3}\,s^{-1} \quad k_2 = 6\times10^{-4}\,s^{-1}$$

Must consider 3 coupled LDE's :

$$\boxed{\begin{aligned}\frac{da}{dt} &= -k_1 a \\ \frac{dx}{dt} &= k_1 a - k_2 x \\ \frac{dp}{dt} &= k_2 x\end{aligned}}$$

Mass balance requires that :

$$p = a_0 - a - x$$

Hence once a(t) and x(t) are evaluated we can determine p(t) .

The solutions to the coupled equations are :

$$\boxed{\begin{aligned}a(t) &= a_0 \exp[-k_1 t] \\ x(t) &= \frac{k_1 a_0}{k_2 - k_1}\{\exp[-k_1 t] - \exp[-k_2 t]\} \\ p(t) &= a_0 - a_0 \exp[-k_1 t] - \frac{k_1 a_0}{k_2 - k_1}\{\exp[-k_1 t] - \exp[-k_2 t]\}\end{aligned}}$$

We different behaviour depending on the ratio of the rate constants k_1 and k_2

Consecutive reactions: Rapid decay of intermediate.

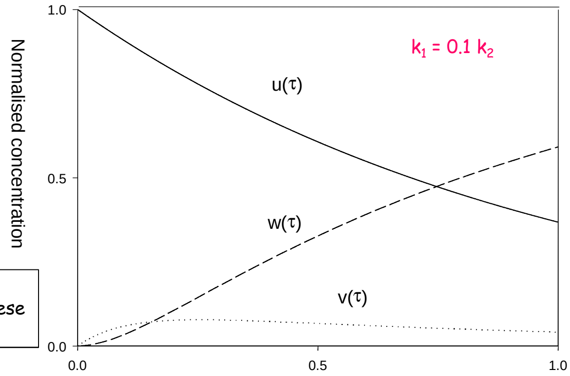
Chemistry³ pp.373-381

$$\frac{dx}{dt} = R_{X,formation} - R_{X,removal} \cong 0$$

Intermediate X is fairly reactive. Concentration of intermediate X will be small at all times.

$$A \xrightarrow{k_1} X \xrightarrow{k_2} P$$

Can use Quasi-Steady State Approximation QSSA under these Conditions.

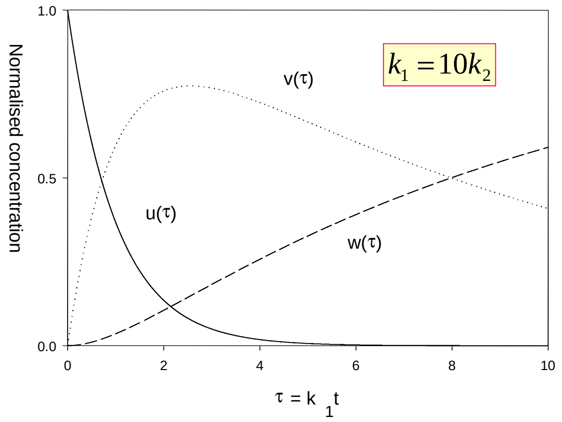


Rate of change of concentration of intermediate species X With respect to time is zero.
X gets used up as fast as it is formed.
Hence the intermediate concentration is approximately small and constant.

Consecutive reactions:
Slow decay of intermediate.

$$\boxed{A \xrightarrow{k_1} X \xrightarrow{k_2} P}$$

$$\boxed{\begin{aligned} u &= \frac{a}{a_0} \\ v &= \frac{x}{a_0} \\ w &= \frac{p}{a_0} \end{aligned}}$$



Initial reactant A more reactive than intermediate X .

Rate determining step in a consecutive reaction is the step that is associated with the highest energy barrier and is therefore kinetically limiting and determines the net reaction rate.

Rate Determining Step

$$\boxed{k_1 >> k_2}$$

$$A \underset{\text{Fast}}{\xrightarrow{k_1}} X \underset{\text{Slow}}{\xrightarrow{k_2}} P$$

- Reactant A decays rapidly, concentration of intermediate species X is high for much of the reaction and product P concentration rises gradually since X --> P transformation is slow .

$$\boxed{k_2 >> k_1}$$

Rate Determining Step

$$A \underset{\text{Slow}}{\xrightarrow{k_1}} X \underset{\text{Fast}}{\xrightarrow{k_2}} P$$

- Reactant A decays slowly, concentration of intermediate species X will be low for the duration of the reaction and to a good approximation the net rate of change of intermediate concentration with time is zero. Hence the intermediate will be formed as quickly as it is removed. This is the *quasi steady state approximation* (QSSA).

Rate Determining Steps (I) .

$A \xrightarrow{k_1} X \xrightarrow{k_2} P$

$\kappa = \frac{k_2}{k_1}$

key parameter

Case I . → $\kappa = \frac{k_2}{k_1} >> 1$

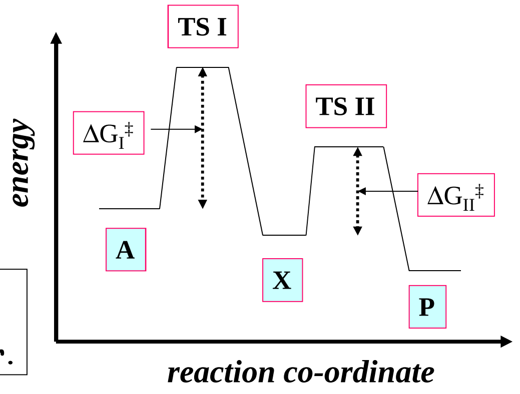
$k_2 >> k_1$

$A \xrightarrow{k_1} X \xrightarrow{k_2} P$

I : slow rds II : fast

$\Delta G_I^\ddagger >> \Delta G_{II}^\ddagger$

Intermediate X fairly reactive.
[X] will be small at all times.



Step I rate determining since it has the highest activation energy barrier.

Rate Determining Steps (II) .

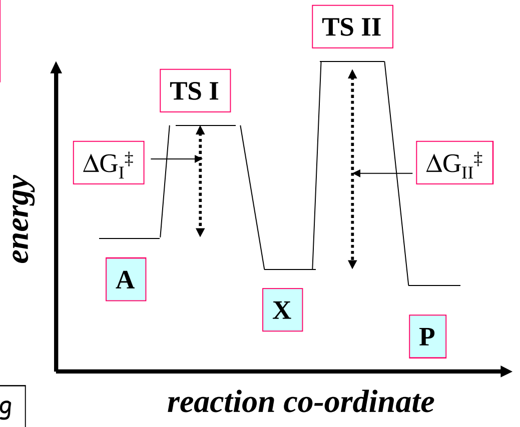
Case II . → $\kappa = \frac{k_2}{k_1} << 1$

$k_2 << k_1$

$A \xrightarrow{k_1} X \xrightarrow{k_2} P$

I : fast II : slow rds

$\Delta G_I^\ddagger << \Delta G_{II}^\ddagger$

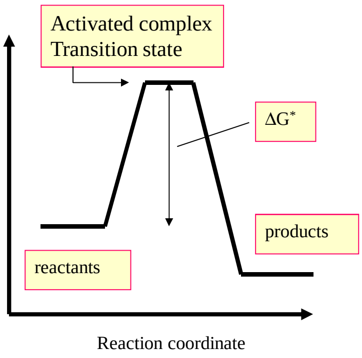


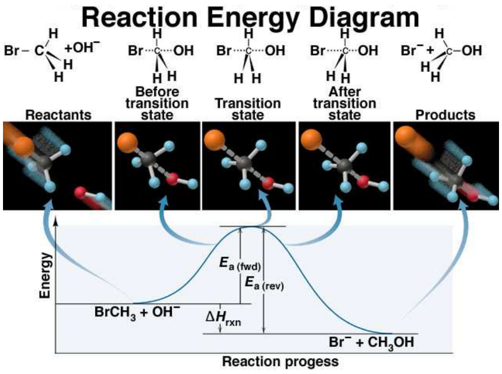
Step II is rate determining since it has the highest activation energy barrier.

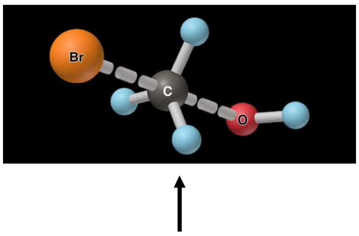
The reactant species A will be more reactive than the intermediate X.

Activated Complex Theory (ACT) of chemical reaction kinetics.

Progress of a chemical reaction can be expressed in terms of a plot of energy versus reaction co-ordinate.
The reaction coordinate may be described in terms of changes in particular bond lengths since these will vary as the reaction progresses.



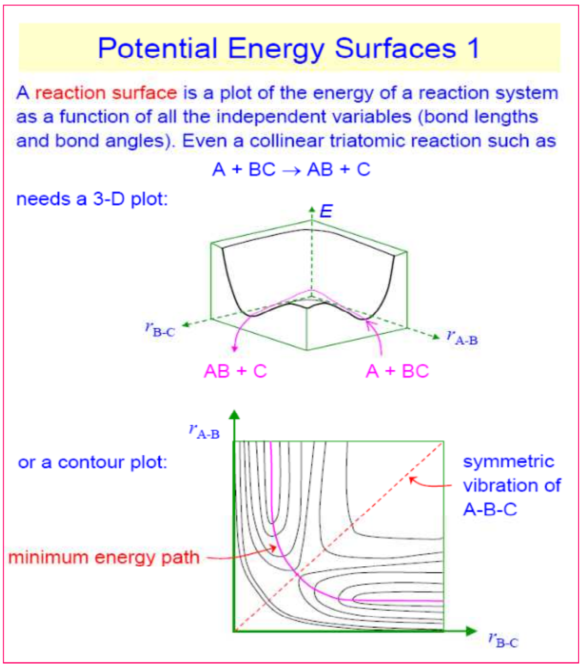




Activated Complex or Transition State

Henry Eyring
1901-1981

Developed (in 1935) the Transition State Theory (TST)
or
Activated Complex Theory (ACT)
of Chemical Kinetics.



Potential Energy Surfaces 1

A reaction surface is a plot of the energy of a reaction system as a function of all the independent variables (bond lengths and bond angles). Even a collinear triatomic reaction such as

$$A + BC \rightarrow AB + C$$

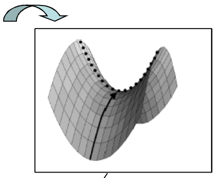
needs a 3-D plot:

or a contour plot:

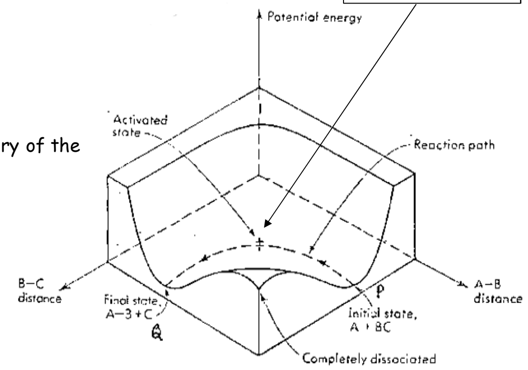
Potential energy surface for a chemical reaction

$$A + BC \rightarrow [ABC]^{*} \rightarrow AB + C$$

Transition
State :
Local max
on a min
Energy path

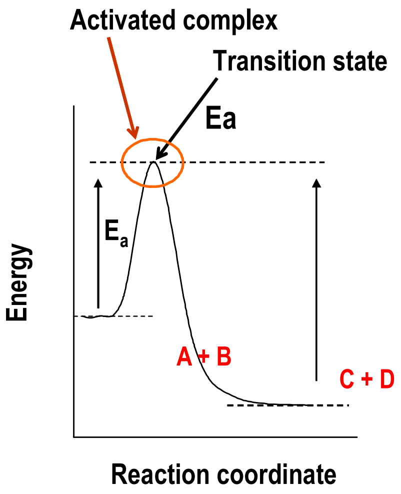


- Calculate potential energy V of System A(g)+ BC(g) -> AB(g) +C(g).
- For a fixed angle of approach θ between reactants (θ = 180°) we plot V versus R_{AB} and R_{BC} to define a 3D Potential energy surface.
- This defines a detailed map of the trajectory of the system as it proceeds from the initial Reactant state to the final Product state.
- This procedure is very computationally intensive and has only been carried out for fairly simple reactions in the gas phase.



Transition state theory (TST) or activated complex theory (ACT).

- In a reaction step as the reactant molecules A and B come together they distort and begin to share, exchange or discard atoms.
- They form a loose structure $AB^{\ddagger}$ of high potential energy called the activated complex that is poised to pass on to products or collapse back to reactants C + D.
- The peak energy occurs at the transition state. The energy difference from the ground state is the activation energy E_a of the reaction step.
- The potential energy falls as the atoms rearrange in the cluster and finally reaches the value for the products
- Note that the reverse reaction step also has an activation energy, in this case higher than for the forward step.



Transition state theory

- The theory attempts to explain the size of the rate constant k_r and its temperature dependence from the actual progress of the reaction (reaction coordinate).
- The progress along the reaction coordinate can be considered in terms of the approach and then reaction of an H atom to an F_2 molecule
- When far apart the potential energy is the sum of the values for H and F_2
- When close enough their orbitals start to overlap
  - A bond starts to form between H and the closer F atom H · · ·F—F
  - The F—F bond starts to lengthen
- As H becomes closer still the H · · · F bond becomes shorter and stronger and the F—F bond becomes longer and weaker
  - The atoms enter the region of the activated complex
- When the three atoms reach the point of maximum potential energy (the transition state) a further infinitesimal compression of the H—F bond and stretch of the F—F bond takes the complex through the transition state.

Thermodynamic approach

$$A + B \overset{K^\ddagger}{\rightleftharpoons} \text{activated complex } AB^\ddagger \xrightarrow{k^\ddagger} \text{products} \qquad \textbf{where } K^\ddagger = \frac{[AB^\ddagger]}{[A][B]}$$

- Therefore rate of formation of products = $k^\ddagger [AB^\ddagger] = k^\ddagger K^\ddagger [A][B]$
- Compare this expression to the rate law: rate of formation of products = $k_r [A][B]$
- Hence the rate constant $k_r = k^\ddagger K^\ddagger$
- The Gibbs energy for the process is given by $\Delta^\ddagger G = -RT\ln(K^\ddagger)$ and so $K^\ddagger = \exp(-\Delta^\ddagger G/RT)$
- Hence rate constant $k_r = k^\ddagger \exp(-(\Delta^\ddagger H - T\Delta^\ddagger S)/RT)$.
- Hence $k_r = k^\ddagger \exp(\Delta^\ddagger S/R)\exp(-\Delta^\ddagger H/RT)$
- This expression has the same form as the Arrhenius expression.
  - The activation energy E_a relates to $\Delta^\ddagger H$
  - Pre-exponential factor $A = k^\ddagger \exp(\Delta^\ddagger S/R)$
  - The steric factor P can be related to the change in disorder at the transition state

Advantages of transition state theory

- Provides a complete description of the nature of the reaction including
    - the changes in structure and the distribution of energy through the transition state
    - the origin of the pre-exponential factor A with units t^{-1} that derive from frequency or velocity
    - the meaning of the activation energy E_a
- Rather complex fundamental theory can be expressed in an easily understood pictorial diagram of the transition state - plot of energy vs the reaction coordinate
- The pre-exponential factor A can be derived *a priori* from statistical mechanics in simple cases
- The steric factor P can be understood as related to the change in order of the system and hence the entropy change at the transition state
- Can be applied to reactions in gases or liquids
- Allows for the influence of other properties of the system on the transition state (e.g., solvent effects).

Disadvantage

- Not easy to estimate fundamental properties of the transition state except for very simple reactions
    - theoretical estimates of A and E_a may be 'in the right ball-park' but still need experimental values