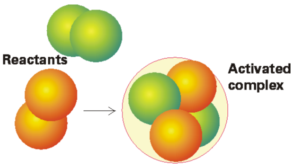
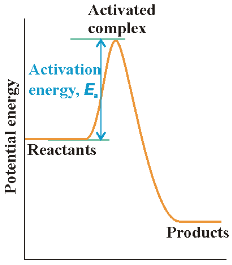
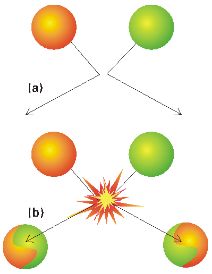




SF Chem 2201.
Chemical Kinetics
2011/2012.

Dr Mike Lyons
Room 3.2 Chemistry Building
School of Chemistry
Trinity College Dublin.
Email : melyons@tcd.ie

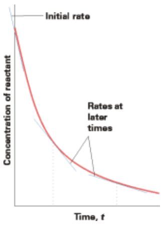


Course Summary.

- Contact short but sweet. **5** Lectures in total (4 this week, 1 next week, **3** tutorials next week).
- We revise quantitative aspects of JF kinetics and discuss some new more advanced topics and introduce the mathematical theory of chemical kinetics.
- Topics include:
  - **Lecture 1-2.** Quantitative chemical kinetics, integration of rate equations, zero, first, second order cases, rate constant . Graphical analysis of rate data for rate constant and half life determination for each case . Dependence of rate on temperature. Arrhenius equation and activation energy. Kinetics of complex multistep reactions. Parallel and consecutive reactions. Concept of rate determining step and reaction intermediate.
  - **Lecture 3,4.** Enzyme kinetics (Michaelis-Menten case) and surface reactions involving adsorbed reactants (Langmuir adsorption isotherm).
  - **Lecture 5.** Theory of chemical reaction rates : bimolecular reactions. Simple Collision Theory & Activated Complex Theory.

Recommended reading.

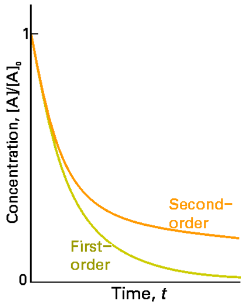
- Burrows et al **Chemistry**^{3}, OUP Chapter 8. pp.339-403.
- P.W. Atkins J. de Paula. ***The elements of physical chemistry.*** 4th edition. OUP (2005). Chapter 10, pp.229-256; Chapter 11, pp.257-284.
- P.W. Atkins and J. de Paula. **Physical Chemistry for the Life Sciences**. 1st edition. OUP (2005). Part II entitled The kinetics of life processes (Chapters 6,7,8) is especially good.
  - Both of these books by well established authors are clearly written with an excellent style and both provide an excellent basic treatment of reaction kinetics with emphasis on biological examples. These books are set at just the right level for the course and you should make every effort to read the recommended chapters in detail. Also the problem sheets will be based on problems at the end of these chapters!
- P.W. Atkins, J. de Paula. ***Physical Chemistry.*** 8th Edition. OUP (2006). Chapter 22, pp.791-829 ; Chapter 23, pp.830-868; Chapter 24, pp.869-908.
  - A more advanced and complete account of the course material. Much of chapter 24 is JS material.
- M.J. Pilling and P/W. Seakins. ***Reaction Kinetics.*** OUP (1995).
  - Modern textbook providing a complete account of modern chemical reaction kinetics. Good on experimental methods and theory.
- M. Robson Wright An introduction to chemical kinetics. Wiley (2005)
  - Another modern kinetics textbook which does as it states in the title, i.e. provide a readable introduction to the subject ! Well worth browsing through.

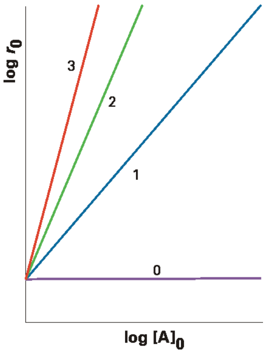


SF Chemical Kinetics.

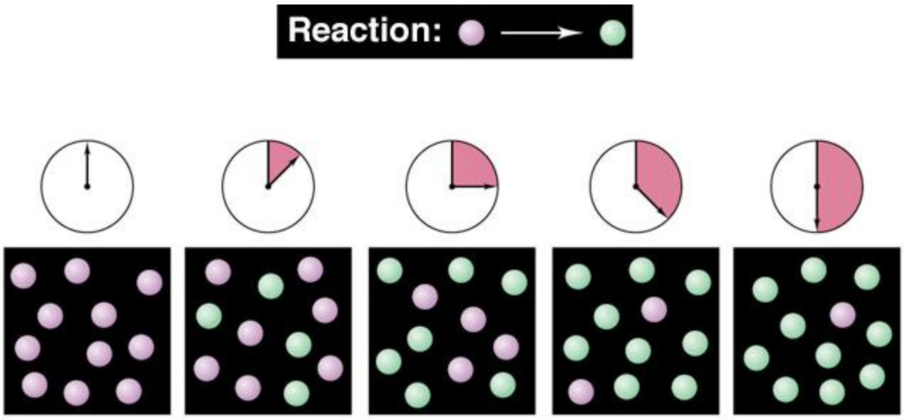
Lecture 1-2.

Quantitative Reaction Kinetics.





Reaction Rate: The Central Focus of Chemical Kinetics

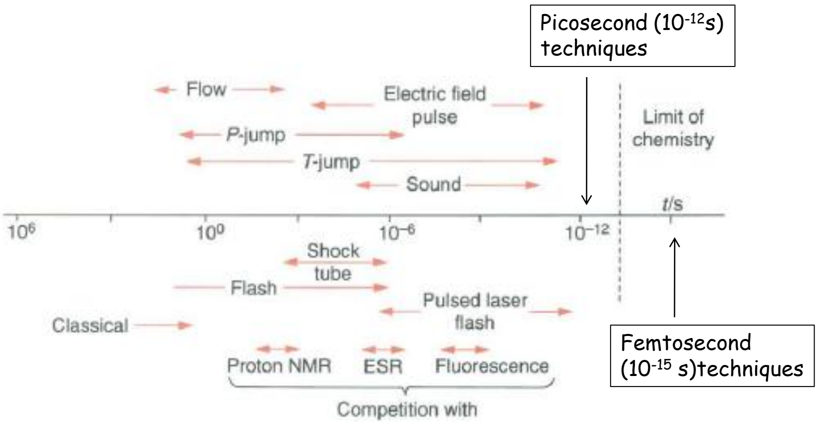


The wide range of reaction rates.

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

Reaction rates vary from very fast to very slow :
from femtoseconds to centuries !

1 femtosecond (fs)
= 10^{-15} s = $1/10^{15}$ s !



Picosecond (10^{-12}s) techniques

Femtosecond (10^{-15} s)techniques

Atkins de Paula, Elements Phys. Chem.
5th edition, Chapter 10, section 10.2, pp.221-222

Reactions studies under constant temperature conditions.
Mixing of reactants must occur more rapidly than reaction occurs.
Start of reaction pinpointed accurately.
Method of analysis must be much faster than reaction itself.

Chemical reaction kinetics.

- Chemical reactions involve the forming and breaking of chemical bonds.
- Reactant molecules (H_2, I_2) approach one another and collide and interact with appropriate energy and orientation. Bonds are stretched, broken and formed and finally product molecules (HI) move away from one another.
- How can we describe the rate at which such a chemical transformation takes place?

reactants products

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

- Thermodynamics tells us all about the energetic feasibility of a reaction : we measure the Gibbs energy ΔG for the chemical Reaction.
- Thermodynamics does not tell us how quickly the reaction will proceed : it does not provide kinetic information.

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.

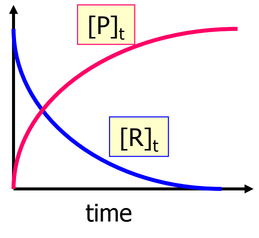
- What do we mean by the term reaction rate?
  - The term rate implies that something changes with respect to something else.
- How may reaction rates be determined ?
  - The reaction rate is quantified in terms of the change in concentration of a reactant or product species with respect to time.
  - 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.

Reactant concentration

Product concentration

$$\boxed{R_\Sigma = -\frac{d[R]}{dt} = \frac{d[P]}{dt}}$$

Net reaction rate
Units : mol dm^{-3} s^{-1}



Geometric definition of reaction rate.

Rate expressed as tangent line
To concentration/time curve at a
Particular time in the reaction.

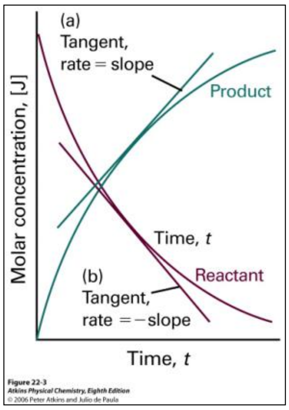
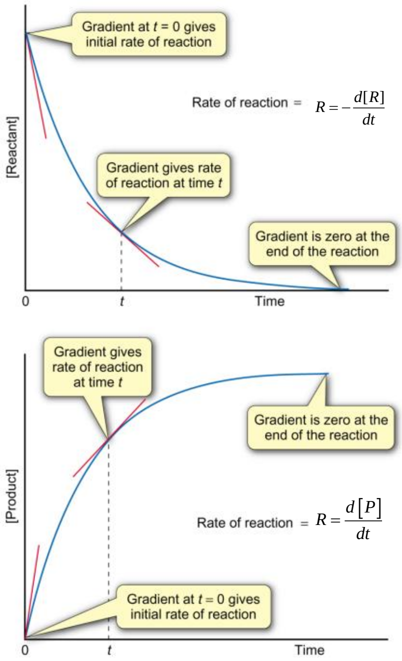


Figure 22-3
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula



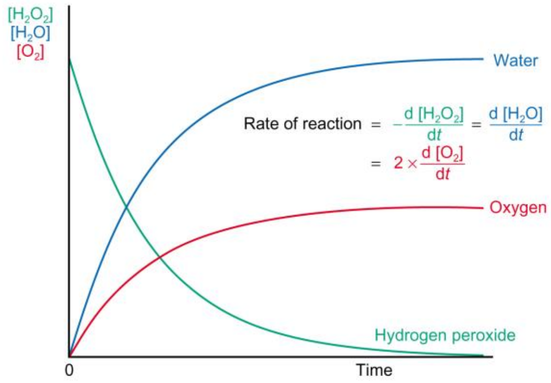
Reaction Rates and Reaction Stoichiometry

$O_3(g) + NO(g) \rightarrow NO_2(g) + O_2(g)$

$$\text{rate} = -\frac{d[O_3]}{dt} = -\frac{d[NO]}{dt} = +\frac{d[NO_2]}{dt} = +\frac{d[O_2]}{dt}$$

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

$2\,H_2O_2\,(aq) \rightarrow 2\,H_2O\,(l) + O_2\,(g)$



The general case.

- Why do we define our rate in this way?
  - removes ambiguity in the measurement of reaction rates in that we now obtain a single rate for the <u>entire equation</u>, not just for the change in a <u>single reactant or product</u>.

$$\boxed{aA + bB \rightarrow pP + qQ}$$

$$\boxed{\begin{aligned} Rate \quad R &= -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} \\ &= +\frac{1}{q}\frac{d[Q]}{dt} = +\frac{1}{p}\frac{d[P]}{dt} \end{aligned}}$$

Rate, rate equation and reaction order : formal definitions.

- 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.

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

$$2H_2(g)+O_2(g)\rightarrow 2H_2O(g)$$
$$R = -\frac{1}{2}\frac{d[H_2]}{dt} = -\frac{d[O_2]}{dt} = \frac{1}{2}\frac{d[H_2O]}{dt}$$

- **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.

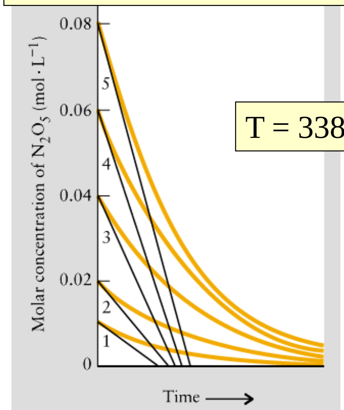
- Rate of reaction is often found to be proportional to the molar concentration of the reactants raised to a simple power (which need not be integral). This relationship is called the ***rate equation***. The manner in which the reaction rate changes in magnitude with changes in the magnitude of the concentration of each participating reactant species is called the ***reaction order***.

Reaction rate and reaction order.

- The reaction rate (reaction velocity) R is quantified in terms ofchanges in concentration [J] of reactant or product species J with respect to changes in time.
- The magnitude of the reaction rate changes (decreases) 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***.
- Hence in other words:
  - the reaction order is a measure of the sensitivity of the reaction rate to changes in the concentration of the reactants.

Working out a rate equation.

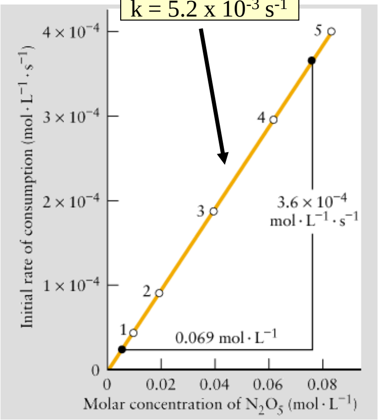
$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$



T = 338 K

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

k = 5.2 x 10^{-3} s^{-1}



Initial rate is proportional to initial concentration of reactant.

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

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

k = rate constant

Rate Equation.

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

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

stoichiometric coefficients

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

rate constant k

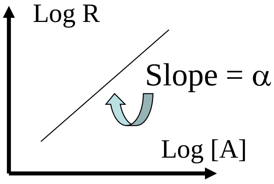
$$R = -\frac{1}{x}\frac{d[A]}{dt} = -\frac{1}{y}\frac{d[B]}{dt} = k[A]^{\alpha}[B]^{\beta}$$

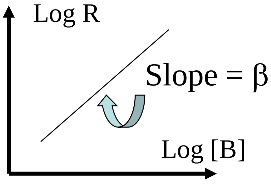
α, β = ***reaction orders*** *for the reactants (got experimentally)*

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.





Different rate equations imply different mechanisms.

$$H_2 + X_2 \rightarrow 2HX$$
$$X = I, Br, Cl$$

$$H_2 + I_2 \rightarrow 2HI$$
$$R = \frac{d[HI]}{dt} = k[H_2][I_2]$$
$$H_2 + Br_2 \rightarrow 2HBr$$
$$R = \frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{1/2}}{1 + \frac{k'[HBr]}{[Br_2]}}$$
$$H_2 + Cl_2 \rightarrow 2HCl$$
$$R = \frac{d[HCl]}{dt} = k[H_2][Cl_2]^{1/2}$$

- The rate law provides an important guide to reaction mechanism, since any proposed mechanism must be consistent with the observed rate law.
- A complex rate equation will imply a complex multistep reaction mechanism.
- Once we know the rate law and the rate constant for a reaction, we can predict the rate of the reaction for any given composition of the reaction mixture.
- We can also use a rate law to predict the concentrations of reactants and products at any time after the start of the reaction.

Integrated rate equation.

Burrows et al Chemistry^3, Chapter 8, pp.349-356.
Atkins de Paula 5th ed. Section 10.7,10.8, pp.227-232

- Many rate laws can be cast as differential equations which may then be solved (integrated) using standard methods to finally yield an expression for the reactant or product concentration as a function of time.
- We can write the general rate equation for the process A → Products as
$$-\frac{dc}{dt} = kF(c)$$
where F(c) represents some distinct function of the reactant concentration c. One common situation is to set $F(c) = c^n$ where n = 0,1,2,... and the exponent n defines the reaction order wrt the reactant concentration c.
- The differential rate equation may be integrated once to yield the solution c = c(t) provided that the initial condition at zero time which is $c = c_0$ is introduced.

Zero order kinetics.

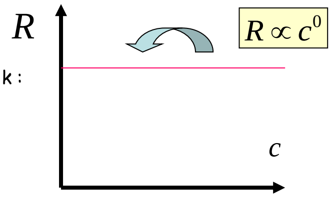
The reaction proceeds at the same rate R regardless of concentration.

Rate equation :

$$R = -\frac{dc}{dt} = k$$

$$c = c_0 \text{ when } \quad t = 0$$

units of rate constant k : mol dm^{-3} s^{-1}

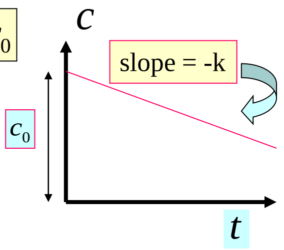


$$R \propto c^0$$

integrate using initial condition

$$c(t) = -kt + c_0$$

diagnostic plot



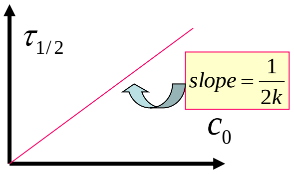
c_0

slope = -k

half life

$$t = \tau_{1/2} \text{ when } \quad c = \frac{c_0}{2}$$

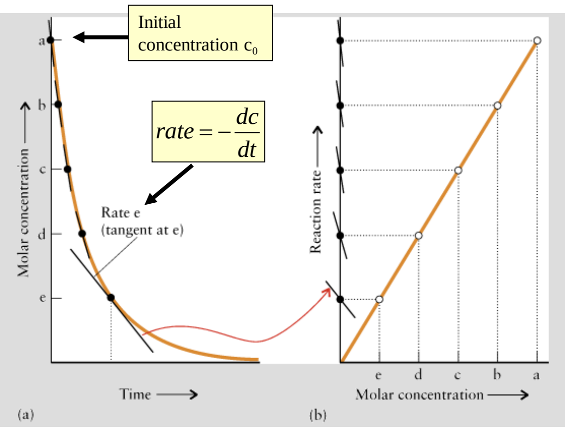
$$\tau_{1/2} = \frac{c_0}{2k} \qquad \tau_{1/2} \propto c_0$$



$$slope = \frac{1}{2k}$$

First order kinetics.

$$A \xrightarrow{k} \text{products}$$



Initial concentration c_0

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

First order differential rate equation.

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

Initial condition

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

Solve differential equation Via separation of variables

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

Reactant concentration as function of time.

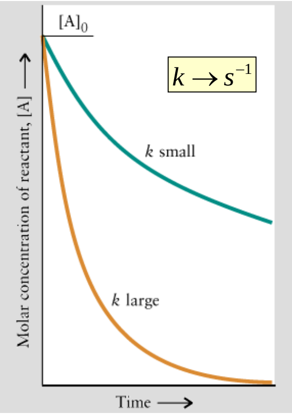
First order reaction

$$(rate)_t \propto c$$

$$(rate)_t = kc$$

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

First order kinetics.



$k \to s^{-1}$

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

$$u = \frac{c(t)}{c_0} = \exp[-\theta]$$

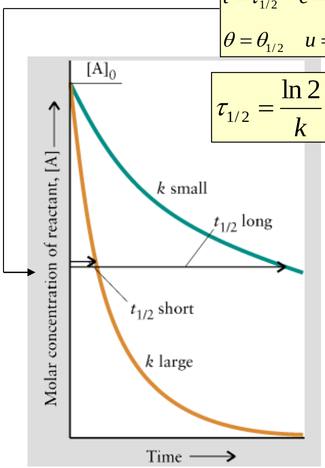
$$\theta = kt$$

Half life $\tau_{1/2}$

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

$\theta = \theta_{1/2} \quad u = 1/2$

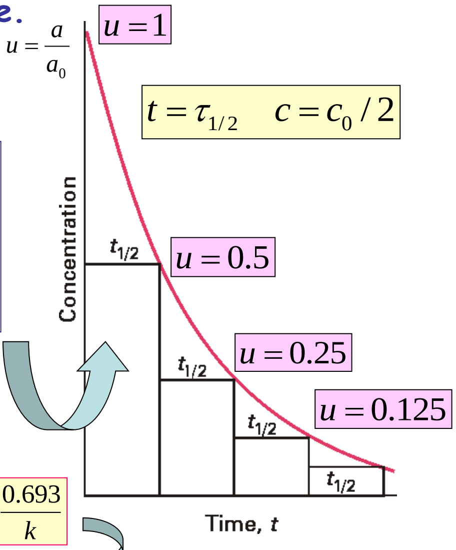
$$\tau_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$



Mean lifetime of reactant molecule

$$\tau = \frac{1}{c_0}\int_0^\infty c(t)\,dt = \frac{1}{c_0}\int_0^\infty c_0 e^{-kt}\,dt = \frac{1}{k}$$

First order kinetics: half life.



$u = 1$

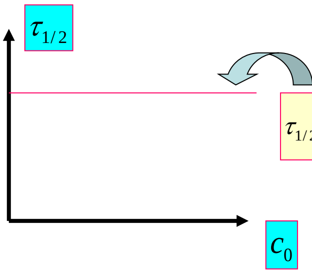
$t = \tau_{1/2} \quad c = c_0 / 2$

$u = 0.5$

$u = 0.25$

$u = 0.125$

In each successive period of duration $t_{1/2}$ 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

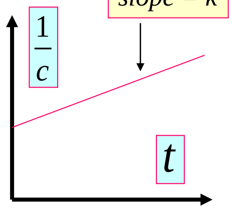
Second order kinetics: equal reactant concentrations.

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

$$-\frac{dc}{dt} = kc^2$$
$$t = 0 \quad c = c_0$$

separate variables
integrate

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



dm^{3}mol^{-1}s^{-1}

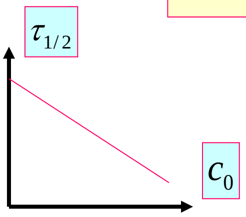
slope = k

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

half life

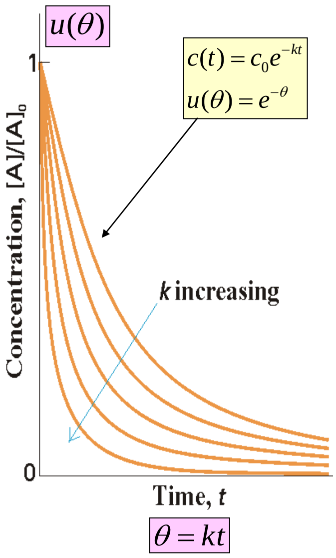
$$t = \tau_{1/2} \quad c = \frac{c_0}{2}$$

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



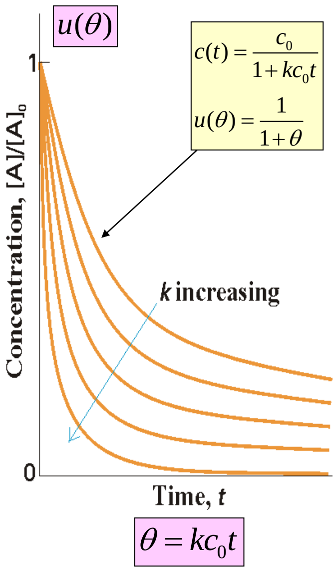
rate varies as square of reactant concentration

1st order kinetics



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

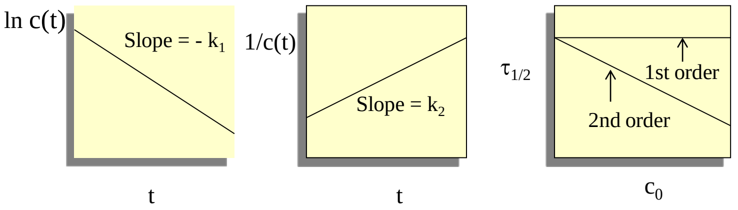
2nd order kinetics



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

1st and 2nd order kinetics : Summary .

Reaction	Differential rate equation	Concentration variation with time	Diagnostic Equation	Half Life
$A \xrightarrow{k_1}$ Products	$-\frac{dc}{dt}=k_1c$	$c(t)=$ $c_0\exp[-k_1t]$	$\ln c(t)=-k_1t+\ln c_0$	$\tau_{1/2}=\frac{\ln 2}{k_1}$
$2A \xrightarrow{k_2}$ Products	$-\frac{dc}{dt}=k_2c^2$	$c(t)=$ $\frac{c_0}{1+k_2c_0t}$	$\frac{1}{c(t)}=k_2t+\frac{1}{c_0}$	$\tau_{1/2}=\frac{1}{k_2c_0}$



Diagnostic Plots .

n th order kinetics: equal reactant concentrations.

$$nA \xrightarrow{k} P$$

$$-\frac{dc}{dt}=kc^n$$
$$t=0 \quad c=c_0$$

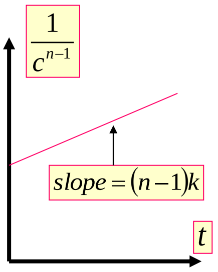
separate variables
integrate

$$\frac{1}{c^{n-1}}=(n-1)kt+\frac{1}{c_0{}^{n-1}}$$

$$n \neq 1$$

$$n = 0, 2, 3, \ldots..$$

rate constant k obtained from slope



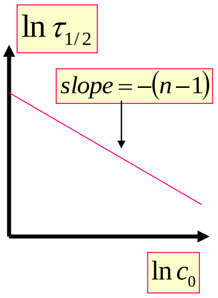
Half life

$$\tau_{1/2}=\frac{2^{n-1}-1}{(n-1)kc_0{}^{n-1}}$$

$$\ln\tau_{1/2}=\ln\left\{\frac{2^{n-1}-1}{(n-1)k}\right\}-(n-1)\ln c_0$$

$$\tau_{1/2}\propto c_0{}^{1-n}$$
$$n>1 \quad \tau_{1/2}\downarrow \; as \; c_0\uparrow$$
$$n<1 \quad \tau_{1/2}\uparrow \; as \; c_0\uparrow$$

reaction order n determined from slope



Summary of kinetic results.

$$nA \xrightarrow{k} P$$

$$t = 0 \quad c = c_0$$
$$t = \tau_{1/2} \quad c = \frac{c_0}{2}$$

Rate equation

Reaction Order	$R = -\frac{dc}{dt}$	Integrated expression	Units of k	Half life $\tau_{1/2}$
0	k	$c(t) = -kt + c_0$	mol dm^{-3}s^{-1}	$\frac{c_0}{2k}$
1	kc	$\ln\left\{\frac{c_0}{c(t)}\right\} = kt$	s^{-1}	$\frac{\ln 2}{k}$
2	kc^2	$\frac{1}{c(t)} = kt + \frac{1}{c_0}$	dm^{3}mol^{-1}s^{-1}	$\frac{1}{kc_0}$
3	kc^3	$\frac{1}{c^2(t)} = 2kt + \frac{1}{c_0{}^2}$	dm^{6}mol^{-2}s^{-1}	$\frac{3}{2kc_0{}^2}$
n	kc^n	$\frac{1}{c^{n-1}} = (n-1)kt + \frac{1}{c_0{}^{n-1}}$		$\frac{1}{n-1}\left\{\frac{2^{n-1}-1}{kc_0{}^{n-1}}\right\}$

Second order kinetics: Unequal reactant concentrations.

$$A + B \xrightarrow{k} P$$

rate equation

$$R = -\frac{da}{dt} = -\frac{db}{dt} = \frac{dp}{dt} = kab$$

initial conditions

$$t = 0 \quad a = a_0 \quad b = b_0 \quad a_0 \neq b_0$$

↓ *integrate using partial fractions*

$$F(a,b) = \frac{1}{b_0 - a_0}\left\{\ln\left(\frac{b/b_0}{a/a_0}\right)\right\} = kt$$

half life

$$\tau_{1/2} = \frac{\ln\left\{2 - \frac{1}{\zeta}\right\}}{ka_0(\zeta - 1)}$$

$$\zeta = \frac{b_0}{a_0}$$

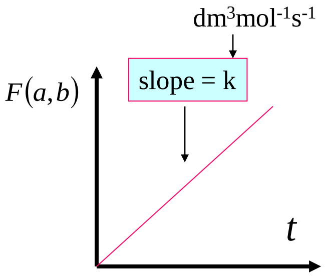
Pseudo first order kinetics when $b_0 >> a_0$

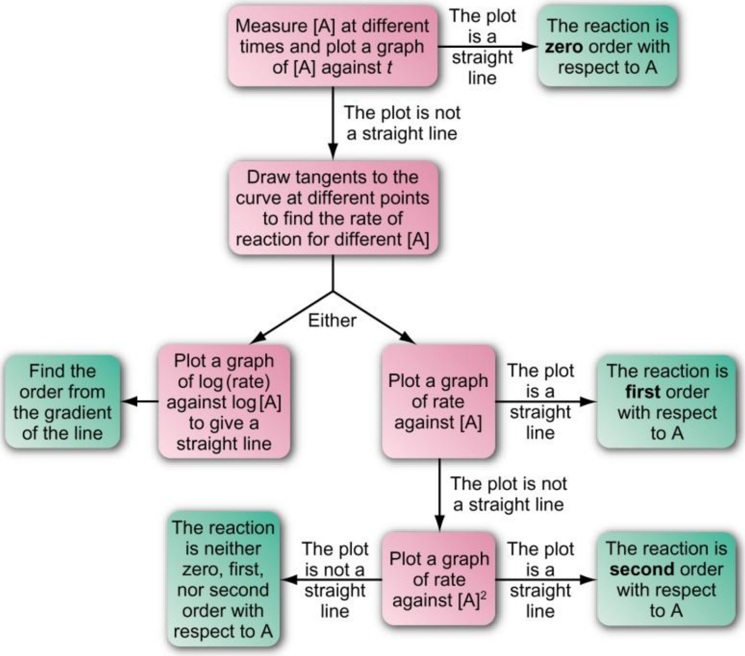
$$\zeta >> 1 \quad \frac{1}{\zeta} \to 0$$

$$\tau_{1/2} \cong \frac{\ln 2}{kb_0} = \frac{\ln 2}{k'}$$

$$k' = kb_0$$

pseudo 1st order rate constant

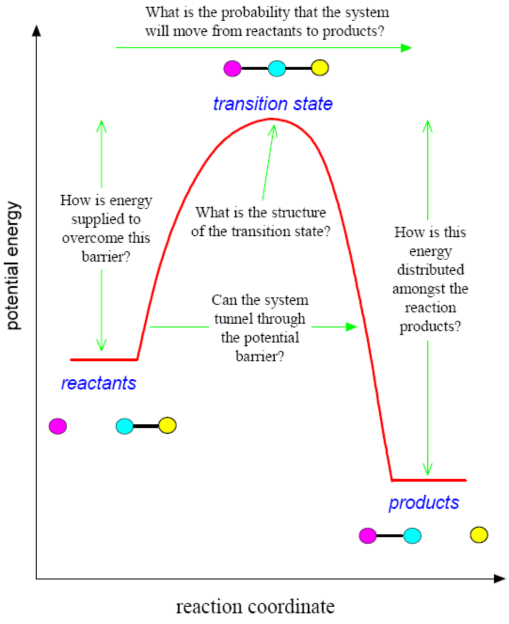




Temp Effects in Chemical Kinetics.

Atkins de Paula
Elements P Chem 5th edition
Chapter 10, pp.232-234

Burrows et al Chemistry^3,
Section 8.7,
pp.383-389.



Van't Hoff expression:

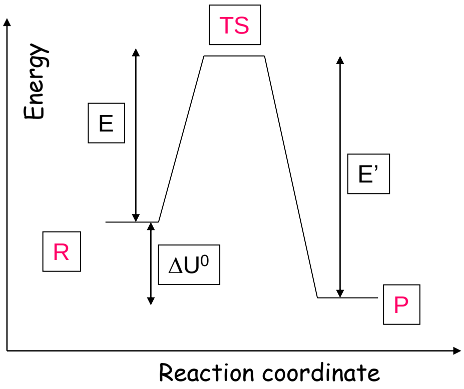
$$\left(\frac{d\ln K_c}{dT}\right)_P = \frac{\Delta U^0}{RT^2}$$

Standard change in internal energy:

$$\Delta U^0 = E - E'$$

$$R \underset{k'}{\overset{k}{\rightleftharpoons}} P$$

$$K_c = \frac{k}{k'}$$



$$\left(\frac{d}{dT}\ln\left(\frac{k}{k'}\right)\right)_P = \frac{d\ln k}{dT} - \frac{d\ln k'}{dT} = \frac{\Delta U^0}{RT^2}$$

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

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

This leads to formal definition of Activation Energy.

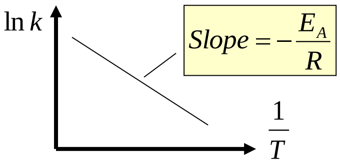
Temperature effects in chemical kinetics.

- 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.

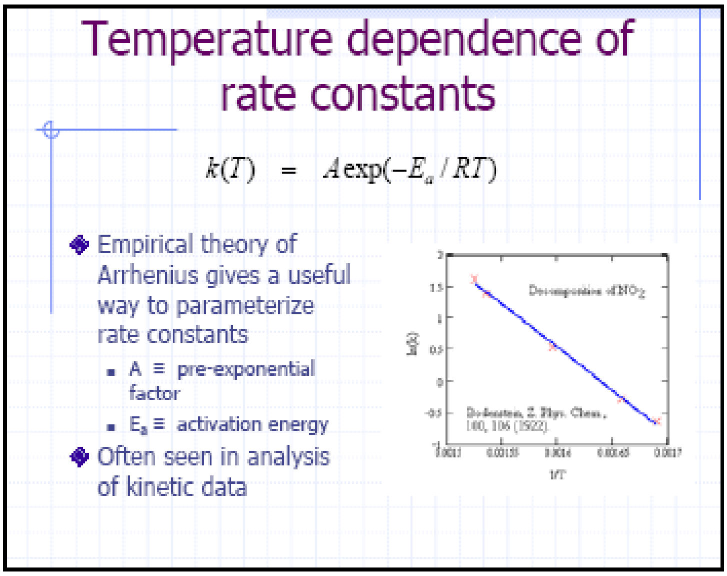
$$k = A\exp\left[-\frac{E_A}{RT}\right]$$

Pre-exponential factor

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



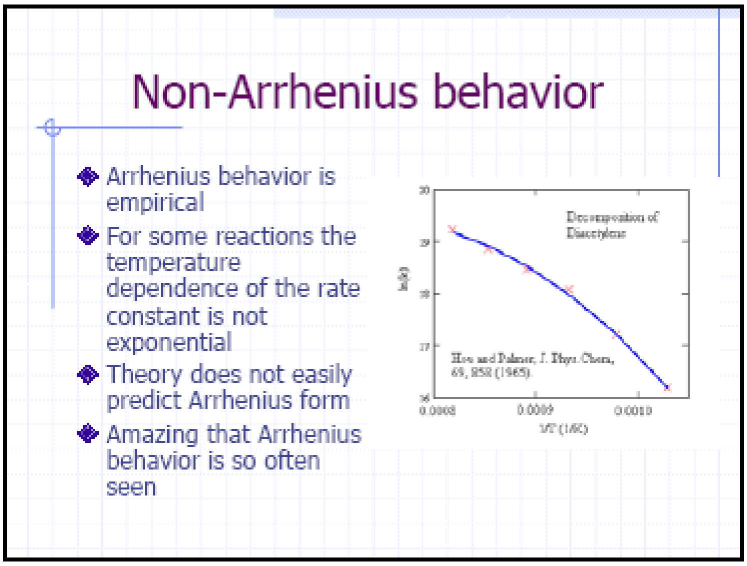
$$Slope = -\frac{E_A}{R}$$



Temperature dependence of rate constants

$$k(T) = A\exp(-E_a / RT)$$

- Empirical theory of Arrhenius gives a useful way to parameterize rate constants
  - A ≡ pre-exponential factor
  - E_a ≡ activation energy
- Often seen in analysis of kinetic data



Non-Arrhenius behavior

- Arrhenius behavior is empirical
- For some reactions the temperature dependence of the rate constant is not exponential
- Theory does not easily predict Arrhenius form
- Amazing that Arrhenius behavior is so often seen

In some circumstances the Arrhenius Plot is curved which implies that the Activation energy is a function of temperature.
Hence the rate constant may be expected to vary with temperature according to the following expression.

$$\boxed{k = aT^m \exp\left[-\frac{E}{RT}\right]}$$

We can relate the latter expression to the Arrhenius parameters A and E_A as follows.

$$\begin{aligned}
&\ln k = \ln a + m \ln T - \frac{E}{RT} \\
&E_A = RT^2\left(\frac{d\ln k}{dT}\right) = RT^2\left\{\frac{m}{T} + \frac{E}{RT^2}\right\} = E + mRT \\
&E = E_A - mRT
\end{aligned}$$

Hence

$$\begin{aligned}
&k = aT^m e^m \exp\left[-\frac{E_A}{RT}\right] = A\exp\left[-\frac{E_A}{RT}\right] \\
&A = aT^m e^m
\end{aligned}$$

Svante August Arrhenius

Consecutive Reactions .

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

- Mother / daughter radioactive decay.

$$^{218}Po \rightarrow {}^{214}Pb \rightarrow {}^{214}Bi$$
$$k_1 = 5\times10^{-3}s^{-1} \quad k_2 = 6\times10^{-4}s^{-1}$$

Mass balance requirement:

$$p = a_0 - a - x$$

3 coupled LDE's define system :

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

The solutions to the coupled equations are :

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

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

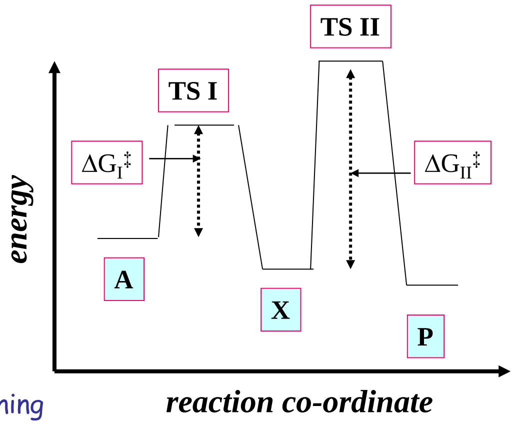
Consecutive reaction : Case I.
Intermediate formation fast, intermediate decomposition slow.

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

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

I : fast *II : slow rds*

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



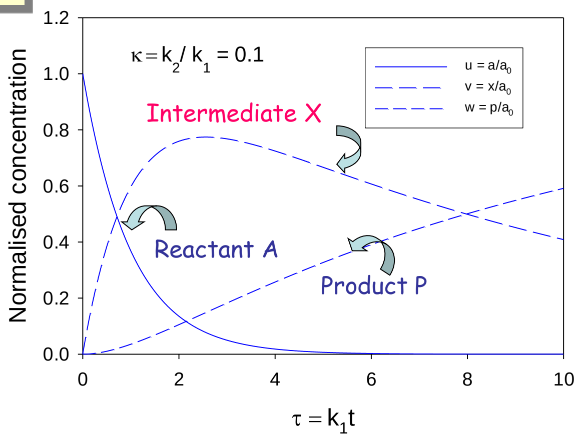
Step II is rate determining since it has the highest activation energy barrier.

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

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

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

$$u = \frac{a}{a_0}$$
$$v = \frac{x}{a_0}$$
$$w = \frac{p}{a_0}$$



Initial reactant A more reactive than intermediate X .

Concentration of intermediate significant over time course of reaction.

Consecutive reactions Case II:
Intermediate formation slow, intermediate decomposition fast.

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

key parameter

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

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

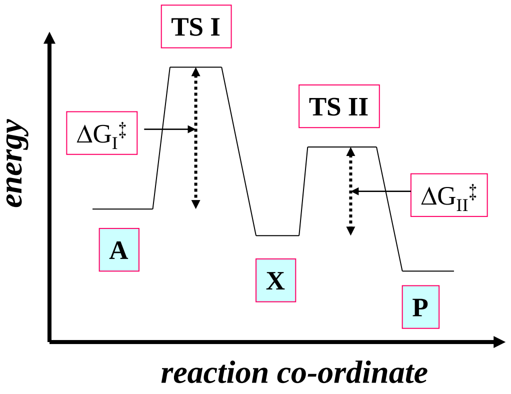
$k_2 >> k_1$

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

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

I : slow rds ***II : fast***

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



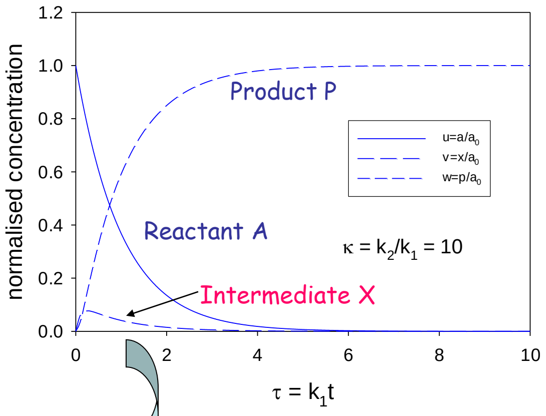
Step I rate determining since it has the highest activation energy barrier.

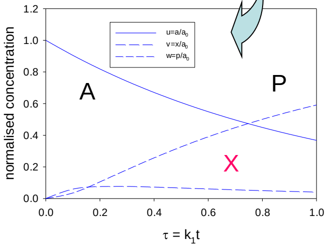
$$A \xrightarrow{k_1} X \xrightarrow{k_2} P$$

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

$k_2 >> k_1$

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





Intermediate concentration is approximately constant after initial induction period.

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

Rate Determining Step

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

Fast Slow

- 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

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

Slow Fast

- 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).

Parallel reaction mechanism.

$$\boxed{\begin{array}{l} A \xrightarrow{k_1} X \\ A \xrightarrow{k_2} Y \end{array}}$$

k_1, k_2 = 1st order rate constants

- We consider the kinetic analysis of a concurrent or parallel reaction scheme which is often met in real situations.
- A single reactant species can form two distinct products.

We assume that each reaction exhibits 1st order kinetics.

- Initial condition : t= 0, $a = a_0$; x = 0, y = 0
- Rate equation:

$$\boxed{R = -\frac{da}{dt} = k_1 a + k_2 a = (k_1 + k_2)a = k_\Sigma a}$$

$$\boxed{a(t) = a_0 \exp[-k_\Sigma t] = a_0 \exp[-(k_1 + k_2)t]}$$

- Half life: $\boxed{\tau_{1/2} = \frac{\ln 2}{k_\Sigma} = \frac{\ln 2}{k_1 + k_2}}$

- All of this is just an extension of simple 1st order kinetics.

We can also obtain expressions for the product concentrations x(t) and y(t).

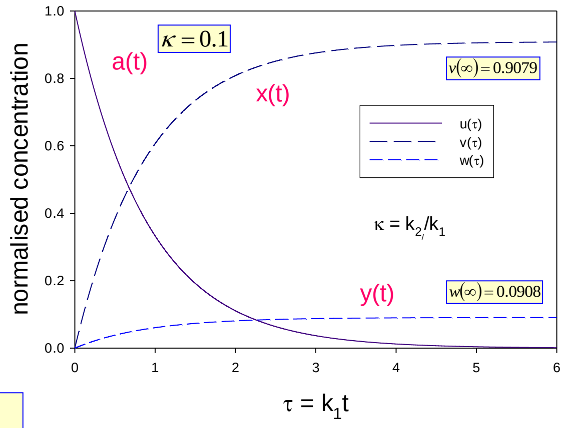
$$\boxed{\begin{aligned} \frac{dx}{dt} &= k_1 a = k_1 a_0 \exp[-(k_1 + k_2)t] \\ x(t) &= k_1 a_0 \int_0^t \exp[-(k_1 + k_2)t]\,dt \\ x(t) &= \frac{k_1 a_0}{k_1 + k_2}\{1 - \exp[-(k_1 + k_2)t]\} \end{aligned}}$$

$$\boxed{\begin{aligned} \frac{dy}{dt} &= k_2 a = k_2 a_0 \exp[-(k_1 + k_2)t] \\ y(t) &= k_2 a_0 \int_0^t \exp[-(k_1 + k_2)t]\,dt \\ y(t) &= \frac{k_2 a_0}{k_1 + k_2}\{1 - \exp[-(k_1 + k_2)t]\} \end{aligned}}$$

Final product analysis yields rate constant ratio.

$$\boxed{\lim_{t \to \infty} \frac{x(t)}{y(t)} = \frac{k_1}{k_2}}$$

Parallel Mechanism: $k_1 >> k_2$

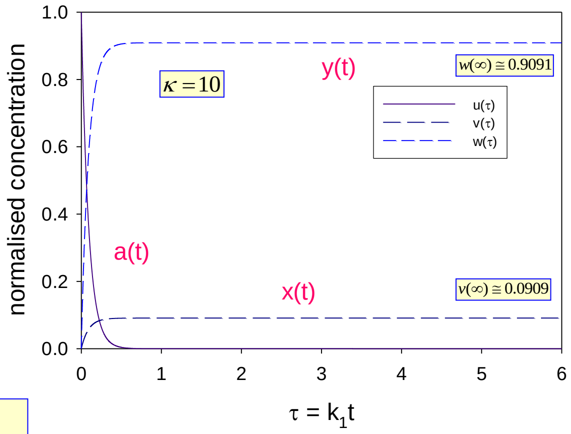


Theory

$$\kappa = \frac{k_2}{k_1} = 0.1$$

$$\frac{k_1}{k_2} = 10 = \frac{v(\infty)}{w(\infty)}$$

Parallel Mechanism: $k_2 >> k_1$

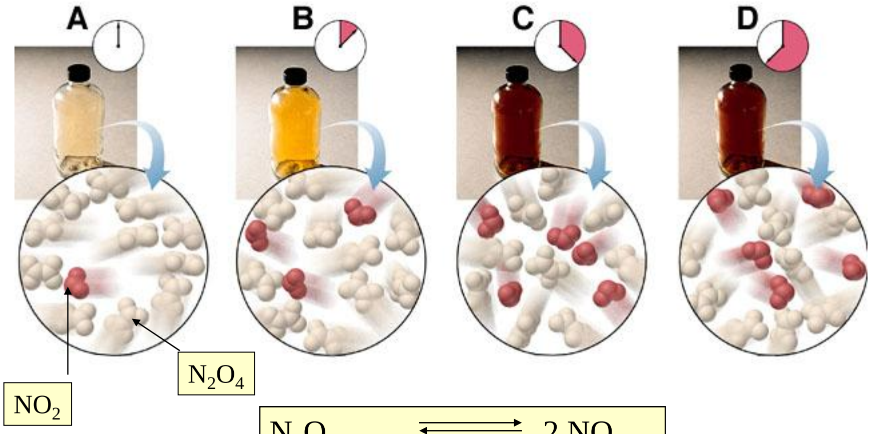


Theory

$$\kappa = \frac{k_2}{k_1} = 10$$

$$\frac{k_1}{k_2} = 0.1 = \frac{v(\infty)}{w(\infty)}$$

Reaching Equilibrium on the Macroscopic and Molecular Level



$$N_2O_{4\,(g)} \rightleftharpoons 2\ NO_{2\,(g)}$$

colourless brown

Chemical Equilibrium : a kinetic definition.

- Countless experiments with chemical systems have shown that in a state of equilibrium, the concentrations of reactants and products no longer change with time.
- This apparent cessation of activity occurs because under such conditions, all reactions are microscopically reversible.
- We look at the dinitrogen tetraoxide/ nitrogen oxide equilibrium which occurs in the gas phase.

$$N_2O_{4\,(g)} \rightleftharpoons 2\ NO_{2\,(g)}$$

colourless brown

Kinetic analysis.

$\vec{R} = k[N_2O_4]$

$\overleftarrow{R} = k'[NO_2]^2$

Valid for any time t

Equilibrium: $t \to \infty$

$\vec{R} = \overleftarrow{R}$

$k[N_2O_4]_{eq} = k'[NO_2]_{eq}^2$

$$\frac{[NO_2]_{eq}^2}{[N_2O_4]} = \frac{k}{k'} = K$$

Equilibrium constant

Concentrations vary with time

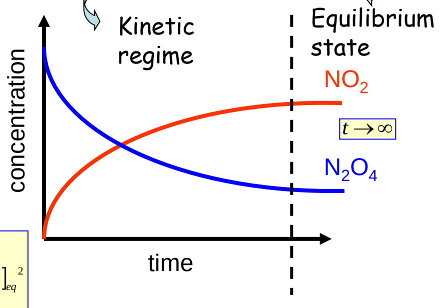
$[NO_2]_t \uparrow$

$[N_2O_4]_t \downarrow$

Concentrations time invariant

$[NO_2]_{eq}$

$[N_2O_4]_{eq}$



First order reversible reactions : understanding the approach to chemical equilibrium.

$$A \underset{k'}{\overset{k}{\rightleftharpoons}} B$$

Rate equation

$$\frac{da}{dt} = -ka + k'b$$

Initial condition

$$t = 0 \quad a = a_0 \quad b = 0$$

Mass balance condition

$$\forall t \quad a + b = a_0$$

Introduce normalised variables.

$$u = \frac{a}{a_0} \quad v = \frac{b}{a_0} \quad \tau = (k + k')t \quad \theta = \frac{k}{k'}$$

$$u + v = 1$$
$$\tau = 0 \quad u = 1 \quad v = 0$$

Rate equation in normalised form

$$\frac{du}{d\tau} + u = \frac{1}{1+\theta}$$

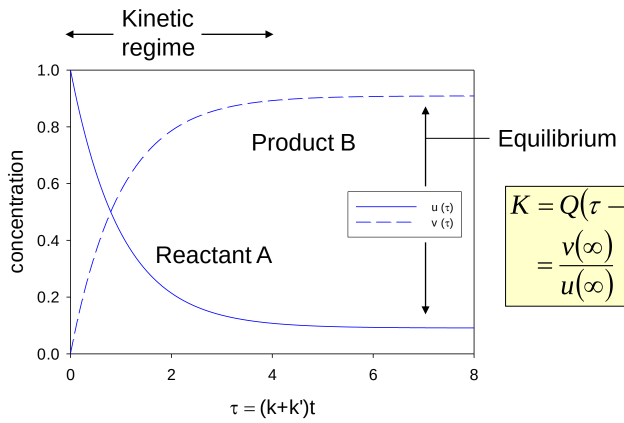
Solution produces the concentration expressions

$$u(\tau) = \frac{1}{1+\theta}\{1 + \theta \exp[-\tau]\}$$
$$v(\tau) = \frac{\theta}{1+\theta}\{1 - \exp[-\tau]\}$$

$$Q(\tau) = \frac{v(\tau)}{u(\tau)} = \theta\left\{\frac{1 - \exp[-\tau]}{1 + \theta \exp[-\tau]}\right\}$$

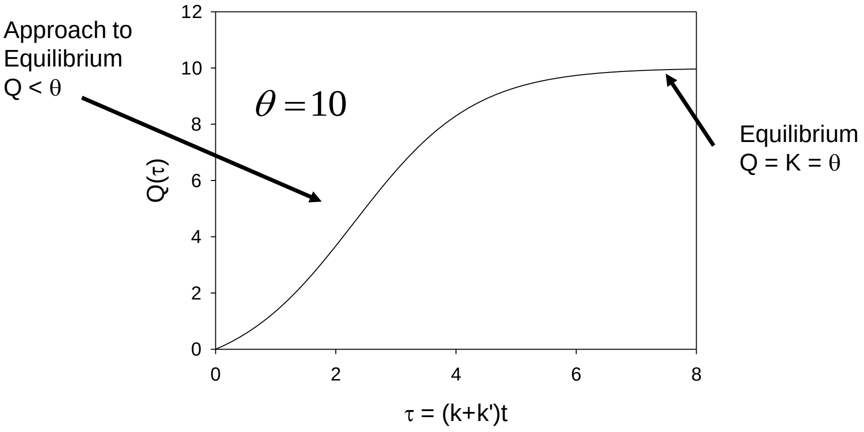
Reaction quotient Q

First order reversible reactions: approach to equilibrium.



$$K = Q(\tau \to \infty) = \frac{v(\infty)}{u(\infty)}$$

Understanding the difference between reaction quotient Q and Equilibrium constant K.



Approach to Equilibrium $Q < \theta$

Equilibrium $Q = K = \theta$

$$Q(\tau)=\frac{v(\tau)}{u(\tau)}=\theta\left\{\frac{1-\exp[-\tau]}{1+\theta\exp[-\tau]}\right\}$$

$$t \to \infty \quad Q \to K = \theta = \frac{k}{k'}$$

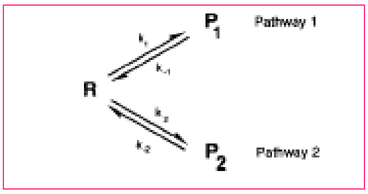
$$K = \frac{v(\infty)}{u(\infty)}$$

Kinetic versus Thermodynamic control.

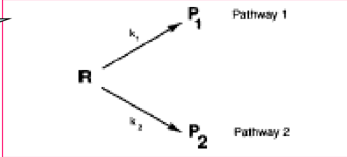
- In many chemical reactions the competitive formation of side products is a common and often unwanted phenomenon.
- It is often desirable to optimize the reaction conditions to maximize selectivity and hence optimize product formation.
- **Temperature** is often a parameter used to modify selectivity.

Refer to JCE papers dealing with this topic given as extra handout.

- Operating at low temperature is generally associated with the idea of high selectivity (this is termed **kinetic** control). Conversely, operating at high temperature is associated with low selectivity and corresponds to **Thermodynamic** control.
- **Time** is also an important parameter. At a given temperature, although the kinetically controlled product predominates at short times, the thermodynamically controlled product will predominate if the reaction time is long enough.



Short reaction times



Assume that reaction product P_1 is less stable than the product P_2. Also its formation is assumed to involve a lower activation energy E_A.

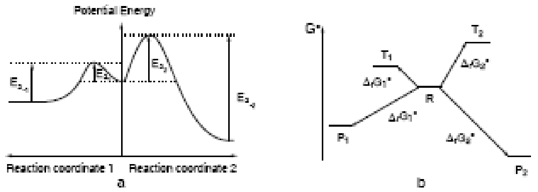
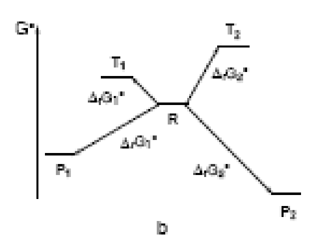


Figure 1. Energy diagrams associated with scheme 1 to illustrate the kinetic or thermodynamic control of reaction. a: Potential energy as a function of the two independent reaction coordinates associated with the pathways 1 and 2. E_a represents the activation energy of the pathway under consideration. b: Horizontally expanded representation of the standard Gibbs free energies of the reactant R, the products P_1 and P_2, and the transition states T_1 and T_2. $\Delta_r G°$ and $\Delta_r G^{°\neq}$ respectively designate the standard Gibbs function and the standard Gibbs free energy of activation for each reaction pathway.

Temperature effect.

- **Kinetic control.**
  - Assume that energy of products $P_1$and P_2 are much lower than that of the reactant R then $E_{A,1} \ll E_{A,-1}$ and $E_{A,2} \ll E_{A,-2}$.
  - At low temperature one neglects the fraction of molecules having an energy high enough to re-cross the energy barrier from products to reactants.
  - Under such conditions the product ratio $[P_1]/[P_2]$ is determined only by the activation barriers for the forward R → P reaction steps.
- Thermodynamic control.
  - At high temperature the available thermal energy is considered large enough to assume that energy barriers are easily crossed. Thermodynamic equilibrium is reached and the product ratio $[P_1]/[P_2]$ is now determined by the relative stability of the products P_1 and P_2.



$$k_j = A\exp\left[-\frac{\Delta G_j^*}{RT}\right]$$

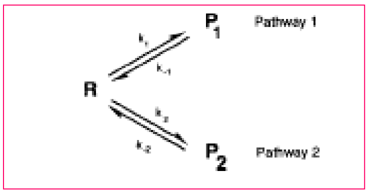
$$\frac{[P_1]}{[P_2]} = \frac{k_1}{k_2} = \exp\left[-\frac{\left(\Delta G_1^* - \Delta G_2^*\right)}{RT}\right]$$

$$\frac{[P_1]}{[P_2]} = \frac{K_1}{K_2} = \exp\left[-\frac{\left(\Delta G_1^0 - \Delta G_2^0\right)}{RT}\right]$$

$$-\frac{d[R]}{dt} = (k_1 + k_2)[R] - k_{-1}[P_1] - k_{-2}[P_2]$$

$$\frac{d[P_1]}{dt} = k_1[R] - k_{-1}[P_1]$$

$$\frac{d[P_2]}{dt} = k_2[R] - k_{-2}[P_2]$$



Short time Approximation. Neglect k$_{-1}$, k$_{-2}$ terms.

Long time approximation.

$$\frac{d[R]}{dt} = \frac{d[P_1]}{dt} = \frac{d[P_2]}{dt} = 0$$

$$[R]_\infty = \frac{[R]_0}{1 + K_1 + K_2}$$

$$[P_1]_\infty = \frac{K_1[R]_0}{1 + K_1 + K_2}$$

$$[P_2]_\infty = \frac{K_2[R]_0}{1 + K_1 + K_2}$$

$$\frac{[P_1]_\infty}{[P_2]_\infty} = \frac{K_1}{K_2}$$

Thermodynamic control limit.

$$[R] = [R]_0 \exp[-(k_1 + k_2)t]$$

$$[P_1] = \frac{k_1[R]_0}{k_1 + k_2}\{1 - \exp[-(k_1 + k_2)t]\}$$

$$[P_2] = \frac{k_2[R]_0}{k_1 + k_2}\{1 - \exp[-(k_1 + k_2)t]\}$$

$$\frac{t}{\tau} = \frac{t}{(k_1 + k_2)} >> 1$$

$$[P_1] \cong \frac{k_1[R]_0}{k_1 + k_2}$$

$$[P_2] \cong \frac{k_2[R]_0}{k_1 + k_2}$$

$$\frac{[P_1]}{[P_2]} = \frac{k_1}{k_2}$$

Kinetic control Limit.

General solution valid for intermediate times.

$$[R] = [R]_0\left\{\frac{k_{-1}k_{-2}}{\lambda_1\lambda_2} + \frac{(\lambda_1 + k_{-2})(\lambda_1 + k_{-1})}{\lambda_1(\lambda_1 - \lambda_2)}\exp[\lambda_1 t] + \frac{(\lambda_2 + k_{-1})(\lambda_2 + k_{-2})}{\lambda_2(\lambda_2 - \lambda_1)}\exp[\lambda_2 t]\right\}$$

$$[P_1] = [R]_0\left\{\frac{k_1k_{-2}}{\lambda_1\lambda_2} + \frac{k_1(\lambda_1 + k_{-2})}{\lambda_1(\lambda_1 - \lambda_2)}\exp[\lambda_1 t] + \frac{k_1(\lambda_2 + k_{-2})}{\lambda_2(\lambda_2 - \lambda_1)}\exp[\lambda_2 t]\right\}$$

$$[P_2] = [R]_0\left\{\frac{k_{-1}k_2}{\lambda_1\lambda_2} + \frac{k_2(\lambda_1 + k_{-1})}{\lambda_1(\lambda_1 - \lambda_2)}\exp[\lambda_1 t] + \frac{k_2(\lambda_2 + k_{-1})}{\lambda_2(\lambda_2 - \lambda_1)}\exp[\lambda_2 t]\right\}$$

$$\lambda_{1,2} = -\frac{\beta \pm \sqrt{\beta^2 - 4\gamma}}{2} = -\frac{\beta}{2}\left\{1 \pm \sqrt{1 - \frac{4\gamma}{\beta^2}}\right\}$$

$$\beta = k_1 + k_2 + k_{-1} + k_{-2}$$

$$\gamma = k_1k_{-2} + k_{-1}k_2 + k_{-1}k_{-2}$$

These expressions reproduce the correct limiting forms corresponding to kinetic and Thermodynamic control in the limits of short and long time respectively.

Quasi-Steady State Approximation. QSSA

- Detailed mathematical analysis of complex reaction mechanisms is difficult.
  Some useful methods for solving sets of coupled linear differential rate equations include **matrix methods** and **Laplace Transforms**.
- In many cases utilisation of the quasi steady state approximation
  leads to a considerable simplification in the kinetic analysis.

The ***QSSA*** *assumes that after an initial induction period (during which the concentration x of intermediates X rise from zero), and during the major part of the reaction, the rate of change of concentrations of all reaction intermediates are negligibly small.*

Mathematically , QSSA implies

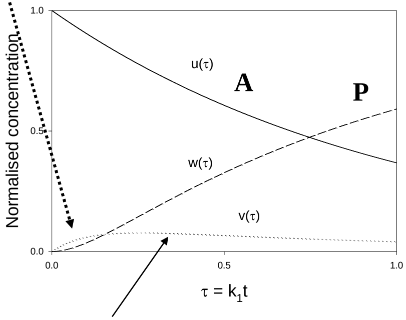
$$\frac{dx}{dt} = R_{X\ formation} - R_{X\ removal} \cong 0$$

$$R_{X\ formation} = R_{X\ removal}$$

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

induction period

Consecutive reactions $k_1 = 0.1\ k_2$.

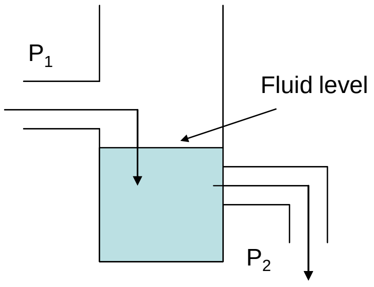


intermediate X

concentration approx. constant

QSSA: a fluid flow analogy.

- QSSA illustrated via analogy with fluid flow.
- If fluid level in tank is to remain constant then rate of inflow of fluid from pipe 1 must balance rate of outflow from pipe 2.
- Reaction intermediate concentration equivalent to fluid level. Inflow rate equivalent to rate of formation of intermediate and outflow rate analogous to rate of removal of intermediate.



Consecutive reaction mechanisms.

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X \xrightarrow{k_2} P$$

Step I is reversible, step II is Irreversible.

Rate equations

$$\frac{du}{d\tau} = -u + \kappa v$$
$$\frac{dv}{d\tau} = u - (\kappa + \phi) v$$
$$\frac{dw}{d\tau} = \phi v$$

Coupled LDE's can be solved via Laplace Transform or other methods.

$$u(\tau) = \frac{1}{\beta - \alpha}\{(\kappa + \phi - \alpha)\exp[-\alpha\tau] - (\kappa + \phi - \beta)\exp[-\beta\tau]\}$$
$$v(\tau) = \frac{1}{\beta - \alpha}\{\exp[-\alpha\tau] - \exp[-\beta\tau]\}$$
$$w(\tau) = 1 - \frac{1}{\beta - \alpha}\{\beta\exp[-\alpha\tau] - \alpha\exp[-\beta\tau]\}$$

$$u = \frac{a}{a_0} \quad v = \frac{x}{a_0} \quad w = \frac{p}{a_0}$$
$$\forall \tau \quad u + v + w = 1$$
$$\tau = 0 \quad u = 1 \quad v = w = 0$$
$$\kappa = \frac{k_{-1}}{k_1} \quad \phi = \frac{k_2}{k_1} \quad \tau = k_1 t$$

Definition of normalised variables and initial condition.

Note that α and β are composite quantities containing the individual rate constants.

$$\alpha\beta = \phi$$
$$\alpha + \beta = 1 + \kappa + \phi$$

QSSA assumes that

$$\frac{dv}{d\tau} \cong 0$$

$$u_{ss} - (\kappa + \phi)v_{ss} = 0$$
$$v_{ss} \cong \frac{u_{ss}}{\kappa + \phi}$$

$$\frac{du_{ss}}{d\tau} = -\frac{\phi}{\kappa + \phi}u_{ss}$$
$$u_{ss} \cong \exp\left[-\frac{\phi}{\kappa + \phi}\tau\right]$$

$$v_{ss} \cong \frac{\exp\left[-\left(\frac{\phi}{\kappa + \phi}\right)\tau\right]}{\kappa + \phi}$$

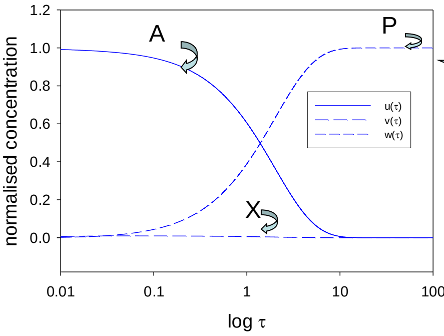
Using the QSSA we can develop more simple rate equations which may be integrated to produce approximate expressions for the pertinent concentration profiles as a function of time.
The QSSA will only hold provided that:

- **the concentration of intermediate is small and effectively constant,**

and so :

- **the net rate of change in intermediate concentration wrt time can be set equal to zero.**

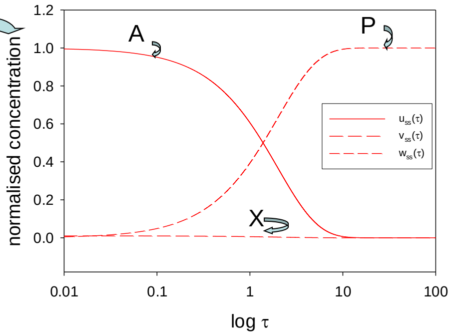
$$\frac{dw_{ss}}{d\tau} \cong \phi v_{ss} = \frac{\phi}{\kappa + \phi}\exp\left[-\left(\frac{\phi}{\kappa + \phi}\right)\tau\right]$$
$$w_{ss} \cong \frac{\phi}{\kappa + \phi}\int_0^{\tau}\exp\left[-\left(\frac{\phi}{\kappa + \phi}\right)\tau\right]d\tau$$
$$= 1 - \exp\left[-\left(\frac{\phi}{\kappa + \phi}\right)\tau\right]$$



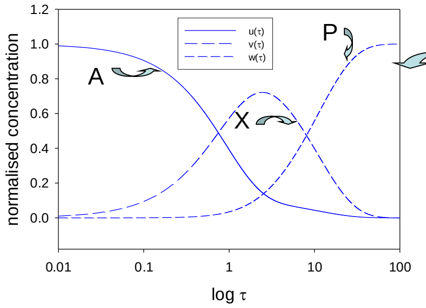
$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X \xrightarrow{k_2} P$$

Concentration versus log time curves for reactant A, intermediate X and product P when full set of coupled rate equations are solved without any approximation.
k_{-1} » k_1, k_2»k_1 and $k_{-1} = k_2 = 50$.
The concentration of intermediate X is very small and approximately constant throughout the time course of the experiment.

Concentration versus log time curves for reactant A, intermediate X, and product P when the rate equations are solved using the QSSA.
Values used for the rate constants are the same as those used above.
QSSA reproduces the concentration profiles well and is valid.



QSSA will hold when concentration of intermediate is **small** and **constant**. Hence the rate constants for getting rid of the intermediate (k_{-1} and k_2) must be much larger than that for intermediate generation (k_1).



$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X \xrightarrow{k_2} P$$

Concentration versus log time curves for reactant A, intermediate X and product P when full set of coupled rate equations are solved without any approximation.
k_{-1} ‹‹ k_1, k_2,,k_1 and $k_{-1} = k_2 = 0.1$
The concentration of intermediate is high and it is present throughout much of the duration of the experiment.

Concentration versus log time curves for reactant A, intermediate X and product P when the Coupled rate equations are solved using the quasi steady state approximation. The same values for the rate constants were adopted as above.

The QSSA is not good in predicting how the intermediate concentration varies with time, and so it does not apply under the condition where the concentration of intermediate will be high and the intermediate is long lived.