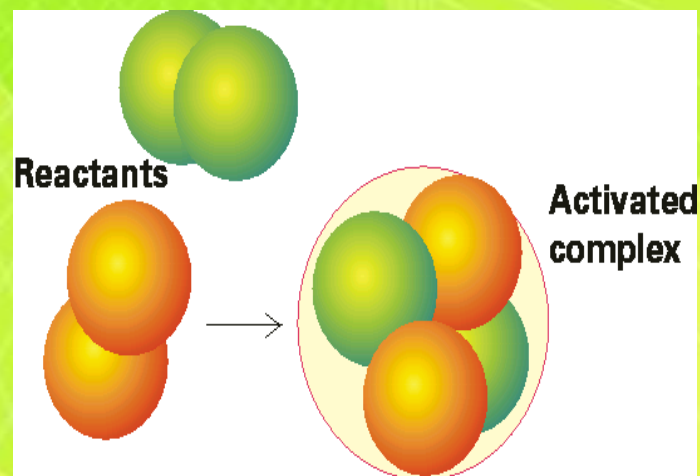
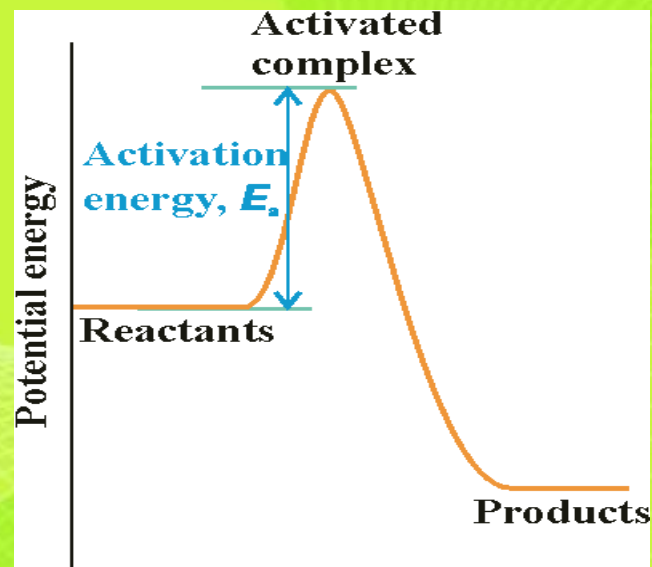


CHEMICAL KINETICS: 1

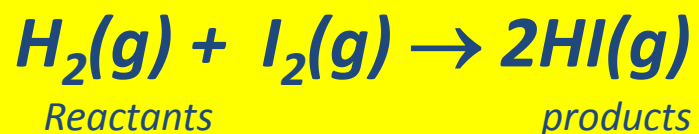
- Rate
- Order
- Rate law
- Rate constant
- Half-life
- Temperature Dependence



Chemical Reactions Kinetics

- Chemical kinetics is the study of time dependence of the change in the concentration of reactants and products.
- Chemical Reaction 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?

Chemical Reaction Kinetics



- Thermodynamics tell 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 proceed (the reaction mechanism)

Basic Ideas in Reaction Kinetics

- Chemical reactions are said to be activated processes: energy (usually thermal (heat) energy) must be introduced into the system so that chemical transformation occur more rapidly when temperature of the system is increased.
- In simple terms an activation energy barrier must be overcome before reactants can be transformed into products.

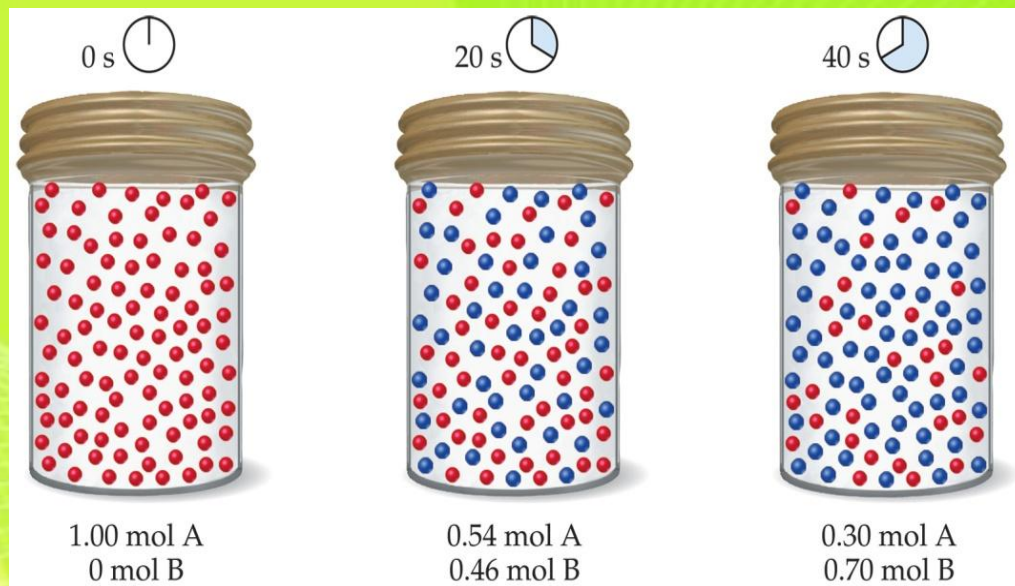
Rate of reaction

- What do we mean by term reaction rate?
- The term rate implies that something changes with respect to something else.
- How many reaction rates can 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.

Rate of reaction

- 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 participating reactants is termed the reaction order.

Rate of reaction



- **Symbol: R , v**
- **Stoichiometric equation:**



- **Rate:**

$$R = -\frac{1}{m} \frac{dA}{dt} = -\frac{1}{n} \frac{dB}{dt} = +\frac{1}{p} \frac{dX}{dt} = +\frac{1}{q} \frac{dY}{dt}$$

- Units of k , rate constant

$$R = -\frac{1}{m} \frac{d[A]}{dt} = k[A]^m[B]^n$$

Annotations for the equation above:

- An arrow points from the text "concentration" to the $d[A]$ term in the numerator.
- An arrow points from the text "time" to the dt term in the denominator.
- An arrow points from the text "(concentration)^m" to the $[A]^m$ term.
- An arrow points from the text "(concentration)ⁿ" to the $[B]^n$ term.
- Two arrows point from the text "not reaction coeff." to the k and the $[A]^m[B]^n$ terms.

Rate Law	Order	Units of k
$R = k$	0	
$R = k[A]$	1	
$R = k[A]^2$	2	
$R = [A][B]$	1 in [A], [B] 2 overall	
$R = k[A]^{1/2}$	1/2	

$$k = \frac{R}{[A]^m[B]^n}$$

$$= \frac{(\text{concentration})^{1-m-n}}{\text{time}}$$

Factors That Affect Reaction Rates

- **Concentration of Reactants**

- As the concentration of reactants increases, so does the likelihood that reactant molecules will collide.



- **Temperature**

- At higher temperatures, reactant molecules have more kinetic energy, move faster, and collide more often and with greater energy.

- **Catalysts**

- Speed rxn by changing mechanism.

Rate Law

- How does the rate depend upon []s?
- Find out by experiment
- *The Rate Law equation*

$$R = k [A]^{\alpha} [B]^{\beta} \dots \quad (\text{for many reactions})$$

- order, $n = \alpha + \beta + \dots$ (dimensionless)
- rate constant, k (units depend on rxn Order)
- Rate = k when each [conc] = unity

Rate laws can be complicated



These rate laws suggest that these two reactions occur via different mechanisms (sets of individual steps).

The first may be an elementary reaction (one step) whereas the latter is certainly a multistep process.

We will soon explore how to obtain complicated rate laws from suggested mechanisms.

Finding rate laws experimentally

There are two common methods for determining rate laws:

Method of isolation

Set up reaction so one reactant is in excess. Any change in rate will be due to changes in other reactant. Repeat for other reactant.

$$R = k'[B]^n \quad \text{where} \quad k' = k[A]^m$$

Method of initial rates

Measure concentration change as a function of time, $\sim v(t)$, for a series of experimental conditions. (Conditions must include sets where the reactant A has the same initial concentration but B changes and vice versa).

Integration of rate laws

- Order of reaction

For a reaction $aA \rightarrow$ products

the rate law is:

$$R = -\frac{1}{a} \frac{d[A]}{dt} = k[A]^n$$

$$\Rightarrow \frac{d[A]}{dt} = -ak[A]^n$$

defining $k_A = ak$

$$R = \frac{d[A]}{dt} = -k_A[A]^n$$

or just written as :

$$R = \frac{d[A]}{dt} = -k[A]^n$$

**rate of change in the
concentration of A**

First-order reaction

$$R = \frac{d[A]}{dt} = -k[A]^1$$

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

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -k \int_0^t dt$$

$$\ln([A]_t - [A]_0) = -k(t - t_0)$$

First-order reaction

$$\ln[A]_t - \ln[A]_0 = -k(t - t_0)$$

$$\ln[A]_t = \ln[A]_0 - kt$$

A plot of $\ln[A]$ versus t gives a straight line of slope $-k_A$ if $r = k[A]^1$

First-order reaction

$$\ln[A]_t - \ln[A]_0 = -k(t - t_0)$$

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$$

$$\frac{[A]_t}{[A]_0} = e^{-kt}$$

$$[A]_t = [A]_0 e^{-kt}$$

First order reactions
decay exponentially.

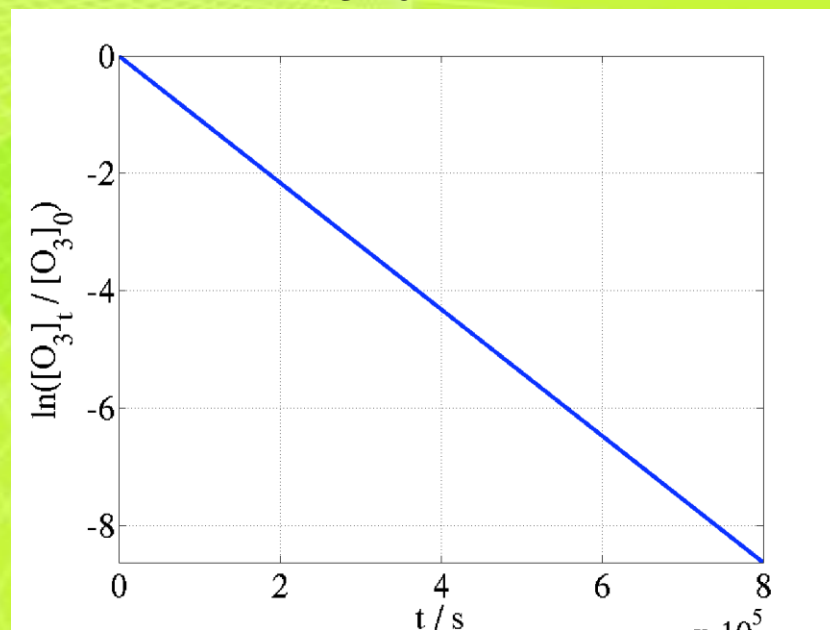
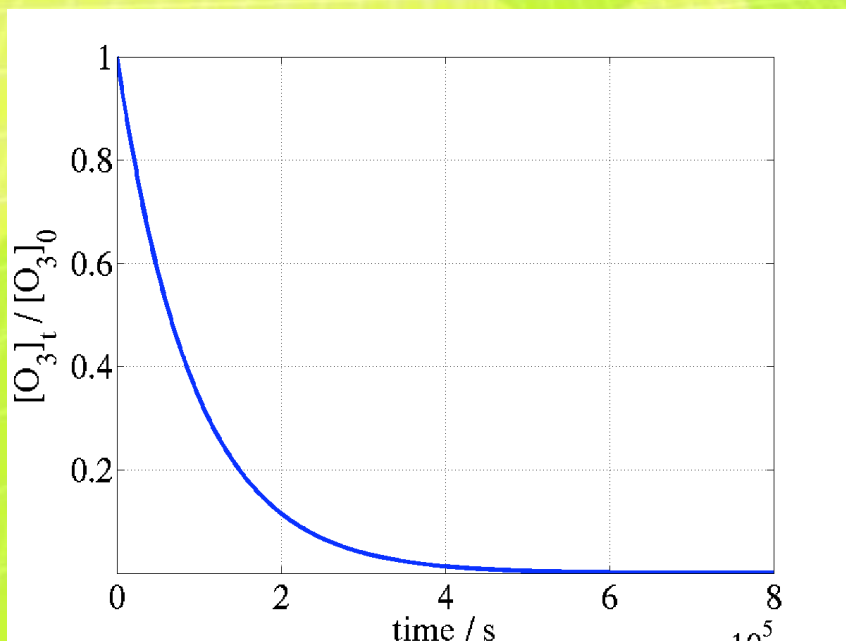
First-order reaction: example

Ozone decays via first order kinetics



$$[\text{O}_3]_t = [\text{O}_3]_0 e^{-kt}$$

$$\ln \frac{[\text{O}_3]_t}{[\text{O}_3]_0} = -kt$$

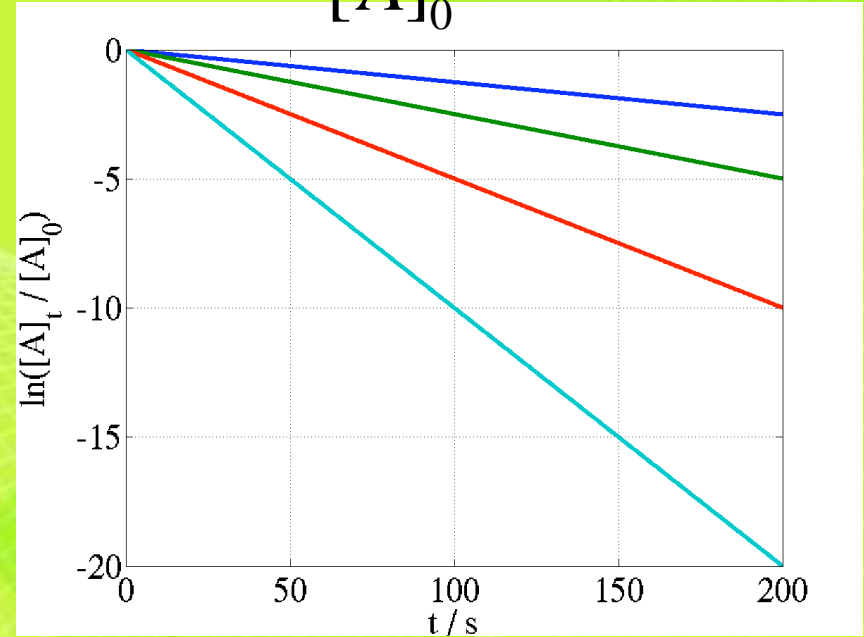
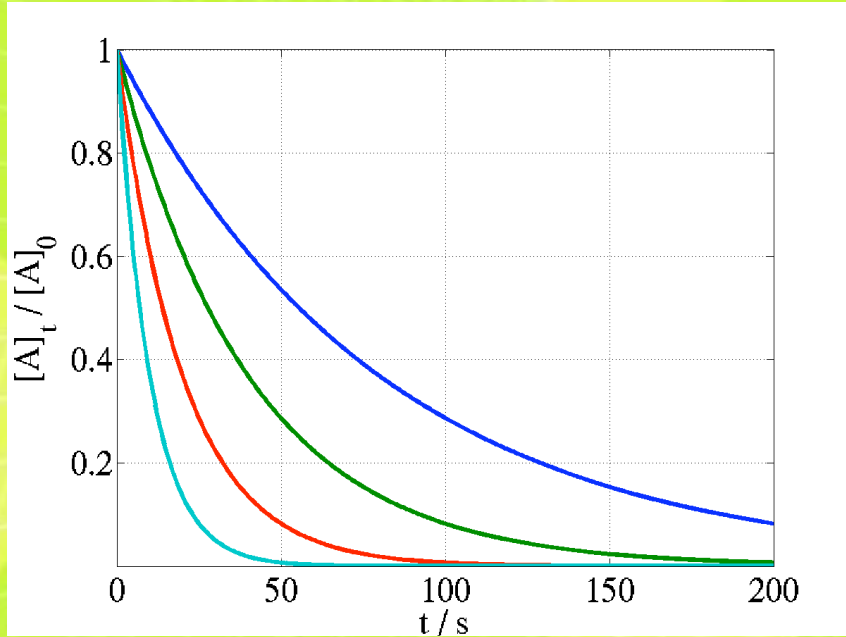


What is slope?

What happens as k increases?

$$[A]_t = [A]_0 e^{-kt}$$

$$\ln \frac{[A]_t}{[A]_0} = -kt$$



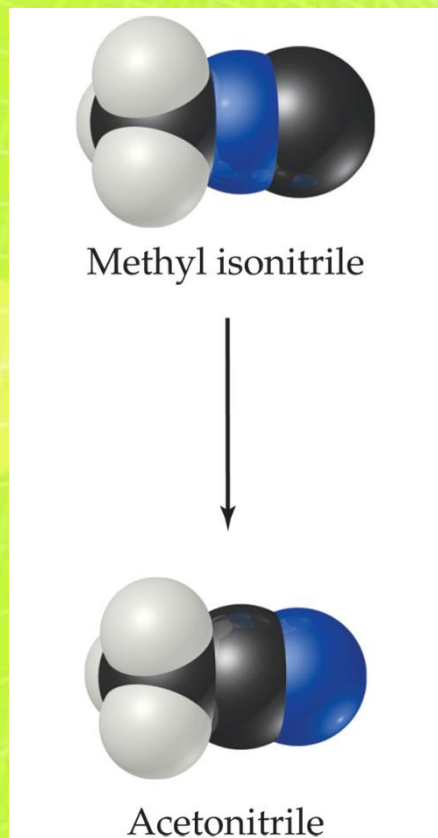
$$k = 0.0125 \text{ s}^{-1}$$

$$k = 0.0250 \text{ s}^{-1}$$

$$k = 0.0500 \text{ s}^{-1}$$

$$k = 0.1000 \text{ s}^{-1}$$

First-order reaction: example



Consider the process in which methyl isonitrile is converted to acetonitrile.



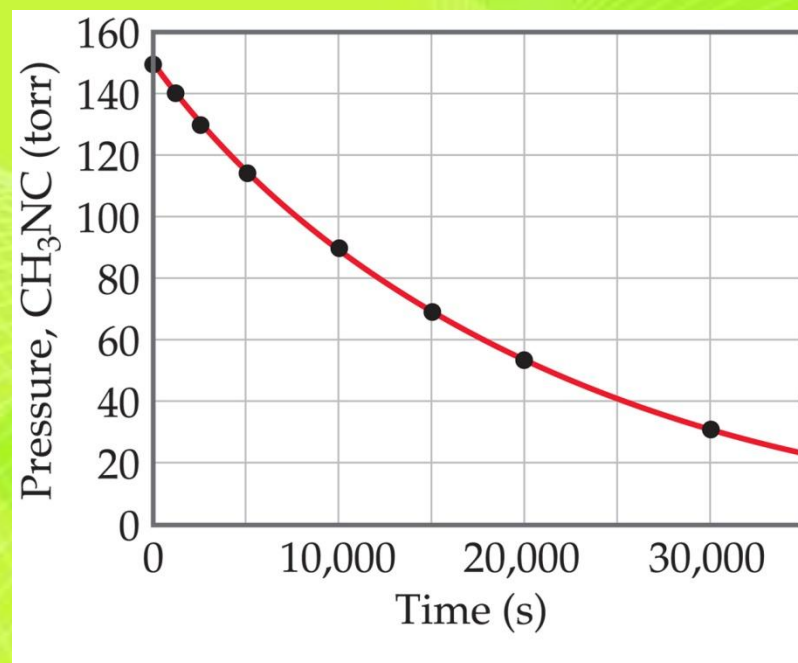
How do we know this is a first order rxn?

First-order reaction: example

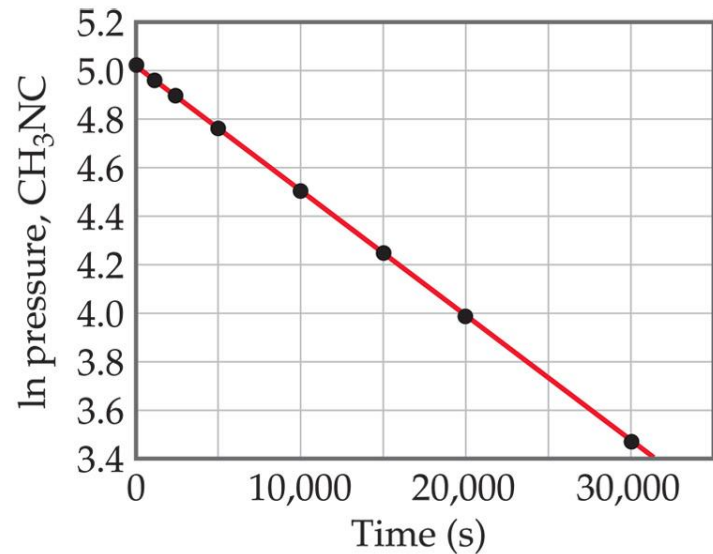
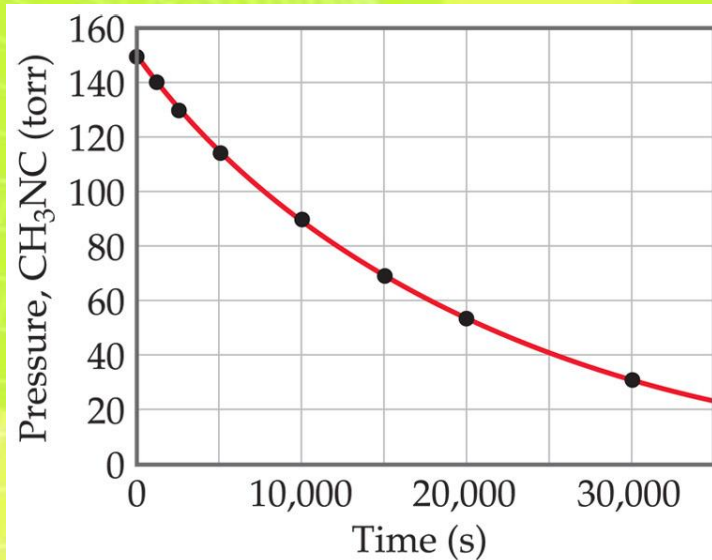


This data was collected for this reaction at 198.9°C.

Does
 $\text{rate} = k[\text{CH}_3\text{NC}]$
for all time intervals?



First-order reaction



$$[A]_t = [A]_0 e^{-kt}$$

$$\ln [A]_t = -kt + \ln [A]_0$$

- When $\ln P$ is plotted as a function of time, a straight line results.
 - The process is first-order.
 - k is the negative slope: $5.1 \times 10^{-5} \text{ s}^{-1}$.

Half life: first-order reaction

- The time taken for [A] to drop to half its original value is called the reaction's half-life, $t_{1/2}$. Setting $[A] = \frac{1}{2}[A]_0$ and $t = t_{1/2}$ in:

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$$

$$\ln\left(\frac{\frac{1}{2}[A]_0}{[A]_0}\right) = -kt_{1/2}$$

Half life: first-order reaction

$$\ln\left(\frac{1}{2}\right) = -kt_{1/2} = -0.693$$

$$\Rightarrow t_{1/2} = \frac{0.693}{k} \quad \text{or} \quad k = \frac{0.693}{t_{1/2}}$$

When is a reaction over?

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

Technically $[A]=0$ only after *infinite* time

Second-order reaction

Similarly, integrating the rate law for a process that is second-order in reactant A:

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

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

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = -k \int_0^t dt$$

Second-order reaction

$$-\frac{1}{[A]_t} - \left(-\frac{1}{[A]_0} \right) = -k(t - t_0)$$
$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

also in the form $y = mx + b$

A plot of $1/[A]$ versus t gives a straight line of slope k_A if $r = k_A[A]^2$

Determining rxn order

The decomposition of NO_2 at 300°C is described by the equation



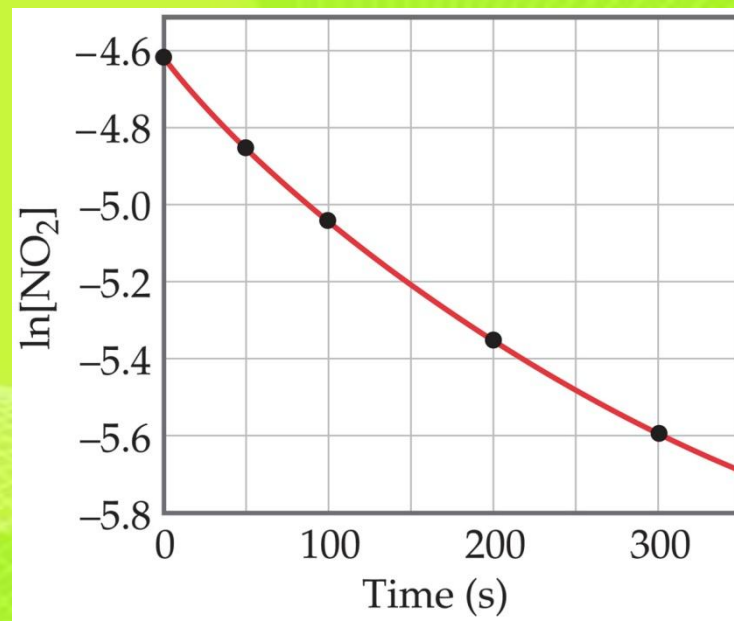
and yields these data:

Time (s)	$[\text{NO}_2], M$
0.0	0.01000
50.0	0.00787
100.0	0.00649
200.0	0.00481
300.0	0.00380

Determining rxn order

Graphing $\ln [\text{NO}_2]$ vs. t yields:

- The plot is *not* a straight line, so the process is *not* first-order in $[\text{A}]$.

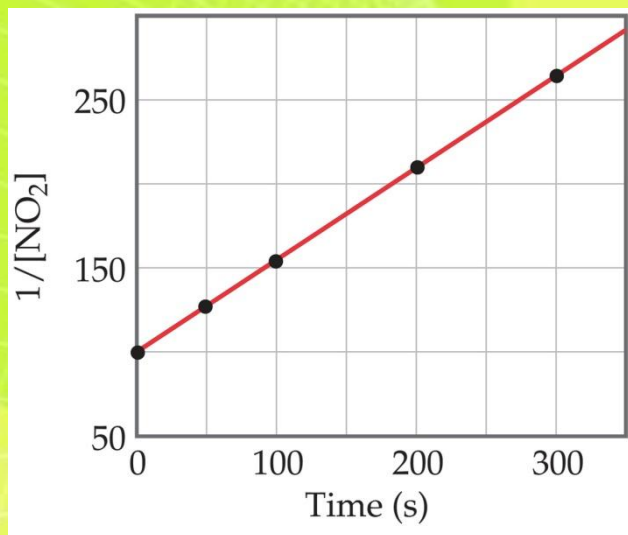


Does not fit:

$$\ln [A]_t = -kt + \ln [A]_0$$

Time (s)	$[\text{NO}_2], M$	$\ln [\text{NO}_2]$
0.0	0.01000	-4.610
50.0	0.00787	-4.845
100.0	0.00649	-5.038
200.0	0.00481	-5.337
300.0	0.00380	-5.573

Second-Order Processes



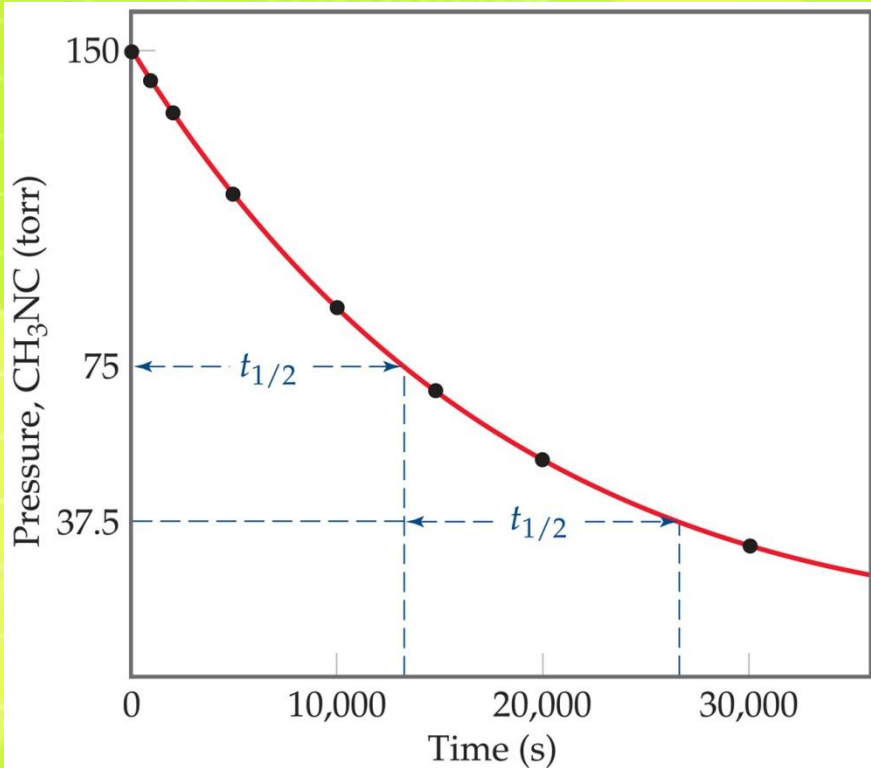
A graph of $1/[\text{NO}_2]$ vs. t gives this plot.

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

Time (s)	$[\text{NO}_2]$, M	$1/[\text{NO}_2]$
0.0	0.01000	100
50.0	0.00787	127
100.0	0.00649	154
200.0	0.00481	208
300.0	0.00380	263

- This *is* a straight line. Therefore, the process is second-order in $[\text{NO}_2]$.

Half-Life



- Half-life is defined as the time required for one-half of a reactant to react.
- Because $[A]$ at $t_{1/2}$ is one-half of the original $[A]$,

$$[A]_t = 0.5 [A]_0.$$

Half life: second-order reaction

For a second-order process, set $[A]_t = 0.5 [A]_0$ in 2nd order equation.

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$

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

Outline: Kinetics

	First order	Second order	Second order (Bimolecular)
Rate Laws	$rate = -k [A]$	$rate = -k [A]^2$	$rate = -k [A] [B]$
Integrated Rate Laws	$\ln \frac{[A]_t}{[A]_0} = -kt$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	complicated (discussed later)
Half-life	$\frac{0.693}{k} = t_{\frac{1}{2}}$	$\frac{1}{k [A]_0} = t_{\frac{1}{2}}$	Complicated (discussed later)

Problems:

- Define/derive **Integrated Rate Laws** and **Half-life** of ***3rd-order*** and ***nth-order reactions*** whose **rate laws** are given below:

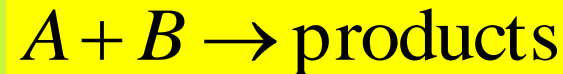
$$R = k[B]^3 \quad \text{where} \quad R = k[A]^n$$

Outline: Kinetics

	Third order	n th -order
Rate Laws	$R = k[A]^3$	$R = k[A]^n$
Integrated Rate Laws	$\frac{1}{2} \left(\frac{1}{[A]_t^2} - \frac{1}{[A]_0^2} \right) = kt$	$\frac{1}{n-1} \left(\frac{1}{[A]_t^{(n-1)}} - \frac{1}{[A]_0^{(n-1)}} \right) = kt$
Half-life	$\frac{3}{(2)k[A]_o^2} = t_{1/2}$	$\frac{2^{n-1} - 1}{(n-1)k[A]_o^{n-1}} = t_{1/2}$

Other order reactions...

Second order reaction:



Second order rate:

$$R = -\frac{1}{2} \frac{d[A]}{dt} = k[A]^2$$

$$R = -\frac{d[A]}{dt} = k[A][B]$$

Integrated rate law:

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + 2kt$$

$$\frac{1}{([A]_0 - [B]_0)} \ln \left(\frac{[B]_0[A]_t}{[A]_0[B]_t} \right) = kt$$

Zero order reaction:



Zero order rate:

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

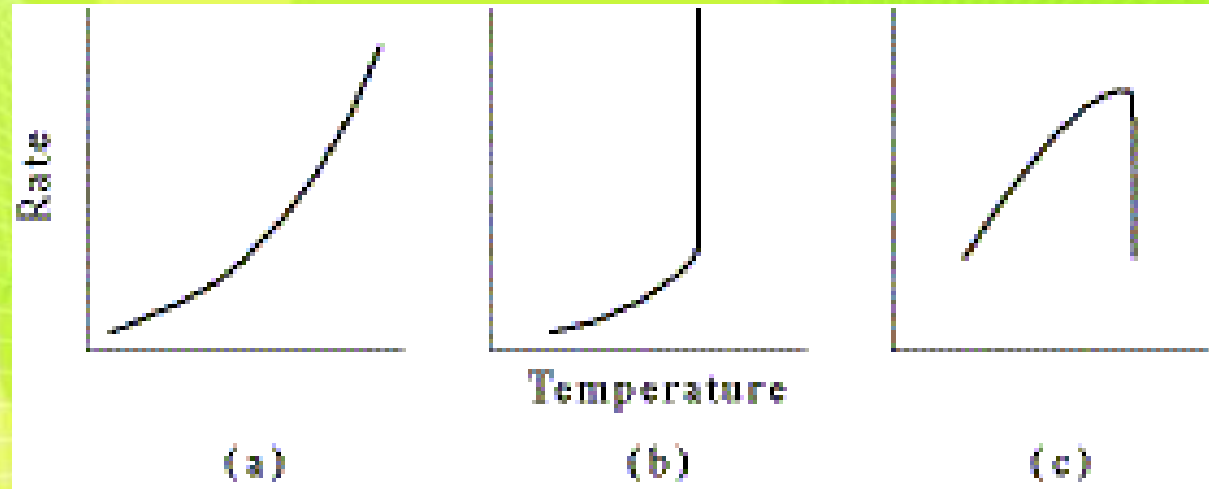
Integrated rate law:

$$[A]_t = [A]_0 - kt$$

Temperature Dependence of k



The rate constant can vary in different ways with T .



Svante Arrhenius
Winner of the 3rd Nobel
Prize in Chemistry

Arrhenius Parameters

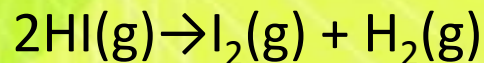
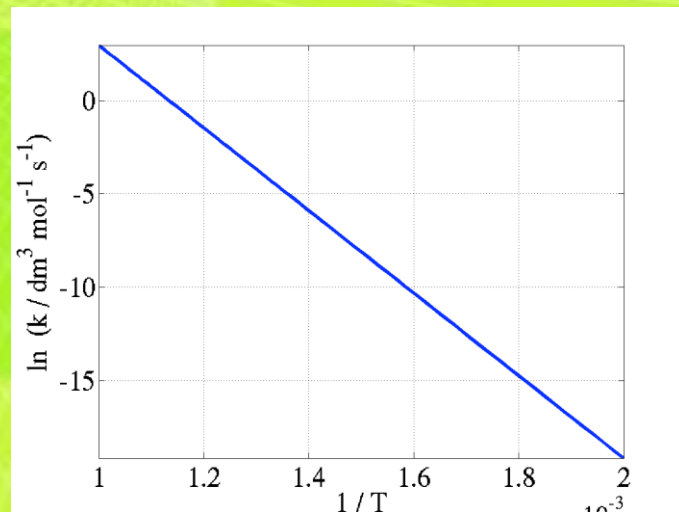
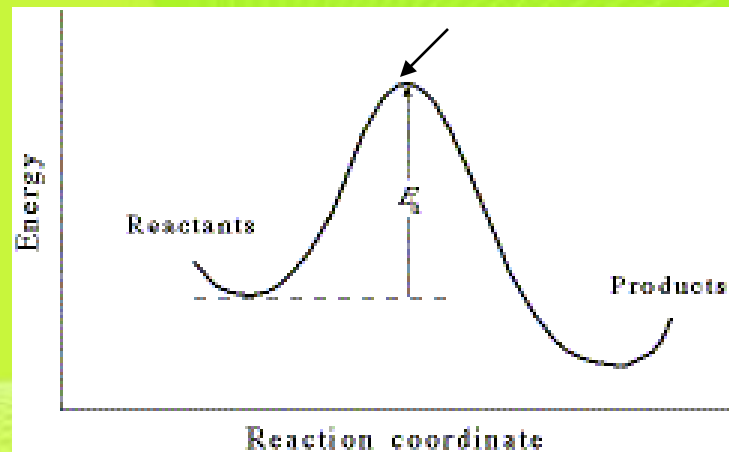
Integrated forms of Arrhenius equation:

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2} \quad \ln k = \ln A - \frac{E_a}{RT}$$
$$k = Ae^{-E_a/RT}$$

E_a is the activation energy. This is the energy required to get over a barrier (at the activated or transition state) between the reactants and products. E_a has units of energy and is T independent.

A is the pre-exponential or Arrhenius factor and is T dependent. A is a measure of rate at which collisions occur (and takes lots of things into acct such as orientation, molecular size, number of molecules per volume, molecular velocity, etc).

Activated (or transition) state

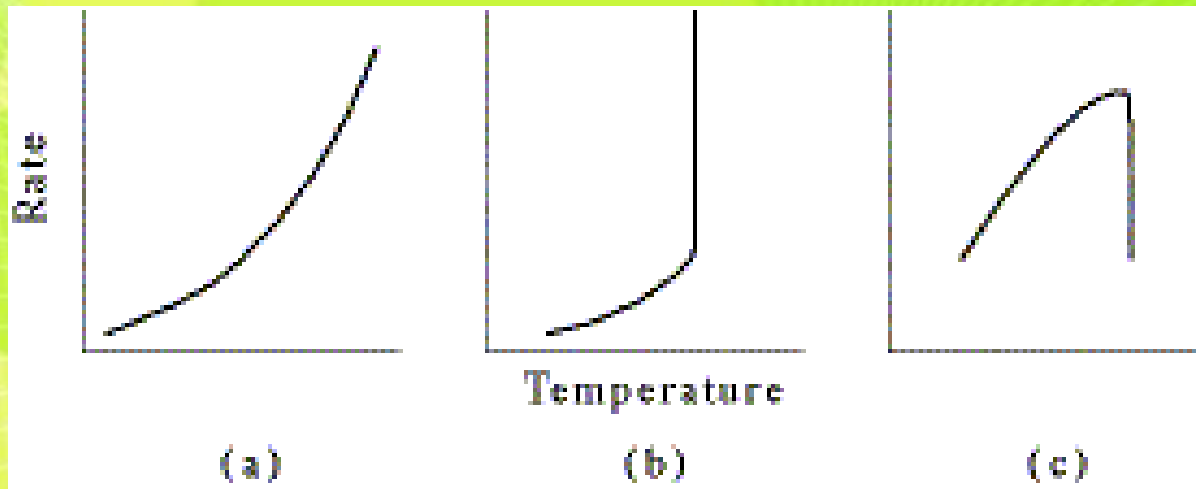


Temperature dependence of k



Svante Arrhenius
Winner of the 3rd Nobel
Prize in Chemistry

The rate constant can vary in different ways with T .



- $\text{C}_2\text{H}_5\text{Cl} \rightarrow \text{C}_2\text{H}_4 + \text{HCl}$
- Rule of thumb: rate \approx doubles for a 10 K rise

No	T / K^{-1}	k / s^{-1}
1	700	6.1×10^{-5}
2	727	30×10^{-5}
3	765	242×10^{-5}

Rate constant expression

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

$$\frac{k_1}{k_2} = \frac{A}{A} \exp\left(\frac{\frac{(-E_A)}{RT_1}}{\frac{(-E_A)}{RT_2}}\right)$$

$$\frac{k_1}{k_2} = \exp\left(\frac{-E_A}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

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

$$\ln\left(\frac{1}{2}\right) = \left(\frac{-E_A}{8.314}\right)\left(\frac{1}{293.15} - \frac{1}{303.15}\right)$$

$$-0.693 = \left(\frac{-E_A}{8.314}\right)\left(1.12526 \times 10^{-4}\right)$$

$$-6158.58 = \left(\frac{-E_A}{8.314}\right) \Rightarrow E_A = 51.202 \text{ kJ mol}^{-1}$$

Relating E_a to thermodynamics!

Necessary Pieces...

Arrhenius Equation: $\ln k = \ln A - \frac{E_a}{RT}$

Differentiate wrt T: $\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$ or $E_a = RT^2 \frac{d \ln k}{dT}$

From Eyring Equation: $\frac{d \ln k}{dT} = \frac{1}{T} + \frac{d \ln K_C^\ddagger}{dT}$

van't Hoff Equation (for K_C): $\frac{d \ln K_C}{dT} = \frac{\Delta U}{RT^2}$

Putting it all together...

$$E_a = RT^2 \left(\frac{1}{T} + \frac{d \ln K_C^\ddagger}{dT} \right) \quad \text{or} \quad E_a = RT + \Delta U^\ddagger$$