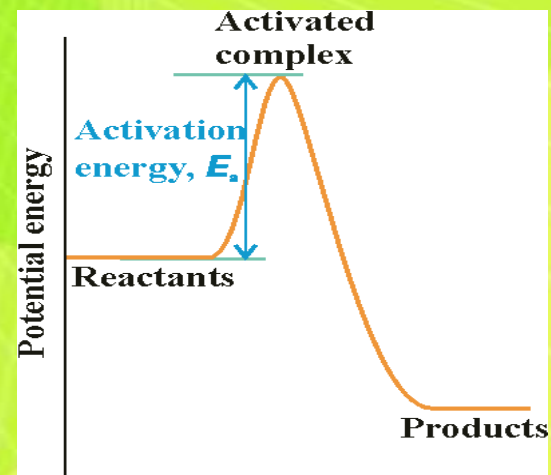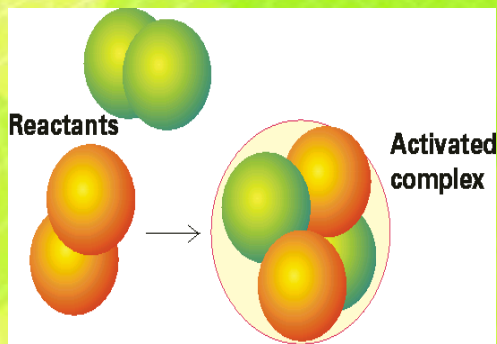# CHEMICAL KINETICS

- Rate
- Order
- Rate law
- Rate constant
- Half-life
- Molecularity
- Elementary

- Complex
- Temperature dependence,
- Steady-state Approximation

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

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

Reactants   *products*
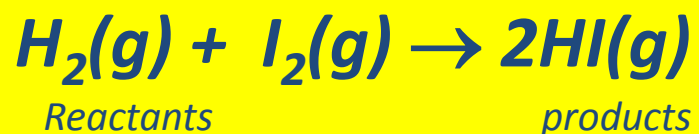
- Thermodynamics tell us all about the energetic feasibility of a reaction: we measure the Gibbs energy ΔG for the chemical reaction.

- 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

0 s   20 s   40 s

1.00 mol A
0 mol B

0.54 mol A
0.46 mol B

0.30 mol A
0.70 mol B
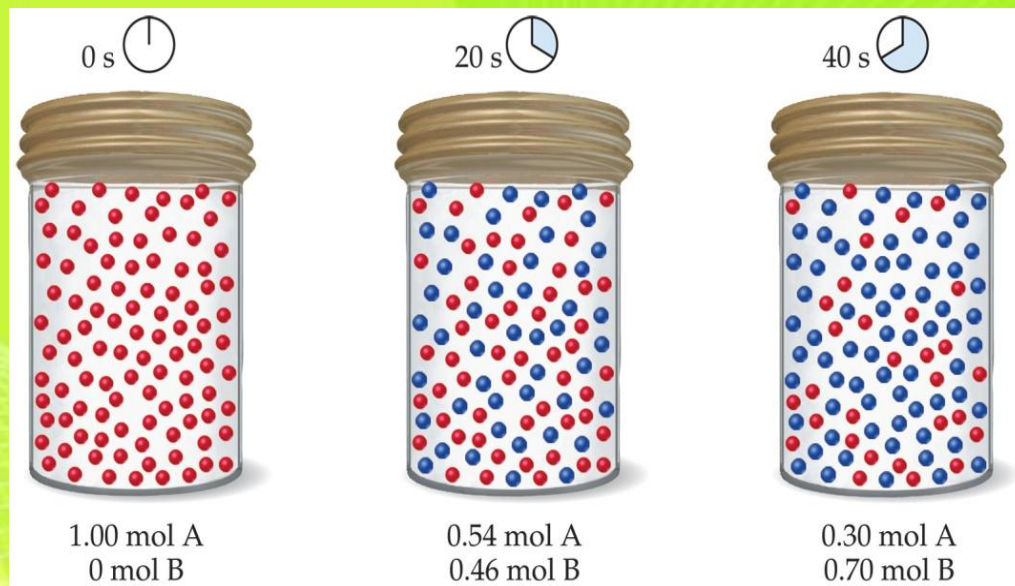
- **Symbol: R, ν**
- **Stoichiometric equation:**

  m **A** + n **B** ⇌ p **X** + q **Y**

- **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

not reaction coeff.

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

$\dfrac{\text{concentration}}{\text{time}}$

(concentration)^m

(concentration)^n

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	

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

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

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*

    $$R = k\,[A]^{\alpha}\,[B]^{\beta}\,\ldots \qquad \text{(for \textit{many} reactions)}$$

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

Rate laws can be complicated

1) $H_2(g) + I_2(g) \rightarrow 2HI(g)$ $R = k[H_2][I_2]$

2) $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$ $R = \dfrac{2k'[H_2][Br_2]^{1/2}}{1 + k''[HBr][Br_2]^{-1}}$

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

The first may be a 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 $\longrightarrow$ products

  the rate law is:
  $$R = -\frac{1}{a}\frac{d[A]}{dt} = k[A]^n$$

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

  $defining \quad k_A = ak$

  rate of change in the concentration of A

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

  $or \ just \ written \ as:$

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

First-order reaction

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

$$\frac{d[A]}{[A]} = -kdt$$

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

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

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

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

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

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

$$[A]_t = [A]_0 \, e^{-kt}$$
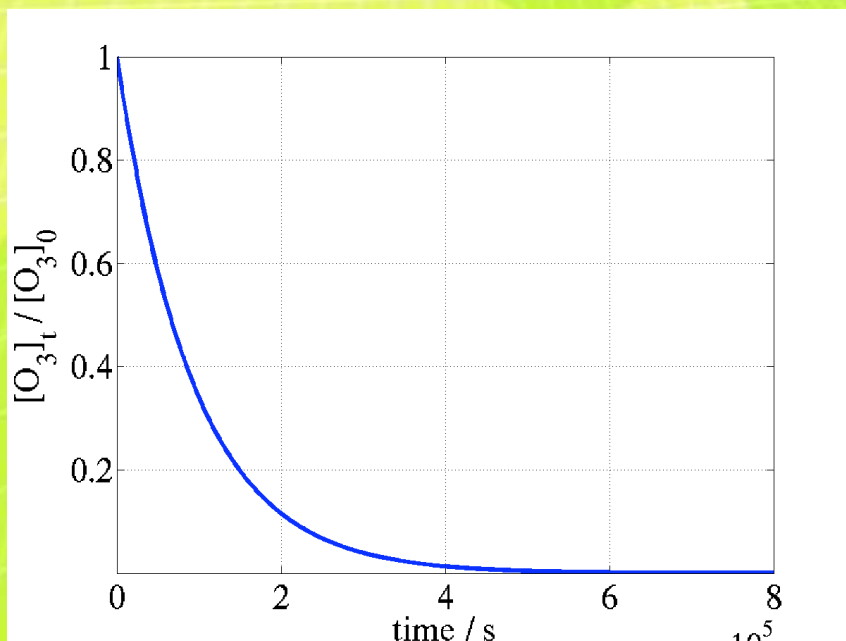
First order reactions decay exponentially.

First-order reaction: example

Ozone decays via first order kinetics

$$O_3(g) \rightarrow O_2(g) + O(g)$$ k = 1.078 × 10^{-5} s^{-1} at 300 K

$$[O_3]_t = [O_3]_0 e^{-kt}$$

$$\ln \frac{[O_3]_t}{[O_3]_0} = -kt$$
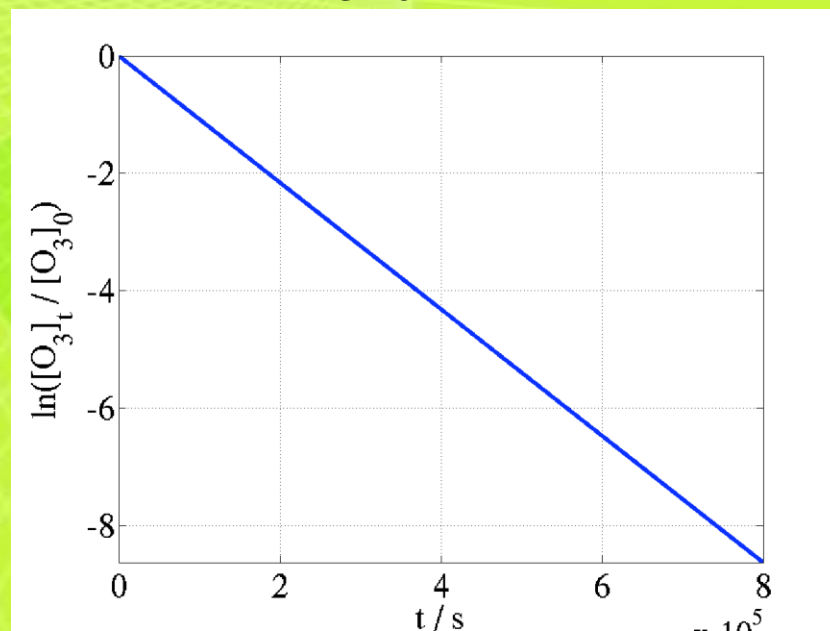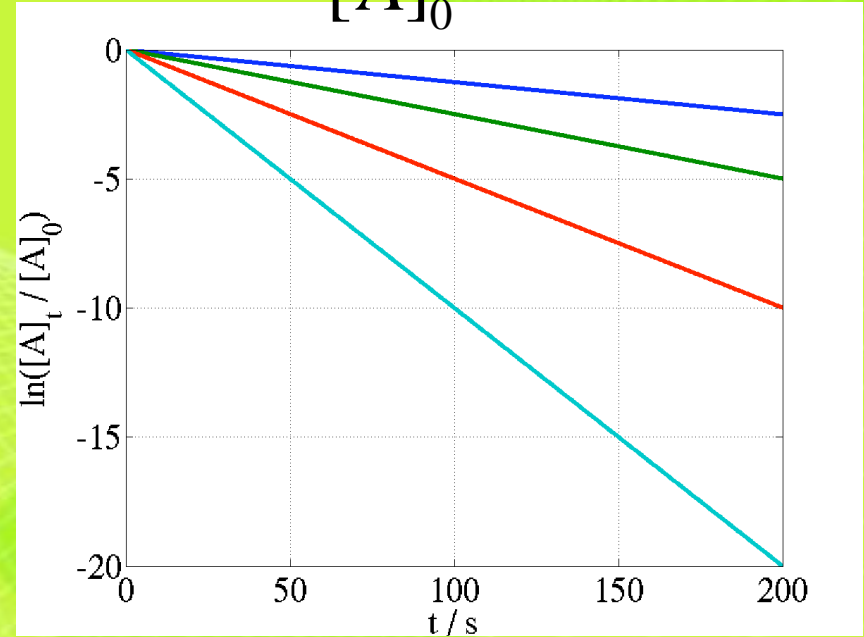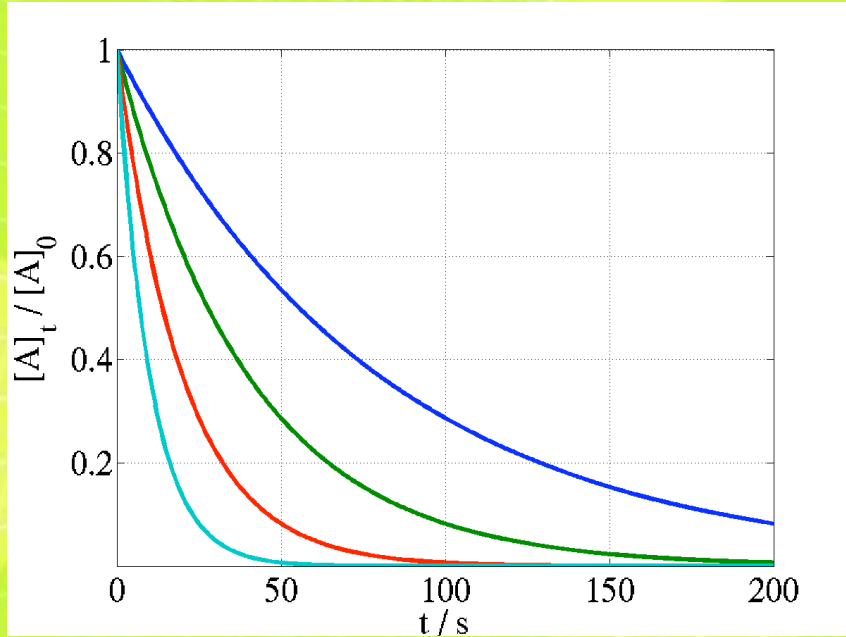

What is slope?

What happens as *k* increases?

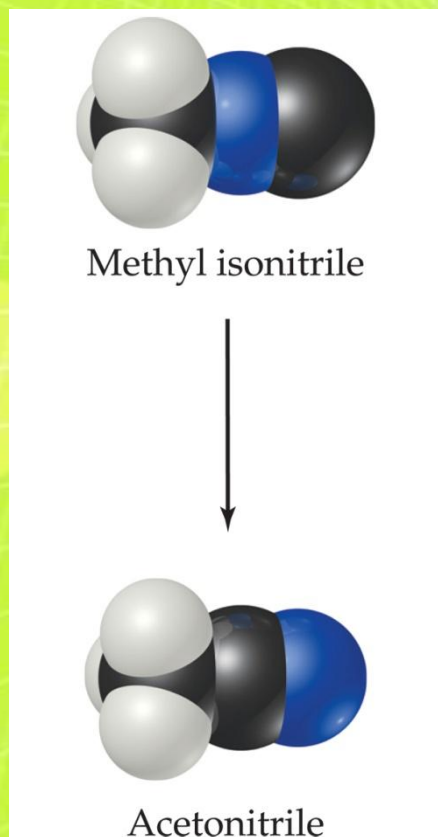$$[A]_t = [A]_0 e^{-kt}$$

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

k = 0.0125 s⁻¹

k = 0.0250 s⁻¹

k = 0.0500 s⁻¹

k = 0.1000 s⁻¹

First-order reaction: example

Methyl isonitrile

Acetonitrile

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

$$CH_3NC \longrightarrow CH_3CN$$

How do we know this is a first order rxn?
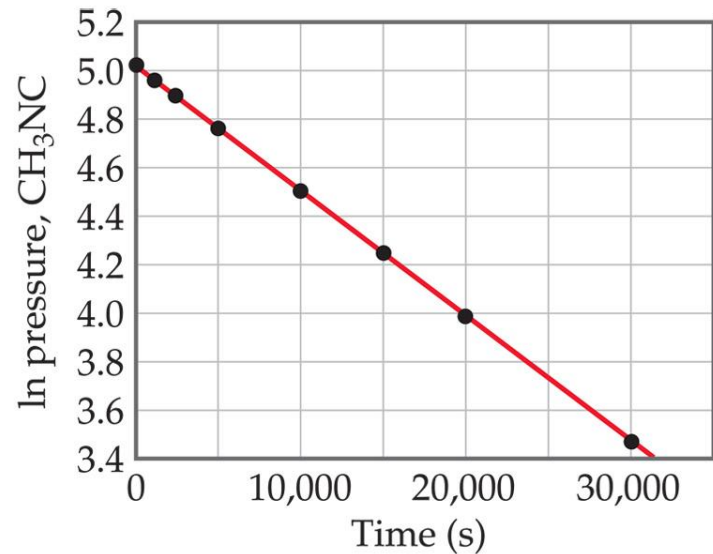
First-order reaction: example

$$CH_3NC \longrightarrow CH_3CN$$
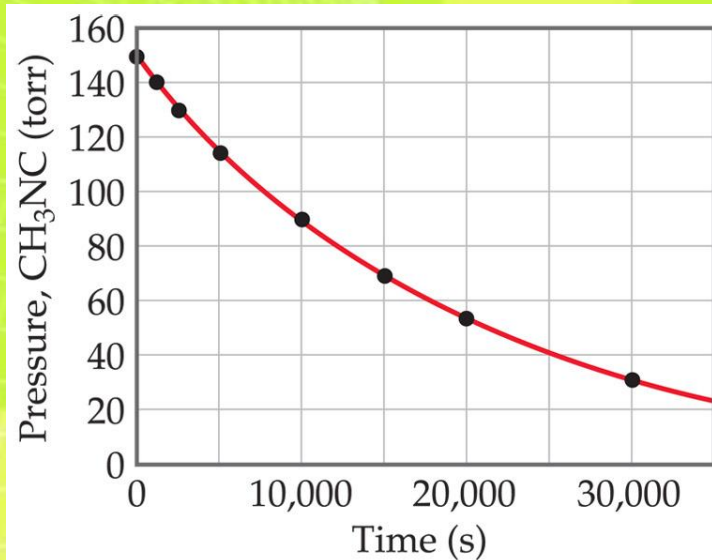
This data was collected for this reaction at 198.9°C.

Does rate=k[CH_3NC] for all time intervals?
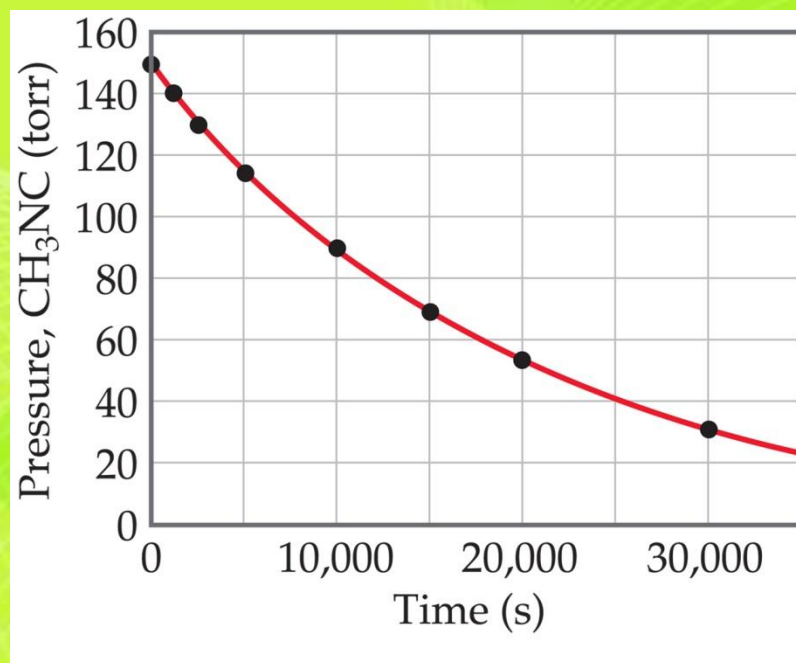
First-order reaction

$$[A]_t = [A]_0\, e^{-kt} \qquad \ln[A]_t = -kt + \ln[A]_0$$

- When ln P is plotted as a function of time, a straight line results.
  - The process is first-order.
  - k is the negative slope: 5.1×10^{-5} 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] = ½[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

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

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

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:

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

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

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

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

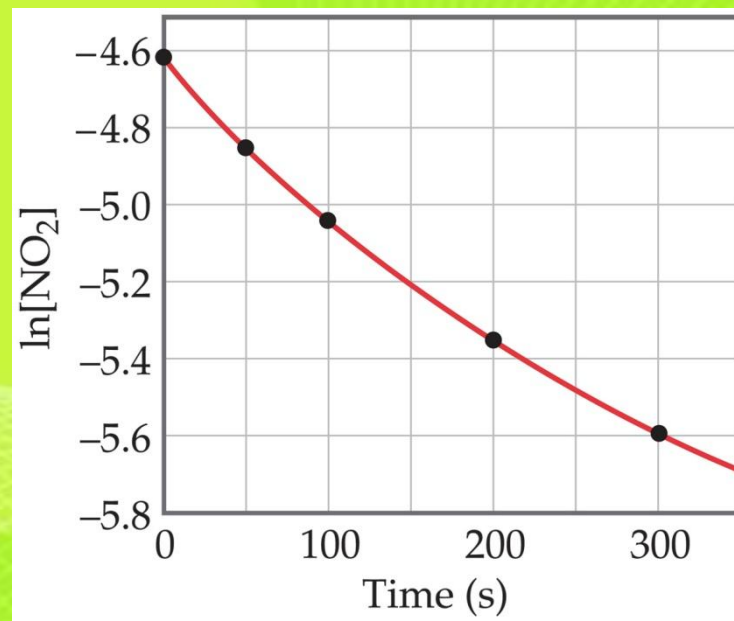The decomposition of NO_2 at 300°C is described by the equation

$$NO_{2\ (g)} \longrightarrow NO_{(g)} + 1/2\ O_{2\ (g)}$$

and yields these data:

Time (s)	[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 $[NO_2]$ vs. t yields:

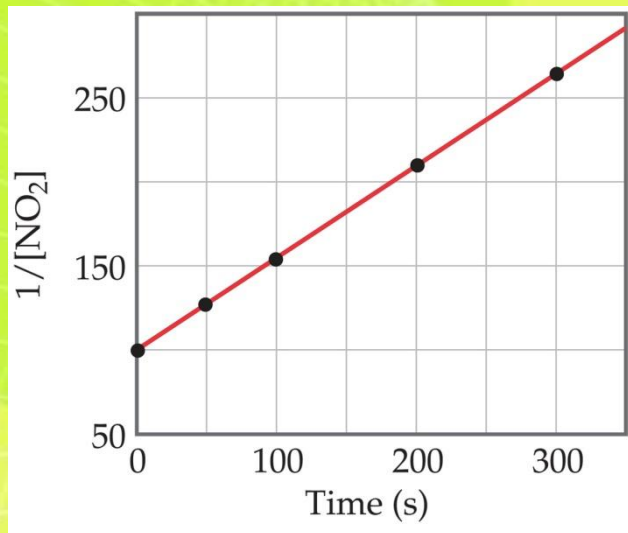- The plot is *not* a straight line, so the process is *not* first-order in [A].

Time (s)	$[NO_2]$, M	ln $[NO_2]$
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

Does not fit:

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

Second-Order Processes

A graph of $1/[NO_2]$ vs. t gives this plot.

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

- This *is* a straight line. Therefore, the process is second-order in $[NO_2]$.

Time (s)	$[NO_2]$, M	$1/[NO_2]$
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
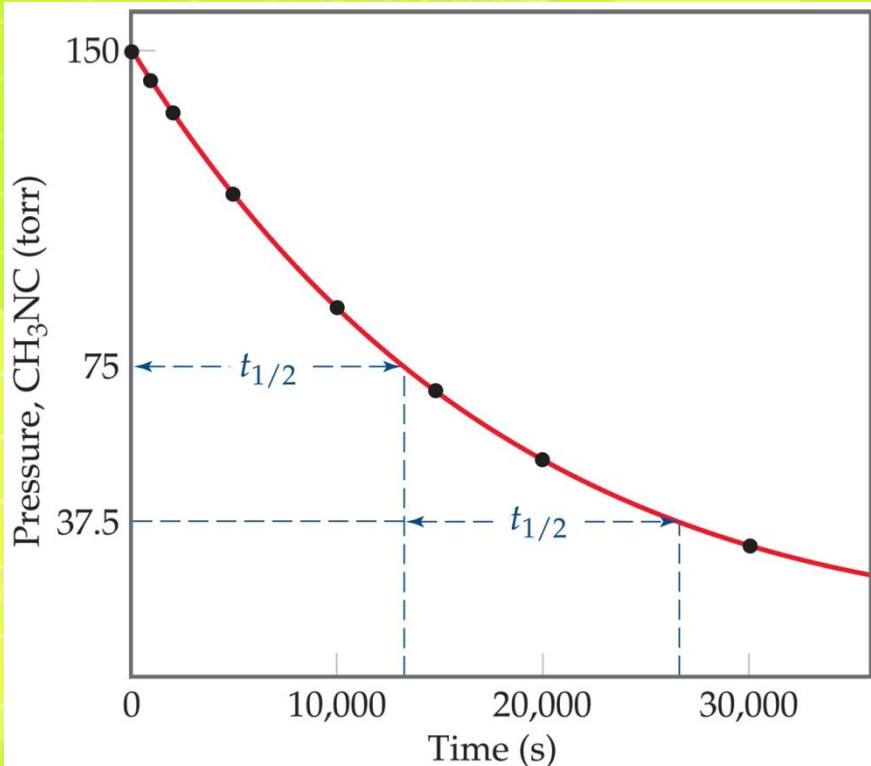
Half-Life

- 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.

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

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

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

Outline: Kinetics

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

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

Outline: Kinetics

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

Rate law for elementary reaction

- Law of Mass Action applies:
  - rate of rxn $\propto$ product of active masses of reactants
  - "active mass" molar concentration raised to power of number of species
- Examples:
  - $A \rightarrow P + Q$ rate = $k_1 [A]^1$
  - $A + B \rightarrow C + D$ rate = $k_2 [A]^1 [B]^1$
  - $2A + B \rightarrow E + F + G$ rate = $k_3 [A]^2 [B]^1$

Molecularity of elementary reactions?

- Unimolecular (decay) $A \rightarrow P$

$$-\frac{d[A]}{dt} = k_1[A]$$

- Bimolecular (collision) $A + B \rightarrow P$
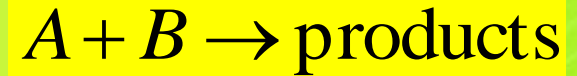
$$-\frac{d[A]}{dt} = k_2[A][B]$$

- Termolecular (collision) $A + B + C \rightarrow P$

$$-\frac{d[A]}{dt} = k_3[A][B][C]$$

- No other are feasible! *Statistically highly unlikely.*

Other order reactions…

Second order reaction:	$2A \rightarrow \text{products}$	$A + B \rightarrow \text{products}$
Second order rate:	$R = -\dfrac{1}{2}\dfrac{d[A]}{dt} = k[A]^2$	$R = -\dfrac{d[A]}{dt} = k[A][B]$
Integrated rate law:	$\dfrac{1}{[A]_t} = \dfrac{1}{[A]_0} + 2kt$	$\dfrac{1}{([A]_0 - [B]_0)}\ln\left(\dfrac{[B]_0[A]_t}{[A]_0[B]_t}\right) = kt$

Zero order reaction: $A \rightarrow \text{products}$

Zero order rate: $R = -\dfrac{d[A]}{dt} = k$

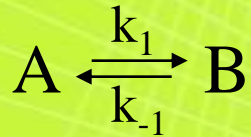Integrated rate law: $[A]_t = [A]_0 - kt$

Pseudo-first order reactions

You can "overload" the other reactants to determine the order with respect to one individual reactant (method of isolation).

For $A + B \rightarrow \text{products}$, what happens if $[B] \gg [A]$?

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

Reversible reactions (small $\Delta_r G$)

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

Assume first order, elementary rxn in both directions

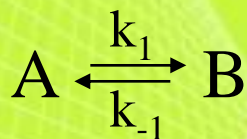Rate: $\quad -\dfrac{d[A]}{dt} = k_1[A] - k_{-1}[B]$

Conservation of Mass:

$$[A]_0 + [B]_0 = [A] + [B]$$

$$[B] = [A]_0 + [B]_0 - [A]$$

$$-\dfrac{d[A]}{dt} = k_1[A] - k_{-1}\left([A]_0 + [B]_0 - [A]\right)$$

Integrate:

$$\ln\left(\dfrac{k_1[A]_t - k_{-1}\left([A]_0 + [B]_0 - [A]_t\right)}{k_1[A]_0 - k_{-1}[B]_0}\right) = -(k_1 + k_{-1})t$$

At equilibrium

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \qquad -\frac{d[A]}{dt} = k_1[A] - k_{-1}[B]$$

At equilibrium... $\quad -\frac{d[A]}{dt} = 0 \longrightarrow k_1[A]_{eq} = k_{-1}[B]_{eq}$

The forward rate equals the reverse at equilibrium.

What is the equilibrium constant for this reaction? $\qquad K_{eq} = \frac{[B]_{eq}}{[A]_{eq}}$

In terms of rate constants? $\qquad K_{eq} = \frac{k_1}{k_{-1}}$

Temperature dependence?

- $C_2H_5Cl \rightarrow C_2H_4 + HCl$

k/s^{-1}	T/K
6.1×10^{-5}	700
30×10^{-5}	727
242×10^{-5}	765

- Conclusion: *very* sensitive to temperature
- Rule of thumb: rate ≈ doubles for a 10 K rise

Details of *T* dependence

Hood

- $k = A \exp\{ -B/T \}$
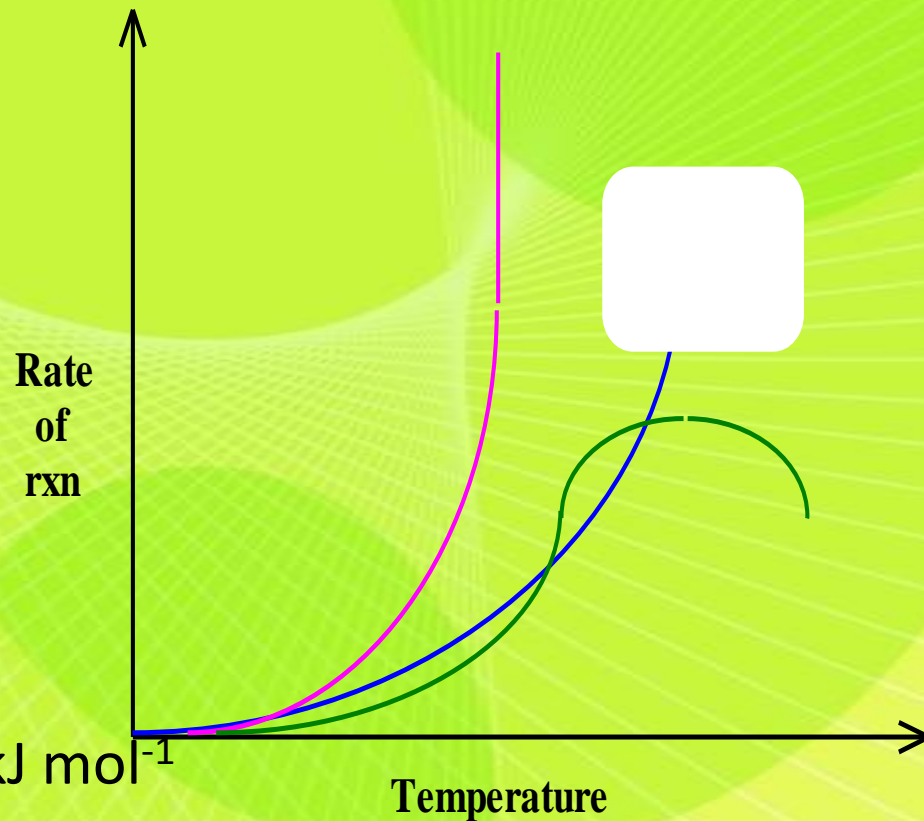
Arrhenius

- $k = A \exp\{ -E / RT \}$

A A-factor or

    pre-exponential factor

     $\equiv k$ at $T \rightarrow \infty$

E activation energy

    (*energy barrier*) J mol^{-1} or kJ mol^{-1}

R gas constant.

Rate
of
rxn

Temperature

Arrhenius eqn. $k=A \exp\{-E/RT\}$

Useful *linear* form: $\ln k = -(E/R)(1/T) + \ln A$
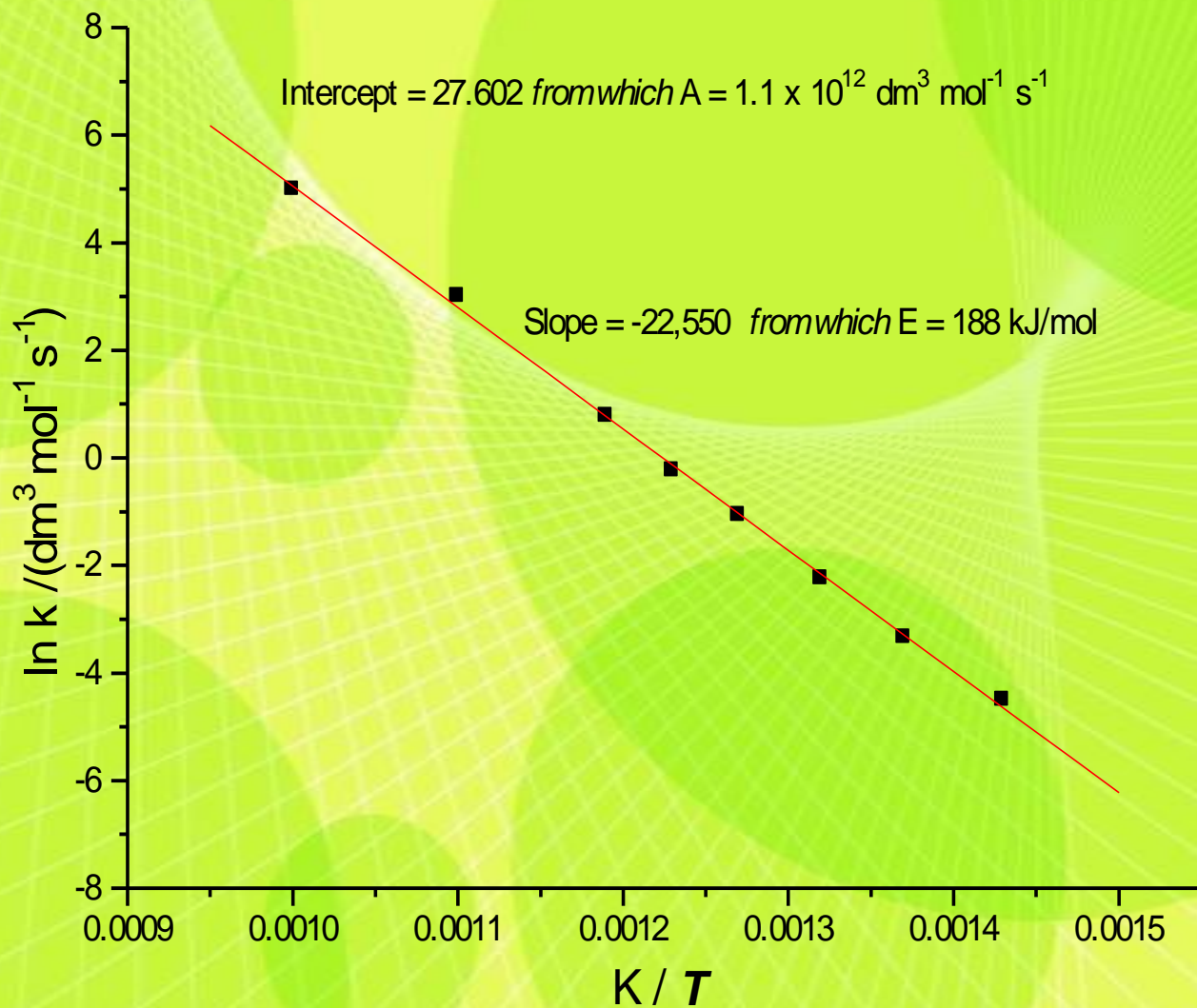
- Plot $\ln k$ along Y-axis *vs* $(1/T)$ along X-axis

Slope is *negative* $-(E/R)$; intercept $= \ln A$

- Experimental Es range from 0 to +400 kJ mol^{-1}

Examples:

- $H^\bullet + HCl \rightarrow H_2 + Cl^\bullet$ 19 kJ mol^{-1}
- $H^\bullet + HF \rightarrow H_2 + F^\bullet$ 139 kJ mol^{-1}
- $C_2H_5I \rightarrow C_2H_4 + HI$ 209 kJ mol^{-1}
- $C_2H_6 \rightarrow 2\,CH_3$ 368 kJ mol^{-1}

Practical Arrhenius plot, origin *not* included

Intercept = 27.602 *from which* A = 1.1×10^{12} dm^3 mol^{-1} s^{-1}

Slope = -22,550 *from which* E = 188 kJ/mol

ln k /(dm^3 mol^{-1} s^{-1})

K / *T*

Rate constant expression

$$k = A\exp\left(\frac{-E_A}{RT}\right)$$

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

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

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

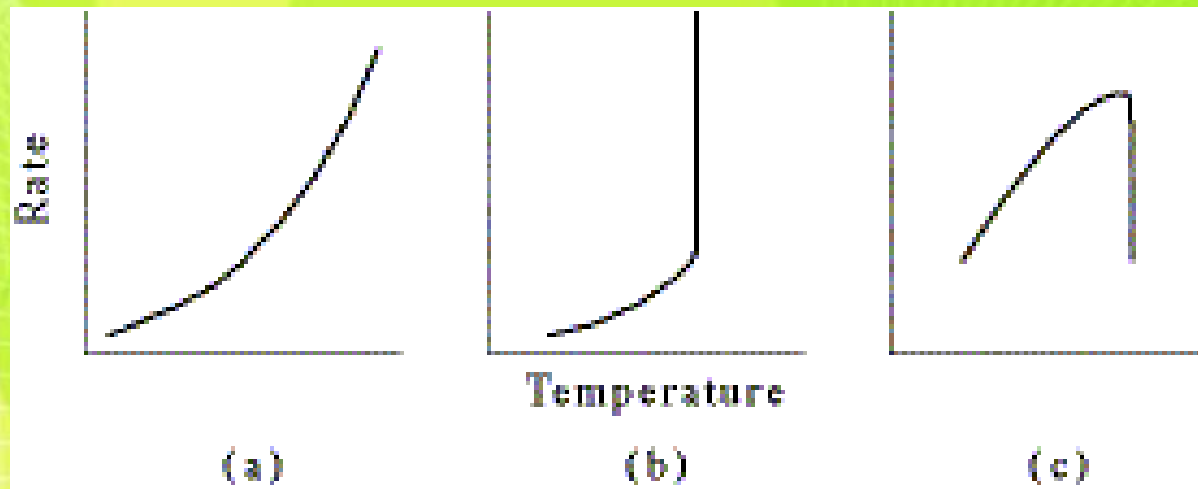$$-0.693 = \left(\frac{-E_A}{8.314}\right)\left(1.12526 \times 10^{-4}\right)$$

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

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

Temperature Dependence of k

Svante Arrhenius
Winner of the 3rd Nobel
Prize in Chemistry

The rate constant can vary in different ways with T.

Differential form of the Arrhenius Equation:

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

Arrhenius Parameters

Integrated forms of Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{RT} \qquad k = Ae^{-E_a/RT}$$

E_a is the <u>activation energy</u>. 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 <u>pre-exponential or Arrhenius factor</u> 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

$2HI(g) \rightarrow I_2(g) + H_2(g)$
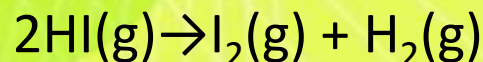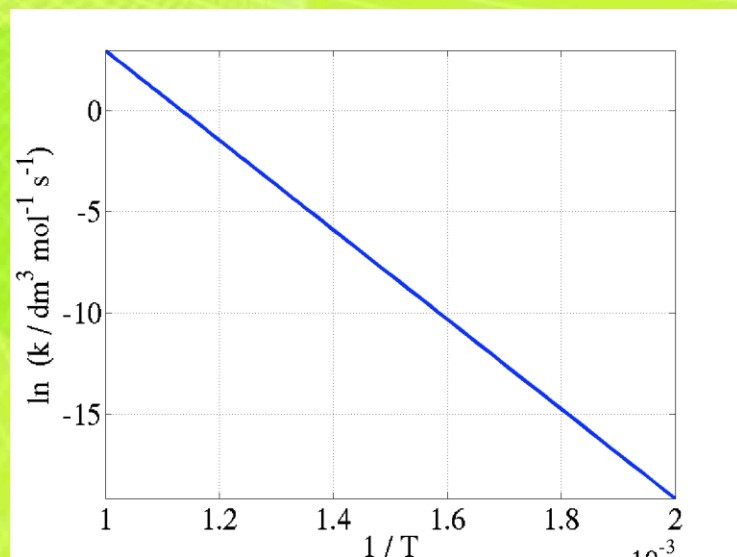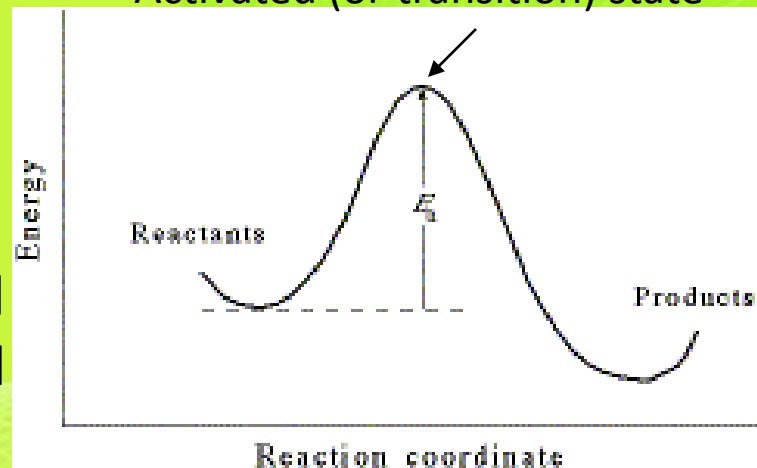
Transition-State Theory
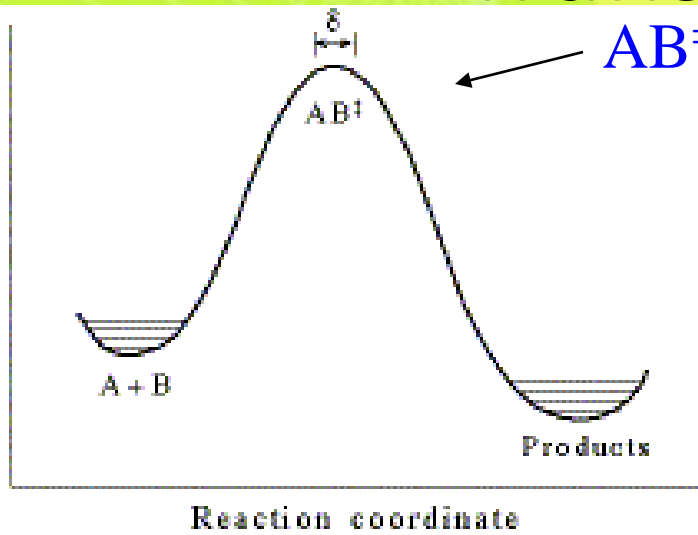
$AB^{‡}$ is the transition state (or activated complex.)

Transition state theory assumes that the transition state and reactants are in equilibrium with each other, and uses concepts from chemical equilibrium and statistical mechanics to find kinetic info such as rate constants!

Eyring Equation (key to transition-state theory)

$$k = \frac{k_B T}{h} K_C^{‡}$$

From CEq:

$$K^{‡} = e^{-\Delta G^{‡}/RT}$$

Change in Gibbs energy from reactants to TS

So…

$$k = \frac{k_B T}{h} e^{-\Delta G^{‡}/RT} \xrightarrow{\Delta G = \Delta H - T\Delta S} k = \frac{k_B T}{h} e^{\Delta S^{‡}/R} e^{-\Delta H^{‡}/RT}$$

Enthalpy of activation

Entropy of activation

Relating E_a to thermodynamics!

Necessary Pieces...

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

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

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

What about A, the pre-exponential?

$$E_a = RT + \Delta U^{\ddagger} \quad \text{and} \quad \Delta U^{\ddagger} = \Delta H^{\ddagger} - RT\Delta^{\ddagger} n_g$$

so $\boxed{E_a = RT + \Delta H^{\ddagger} - RT\Delta^{\ddagger} n}$

Unimolecular Gas Phase Reaction
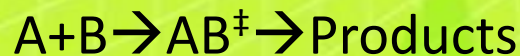
A→A‡→Products   so $E_a = RT + \Delta H^{\ddagger}$

$$k = \frac{k_B T}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT}$$

$$k = e\frac{k_B T}{h} e^{\Delta S^{\ddagger}/R} e^{-E_a/RT}$$

Same for reactions in solution

Bimolecular Gas Phase Reaction

A+B→AB‡→Products   so $E_a = \Delta H^{\ddagger} + 2RT$

$$k = e^2 \frac{k_B T}{h} e^{\Delta S^{\ddagger}/R} e^{-E_A/RT}$$

What is A?

Transition State Theory and NMR Lab

In the NMR/N,N-DMA Paper, Gasparro et al. found an activation energy of 70.3 kJ/mol and a pre-factor of 1.87×10^{10} s^{-1}. Using these values, and a temperature of 298 K, find…

$$\Delta H^{\ddagger} \qquad \Delta S^{\ddagger} \qquad \Delta G^{\ddagger}$$

Why is TST important?

1. Provides details of a reaction on the molecular scale.
2. Connects quantum mechanics and kinetics.
3. Currently used for many computational studies on reaction rates.
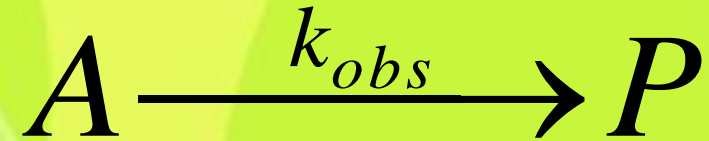
Reaction Mechanisms
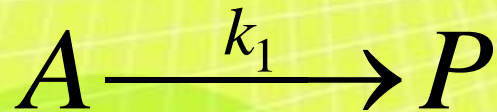
Always remember….

- One can <u>never prove</u> a reaction mechanism, although evidence may disprove a mechanism.

- Verifying proposed mechanisms requires extensive experimental verification of each proposed step!

Let's examine a reaction ...

$$A \xrightarrow{k_{obs}} P$$

Reaction could progress in multiple ways... How can we distinguish?

Case 1: One elementary step

Case 2: Two step reaction

$$A \xrightarrow{k_1} P$$

$$A \xrightarrow{k_1} I$$

$$I \xrightarrow{k_2} P$$

let's focus on the intermediate...

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$
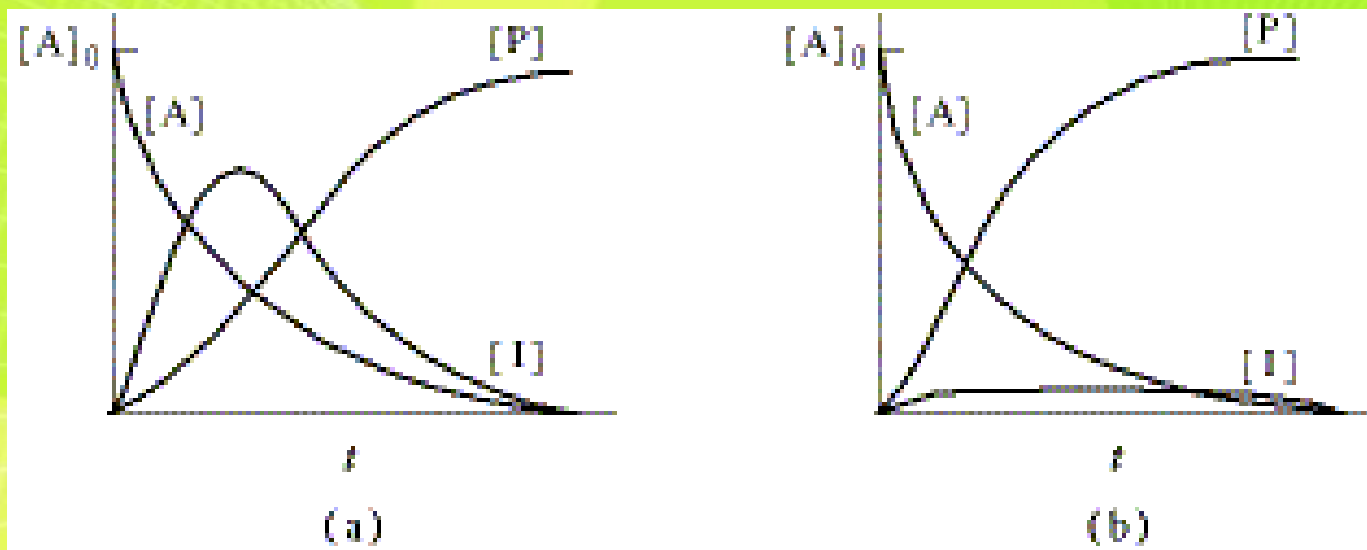
How do k_1 and k_2 relate in case a? in case b?

(a) I forms quickly but decays slowly... k_1 is fast relative to k_2.

(b) I builds up to a constant, nearly negligible, concentration until near end of reaction. ... k_1 is slow relative to k_2.

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

Steady state approximation... Valid only if k2 > k1.

Rate Laws do not yield unique mechanisms

An empirically determined rate law does not imply a unique reaction mechanism!

Consider reaction: $2\mathrm{NO}(g) + \mathrm{O}_2(g) \xrightarrow{\ k_{obs}\ } 2\mathrm{NO}_2(g)$
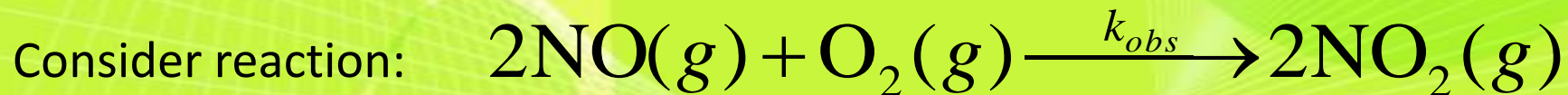
Experimentally, it was determined that the rate is given by:

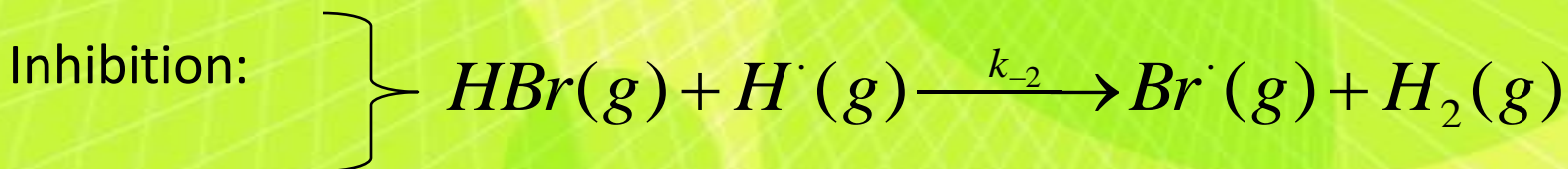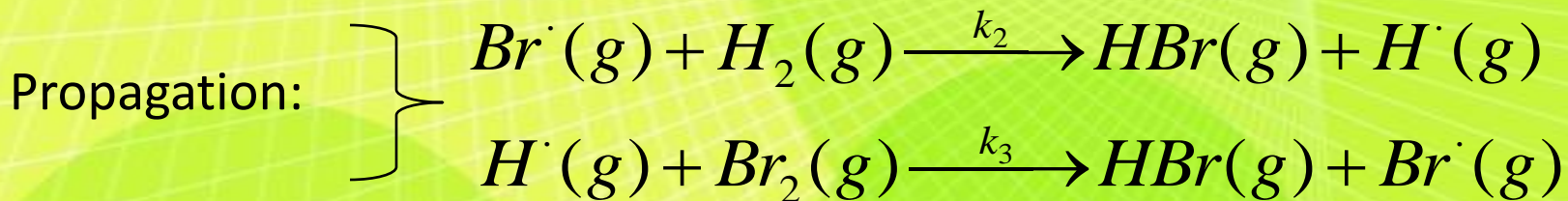$$v(t) = k_{obs}[\mathrm{NO}]^2[\mathrm{O}_2]$$

Researchers proposed two possible mechanisms. They need to determine if one of them is correct.

So how would researchers distinguish between the mechanisms?

Remember the Chain Rxn from CK-6?

$$H_2(g) + Br_2(g) \rightarrow 2HBr(g) \qquad v(t) = \frac{2k'[H_2][Br_2]^{1/2}}{1 + k''[HBr][Br_2]^{-1}}$$

<u>Proposed Mechanism</u>

Initiation:
$$Br_2(g) + M(g) \xrightarrow{\quad k_1 \quad} 2Br^{\cdot}(g) + M(g)$$

Propagation:
$$Br^{\cdot}(g) + H_2(g) \xrightarrow{\quad k_2 \quad} HBr(g) + H^{\cdot}(g)$$
$$H^{\cdot}(g) + Br_2(g) \xrightarrow{\quad k_3 \quad} HBr(g) + Br^{\cdot}(g)$$

Inhibition:
$$HBr(g) + H^{\cdot}(g) \xrightarrow{\quad k_{-2} \quad} Br^{\cdot}(g) + H_2(g)$$

Termination:
$$2Br^{\cdot}(g) + M(g) \xrightarrow{\quad k_{-1} \quad} Br_2(g) + M(g)$$

A reaction: $CO + Cl_2 \xrightarrow{\quad\times\quad} COCl_2$ ...... ??

- Exptal rate law:

$$-\frac{d[CO]}{dt} = k[CO][Cl_2]^{\frac{1}{2}}$$

- Conclusion?: reaction does *not* proceed as written

- "Elementary" reactions; rxns. that proceed as written at the *molecular level*.

  - $Cl_2 \rightarrow Cl + Cl$ (1)   ● Decay
  - $Cl + CO \rightarrow COCl$ (2)   ● Collisional
  - $COCl + Cl_2 \rightarrow COCl_2 + Cl$ (3)   ● Collisional
  - $Cl + Cl \rightarrow Cl_2$ (4)   ● Collisional

- Steps 1 through 4 comprise the "mechanism" of the reaction.

$$-\frac{d[CO]}{dt} = k_2[CO][Cl_2]^{\frac{1}{2}}$$
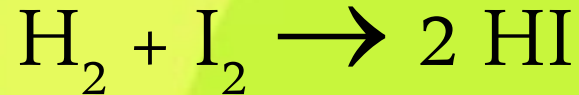
- If steps 2 & 3 are **slow** in comparison to 1 & 4. ....then,

  – $Cl_2 \rightleftharpoons 2Cl$ or $K = [Cl]^2 / [Cl_2]$

  – So $[Cl] = \sqrt{K} \times [Cl_2]^{1/2}$

  – Hence: $$-\frac{d[CO]}{dt} = k_2^{\frac{1}{2}}.[CO].[Cl_2]^{\frac{1}{2}}$$

  Predict that: *observed* $k = k_2 \times \sqrt{K}$

- Therefore mechanism confirmed (?)

$$H_2 + I_2 \longrightarrow 2\,HI$$

- Predict: $+\,(1/2)\,(d[HI]/dt) = k\,[H_2]\,[I_2]$

- But if via:
  - $I_2 \longrightarrow 2\,I$
  - $I + I + H_2 \longrightarrow 2\,HI$ **rate** $= k_2\,[I]^2\,[H_2]$
  - $I + I \longrightarrow I_2$
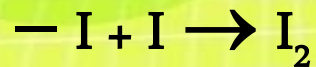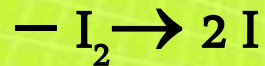
Assume, as before, that 1 & 3 are *fast* cf. to 2

Then: $I_2 \rightleftharpoons 2\,I$ or $K = [I]^2 \,/\, [I_2]$

- Rate $= k_2\,[I]^2\,[H_2] = k_2\,K\,[I_2]\,[H_2]$ (identical)

Check? $I_2 + h\nu \longrightarrow 2\,I$ (light of 578 nm)

Problem

- In the decomposition of azomethane, A, at a pressure of 21.8 kPa & a temperature of 576 K the following concentrations were recorded as a function of time, *t*:

Time, *t* /mins	0	30	60	90	120
[A] / mmol dm^{-3}	8.70	6.52	4.89	3.67	2.75

- Show that the reaction is 1st order in azomethane & determine the rate constant at this temperature.

Recognise that this is a rate law question dealing with the integral method.

$$- (d[A]/dt) = k\,[A]^? = k\,[A]^1$$

Re-arrange & integrate
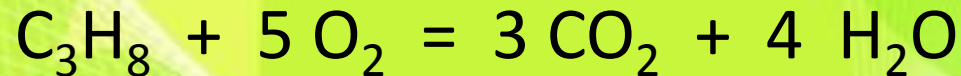
- Test: $\ln[A] = -k\,t + \ln[A]_0$

Complete table:

Time, t /mins	0	30	60	90	120
ln [A]		2.16	1.88	1.59	1.30	1.01

- Plot ln [A] *along* y-axis; t *along* x-axis
- Is it linear? *Yes.* Conclusion follows.

Calc. slope as: -0.00959 so $k = +\,9.6 \times 10^{-3}\,min^{-1}$

More recent questions …

- Write down the rate of rxn for the rxn:

$$C_3H_8 + 5\,O_2 = 3\,CO_2 + 4\,H_2O$$

- for <u>both</u> products & reactants   [8 marks]

For a 2nd order rxn the rate law can be written:

$$- (d[A]/dt) = k\,[A]^2$$

What are the units of k ?   [5 marks]

- Why is the elementary rxn $NO_2 + NO_2 \Rightarrow N_2O_4$ referred to as a bimolecular rxn?
          [3 marks]