

Module 2, Lecture 5

Chemical Kinetics

Part 2

Learning objectives:

- Use graphical methods to determine the rate constant for a first order reaction
- Understand the concept of half-life and be able to determine half-life from experimental data
- Understand the terms *elementary step*, *reaction mechanism*, *reaction intermediate*, *rate-determining step*.
- Derive rate laws for each of two types of mechanism
- Draw a reaction energy profile for a given reaction mechanism.

Textbook: Chapter 14

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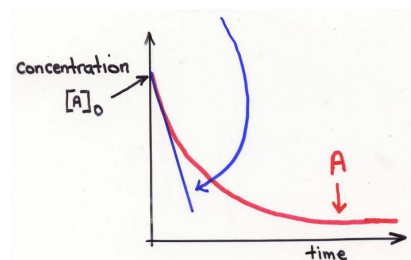
Recap: Initial rates method

- Allows us to deduce x and y.
- Can find the rate constant, k.

$$k = \frac{\text{initial rate}}{[A]_0^x [B]_0^y}$$

However, it would be useful to be able to have an equation that allows us to:

- Not be restricted only to information about the start of the reaction.
- Be able to find the concentration of reactants at ANY point in the reaction.



Alternative method: **integrated rate law**

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Integrated rate law for first order reactions

- Relates concentration to time t .
- Alternative method for finding k .

For a 1st order reaction: $\text{rate} = -\frac{d[A]}{dt} = k[A]$

Mathematical manipulation (integration) gives

$$\ln [A]_t = \ln [A]_0 - kt \quad \text{NB: Don't need to know how to do the math}$$

For 1st order reaction **if we know initial concentration $[A]_0$ and k , we can calculate concentration of A, $[A]_t$, after some time t .**

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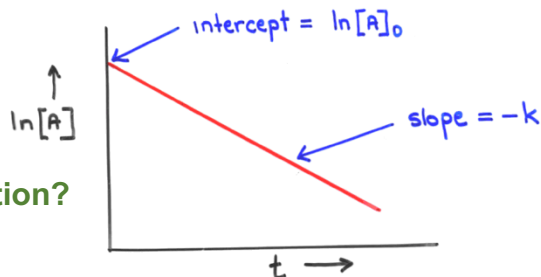
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Q: What if we don't know the rate constant, k , or the initial concentration, $[A]_0$?

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

$y = mx + c$ equation of a straight line!

A: Plot of $\ln [A]_t$ versus t will be linear with
 slope = $-k$
 intercept = $\ln [A]_0$



Q: What if we don't know the order of reaction?

A: To show a reaction is 1st order

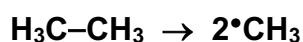
- show that a plot of $\ln [A]$ versus t is linear
- **can obtain k from slope of plot**

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Example

For the decomposition of ethane C_2H_6 :



Use data obtained at 1000 K to show the reaction is **1st order** and **determine k** .

time / s	0	1000	2000	3000	4000
$[\text{C}_2\text{H}_6]$ / mol L ⁻¹	1.59	0.92	0.53	0.31	0.18
$\ln[\text{C}_2\text{H}_6]$	0.46	-0.083	-0.64	-1.17	-1.71

Concentration data must be converted to ln form. 

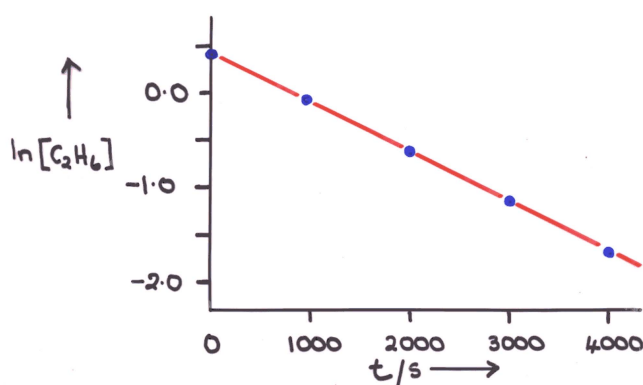
$\ln[\text{C}_2\text{H}_6]_0$

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This gives the following graph – a straight line
i.e. first order reaction

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



$$\begin{aligned} \text{slope} &= \frac{(-1.71) - (0.46)}{4000 - 0} \\ &= -5.43 \times 10^{-4} \text{ s}^{-1} = -k \\ \therefore k &= 5.43 \times 10^{-4} \text{ s}^{-1} \end{aligned}$$

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Half-life, $t_{1/2}$

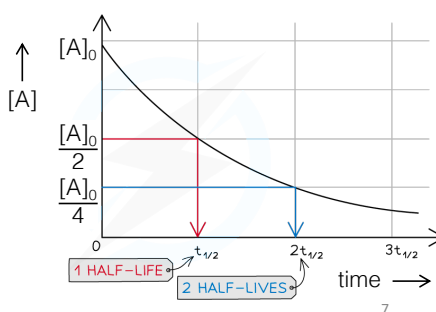
Convenient way to describe how fast a reaction occurs.
Common in nuclear physics, medicine.



Half-life: Time taken for [reactant] to reach $\frac{1}{2}$ its initial value.

For a reactant A, half life occurs when $[A]_{t_{1/2}} = \frac{[A]_0}{2}$

Can show graphically



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$t_{1/2}$ and k

For **1st order reaction** value of $[A]_0/2$ at $t=t_{1/2}$ can be substituted into integrated rate equation.

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

$$\ln[A]_t - \ln[A]_0 = \ln \frac{[A]_t}{[A]_0} = -kt \quad \text{property of logs i.e. } \ln a - \ln b = \ln \frac{a}{b}$$

At half life $t=t_{1/2}$: $[A]_t = \frac{[A]_0}{2} = 0.5[A]_0$

So: $\ln \frac{0.5[A]_0}{[A]_0} = \ln(0.5) = -kt_{1/2}$

$$\therefore t_{1/2} = -\frac{\ln(0.5)}{k} = \frac{0.693}{k}$$

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

For 1st order kinetics, **$t_{1/2}$ is independent of the initial concentration** of A, i.e. $[A]_0$.

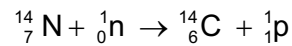
(For the other order reactions, $t_{1/2}$ depends on $[A]_0$ and half-life concept little used.)

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Radioactive decay

1st order process for which $t_{1/2}$ is useful - basis of **radio dating** methods



Radiocarbon Dating

- Radioactive ${}^{14}\text{C}$ formed in atmosphere as ${}^{14}\text{CO}_2$ by collision of neutrons with ${}^{14}_7\text{N}$
- ${}^{14}\text{C}/{}^{12}\text{C}$ ratio in living matter kept constant by exchange of CO_2 from atmosphere via photosynthesis. This exchange stops when living object dies.
- ${}^{14}\text{C}$ decays ${}^{14}_6\text{C} \rightarrow {}^{14}_7\text{N} + {}^0_{-1}\beta$ $t_{1/2} = 5780 \text{ y}$
- ${}^{14}\text{C}/{}^{12}\text{C}$ ratio diminishes with time
- Calculate time since death by **measuring amount of remaining ${}^{14}\text{C}$** and **using $t_{1/2}$ of ${}^{14}\text{C}$**
– useful range – 1000 to 50 000 y

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Radioactive decay in medicine

Common nuclear medicine (unsealed source) therapies

Substance	Condition
${}^{131}\text{I}$ - sodium iodide	hyperthyroidism and throat cancer
${}^{90}\text{Y}$ - Ibritumomab tiuxetan (Zevalin) ${}^{131}\text{I}$ - tositumomab (Bexxar)	refractory lymphoma
${}^{131}\text{I}$ - MIBG metaiodobenzylguanidine	neuroendocrine tumors
${}^{151}\text{Sm}$ or ${}^{89}\text{Sr}$	palliative bone pain treatment



Neuroendocrine tumor seen after MIBG treatment

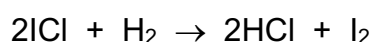
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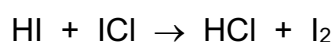
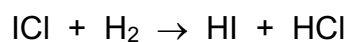
Reaction mechanisms

Elementary reactions - The reason we cannot predict the rate law from the overall chemical equation is that almost all reactions take place in a series of steps called elementary reactions (steps).

Overall reaction:



Elementary reactions:

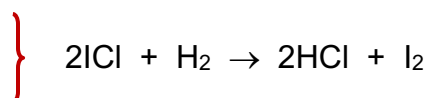
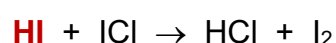
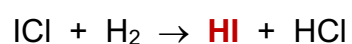


} **reaction mechanism**

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Elementary reactions



Elementary steps are usually **unimolecular** or **bimolecular**.

They may involve **reaction intermediates** – species which play a role in the reaction but which do not appear in the overall equation (e.g. **HI**).

Because intermediates are neither a reactant (or product) they do not appear in the overall rate law.

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Reaction mechanisms

A series of elementary reactions describing an overall reaction is called a **reaction mechanism**.

In a reaction mechanism, the sum of the elementary steps must equal the overall equation.

Writing rate laws from chemical equations, using stoichiometric coefficients, is allowed **ONLY** for elementary reactions



Careful! NOT for the overall reaction

e.g. For step 1 $\text{rate} = k [\text{ICl}] [\text{H}_2]$
 For step 2 $\text{rate} = k [\text{HI}] [\text{ICl}]$

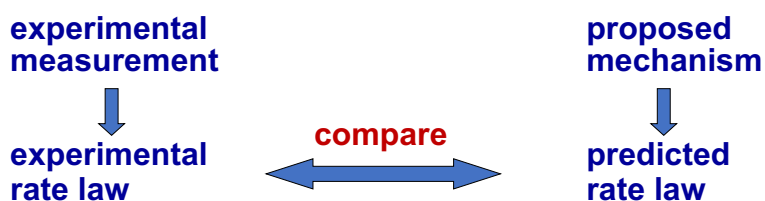
Tricky matter of collecting these individual rate laws into an overall rate law, which should agree with the **experimentally determined rate law**.

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Deducing the reaction mechanisms

Two paths are used to find the reaction mechanism and overall rate law



Although predicted rate law may agree with experimental rate law. The proposed mechanism may be incorrect – a different mechanism may lead to the same rate law.

Experimental rate law can only support proposed mechanism – **it can never prove it**.

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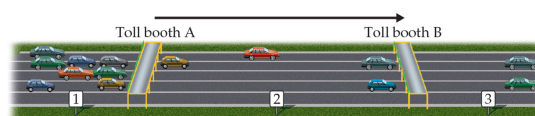
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Rate-determining step

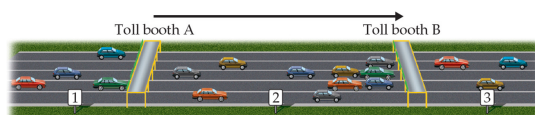
To derive a predicted rate law we need to propose a **rate-determining step**.

The rate-determining step:

- The elementary step in a reaction mechanism that is considered **slower** than any other step.
- Controls the overall rate of reaction.
- “Bottleneck” of the reaction



(a) Cars slowed at toll booth A, rate-determining step is passage through A



(b) Cars slowed at toll booth B, rate-determining step is passage through B

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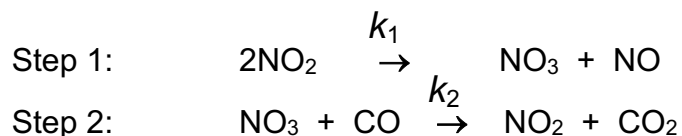
Case #1: First step is rate determining

Derive a mechanism for



Experimental rate law: $\text{rate} = k[\text{NO}_2]^2$

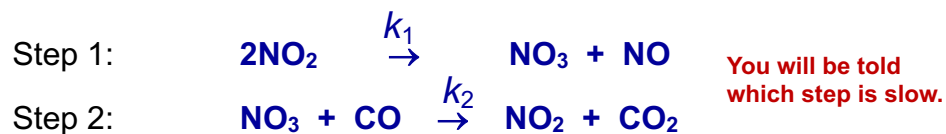
Propose possible mechanism – involves two elementary steps



You will be provided with elementary steps - you don't need to write them yourself.

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Proposed that step 2 is much faster than step 1 i.e. step 1 is **rate determining**

Predicted rate law can be written down directly from stoichiometry of slow step.

$$\text{rate} = \text{rate of rate-determining step} = k_1[\text{NO}_2]^2$$

Predicted rate law same as experimental rate law

- Proposed mechanism **possibly** correct – mechanism is consistent with exptl rate law.
- Further confirmation needs other measurements e.g. detection of NO_3 **reaction intermediate**.

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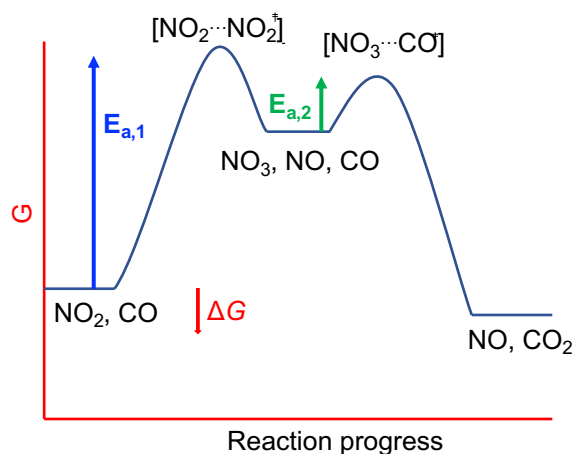
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Reaction energy profile

Plot of energy changes during reaction.

For proposed mechanism two 'peaks' correspond to two elementary reactions.

Because step 1 is slower (rate determining) it must have a **higher activation energy**, E_a (see Lecture 6)



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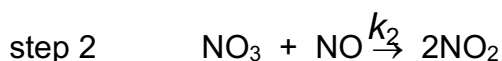
Case #2: Second step is rate determining

Derive a mechanism for:



Experimental rate law: $\text{rate} = k[\text{NO}]^2[\text{O}_2]$

Possible mechanism – fast pre-equilibrium step **followed** by slow step



If step 2 **rate determining** – write rate law down directly.

$$\text{rate} = k_2 [\text{NO}_3] [\text{NO}]$$

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$$\text{rate} = k_2 [\text{NO}_3] [\text{NO}] \quad (1)$$

Expression involving concentration of reactive intermediate NO_3 but this is of little value (difficult to determine $[\text{NO}_3]$).

Need to involve reactants of known concentration.

So use expression for equilibrium constant for step 1:

$$K_1 = \frac{[\text{NO}_3]}{[\text{NO}][\text{O}_2]}$$

If an intermediate appears in the rate law we need to use K to get rid of it.

$$\therefore [\text{NO}_3] = K_1 [\text{NO}][\text{O}_2] \quad (2)$$

And then substitute for $[\text{NO}_3]$ in Eq. (1) from Eq. (2): $\text{rate} = k_2 [\text{NO}] K_1 [\text{NO}][\text{O}_2]$

$$= k_2 K_1 [\text{NO}]^2 [\text{O}_2]$$

$$= k [\text{NO}]^2 [\text{O}_2]$$

Same as experimental rate law!

(constant x another constant = new constant i.e. $k_2 K_1 = k$)

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*** Homework ***

Chemistry – the central science 15th Ed

Brown et al.

Problems 14.20 14.35

Answers on Blackboard

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