1st Order Kinetics

- The rate of a process can be empirically expressed through a ‘rate law’
- Integration of the rate law allows us to describe how concentrations change with time
- The half-life ($t_{1/2}$) is a way of quantifying how quickly the transformation happens and for a first order reaction is related to the rate constant $k = \ln(2)/t_{1/2}$
- Radioactive decay follows first order kinetics and can be used to find the age of a material
- Most chemical reactions do not follow first order kinetics but can, in some cases, be made to follow pseudo-first order kinetics

Kinetics is the study of the rate of change and lies at the heart of modern chemistry. Over the course of the 20th century eight Nobel Prizes were *directly* awarded for work in this field. This lecture provides an introduction to 1st Order Kinetics.

“Nobody, I suppose, could devote many years to the study of chemical kinetics without being deeply conscious of the fascination of time and change: this is something that goes outside science into poetry; but science, subject to the rigid necessity of always seeking *closer approximations* to the truth, itself contains many poetical elements.”
C.N. Hinshelwood

Rate of a Reaction

When we talk about the ‘rate of a reaction’, we mean the rate at which either the reactants are consumed or the rate at which the products are formed. Fig 1 shows an example plot of how the concentrations of the reactant (R) and product (P) changes as a function of time. As the reactants are used up the rate of the reaction slows down.

$$\text{rate} = \frac{\text{change in concentration}}{\text{change in time}} \quad (1)$$

more succinctly we can write this as:

$$\nu = \frac{dC}{dt} \quad (2)$$

Figure 1: *Example variation of the con reactant (R) and product (P) as a functi slope of the plot gives a measure of the ra R is defined by Eq. 10, with k = 1 s^{-1} dm^{-3}.*

where ν is the rate ($dm^{-3}\,s^{-1}$), C (mol dm^{-3}) and t is the time (the disproportionation of hyd

$$2H_2O_2 \rightleftharpoons$$

we could define the rate itoring the productio of hydrogen perox reaction in an ac duction of wat to the stoich peroxide this me two

Introduction: First Order Kinetics

Dr. C . Batchelor-McAuley
Oxford University, UK

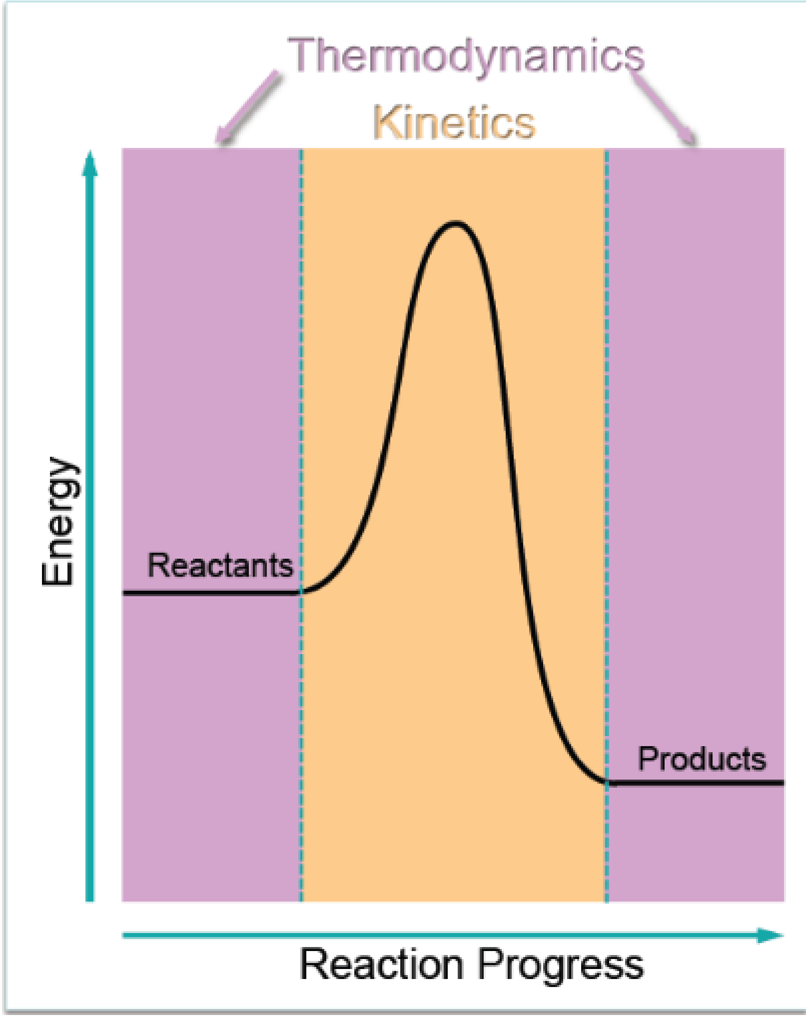
What is "Kinetics"?

Thermodynamics

- *Can* a reaction happen?

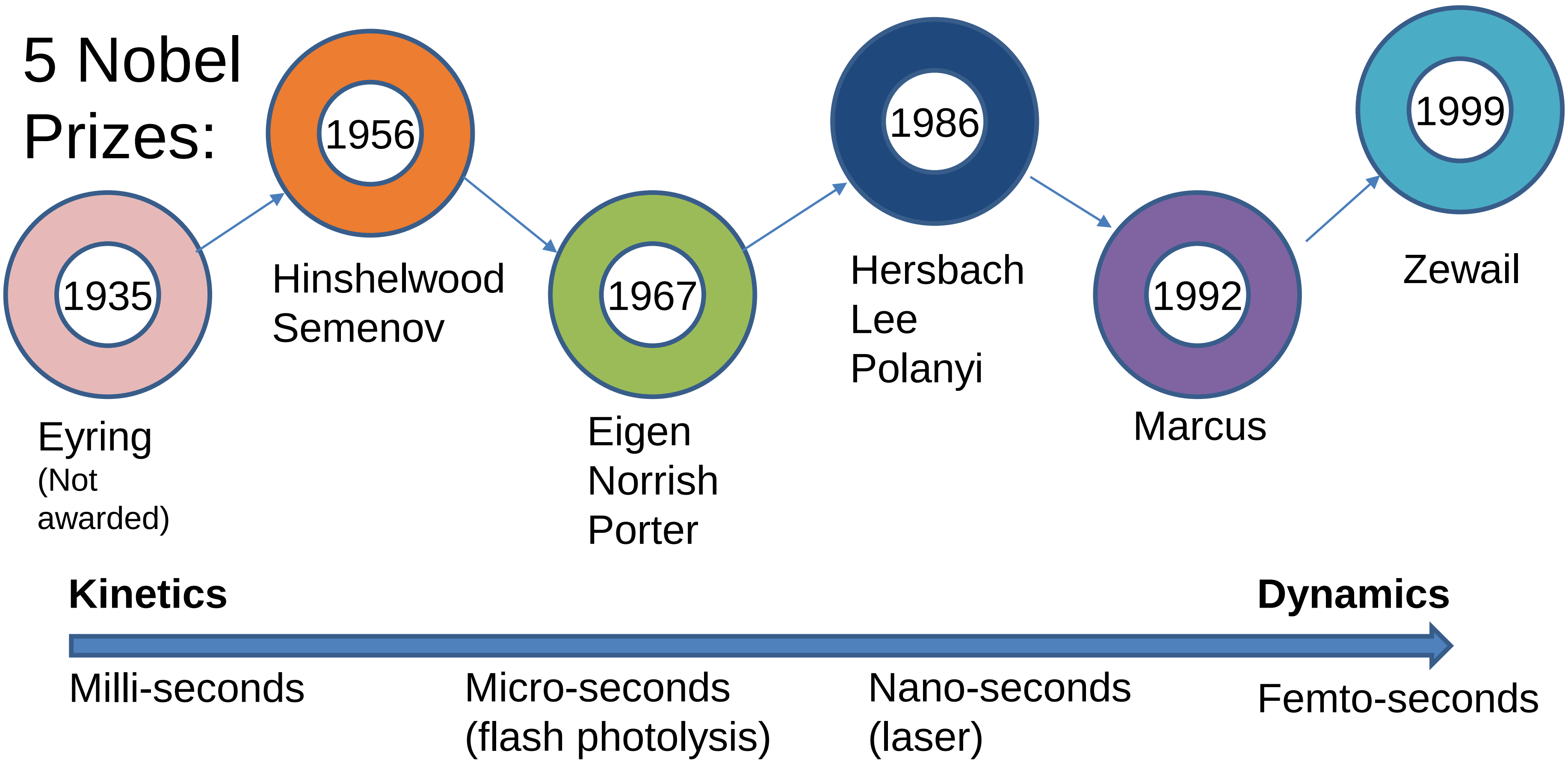
Kinetics

-How *fast* does a reaction happen?



"Nobody, I suppose, could devote many years to the study of chemical kinetics without being deeply conscious of the fascination of time and change: this is something that goes outside science into poetry; but science, subject to the rigid necessity of always seeking **closer approximations** to the truth, itself contains many poetical elements." *C.N. Hinshelwood*
(1956 Nobel Prize: Research on ***Reaction Mechanisms****)*

5 Nobel Prizes:

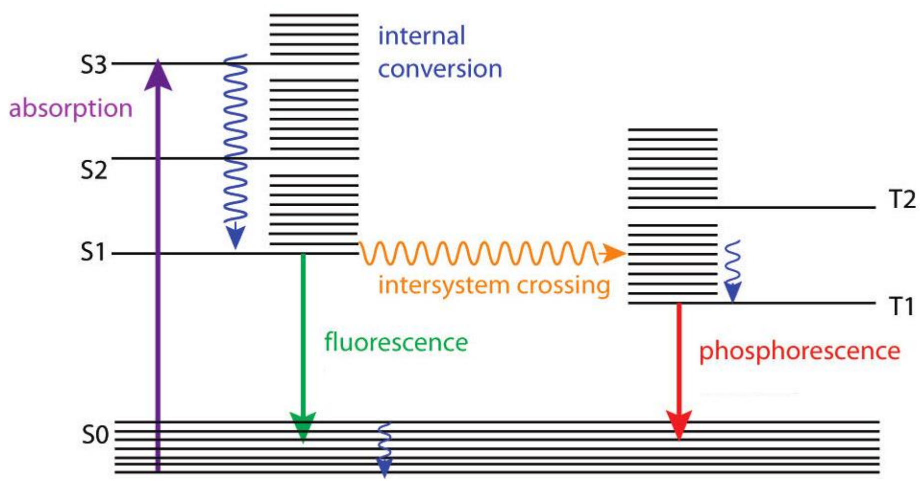


Builds on (recap):
- Definition of a Rate
- Rate Laws

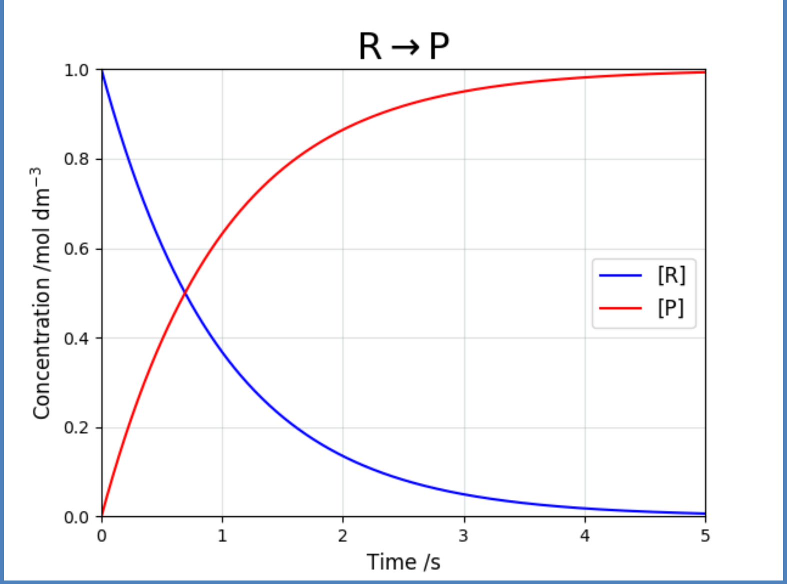
Calculus:
- A closer look

Primary Objectives:
- Integrated Rate Law
- Definition of a half-life
- What are the applications?

Links to:
- Arrhenius equation
- Photochemistry
- Reaction Dynamics



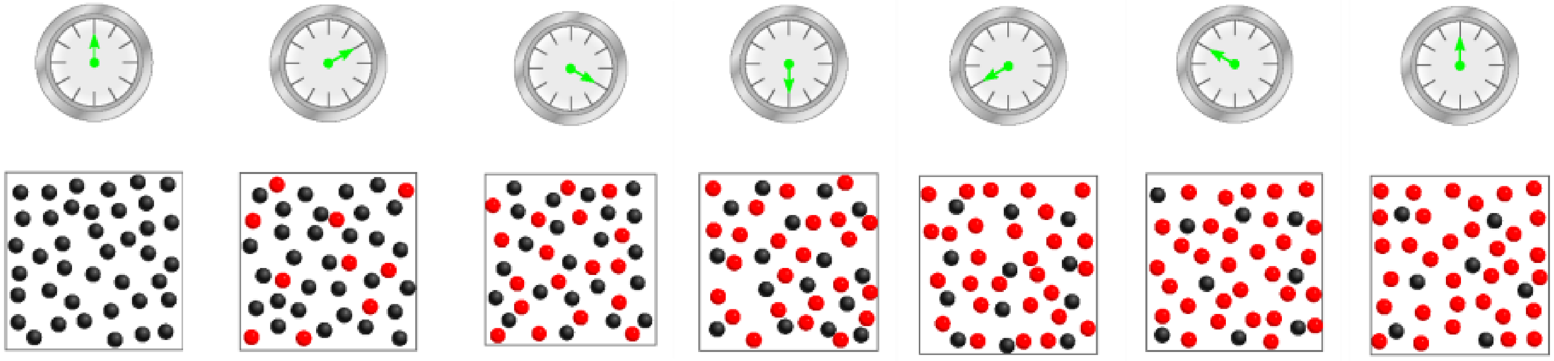
Recap: Rates



Rate = $\frac{\text{Change in Concentration}}{\text{Change in Time}}$

$$v = \frac{dC}{dt}$$

R ⟶ P



Recap: Rate laws

Definition: General Rate Law

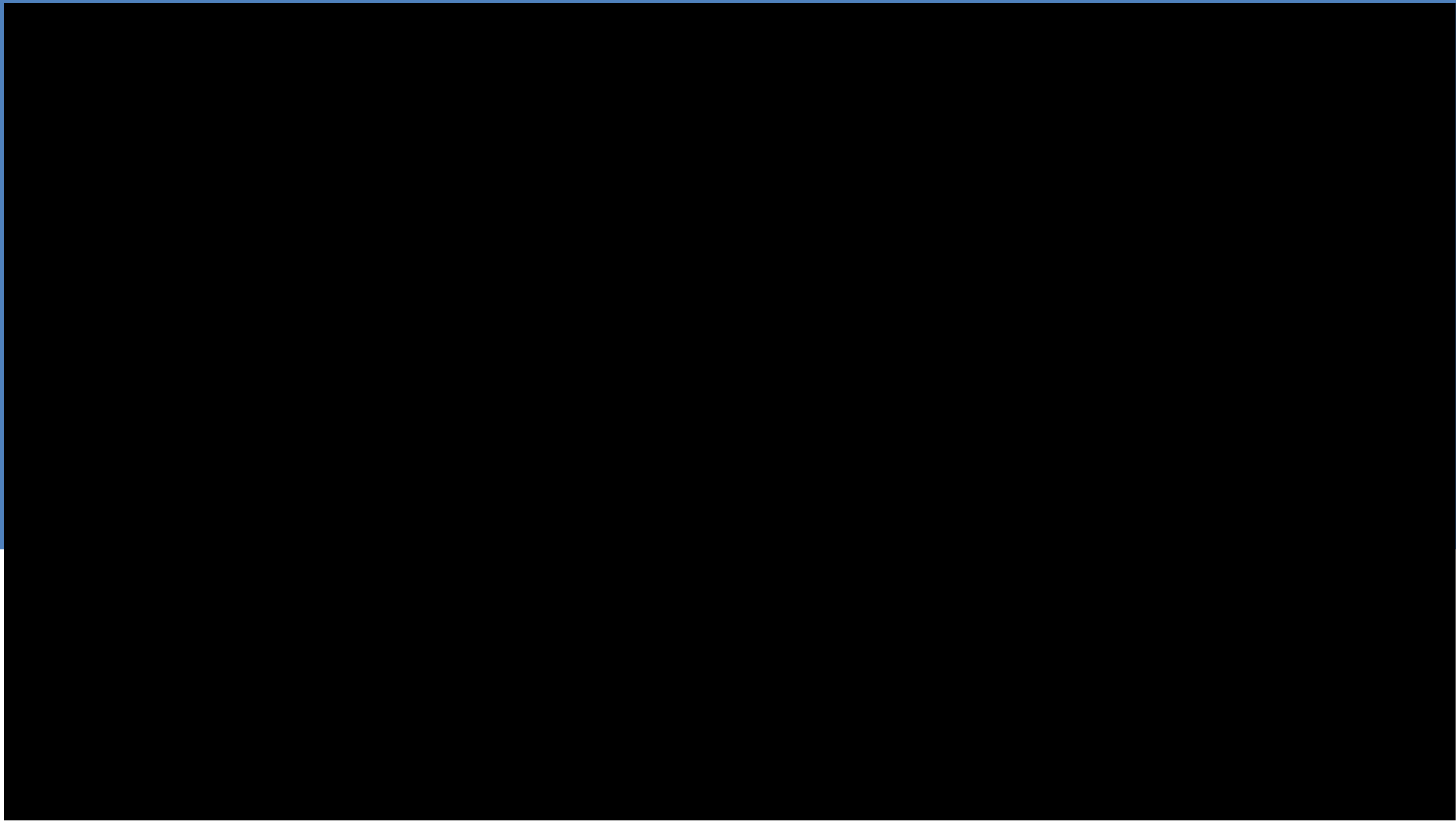
$$\nu = kC_A^a C_B^b C_C^c \ ...$$

Reaction is a order in A
Reaction is b order in B
Reaction is (a+b+c..) order overall

The **rate law** expresses the relationship of the rate of a reaction to the rate constant (k) and the concentrations of the reactants, products and catalysts raised to some power.

We find the rate law *empirically*.

Calculus: Exponential



Integrated Rate Law

We want to know how the concentrations change during a reaction...

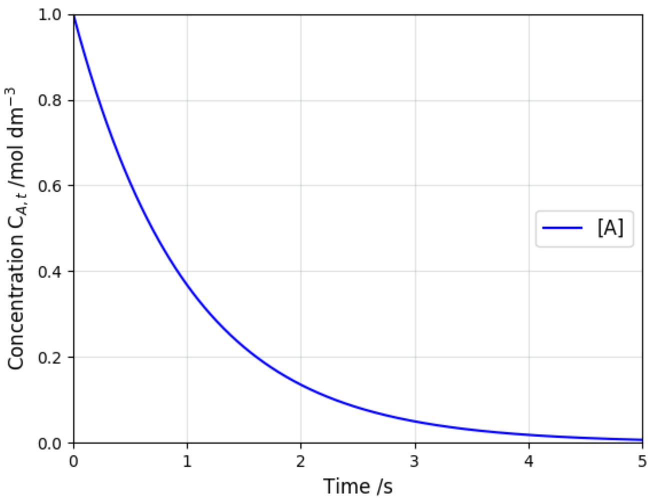
$$A \rightarrow B$$

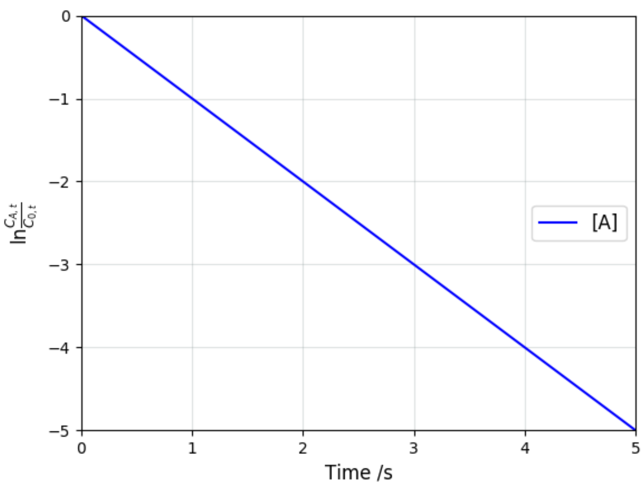
$$\frac{dC_A}{dt} = -kC_A$$

$$\int_{C_{A.0}}^{C_{A,t}} \frac{1}{C_A} dC_A = -\int_0^t kdt$$

$$\ln \frac{C_{A,t}}{C_{A,0}} = -kt$$

$$C_{A,t} = C_{A,0}e^{-kt}$$



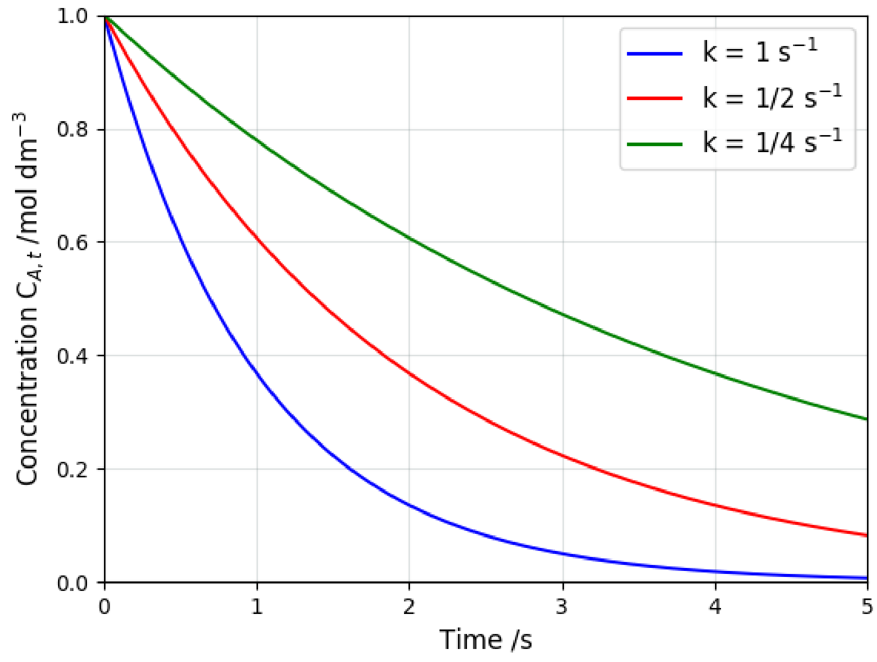


Changing the Rate Constant

We want to know how the concentrations change during a reaction...

$$A \rightarrow B$$

$$C_{A,t} = C_{A,0}e^{-kt}$$



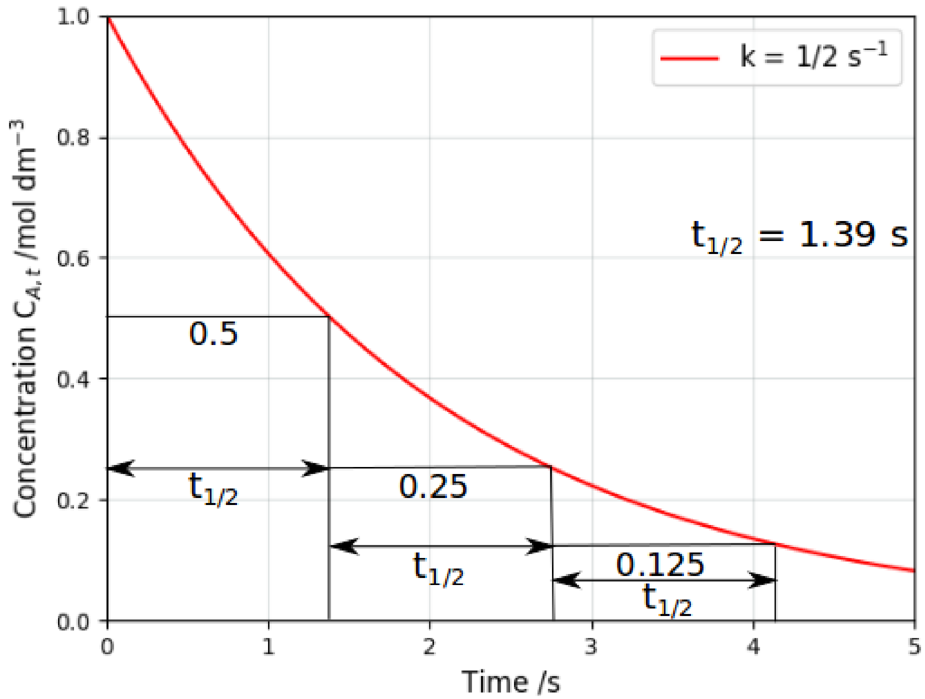
Half-Life

How long does it take for the reactant to drop to half of its original concentration?

$$A \rightarrow B$$

$$C_{A,t} = C_{A,0}e^{-kt}$$

Set: $C_{A,t} = \frac{1}{2}C_{A,0}$



Definition: First Order half-Life

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

Neutron Emitter: ^{252}Cf

Half-life = 2.7 yrs

- 1 microgram releases 170 million neutrons per minute

How long will it take the activity of 1 microgram to drop to 85 million neutrons per minute?

A) 27 years

B) It'll never happen

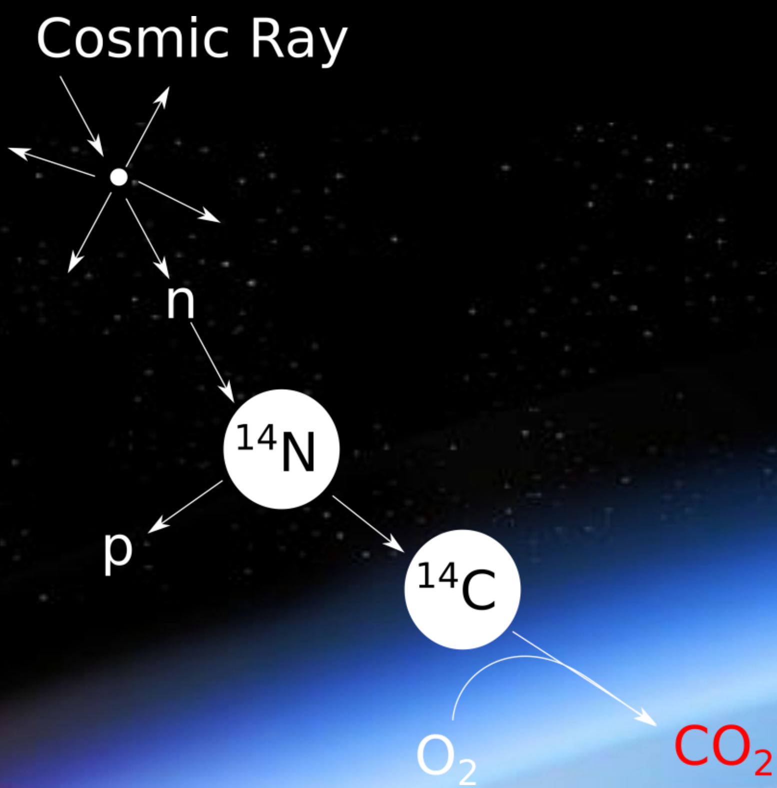
C) 2.7 years

D) Within a few seconds

"... the investigation of human history through the use of chemistry..."

*W. Libby (1956 Nobel Prize: Research on **Carbon Dating**)*

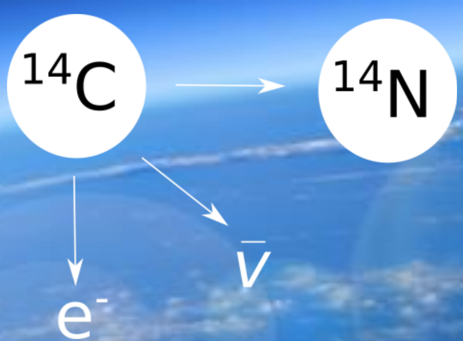
Formation:



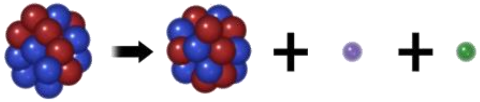
Beta Decay:

14C to 14N

Half-life 5730±40 yrs



Beta Decay ^{14}C to ^{14}N
Half-life 5730±40 yrs



Measured decay rate of (recently) living material: 13.56 atoms min^{-1} gC^{-1}

Libby's original Carbon-14 decay rate Geiger Counter

What is the abundance of 14C?

Main isotopes of carbon				
Isotope	Abundance	Half-life ($t_{1/2}$)	Decay mode	Product
^{11}C	syn	20 min	β^+	^{11}B
^{12}C	98.9%	stable		
^{13}C	1.1%	stable		
^{14}C	trace	5730 y	β^-	^{14}N
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Wikipedia

$$\frac{dN}{dt} = -kN$$

$$\begin{aligned} k &= \frac{\ln(2)}{t_{1/2}} \\ &= \frac{\ln 2}{5730 * 365.24 * 24 * 60} \\ &= 2.3 \times 10^{-10}\ \text{min}^{-1} \end{aligned}$$

$$13.56\ \text{atoms min}^{-1}\text{gC}^{-1} = N\ 2.3 \times 10^{-10}\ \text{min}^{-1}$$

$$N = 5.9 \times 10^{10} \text{atoms gC}^{-1}$$

Objectives:

- **Integrated Rate Law**

  -Allows us to describe how the concentration of a species changes with time

- **Half-life**

  -Provides a measure of how quickly a reaction happens and is related to the rate constant

- **What are the applications?**

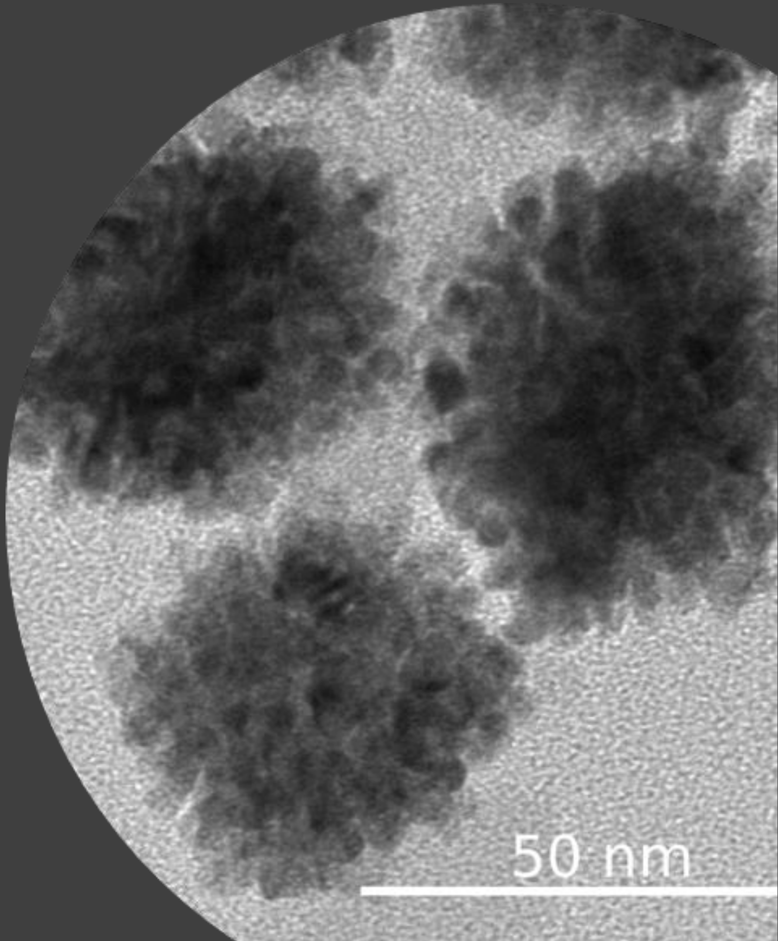
  -Gain insight into chemical mechanism

  -Radioactive Decay- Carbon dating

Hydrogen Peroxide

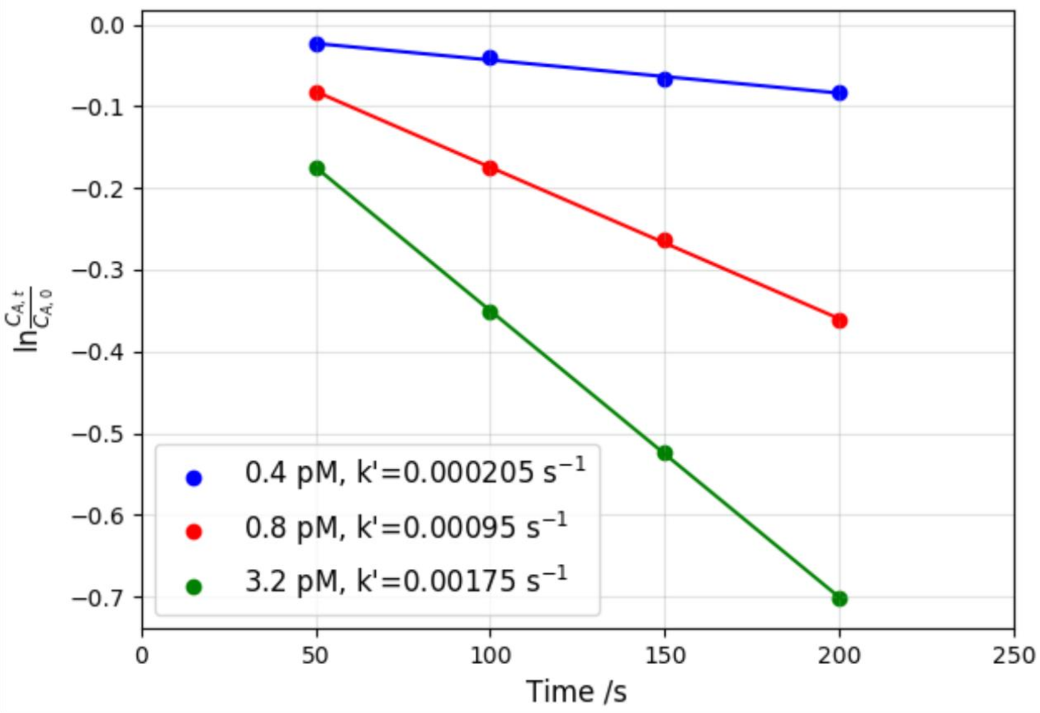
$$2\mathrm{H_2O_2} \rightleftharpoons \mathrm{O_2} + 2\mathrm{H_2O}$$

$$\frac{dC_{H_2O_2}}{dt} = -2kC_{H_2O_2}C_{NP}$$



Hydrogen Peroxide
Decomposition

$$2\mathrm{H_2O_2} \rightleftharpoons \mathrm{O_2} + 2\mathrm{H_2O}$$



$$\frac{dC_{H_2O_2}}{dt} = -2kC_{H_2O_2}C_{NP}$$

$$\ln\frac{C_{H_2O_2,t}}{C_{H_2O_2,0}} = -2kC_{NP}t$$

$$k = 5.4 \times 10^8\ \mathrm{mol^{-1}\ dm^3\ s^{-1}}$$

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