Unit 2 – Day 3

Kinetics

Radioactivity and multistep reactions

Last time

- First Order Integrated Rate Laws

- Half-Lives of First-Order Reactions

- Second Order Integrated Rate Laws
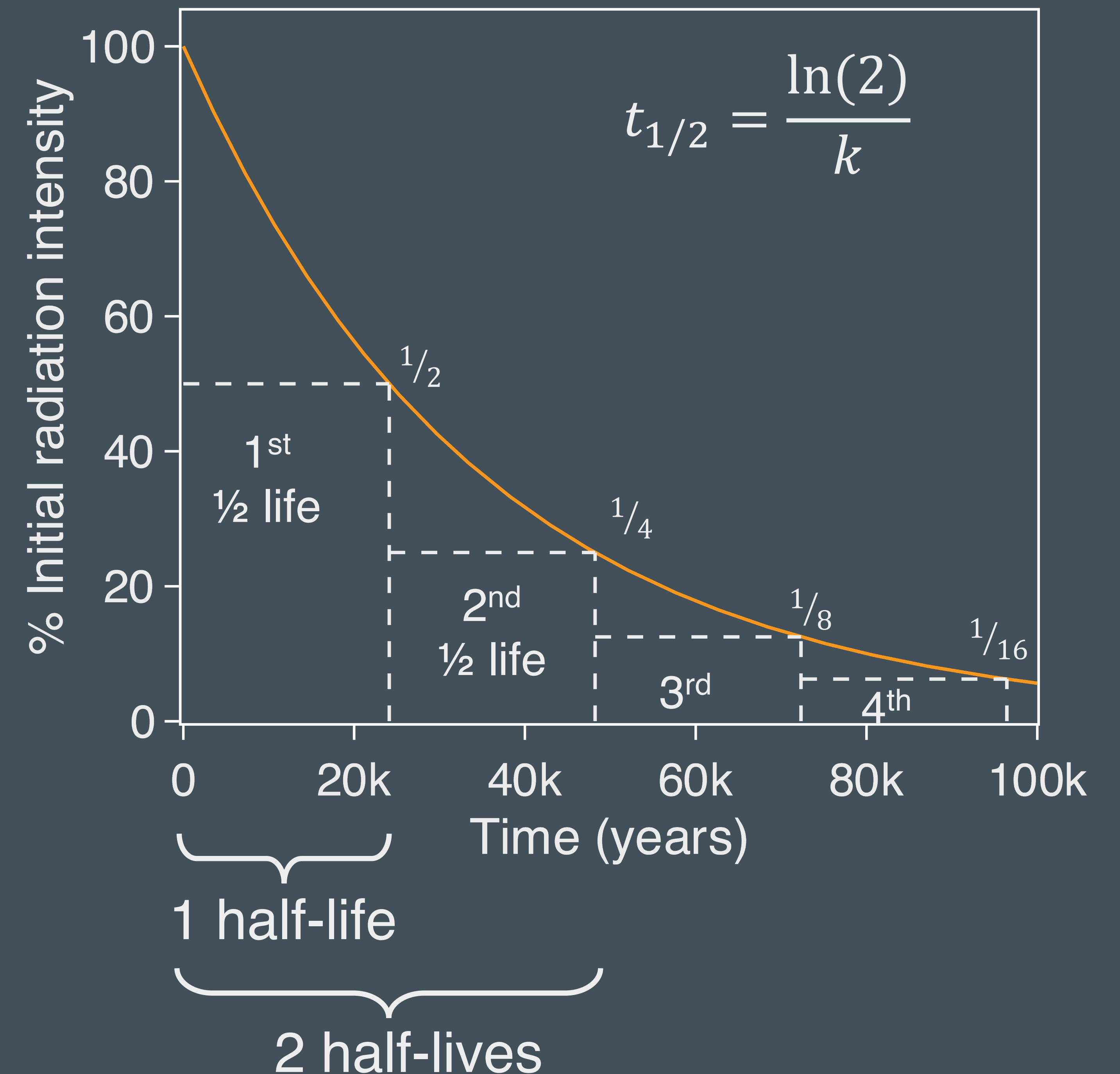
Lecture Topics (Part I)

- Measuring the rate of nuclear decay

- Uses of radioisotopes

- Elementary reactions

- Reaction Mechanisms

- Rate-Determining Step

- Rates and Equilibrium

- Chain Reactions

Pu–239 Radioactive Decay

This curve shows typical radioactive decay kinetics

As the concentration decreases, the half-life **remains constant.** The half-life for Pu–239 is 24,110 years.

All radioactive decay is first-order

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

% Initial radiation intensity

$^{1}/_{2}$

1st ½ life

$^{1}/_{4}$

2nd ½ life

$^{1}/_{8}$

3rd

$^{1}/_{16}$

4th

Time (years)

1 half-life

2 half-lives

Recap: half-lives

	Zeroth order	Radioactivity **First order**	**Second order**
Rate law	$rate = k[A]^0 = k$	$rate = k[A]^1$	$rate = k[A]^2$
Integrated rate law	$[A] = [A]_0 - kt$	$\ln([A]) = \ln([A]_0) - kt$	$\dfrac{1}{[A]} = \dfrac{1}{[A]_0} + kt$
Units of k	$\dfrac{M}{s}$	$\dfrac{1}{s}$	$\dfrac{1}{M \cdot s}$
First half-life	$[A]_{1/2} = [A]_0 - kt_{1/2}$ $t_{1/2} = \dfrac{[A]_0}{2k}$	$\ln([A]_{1/2}) = \ln([A]_0) - kt_{1/2}$ $t_{1/2} = \dfrac{\ln(2)}{k}$	$\dfrac{1}{[A]_{1/2}} = \dfrac{1}{[A]_0} + kt_{1/2}$ $t_{1/2} = \dfrac{1}{k[A]_0}$

Example

U-238 has a half-life of 4.5 billion years. What percentage of the world's U-238 will be left in one billion years?
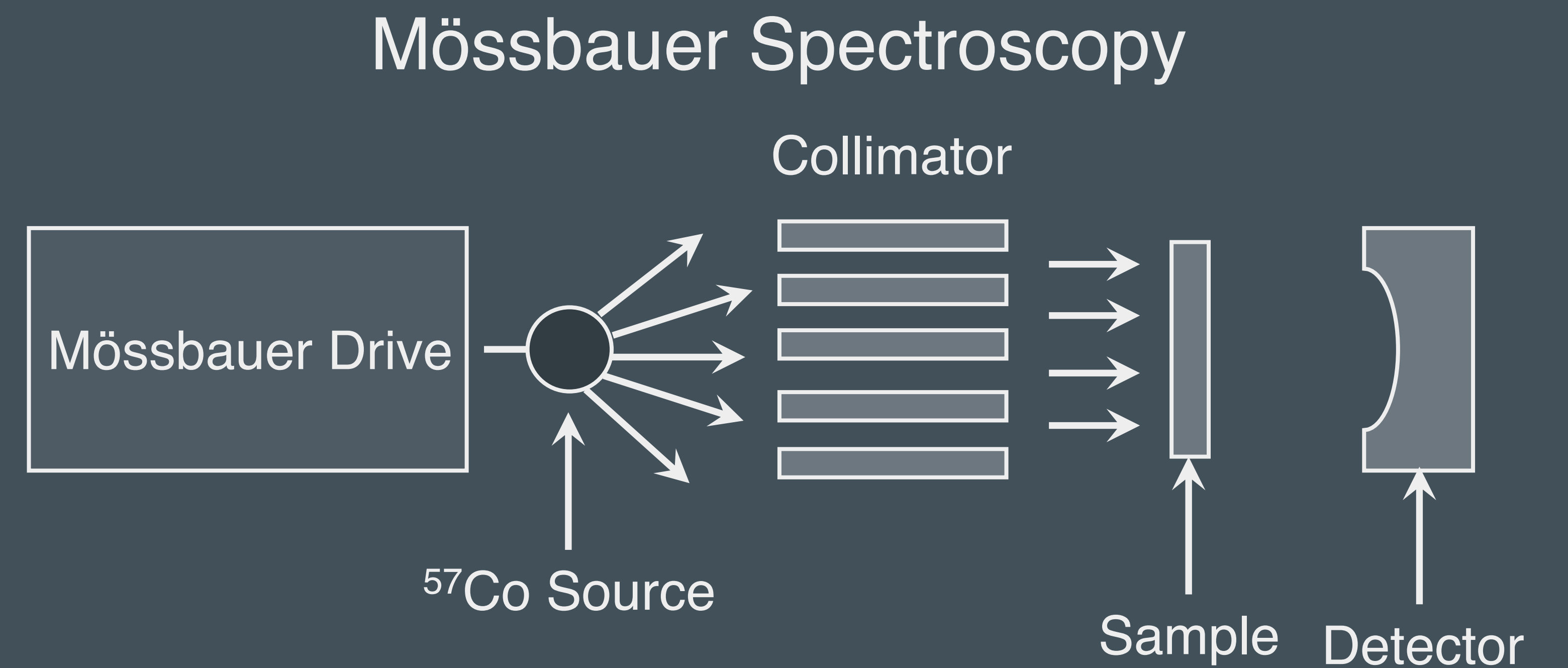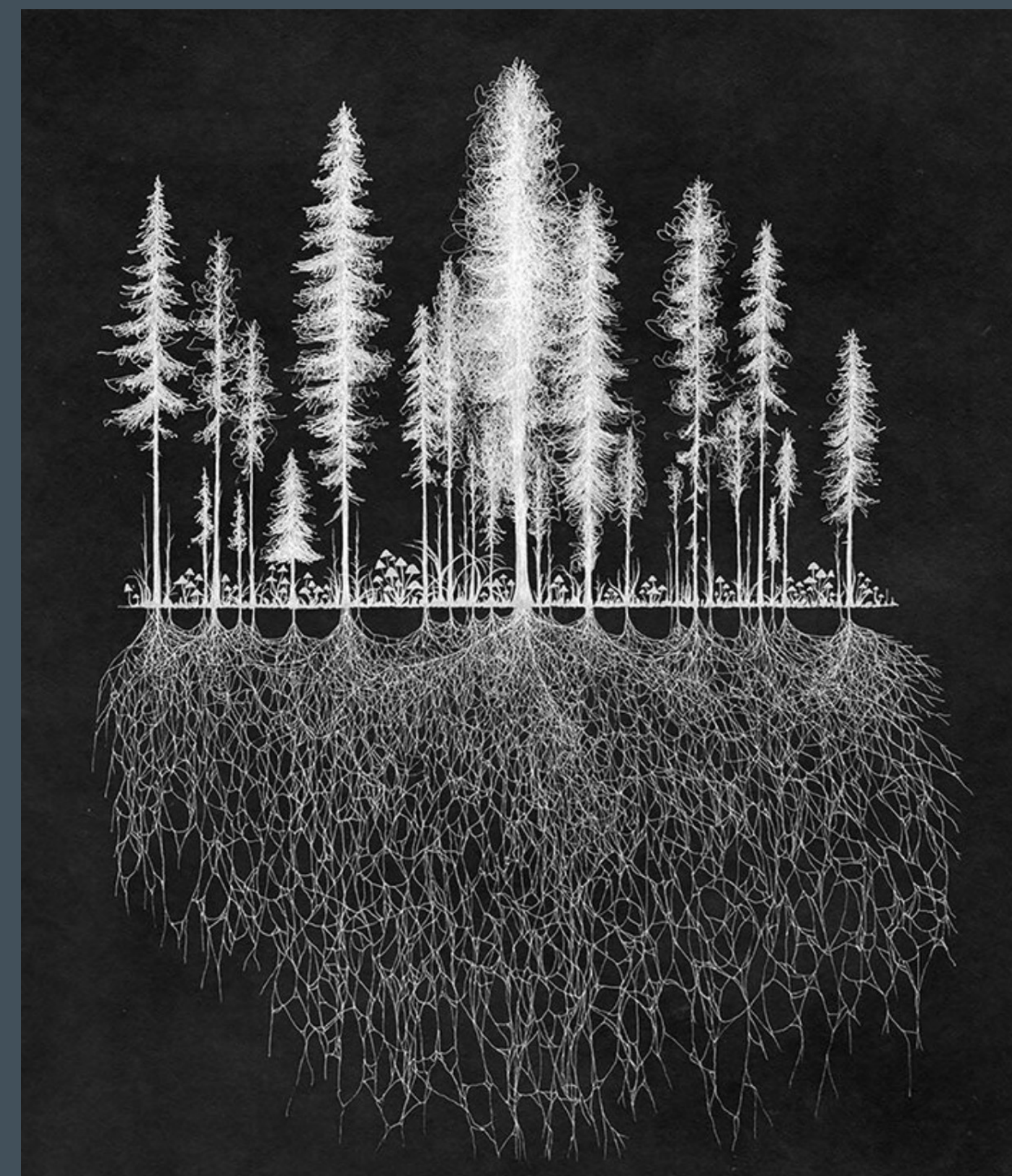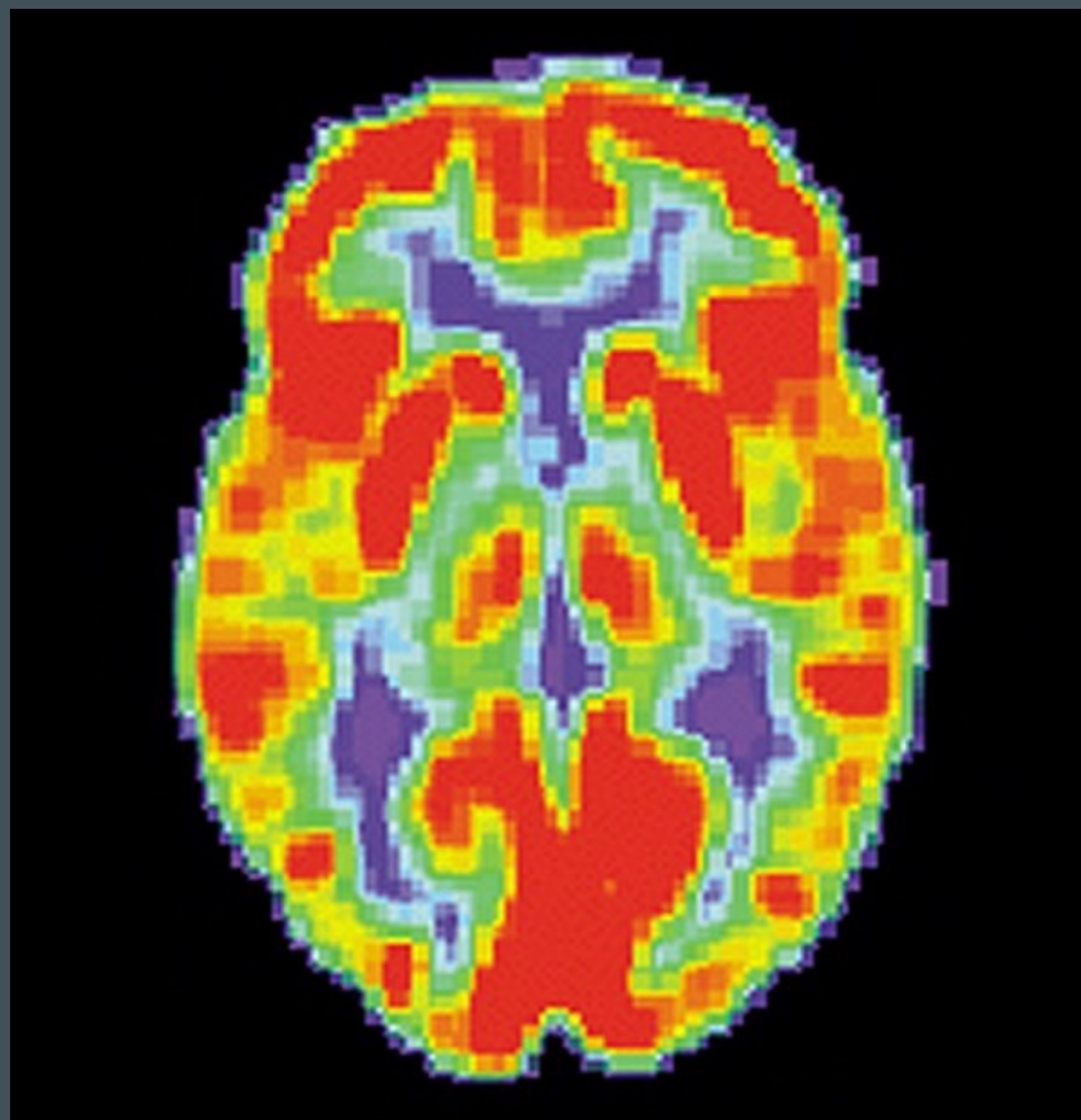
Example

Strontium-90 is one of the most dangerous isotopes released in the Chernobyl disaster in 1986. It has a half-life of 28.8 years. In what year will 99% of the released Sr-90 have decayed away?

Types of Nuclear Decay

Applications of Nuclear Chemistry

① Tracers

② Radiotherapy

③ Spectroscopy

Mössbauer Spectroscopy

Lecture Topics (Part II) – Multistep Reactions

- Mechanism and Multistep Reactions

- Elementary Reactions

- Reaction Mechanisms

- Rate Laws of Elementary Reactions

- Relation Between Microscopic and Macroscopic Rates

- Rate-Determining Step

- Dynamic Equilibrium as a Balancing of Rates

- Chain Reactions

Definitions

Elementary Reaction: a distinct event in the progress of a reaction, often a collision of particles

$$A_3 \rightleftharpoons A_2 + A \qquad\qquad A + A_3 \rightleftharpoons 2A_2$$

Molecularity: the number of reactant molecules, atoms, or ions in a specific elementary reaction

- Unimolecular = 1 reactant
- Bimolecular = 2 reactants
- Termolecular = 3 reactants

Definitions

Reaction Mechanism: a sequence of elementary reactions or steps that take place as reactants are transformed into products

Step 1: $A_3 \rightleftharpoons A_2 + A$

Step 2: $A + A_3 \rightleftharpoons 2A_2$

Overall: $2A_3 \rightarrow 3A_2$

Intermediates: decomposition of ozone

In this mechanism **O** is an *intermediate*. **O** is produced early in the mechanism and then consumed later, so it doesn't appear in the overall reaction.

Step 1: $O_3 \rightleftharpoons O_2 + $ **O**   *slow*

Step 2: **O** $+ O_3 \rightarrow 2O_2$ *fast*

Overall: $2O_3 \rightarrow 3O_2$

DEF: Rate Determining Step (RDS) – the slowest microscopic reaction step in a mechanism

Rate laws for mechanisms

Rate laws for chemical reactions cannot be reliably predicted from the overall equation for the reaction.

If you know the *individual* steps of a reaction mechanism, the rate law for the overall reaction can be predicted from the slowest elementary step.

The rate of the overall reaction is determined by the rate of the slowest elementary step. The slowest step is called the rate limiting step (rls) or the rate determining step (rds).

Example

Suppose the reaction $2O_3 \rightarrow 3O_2$ takes place by the following mechanism

Step 1: $O_3 \rightleftharpoons O_2 + O$ *slow*

Step 2: $O + O_3 \rightarrow 2O_2$ *fast*
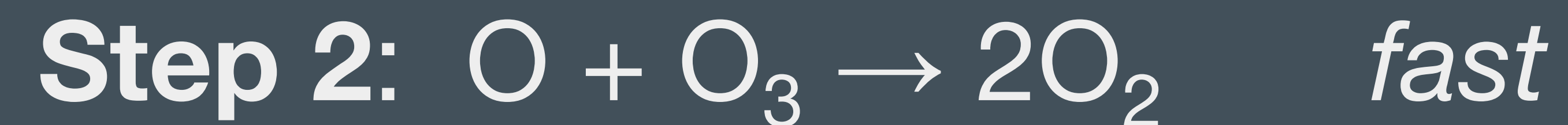
The rate law will depend on the reactants in the slow elementary step. In this example, the rate determining step is Step #1.
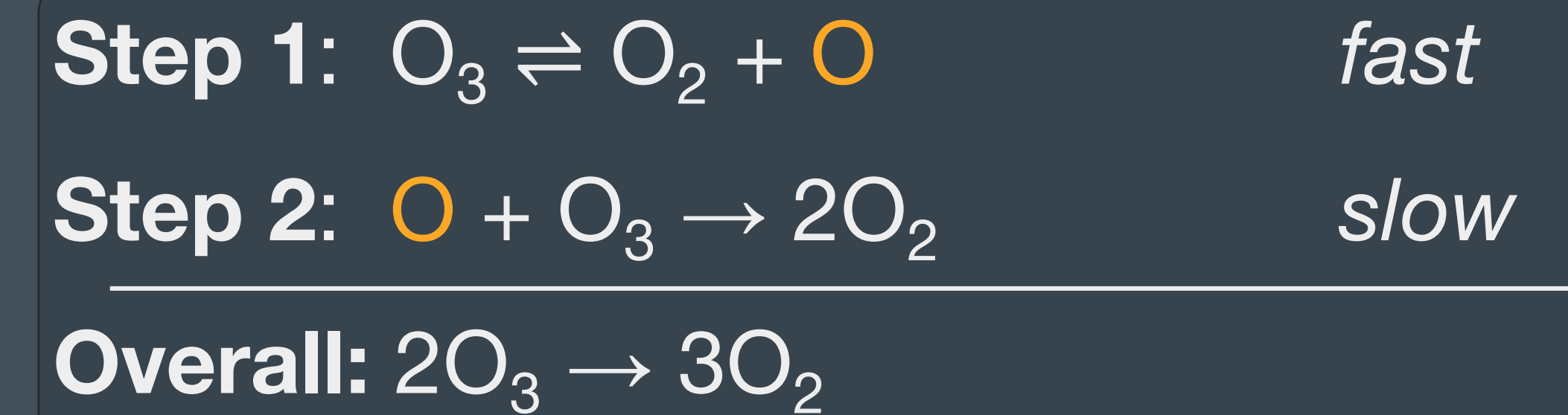
rate = $k[O_3]$

Rate laws and intermediates

① Rate laws include *only* the reactant species whose concentrations that either you can control or significantly change on their own!

② <u>Intermediates can never appear in rate laws</u> because you cannot control their concentration directly.

③ If there is an intermediate in the slow step, you must find a way to swap out the reactant(s) that lead to the production of the intermediate.

Exercise: rate laws with intermediates

What is the rate law for this reaction?

Step 1: $O_3 \rightleftharpoons O_2 + O$ *fast*

Step 2: $O + O_3 \rightarrow 2O_2$ *slow*

Overall: $2O_3 \rightarrow 3O_2$

How to replace an intermediate

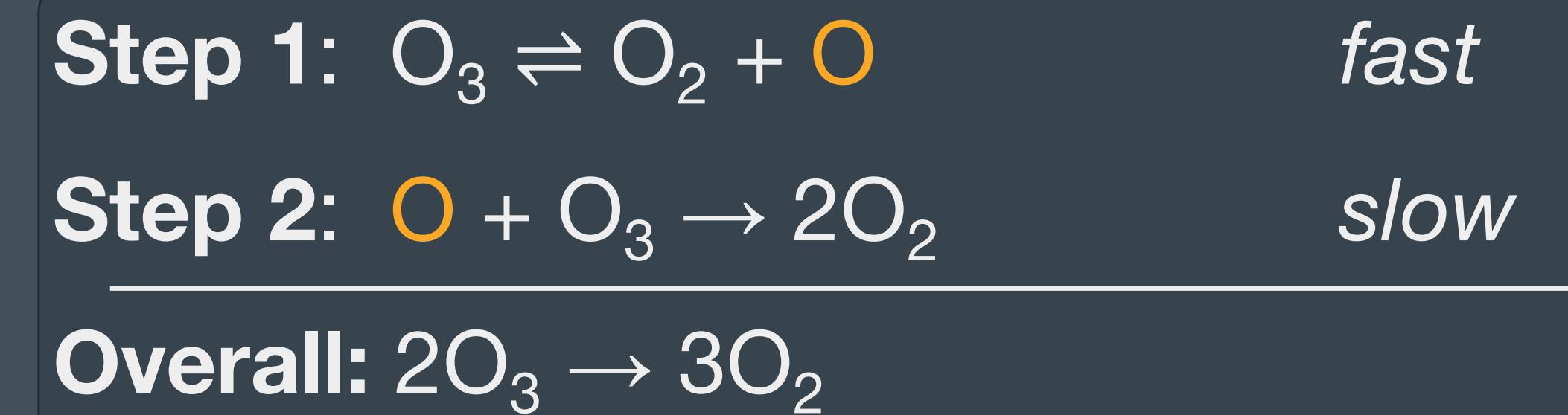|		
Step 1: $O_3 \rightleftharpoons O_2 + O$		*fast*
Step 2: $O + O_3 \rightarrow 2O_2$		*slow*
Overall: $2O_3 \rightarrow 3O_2$		

We can write the rate laws for the rate of consumption and formation of O

rate of formation: $\quad \dfrac{d[O]}{dt} = k_1[O_3] \quad$ (step 1 forward)

rate of consumption of $\dfrac{-d[O]}{dt} = k_{-1}[O_2][O] + k_2[O][O_3]$ (step 1 reverse & step 2 forward)

How to replace an intermediate (SSA)

Numerically one can write the rate equations for the consumption and formation of every product and solve the rate constants using the system of equations. However experimentally often much simpler rate laws are actually observable and can be derived with a few simple approximations. The **Steady State Approximation (SSA)** assumes that for the vast majority of a reaction's progress the intermediate concentrations are constant.

$$\frac{d[O]}{dt} = \frac{-d[O]}{dt} = k_1[O_3] = k_{-1}[O_2][O] + k_2[O][O_3]$$

Solve for the intermediate *O*:

$$[O] = \frac{k_1[O_3]}{k_{-1}[O_2] + k_2[O_3]}$$

How to replace an intermediate

In reaction mechanisms, fast steps may reach **pre-equilibrium** when they are followed by slow steps. During this process, the intermediate is formed and sustained in a rapid formation reaction and its reverse. If this process is *much faster* than the following slow step then. The rate equation can be simplified.

Step 1: $O_3 \rightleftharpoons O_2 + O$ *fast*

Step 2: $O + O_3 \rightarrow 2O_2$ *slow*

Overall: $2O_3 \rightarrow 3O_2$
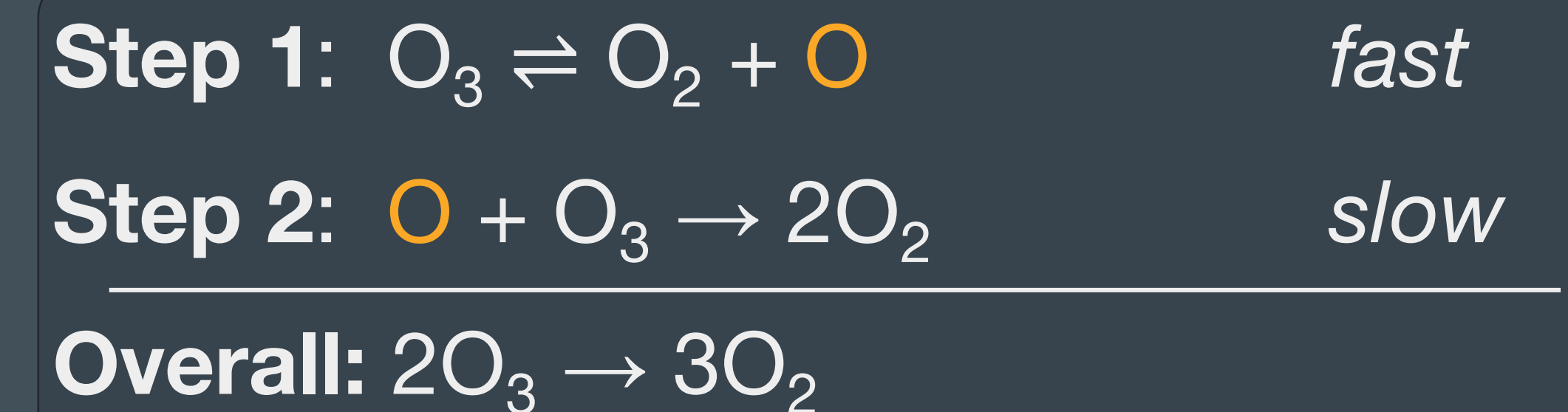
From the last slide:

$$[O] = \frac{k_1[O_3]}{k_{-1}[O_2] + k_2[O_3]} = \frac{k_1[O_3]}{k_{-1}[O_2]}$$

k_2 Slow & too small to matter.
Denominator $\cong k_{-1}[O_2]$

This is just K_{eq} for step 1!

$$\frac{[O][O_2]}{[O_3]} = \frac{k_1}{k_{-1}} = K_{eq1}$$

Careful! Assumptions are not always valid (e.g. high O_3 concentration). Best we just use SSA and rely on this only if the rate law can't be solved or experimental evidence supports the preequilibrium approximation!

How to replace an intermediate

① From the rate-determining step, we have

$$\text{rate} = k_2[O][O_3]$$

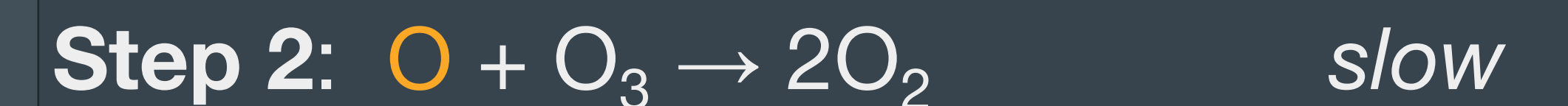② Write the rate laws for the intermediate's formation and consumption and set them equal (SSA)

$$\frac{d[O]}{dt} = \frac{-d[O]}{dt} = k_1[O_3] = k_{-1}[O_2][O] + k_2[O][O_3]$$

③ Substitute the new expression for the intermediate

$$[O] = \frac{k_1[O_3]}{k_{-1}[O_2] + k_2[O_3]}$$

④ Solve for the new rate law

$$\text{rate} = k_2 \frac{k_1[O_3]}{k_{-1}[O_2] + k_2[O_3]}[O_3] \cong \frac{k_1 k_2[O_3]^2}{k_{-1}[O_2]} = k'\frac{[O_3]^2}{[O_2]}$$

           (SSA)   (pre-equilibrium)

K_{eq} can be defined using rates of reaction

At equilibrium, the rates of of the forward and reverse overall reactions are equal

$$@ \; K_{eq} \rightarrow \frac{rate_{forward}}{rate_{reverse}} = 1$$

For an elementary reaction: $K_{eq} = \frac{k_{forward}}{k_{reverse}}$

With multiple elementary steps:

$$K_{eq} = \frac{k_1}{k_{-1}} \frac{k_2}{k_{-2}} \frac{k_3}{k_{-3}} \ldots$$

When $K \gg 1$, the rate constant for the forward reaction is much larger than the rate constant for the reverse reaction. The rates are equal at equilibrium. This is a product favored reaction.

When $K \ll 1$, the rate constant for the reverse reaction is much larger than the rate constant for the forward reaction. The rates are equal at equilibrium. This is a reactant favored reaction.

Example

What is the rate law for this reaction?

Step 1: $B_2 \rightleftharpoons 2B$ *fast*

Step 2: $2B + A_2 \rightarrow 2AB$ *slow*

Overall: $A_2 + B_2 \rightarrow 2AB$

Next time

- The Effect of Temperature

- Arrhenius Behavior

- Collision Theory