

Unit 2 – Day 4

Kinetics

Arrhenius and Collision Theory



Last time

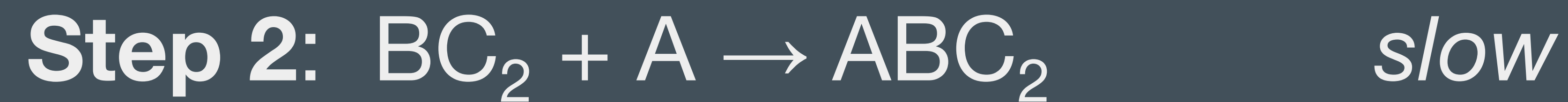
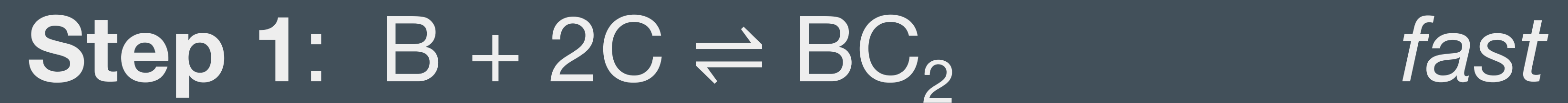
- Measuring the rate of nuclear decay
- Uses of radioisotopes
- Elementary reactions
- Reaction Mechanisms
- Rate-Determining Step
- Rates and Equilibrium

Lecture Topics

- Chain Reactions
- Physical Factors Impacting Rates of Reaction
- Arrhenius Behavior
- Collision Theory
- Analysis of Reaction Coordination Diagrams

Review: Example

What is the rate law for this reaction?



Chain reaction

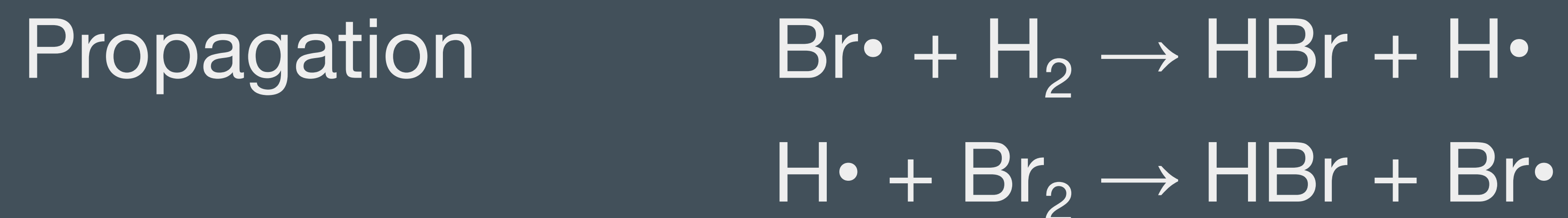
A highly reactive intermediate reacts to produce another highly reactive intermediate, which reacts to produce another, and so on.

In this context, the intermediate is referred to as the chain carrier

Examples:

- Radical chain reaction (chain carrier = radical)
- Radical polymerizations
- Branch chain explosion (chain carrier = neutron)

Radical chain reaction

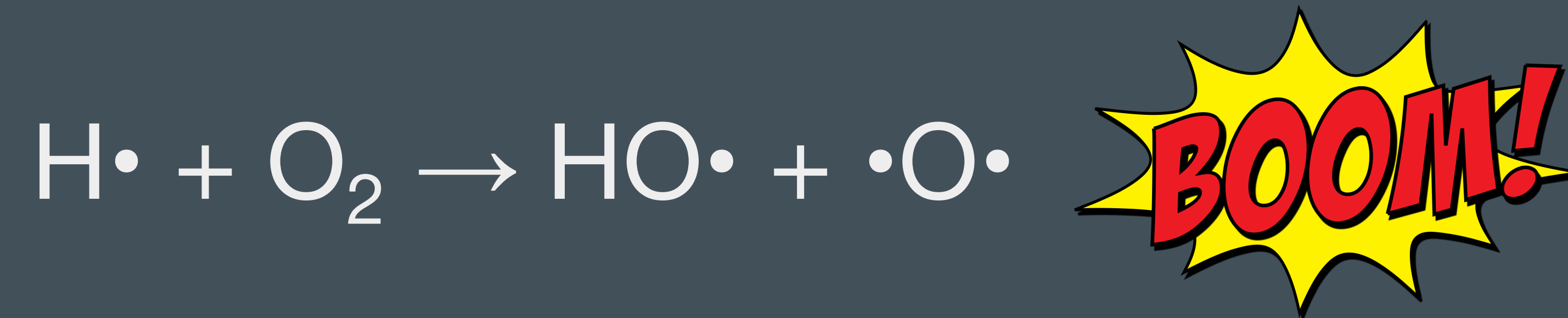


Explosions occur in reactions with chain branching

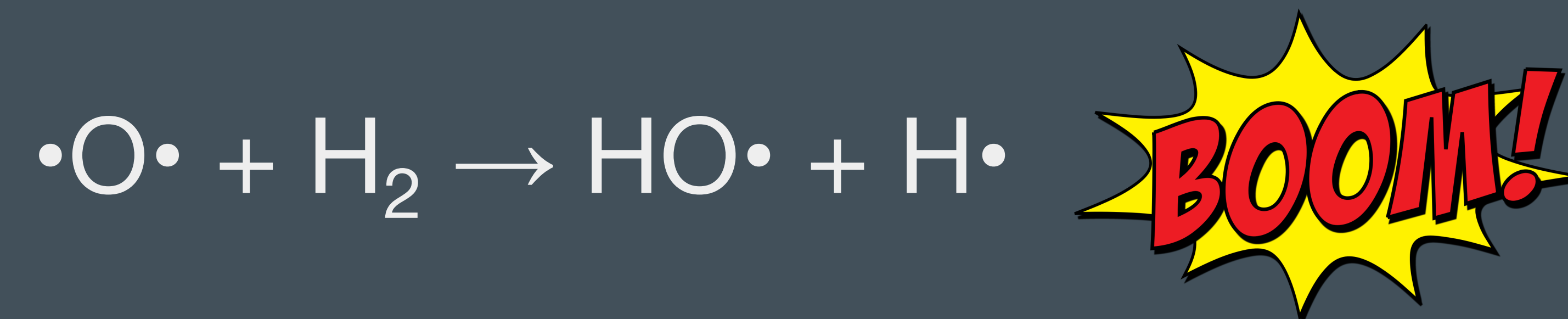
Initiation



Branching



Branching



The nature of explosions

Type 0: Over-pressurization



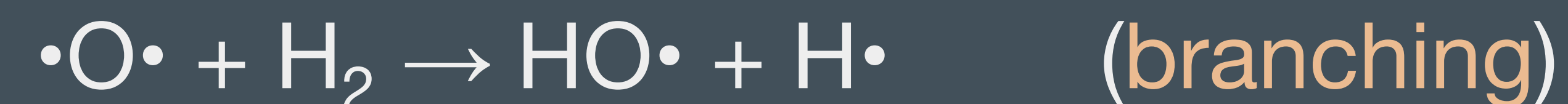
A gas evolving reaction in a sealed container

Type 1: Thermal explosion



A reaction generates heat. Heat speeds up the reaction in a positive feedback loop.

Type 2: Branched-chain explosion



1 reactive intermediate in, 2 reactive intermediates out

Summary

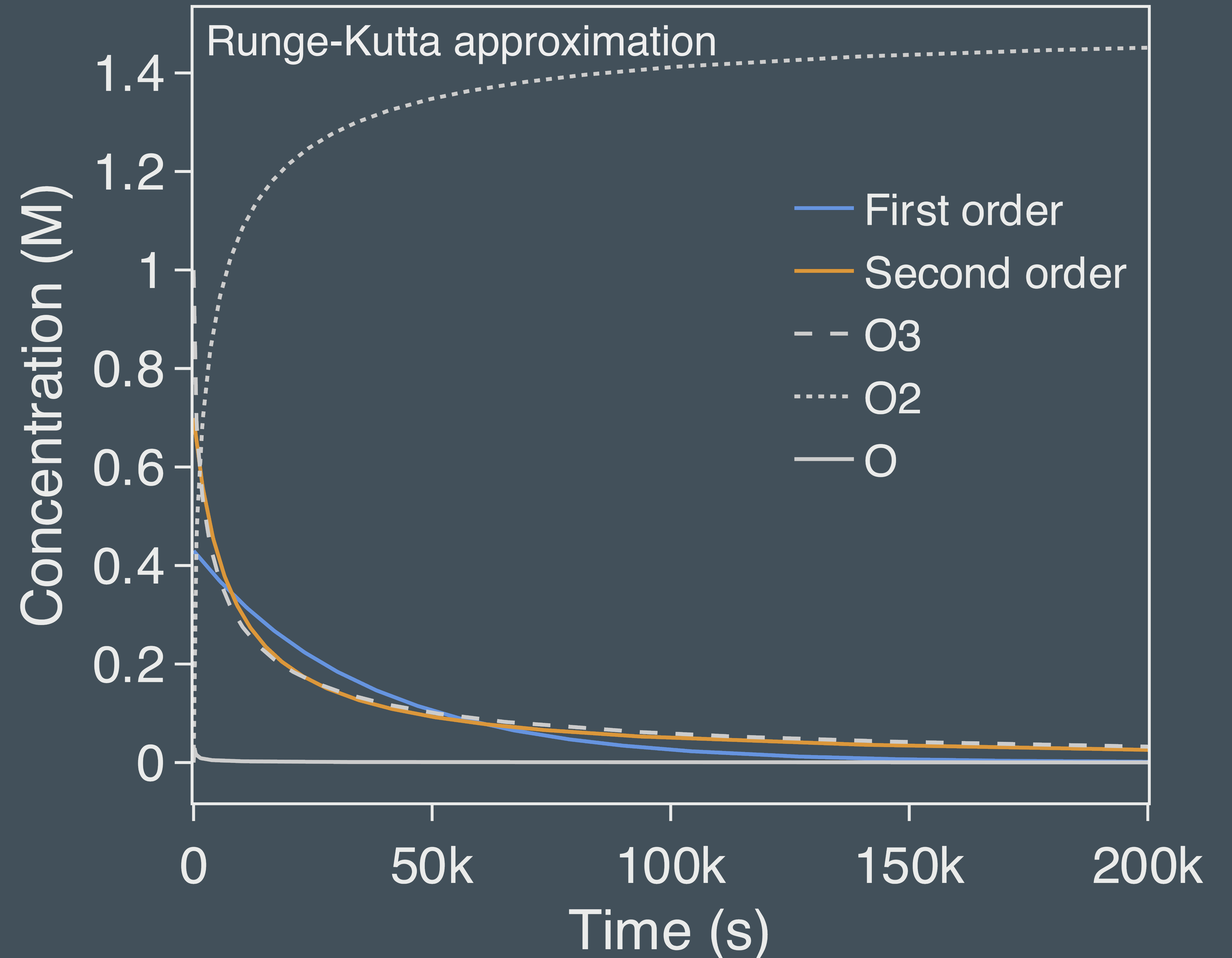
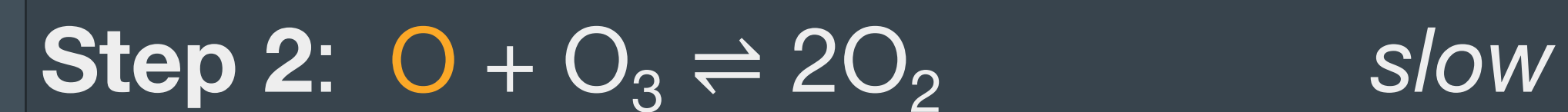
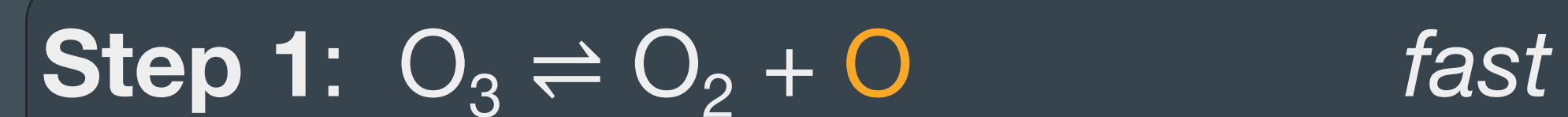
1. Mechanism steps can be **unimolecular**, **bimolecular**, trimolecular (rare),
2. Rate of change depends on the concentration.
3. Rate laws can be *observed* in experimental data and *derived* from **elementary reactions** in a mechanism. We've done both.
4. We can use the **method of initial rates** to support a proposed mechanisms based on elementary reactions.
5. A **rate law** determined from the method of initial rates should match the rate law derived from the **rate-determining step** (slowest elementary reaction) in the mechanism.
6. The observed overall rate law *must* support the proposed mechanism.

Beyond the basics: Numerical solutions to differential equations

$$k_1 = 1,000$$

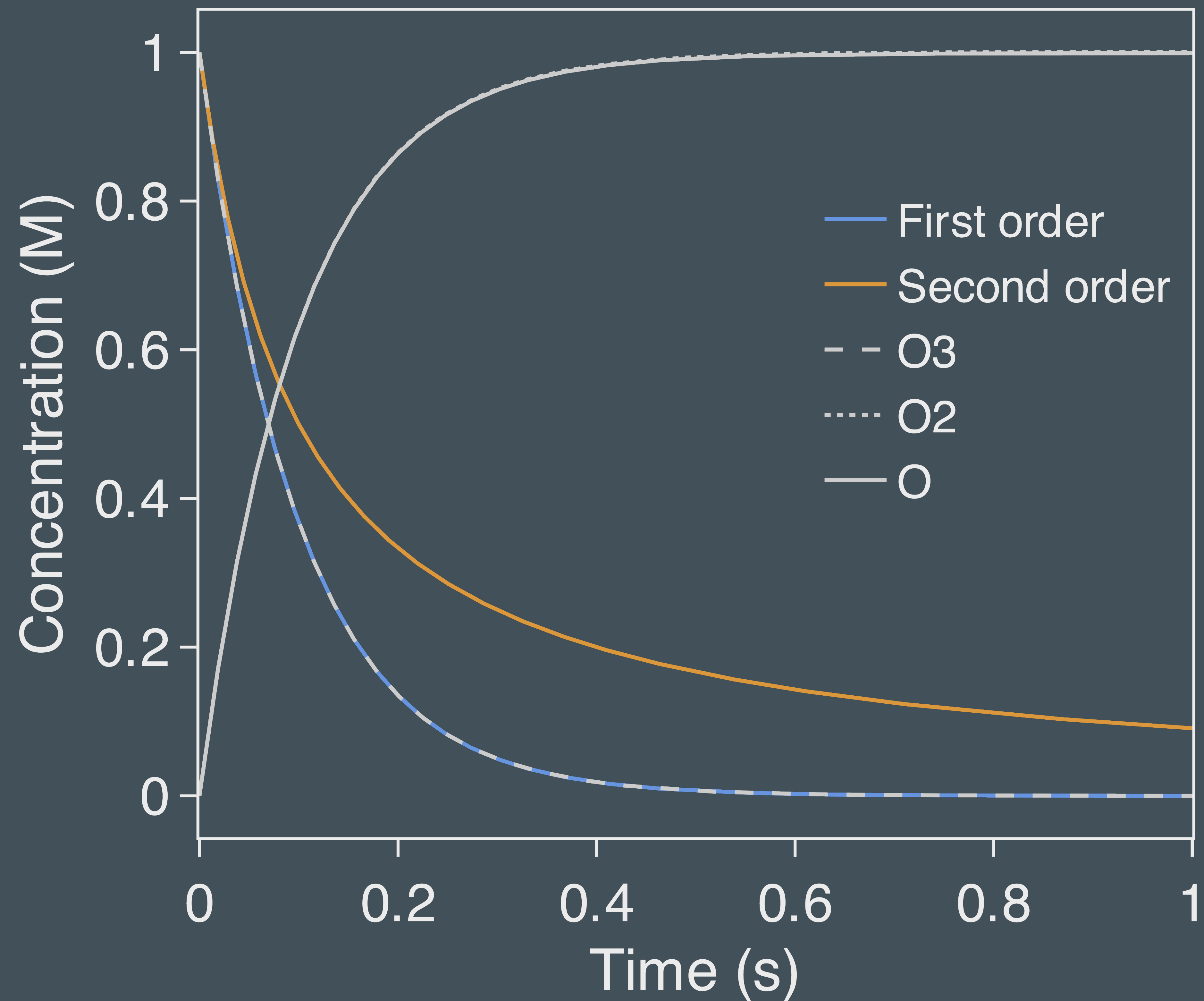
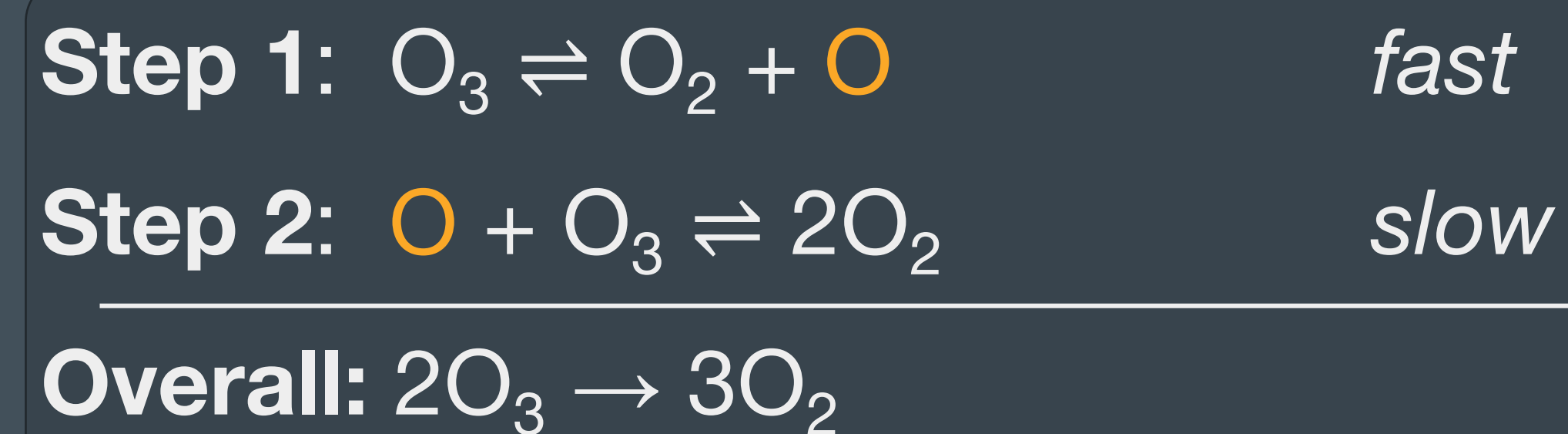
$$k_{-1} = 100,000$$

$$k_2 = 0.01$$



Beyond the basics: Numerical solutions to differential equations

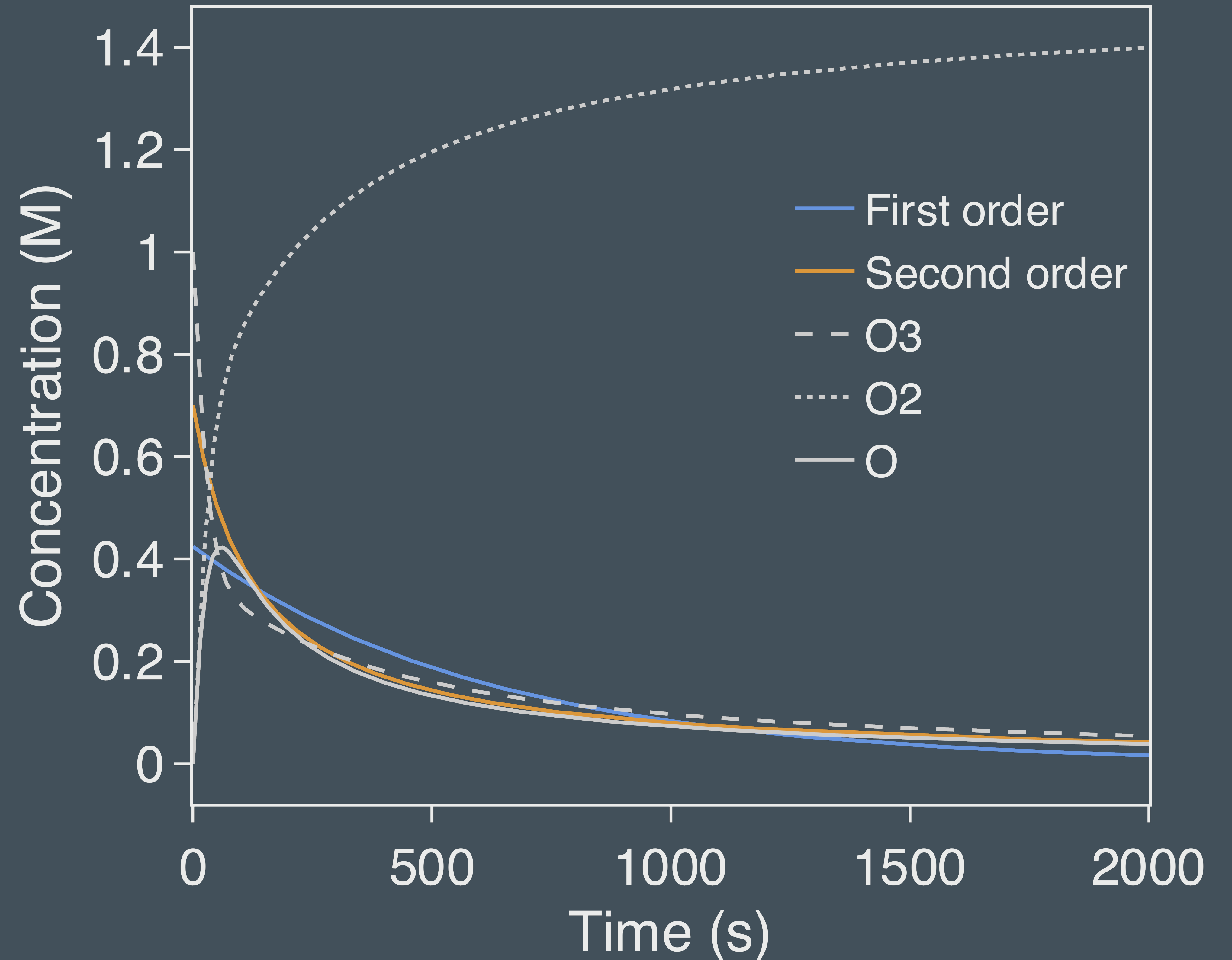
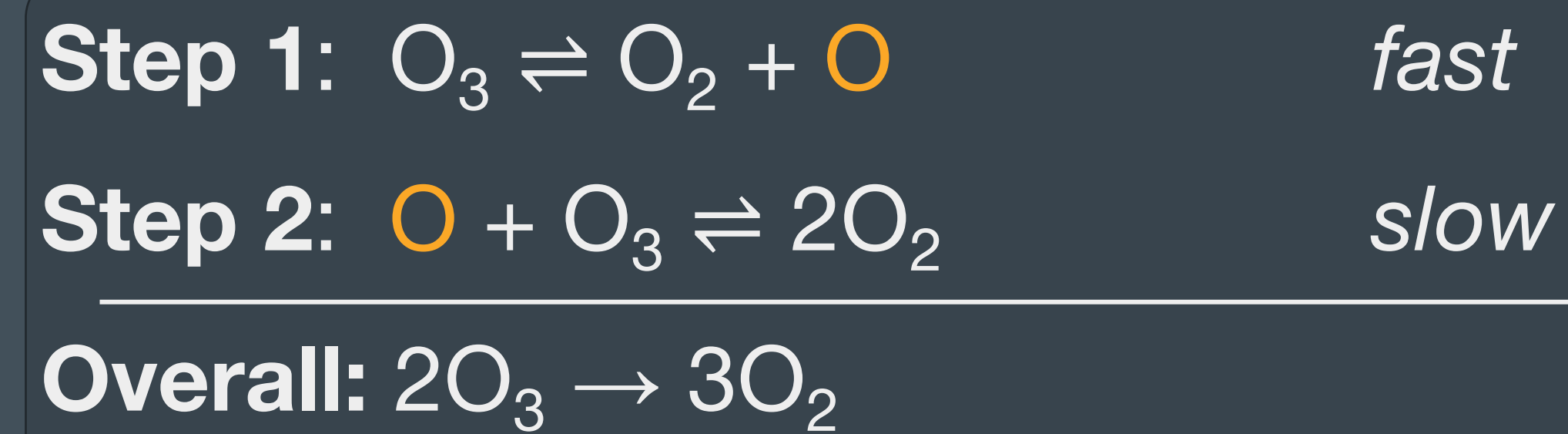
$$k_1 = 10$$
$$k_{-1} = 0$$
$$k_2 = 0.01$$



Why does this reaction stop at 1M O₂?

SSA breaks down when rates are too similar

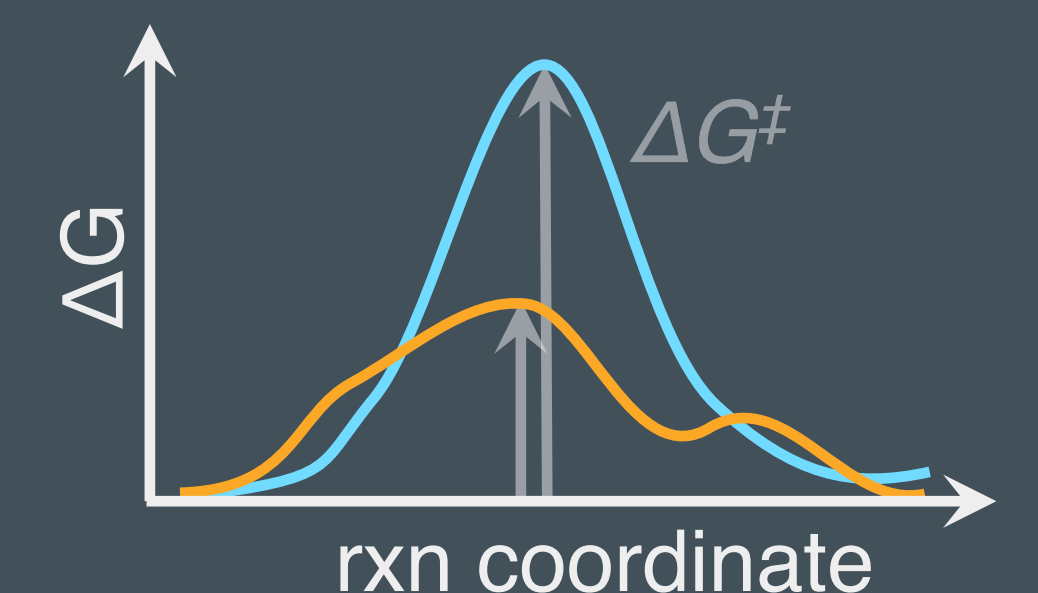
$$k_1 = 0.02$$
$$k_{-1} = 0.02$$
$$k_2 = 0.01$$



Rate of Reaction

There are *4 chemical factors* that affect the speed of a reaction:

- ① **Concentration** – Concentration increases, # collisions increase, reaction rate increases.
- ② **Medium** – diffusion: gas > liquid > solid. Reaction rates between phases & increase as the surface area of their interface increases (e.g. fine powder dissolve faster than large crystals).
- ③ **Temperature** – reactant molecules have more kinetic energy at higher temperatures. At higher temperatures, a larger number of reactant molecules can therefore get exceed the activation energy and proceed to products.
- ④ **Catalysis** – some species can speed up the rate of a reaction but are not used up in the reaction. How does this happen?
(We'll talk about catalysts later.)



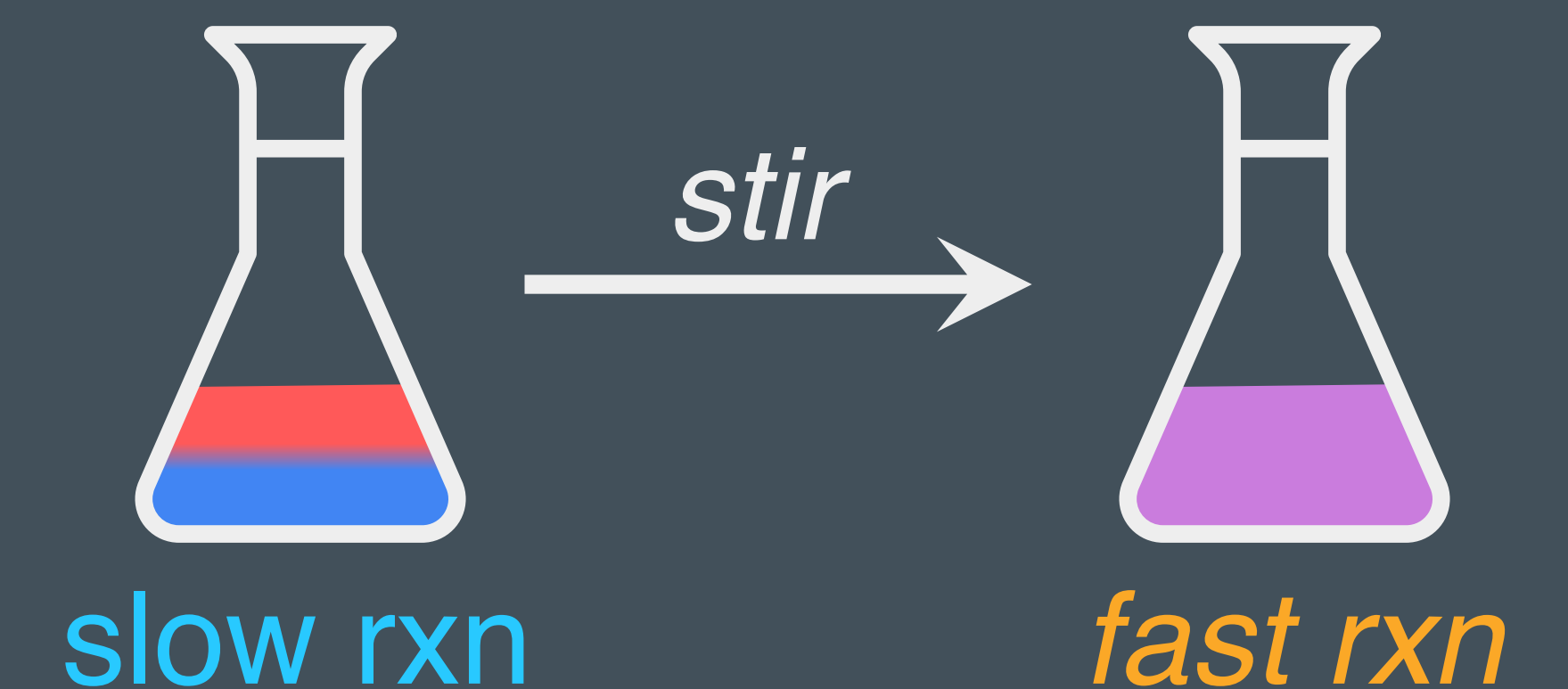
Rate of Reaction

There are *2 engineering factors* that affect the speed of a reaction:

① **Thermal Transport** – when you heat a pot of water the water at the top is colder than the water at the bottom.



② **Mass Transport** – stirring makes inhomogeneous solution homogenous. Homogenous solutions of reactants usually react faster.



Reaction Rate vs Temperature

Why are reactions faster at higher temperatures?

- More molecules have sufficient energy to get over the energy barrier (large effect).
- More molecules have collisions (small effect)

Arrhenius Law – temperature and rate constant

The rate constant k increases with increasing temperature.

At higher temperatures, more molecules have enough energy to make it over the barrier, so the reaction goes faster.

This means that all reactions go faster at higher temperatures.

$$k = A e^{\frac{-E_a}{RT}}$$

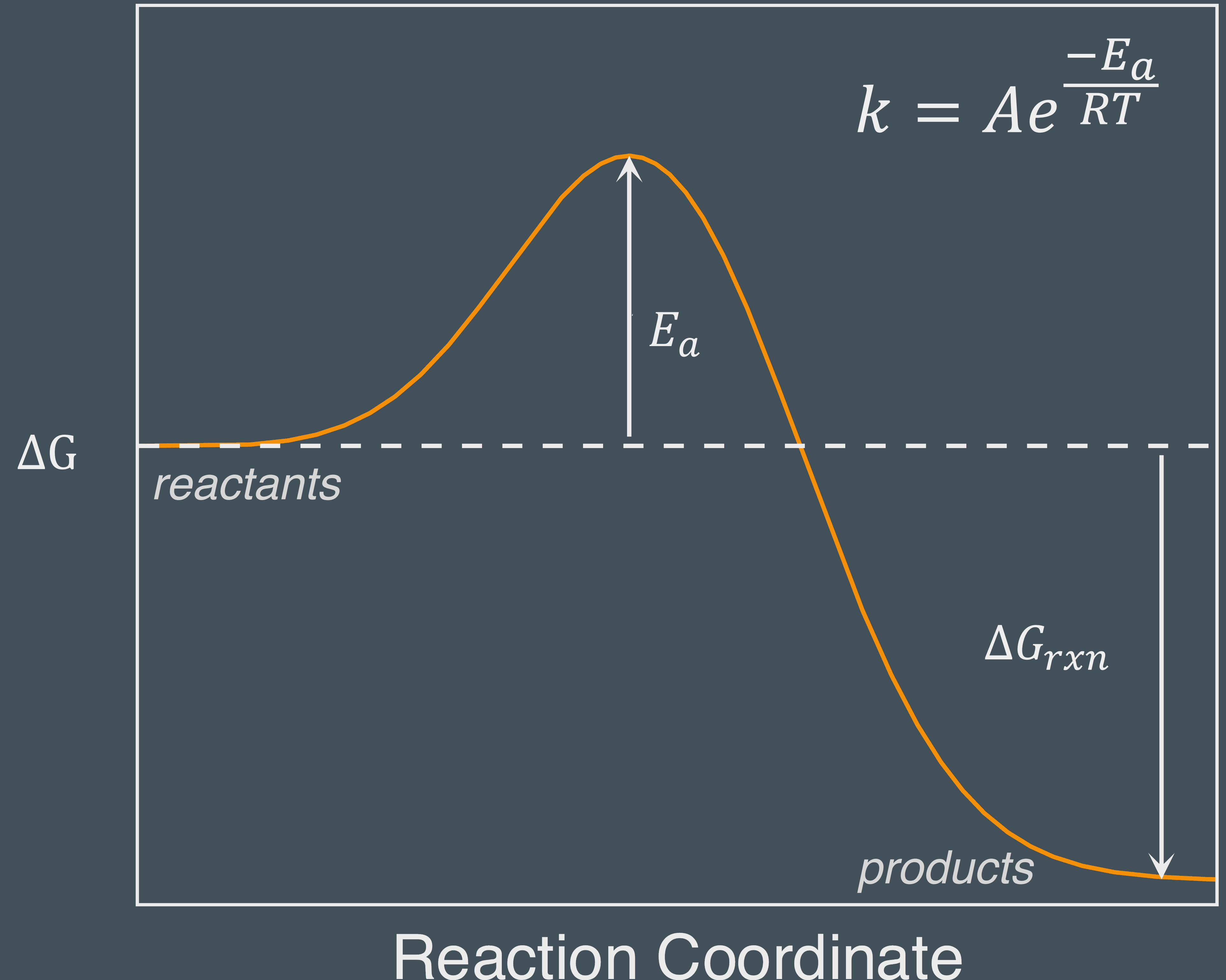
Arrhenius relation

Definitions – Components of Arrhenius relation

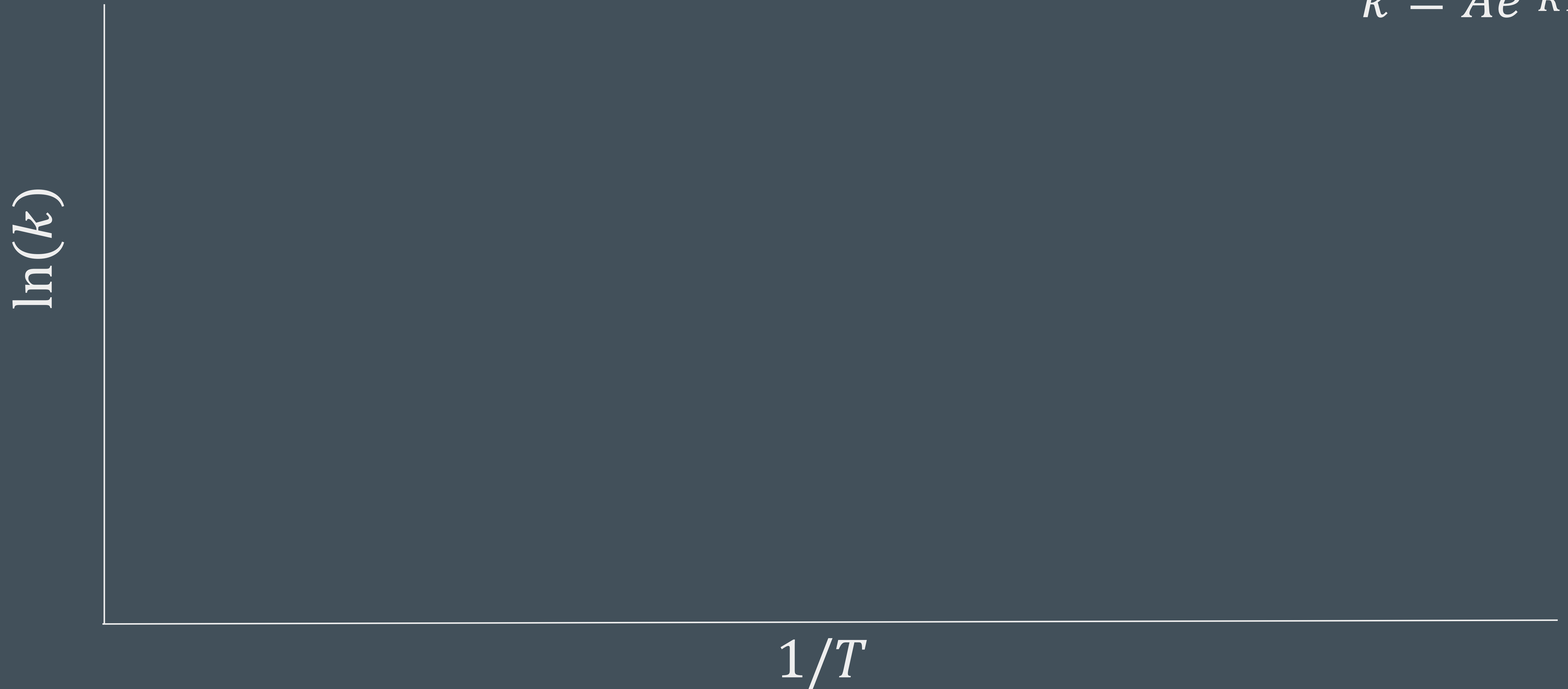
DEF **pre-exponential factor A** : the rate constant at infinite temperature, or the theoretical maximum reaction rate possible.

DEF **Activation Energy E_a** : the minimum amount of energy that the reactants need in order to undergo a chemical reaction

DEF **Reaction Coordinate** :
Progress of a reaction describe at each point as a particular arrangement and trajectory of atoms and molecules in space



Arrhenius Plot



$$k = Ae^{\frac{-E_a}{RT}}$$

E_a vs. rate constants

The higher the activation energy, the stronger the temperature dependence of the rate constant

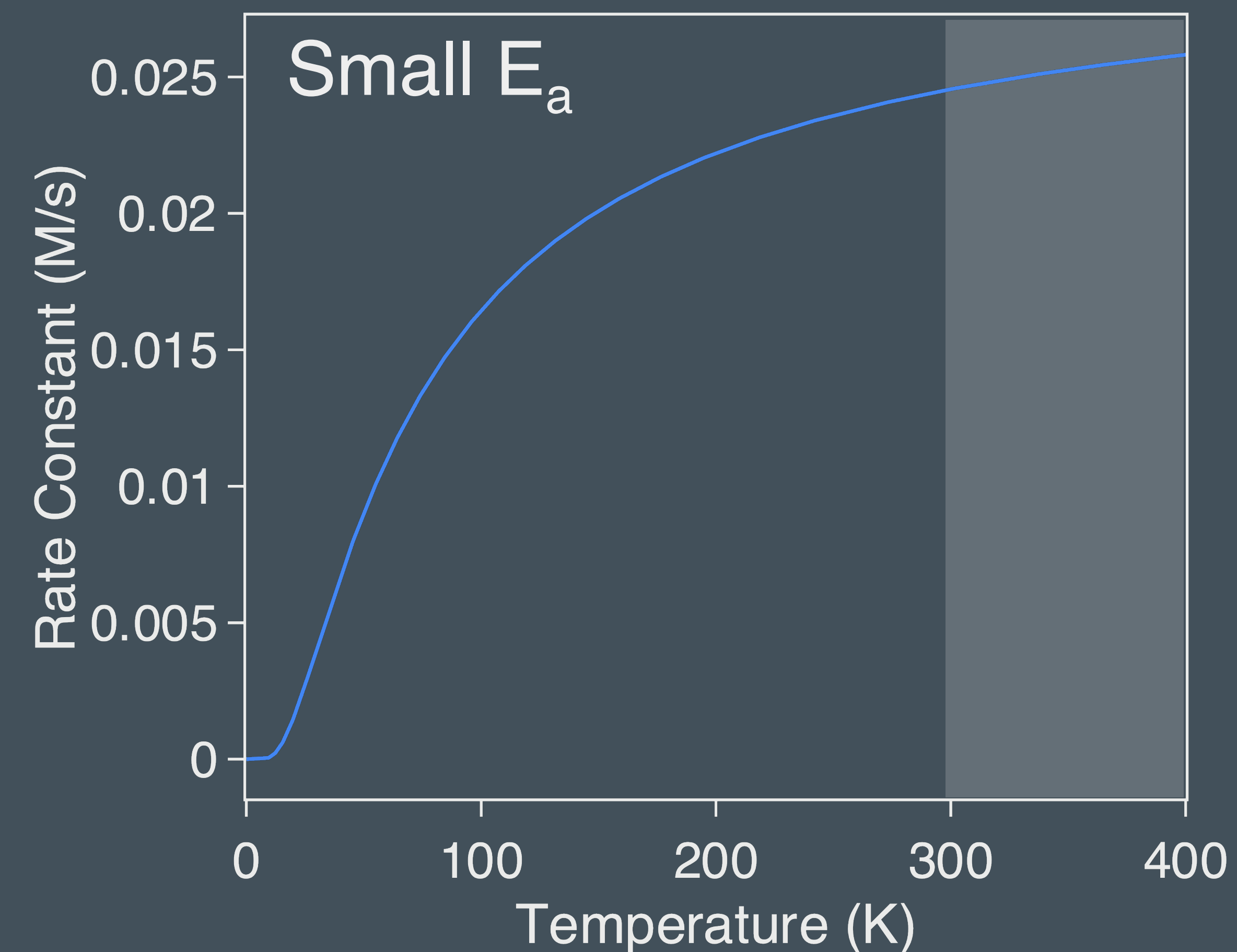
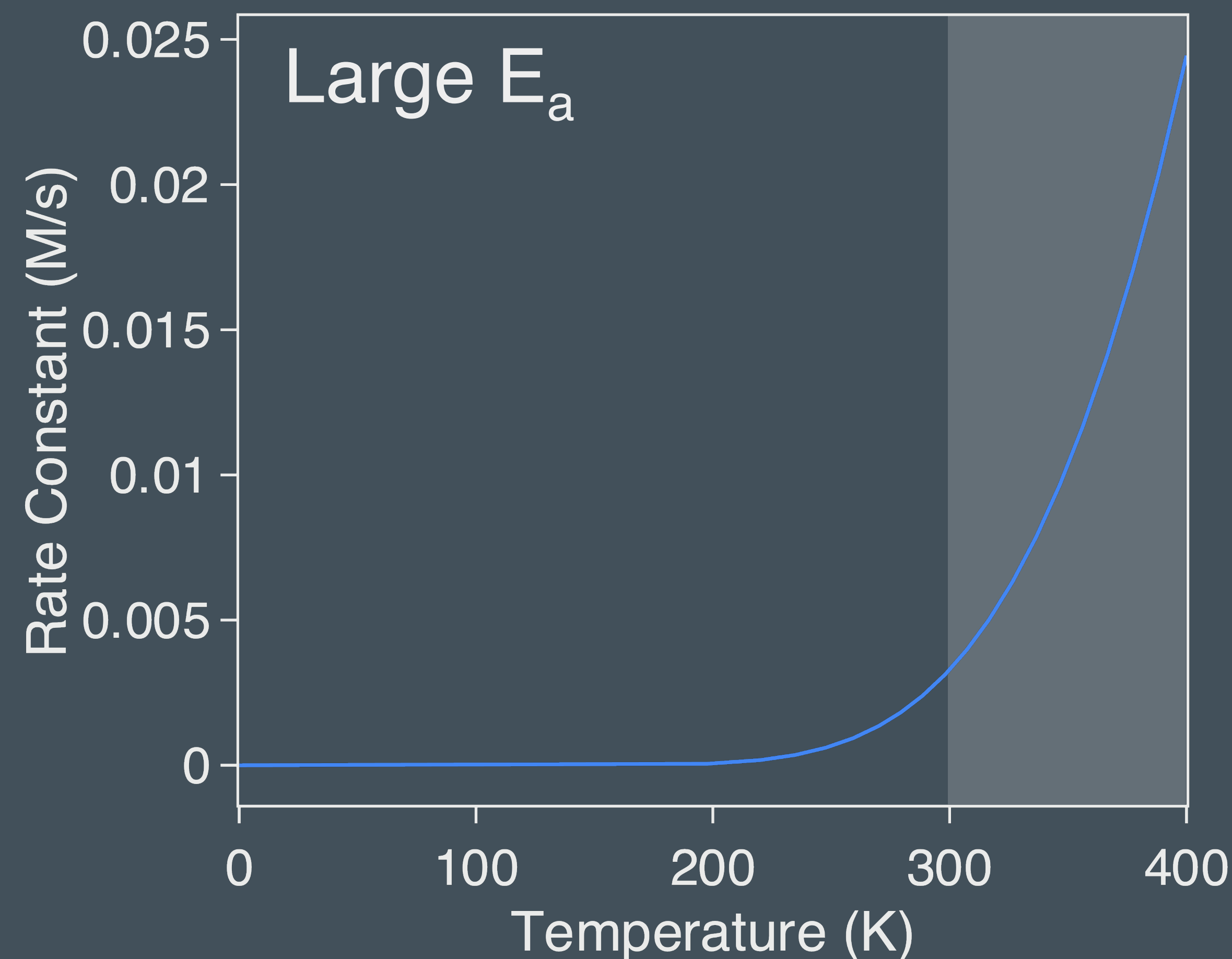
- Low activation energies ≈ 10 kJ/mol
- High activation energies ≈ 60 kJ/mol

temperature “independent”

temperature “dependent”

$$k = Ae^{\frac{-E_a}{RT}}$$

We can use the relationship between activation energy and temperature to predict rate constants



Rate Constant vs. Temperature

The same reaction at two different temperatures will have two different rate constants.

We can combine these two equations:

$$k_1 = Ae^{-\left(\frac{E_a}{RT_1}\right)}$$

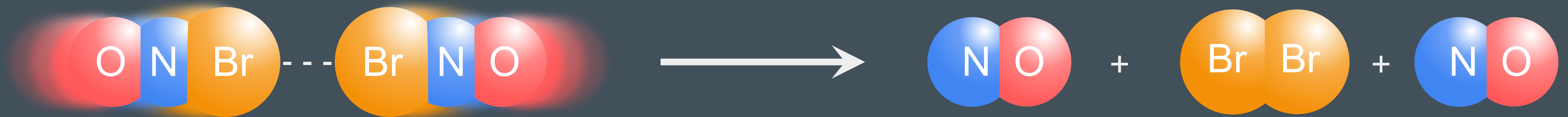
$$k_2 = Ae^{-\left(\frac{E_a}{RT_2}\right)}$$

We get the Arrhenius equation:

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

Collision theory

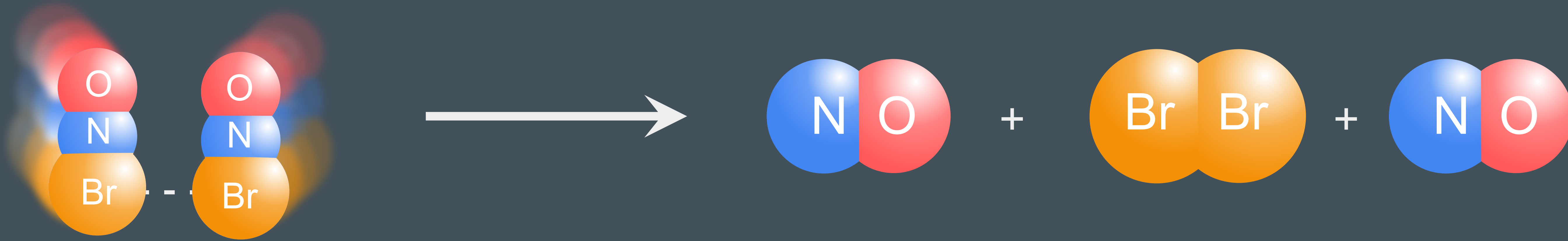
Even if all the molecules have sufficient energy, not all interactions between reactants will lead to products.



Collision theory

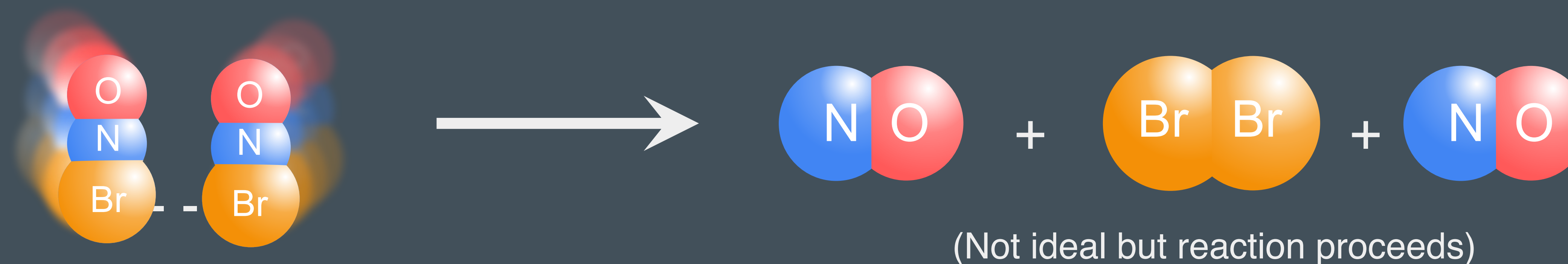
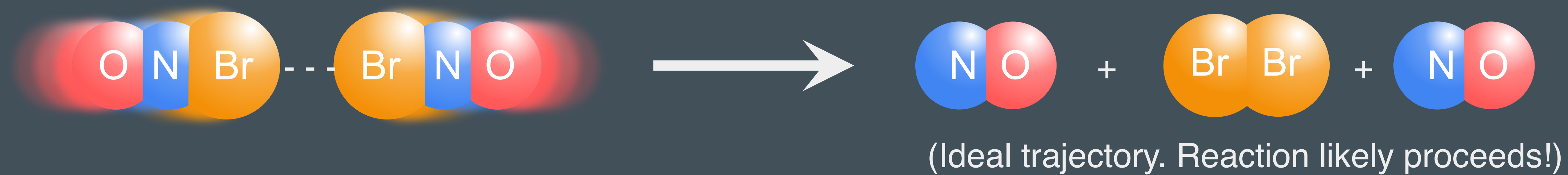


Collision theory



The angle of approach determines reactivity!

Even if all the molecules have sufficient energy, not all interactions between reactants will lead to products.



Collision frequency

The number of collisions per second between Molecule A and Molecule B at a specific temperature

$$\text{collision frequency} = \sigma \bar{v}_{rel} N_A^2 [A][B]$$

σ = collision cross sectional area

Units (collisions per second per liter)

\bar{v}_{rel} = mean relative speed

[A] = Number of atoms A

[B] = Number of atoms B

N_A = Avogadro's number

Collision frequency

$$\text{collision frequency} = \sigma \bar{v}_{rel} N_A^2 [A][B]$$

σ = collision cross section

- The area the molecule presents as a target during a reaction
- The bigger the collision cross section, the greater the collision frequency
- Bigger molecules are easier targets than smaller molecules

Collision frequency

$$\text{collision frequency} = \sigma \bar{v}_{rel} N_A^2 [A][B]$$

\bar{v}_{rel} = mean relative speed

- The mean speed at which the molecules approach each other
- Calculated by multiplying each possible speed by the fraction of molecules that have that speed and then adding all the products together

$$\bar{v}_{rel} = \left(\frac{8RT}{\pi M^*} \right)^{1/2}$$

$$M^* = \frac{\text{mass}_A \text{mass}_B}{\text{mass}_A + \text{mass}_B}$$

(reduced mass)

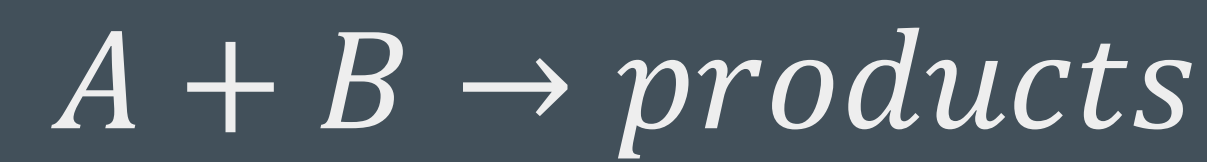
Factoring in Sterics and Activation Energies

These equations predict that an increase in temperature from 273 K to 283 K will increase the collision frequency by a factor of about 1.02.

Experimentally, many reaction rates double over that temperature range...

There must be another factor!

Factoring in Sterics and Activation Energies



$$\text{rate} = k[A][B]$$

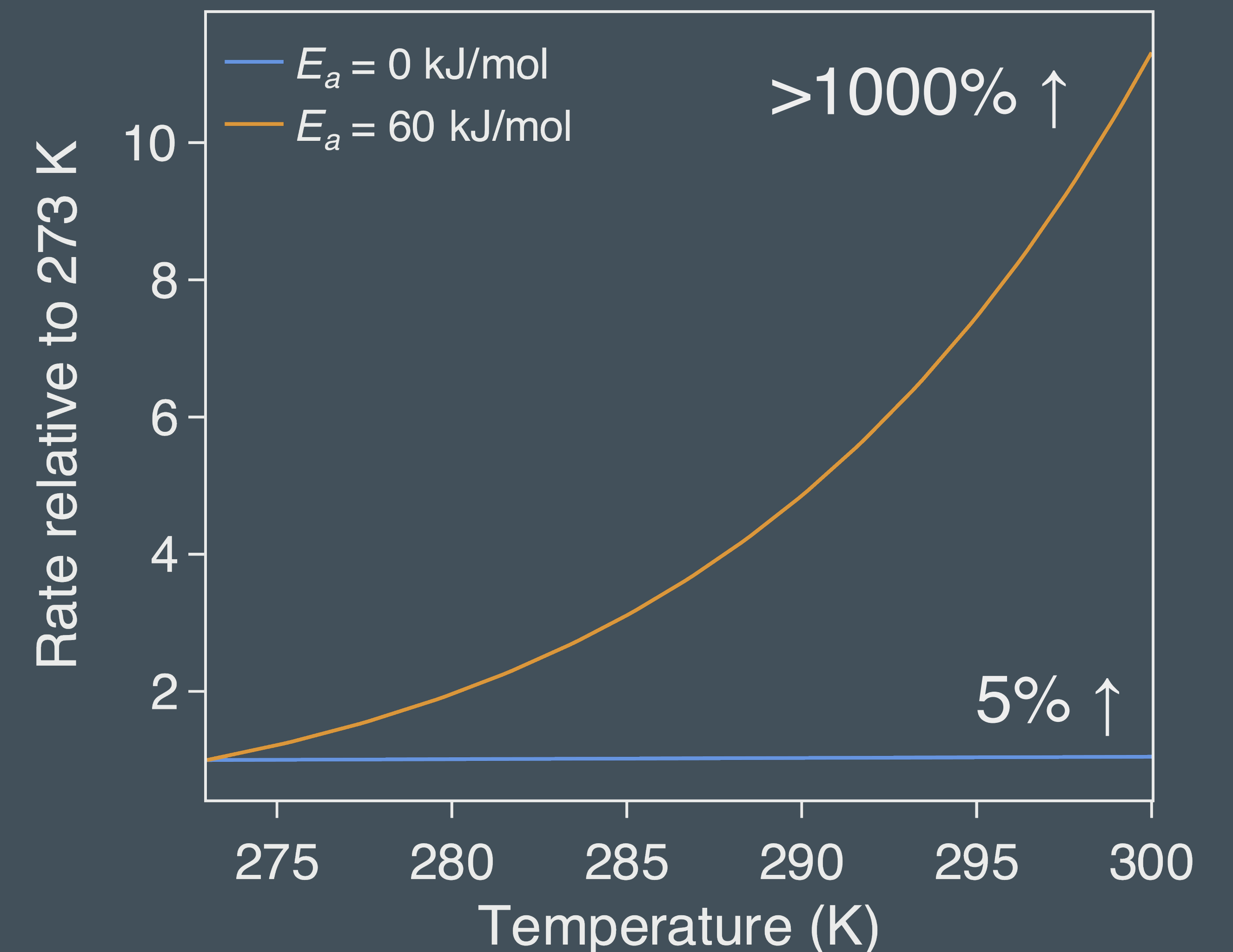
$$\text{rate} = \sigma \bar{v}_{rel} N_A^2 [A][B] \rho e^{-\frac{E_A}{RT}}$$

$\rho = \text{steric factor } (< 1)$

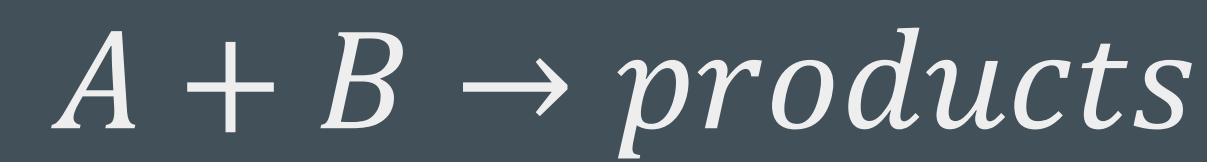
$e^{-\frac{E_A}{RT}} = \text{fraction atoms with sufficient KE to react}$

$$k = \sigma \bar{v}_{rel} N_A^2 \rho e^{-\frac{E_A}{RT}}$$

1. Large activation energies make reactions more temperature sensitive!
2. Absolute rates are of course also make them much slower at same T !



Factoring in Sterics and Activation Energies



$$\text{rate} = k[A][B]$$

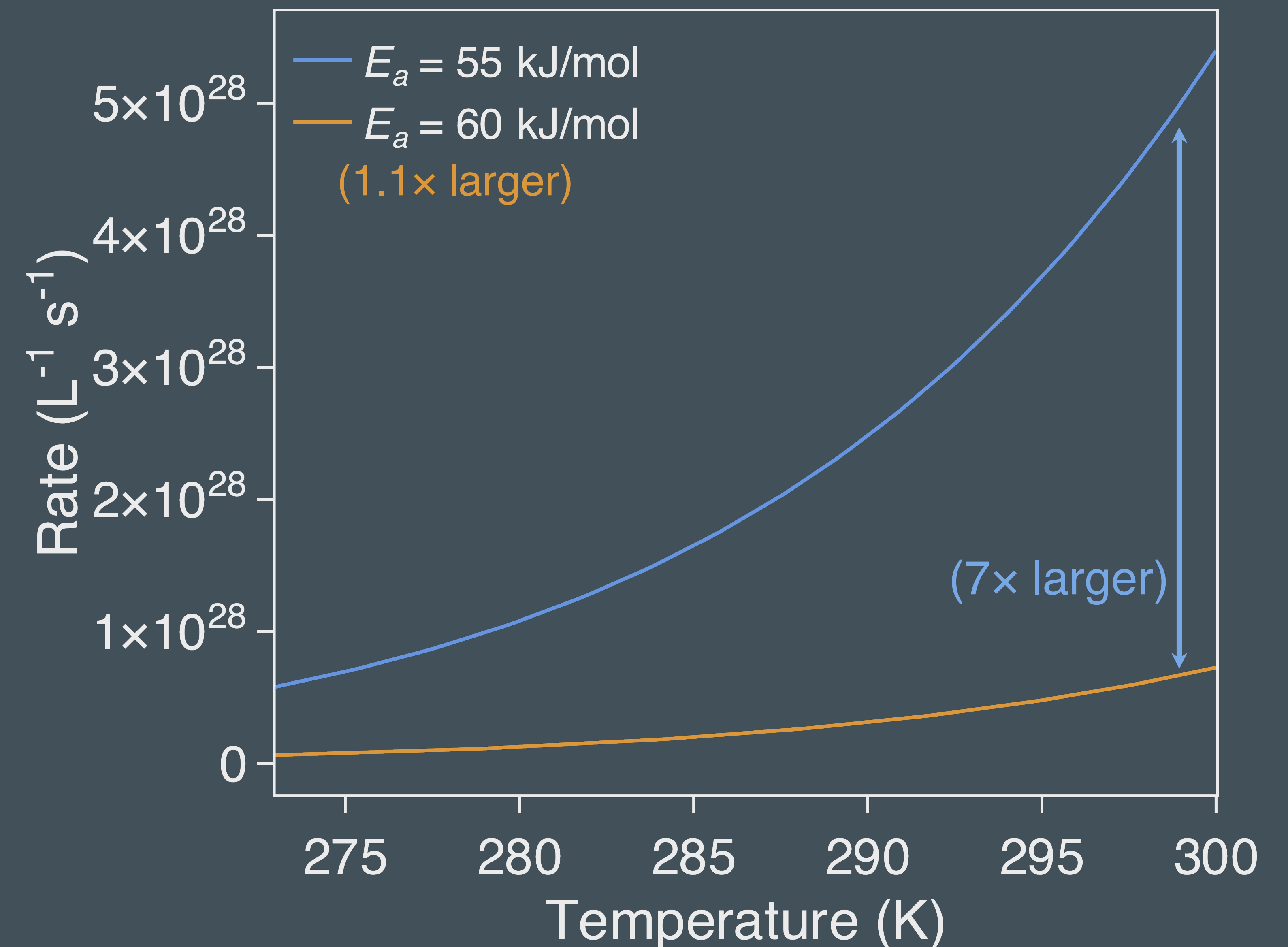
$$\text{rate} = \sigma \bar{v}_{rel} N_A^2 [A][B] \rho e^{-\frac{E_A}{RT}}$$

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$$k = \sigma \bar{v}_{rel} N_A^2 \rho e^{-\frac{E_A}{RT}}$$

1. Large activation energies make reactions more temperature sensitive!
2. Absolute rates are of course also much slower at same T even for small change in E_A !



Definitions

Minimum Energy E_{min} is the minimum amount of kinetic energy needed for energetic collisions to result in chemical reactions.

Collision theory and *rate constants*

According to Collision Theory, the **rate constant** is

$$k_r = \sigma \bar{v}_{rel} N_A^2 e^{\frac{-E_{min}}{RT}}$$

N_A = Avogadro's number

E_{min} = Minimum Energy

$$\bar{v}_{rel} = \left(\frac{8RT}{\pi M^*} \right)^{1/2}$$

$$M^* = \frac{mass_A mass_B}{mass_A + mass_B}$$

(reduced mass)

In the lab

The experimental rate constant is normally smaller than what collision theory predicts.

To Improve predictions, consider the orientation of the molecules! This is called the steric requirement or *sterics*.

Steric Factor

We use the steric factor **P** to adjust our equation for k

- When the molecules are very large, it has a large steric requirement
- A large steric requirement will have a very small steric factor **P**
- A small steric factor barely affects the rate constant

$$k_r = P \sigma \bar{v}_{rel} N_A^2 e^{\frac{-E_{min}}{RT}}$$

Example

Which of the below reactions would you expect to have the largest value for P?



Minimum energy vs. activation energy

Over time, we learned that $E_{\min} = E_a$

Minimum Energy E_{\min} is the minimum amount of kinetic energy needed for energetic collisions to result in chemical reactions

- Usually in reference to **collisions** and **velocity**

Activation Energy E_a is the minimum amount of energy that the reactants need in order to undergo a chemical reaction

- Usually in reference to **temperature**

$\sigma \overline{v_{rel}} N_A$ Vs. Pre-Exponential factor

We also learned that $\sigma \overline{v_{rel}} N_A = A$

$\sigma \overline{v_{rel}} N_A$ is a measure of the rate at which the molecules collide

- Usually in reference to **collisions** and **velocity**

Pre-exponential factor **A** is the rate constant at infinite temperature, or the theoretical maximum reaction rate possible.

- Usually in reference to **temperature**

Summary

Collision Theory

- Collisions and Velocity
- E_{\min}
- $\sigma v_{\text{rel}} N_A$

Arrhenius Theory

- Temperature
- E_a
- A

$$E_a = E_{\min}$$

$$A = \sigma \bar{v}_{\text{rel}} N_A$$

Reaction profile: Endothermic



K_{eq} for Endothermic Reactions

If the reaction is endothermic in the forward direction, the activation energy is higher for the forward direction than for the reverse direction.

The higher E_A means that the rate constant of the forward reaction depends more strongly on temperature than does the rate constant of the reverse reaction.

K_{eq} for Endothermic Reactions

When the temperature increases, the forward rate constant increases more than that of the reverse reaction.

K_c will increase and the reaction will then be able to form products.

What does this mean? An endothermic reaction needs heat to run!

Reaction profile: Exothermic



K for Exothermic Reactions

If the reaction is exothermic in the forward direction, the activation energy is lower for the forward direction than for the reverse direction.

The low E_a means that the rate constant of the reverse reaction depends more strongly on temperature than does the rate constant of the forward reaction.

K for Exothermic Reactions

When the temperature increases, the reverse rate constant increases more than that of the forward reaction.

K_c will decrease and the formation of products will be less favored.

What does this mean? If you increase the heat on an exothermic reaction, the reactants start to become more favored.

Next time

- Transition State Theory
- Catalysis