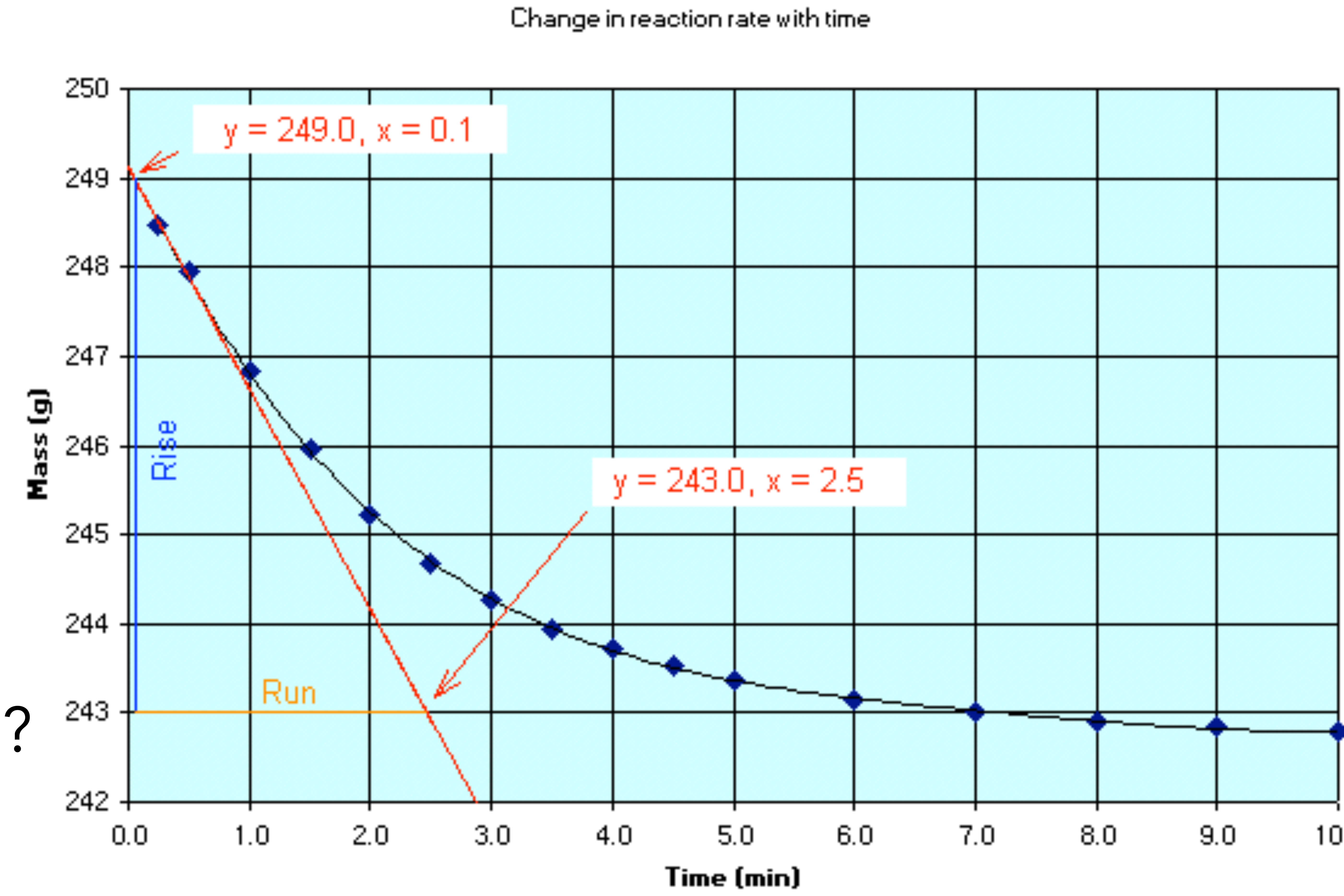
Unit 6

Kinetics

Reaction Rates/Mechanisms
Collision Theory
Rate Expression
Activation Energy

Rates of Reaction:

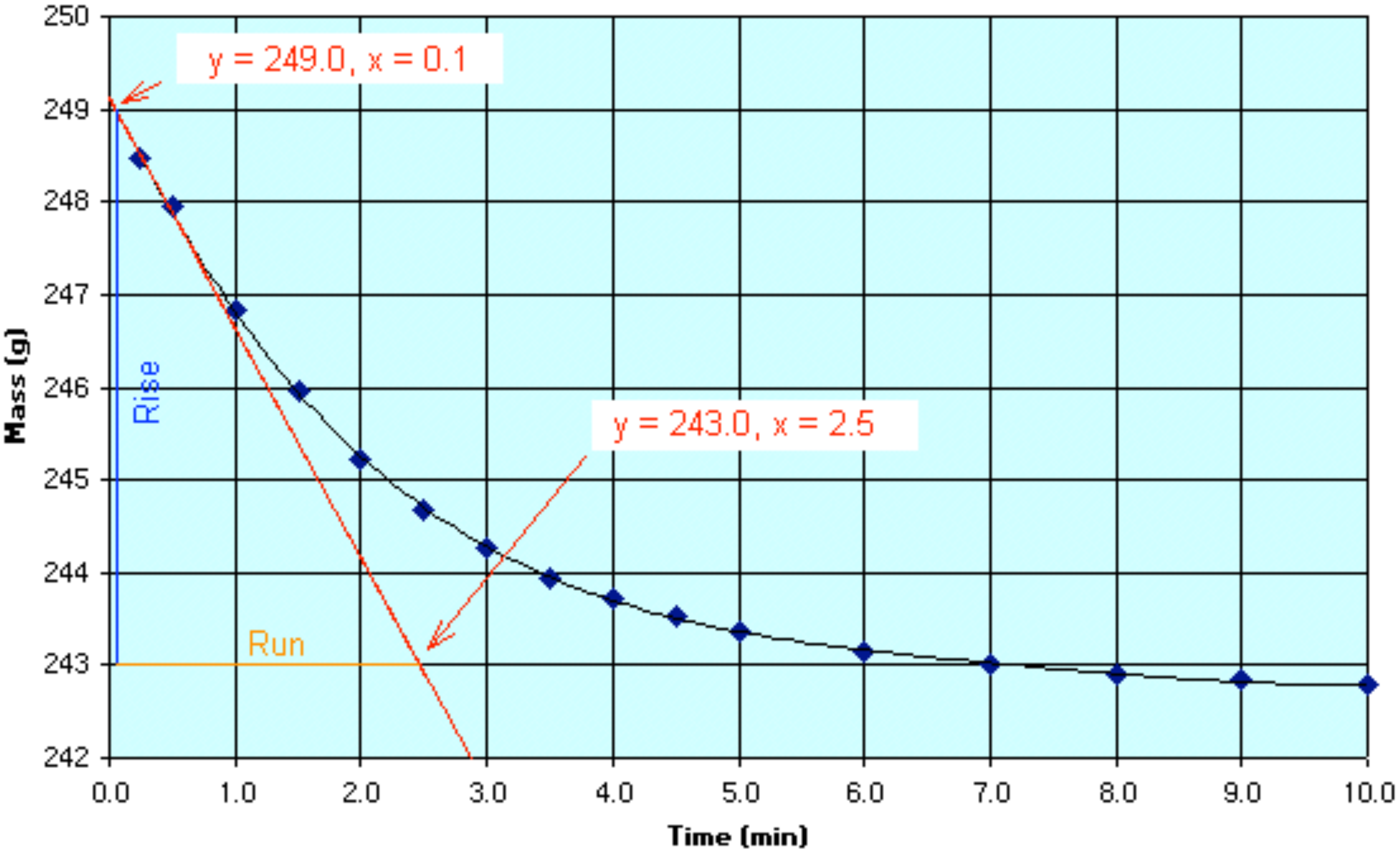


- time vs. rate: what's the difference?
  - units of each?
    - time: seconds
    - rate: 1/seconds
- reaction rate: describes how quickly a reaction happens
  - how quickly the reactants are converted into products

Rate of Reaction:

=change of product concentration / time

- units?
    - concentration = mol dm^{-3}
    - rate = 1/sec
    - rate of reaction = mol dm^{-3} s^{-1}

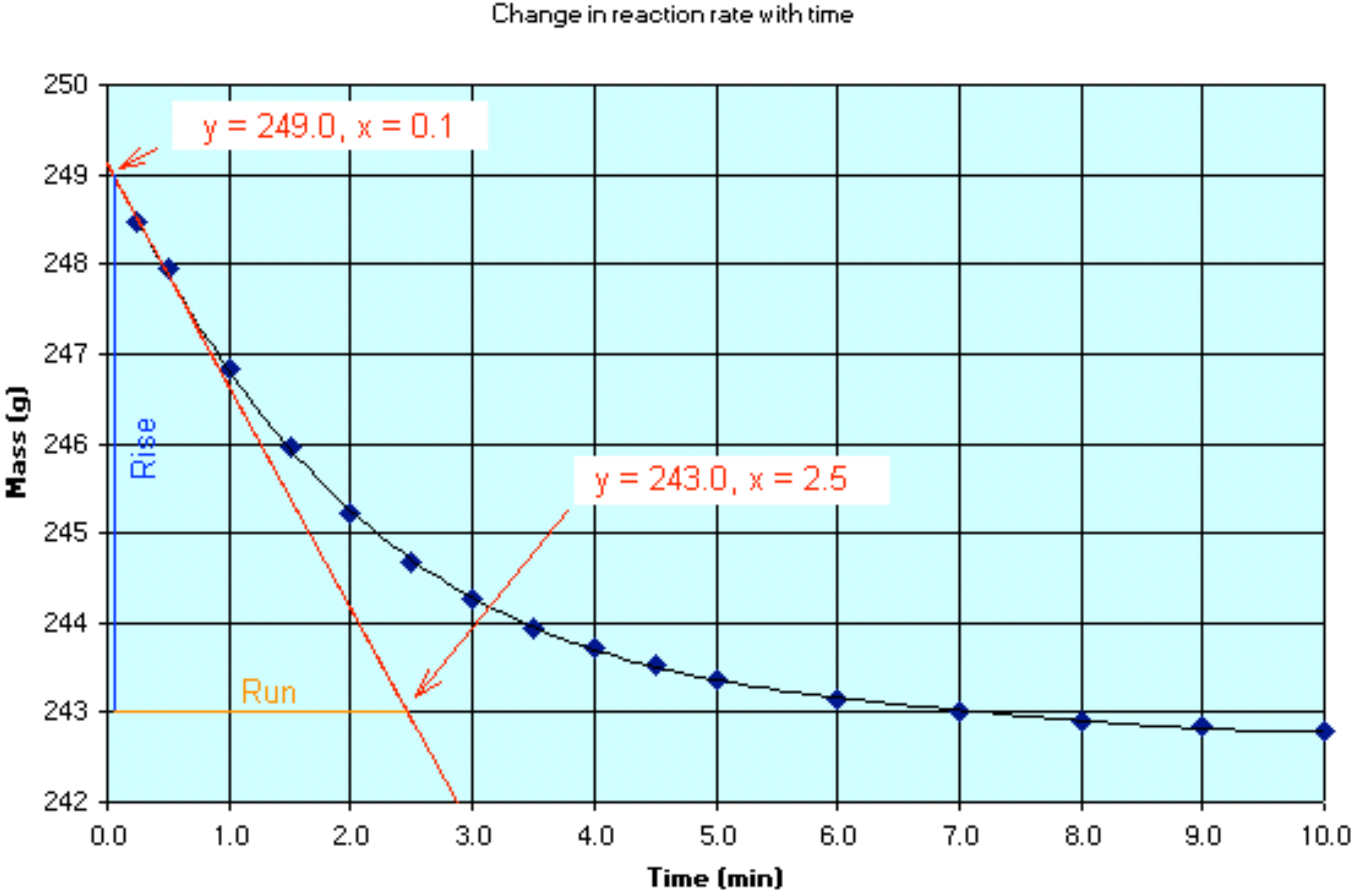


Change in reaction rate with time

Rate of Reaction

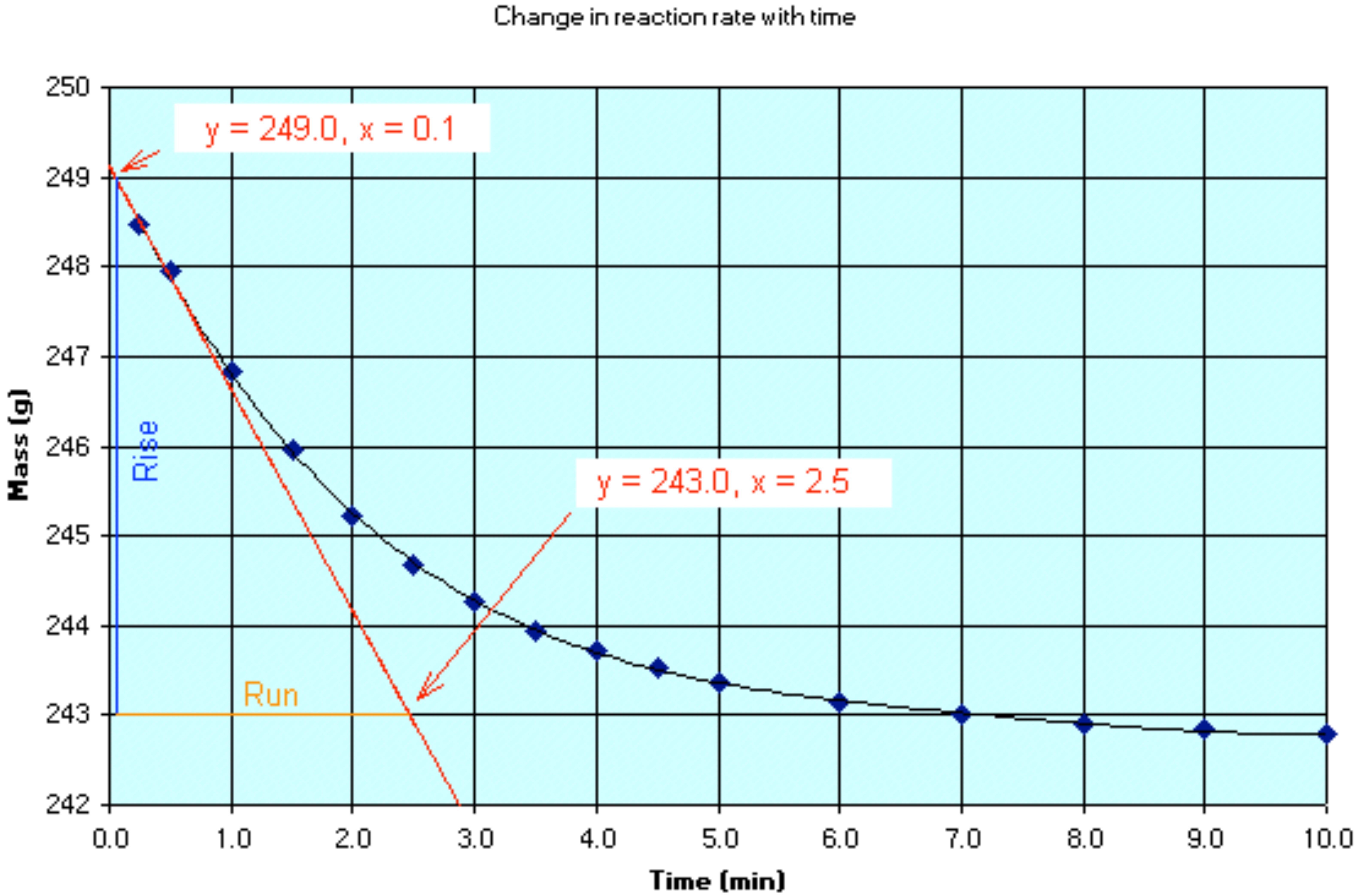
- how to find rate of reaction on a curve...
  - use the tangent, will treat a curve as a single point

gradient might be negative, rate will be positive (always)



Overall...

- What do you notice about the overall rate of reaction?
- The beginning of reaction? The end?



Measuring rates of reaction

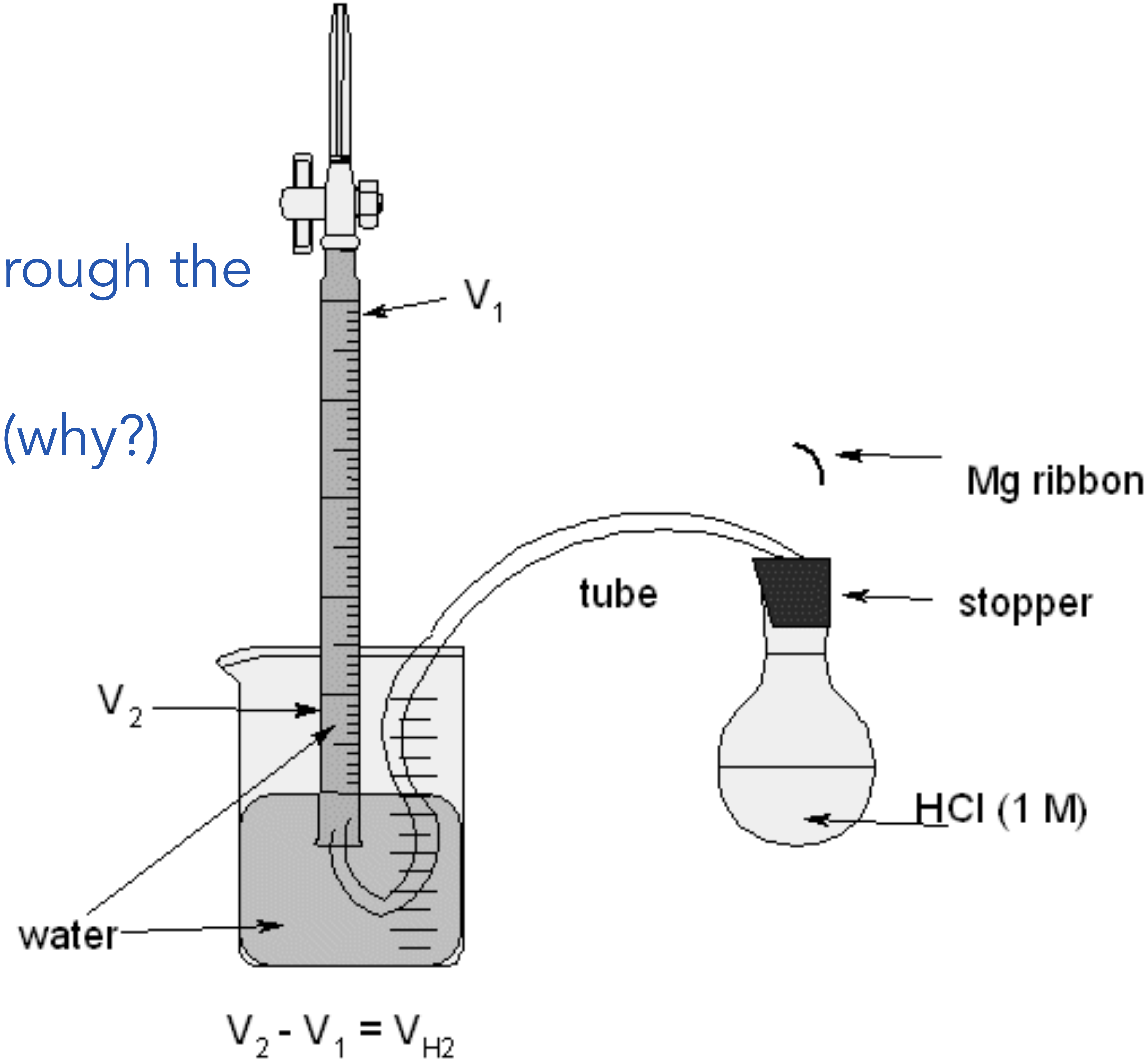
Different Techniques:

- change in volume of a gas
- change in mass
- change in transmission of light (colorimetry/spectrophotometry)
- Titration
- Conductivity
- Clock reactions

Change in Volume of Gas

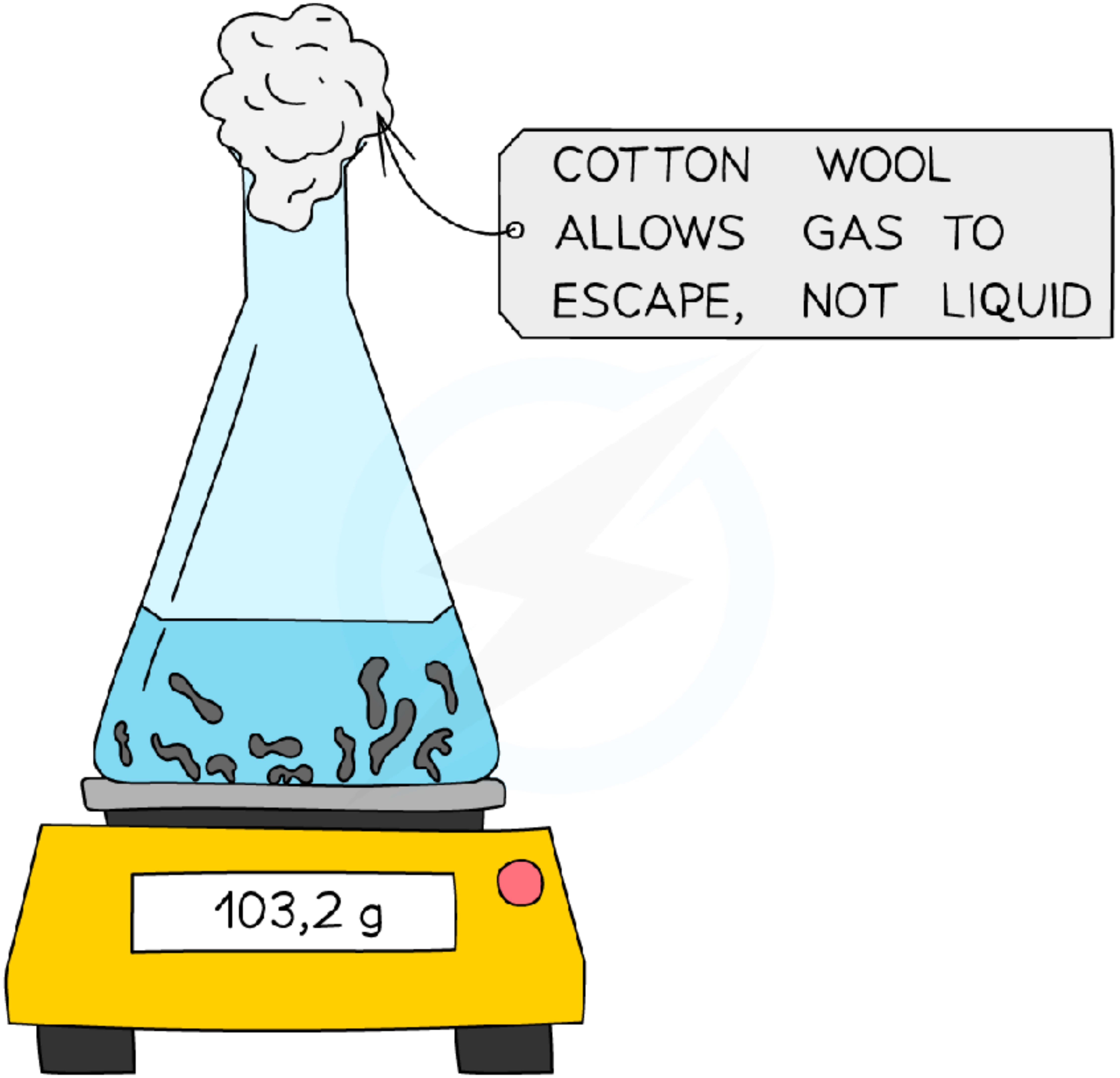
measuring techniques:

- gas syringe
- inverted burette - bubble the gas through the liquid
  - to minimize error use warm water (why?)



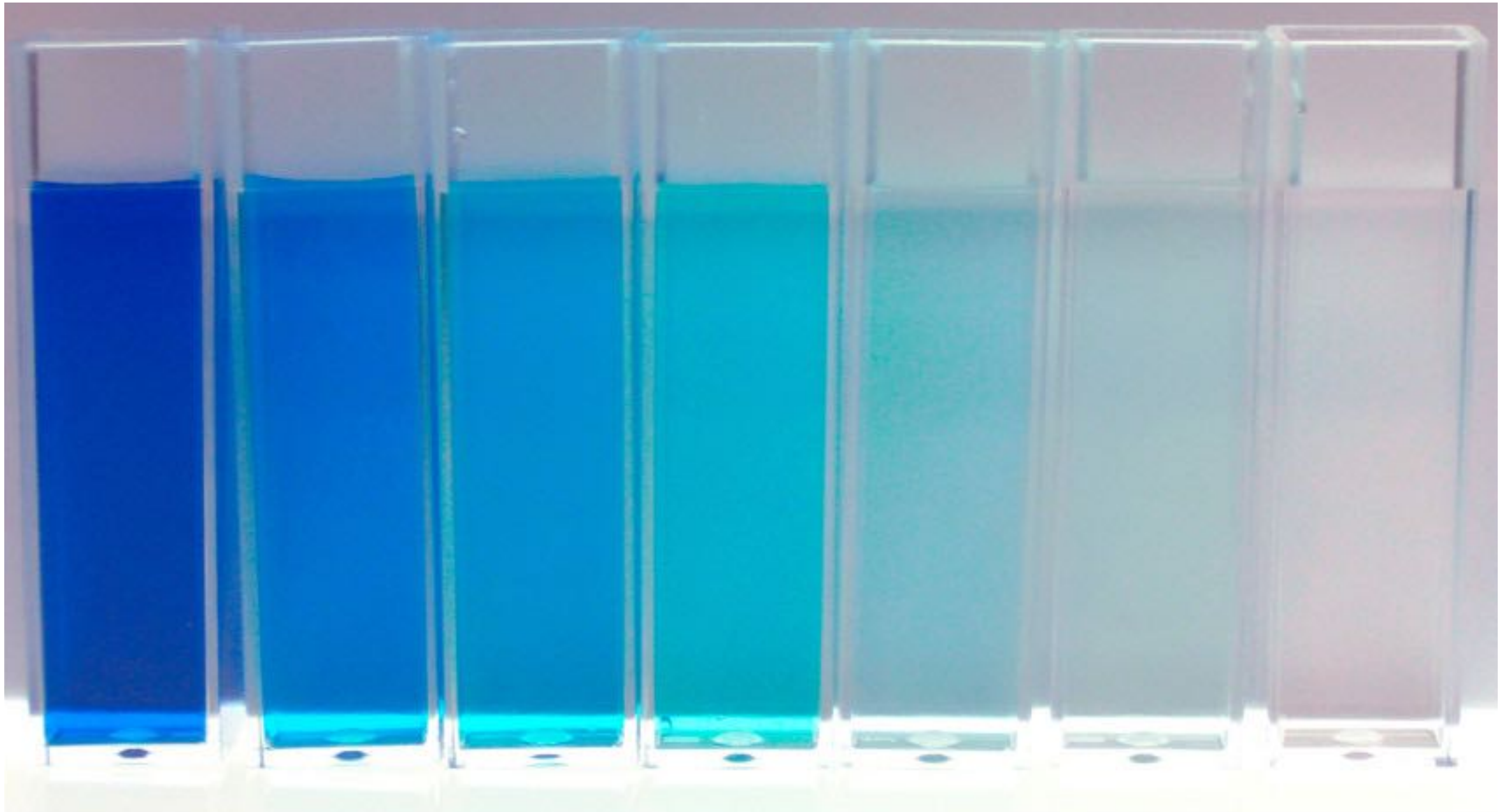
Change in mass

- use a porous membrane to allow gas to escape (cotton balls will work)
- measure the change
- doesn't work well with hydrogen…why?



Change in Color

- works with coloured solutions (transition metals…etc)
- change in absorbance of the solution is measured over time



Titration and Conductivity

- Titration - measure the concentration of the reactants or products by titrating the solution with a ‘standard’ solution of known concentration

- Conductivity - can be measured and compared to the total number of ions in solution (side of the rxn with more ions will be more conductive)

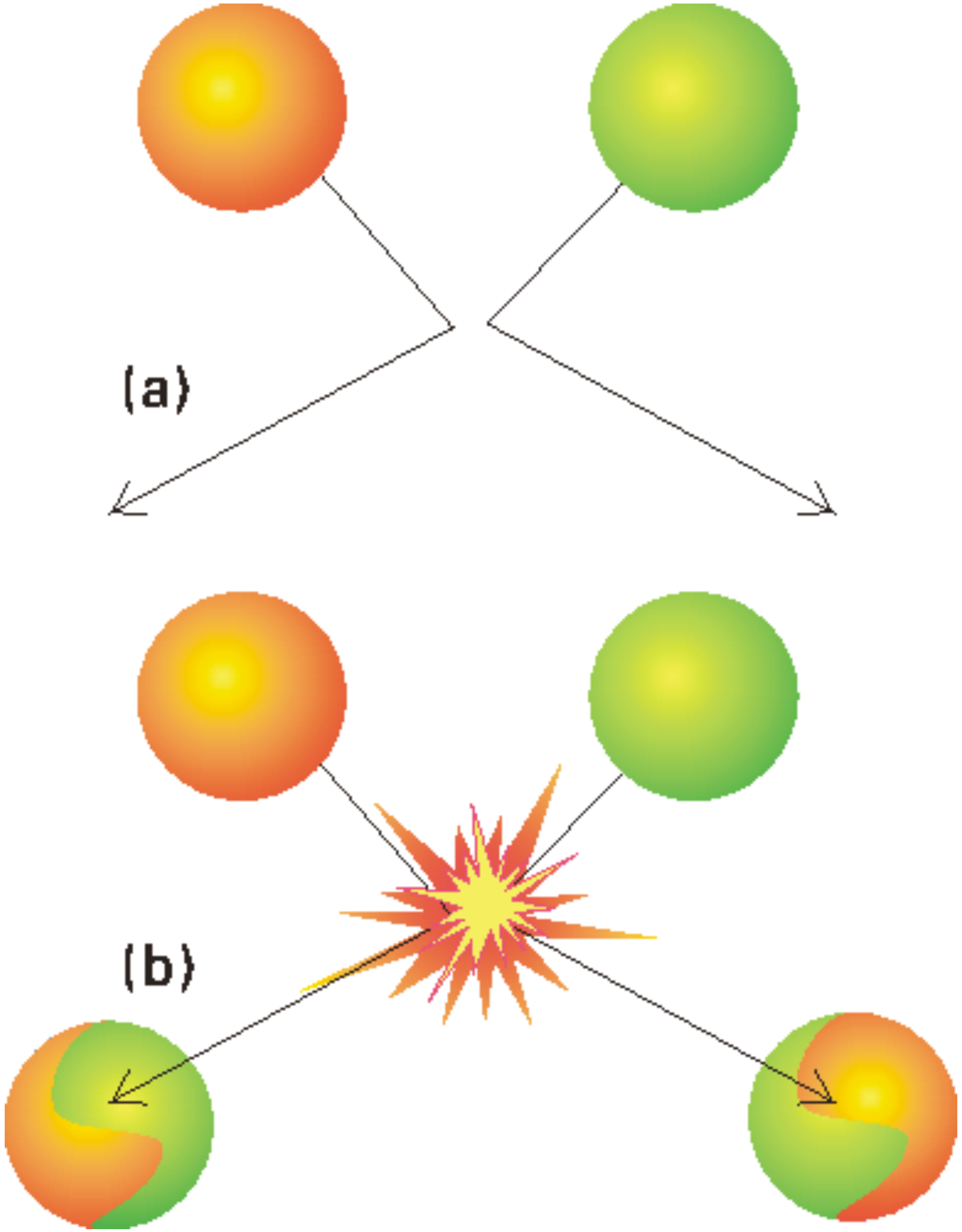
Clock Reactions

- Video!
- Using something observable as an arbitrary 'endpoint'

Collision Theory

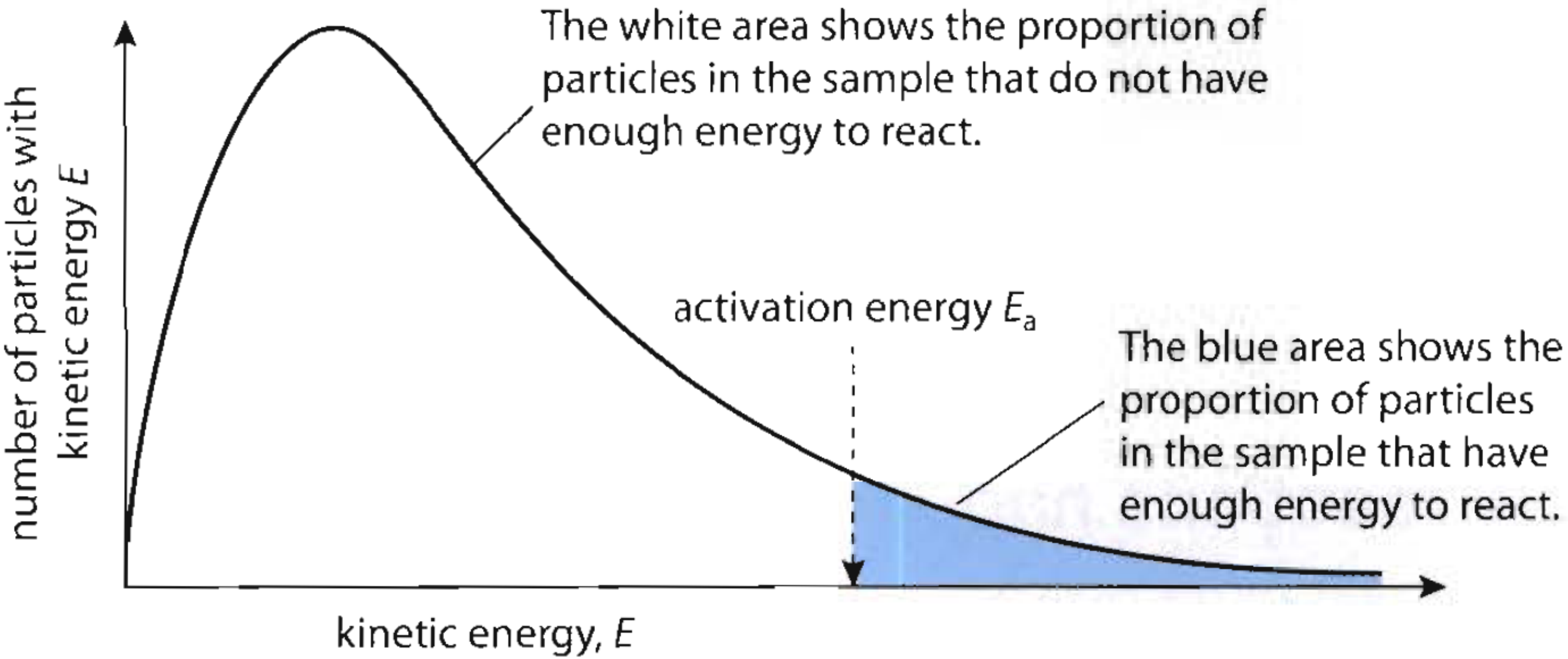
how to have a successful collision...

what do we need?



Kinetic Energy and Temperature

- Not all particles have same KE (avg. KE -- temperature)
- Shown by Maxwell-Boltzmann distribution curve
- simulation



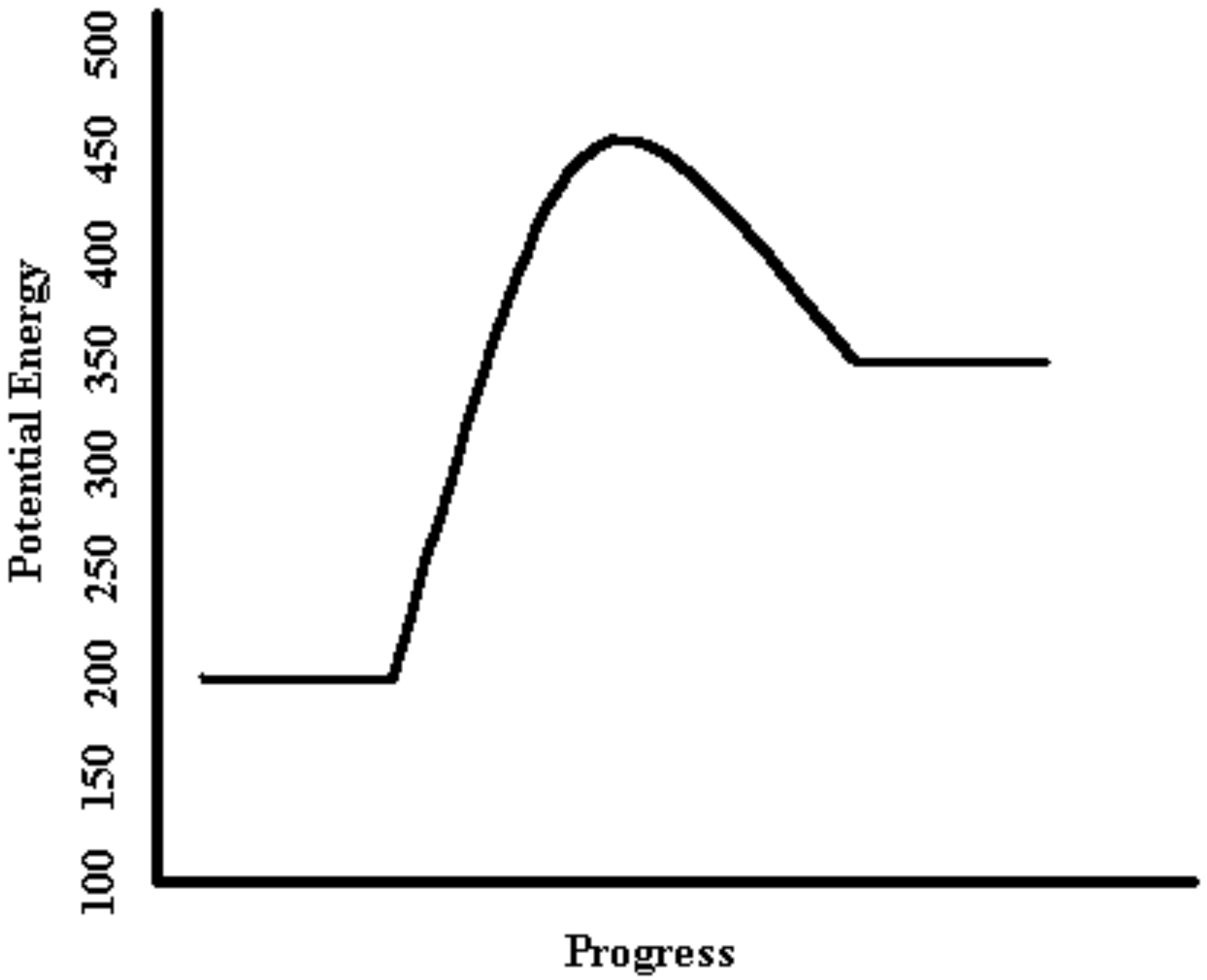
The white area shows the proportion of particles in the sample that do not have enough energy to react.

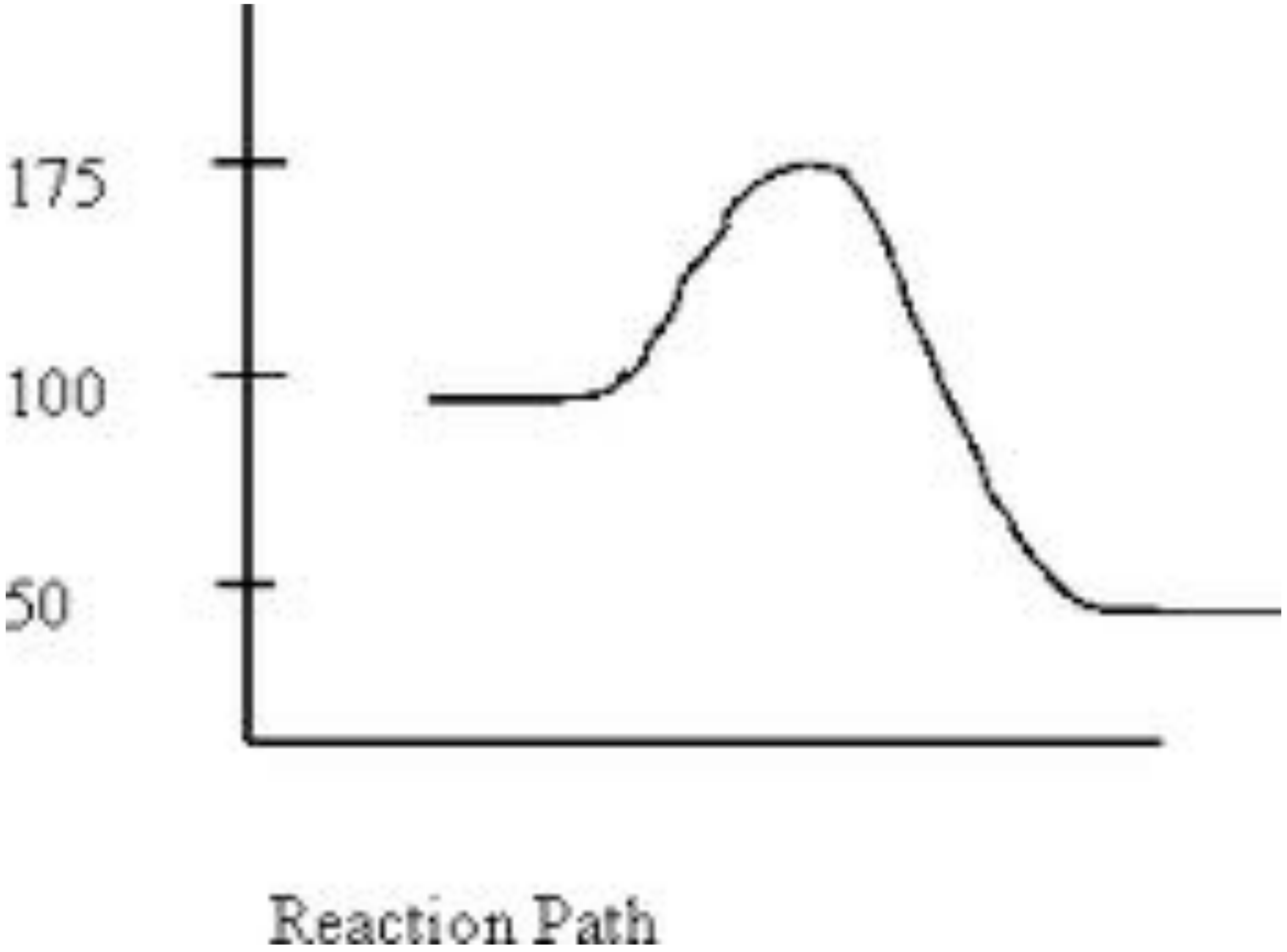
activation energy E_a

The blue area shows the proportion of particles in the sample that have enough energy to react.

Energy of collision

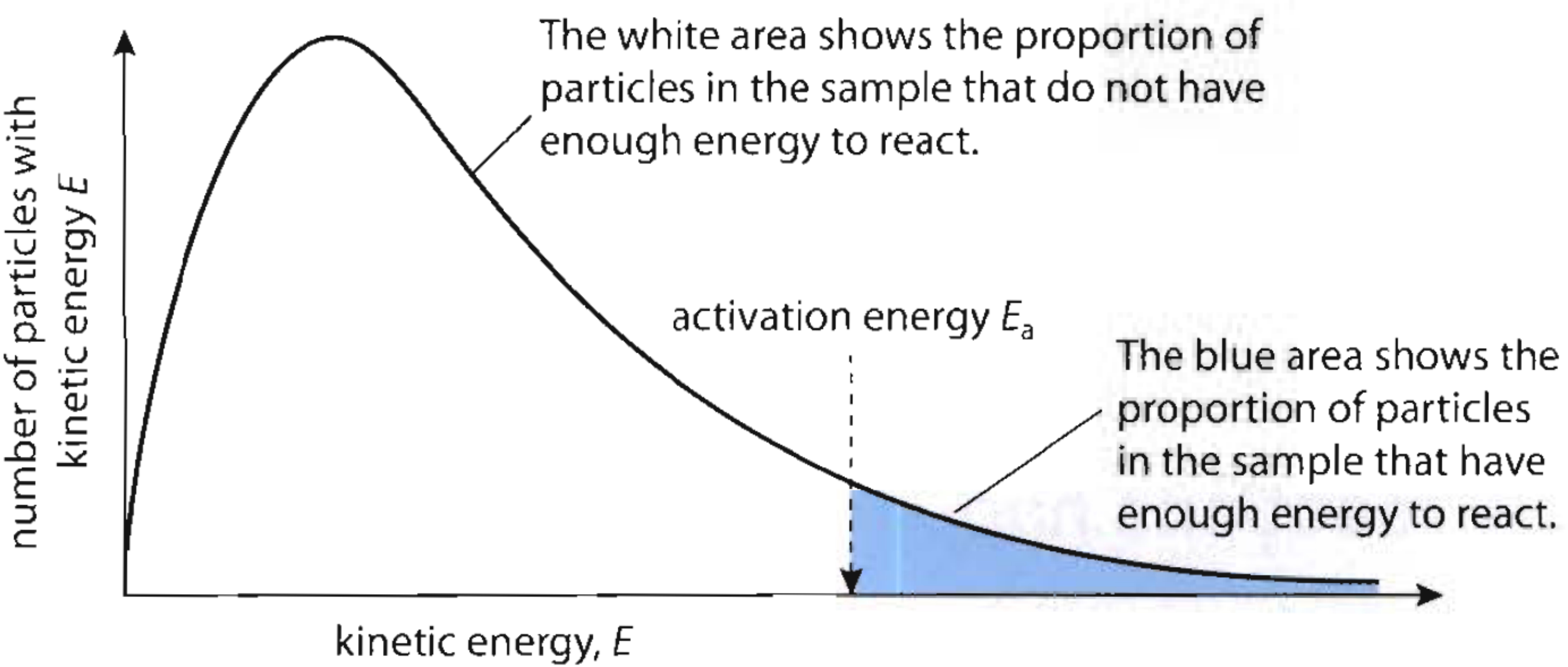
- what's the minimum amount of kinetic energy needed to react called?
  - ACTIVATION ENERGY





Energy

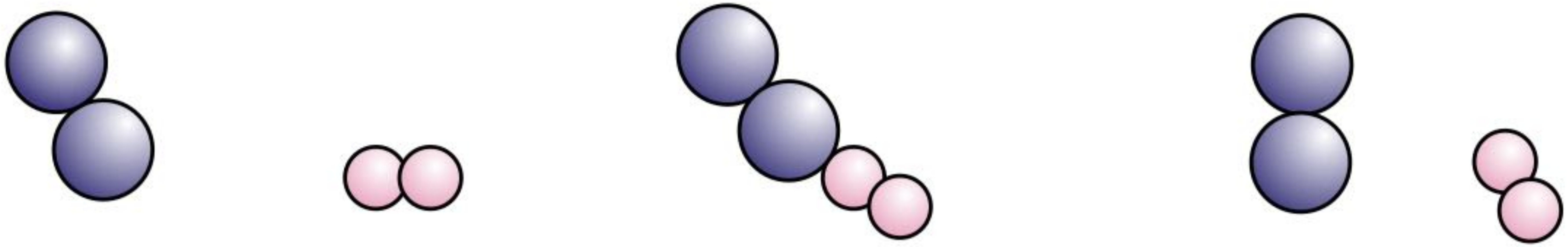
- Only certain particles will have the energy to reach the threshold and are able to complete the reaction



Geometry of Collision

- Do they collide with the proper orientation?
- Will the collision be effective?

(a)

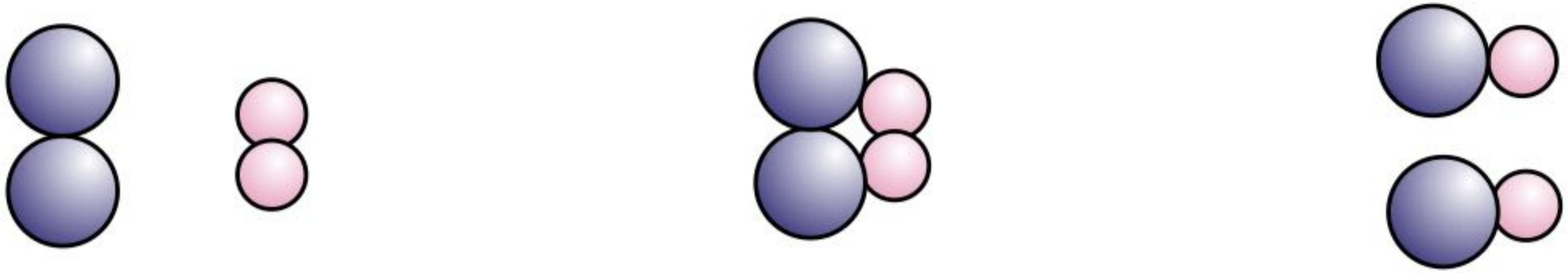


reactant molecules approach each other

ineffective collision – no reaction occurs

reactant molecules separate – no product formed

(b)



reactant molecules approach each other

effective collision – particles have correct collision geometry so reaction occurs

product molecules formed

Factors Affecting Rate of Reaction

You know these:

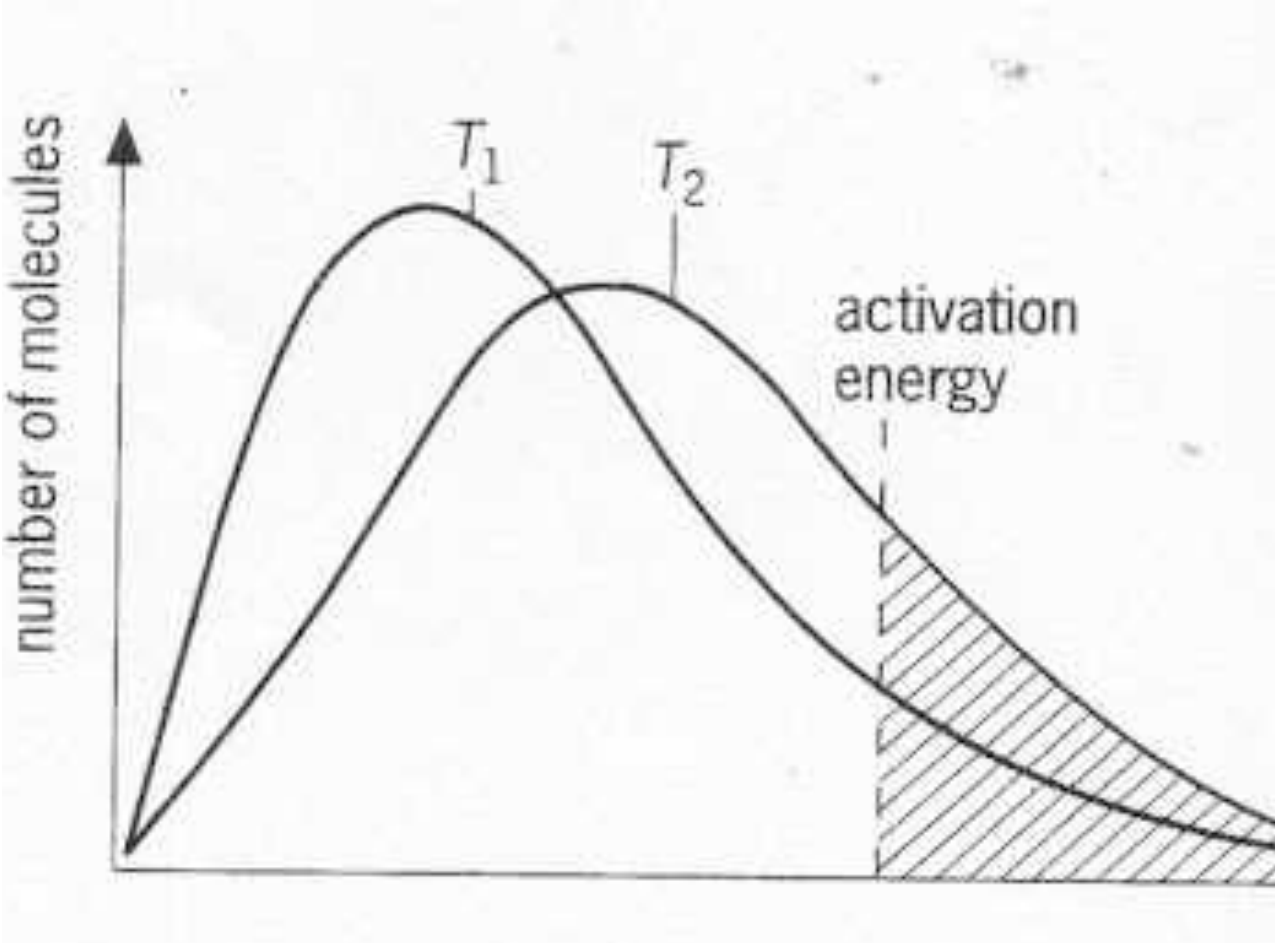
- Temperature
- Concentration
- Particle size

You may know these:

- Pressure
- Catalyst

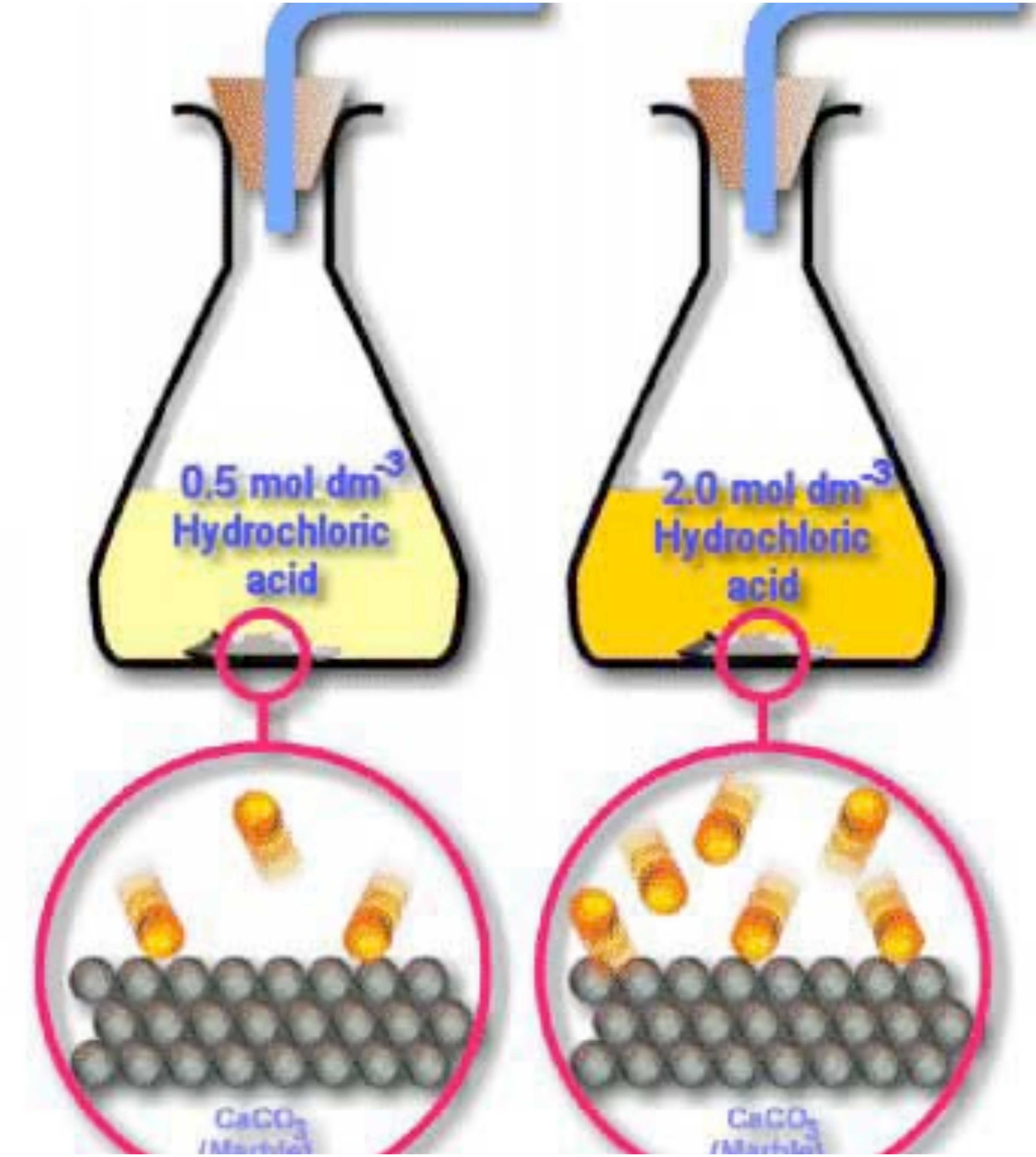
Temperature

- What happens to the kinetic energy if we increase the Temperature?
- Many reactions double their rate with a 10°C increase



Concentration

- Higher concentration has more particles involved and therefore will have more collisions and more of those collisions will be successful

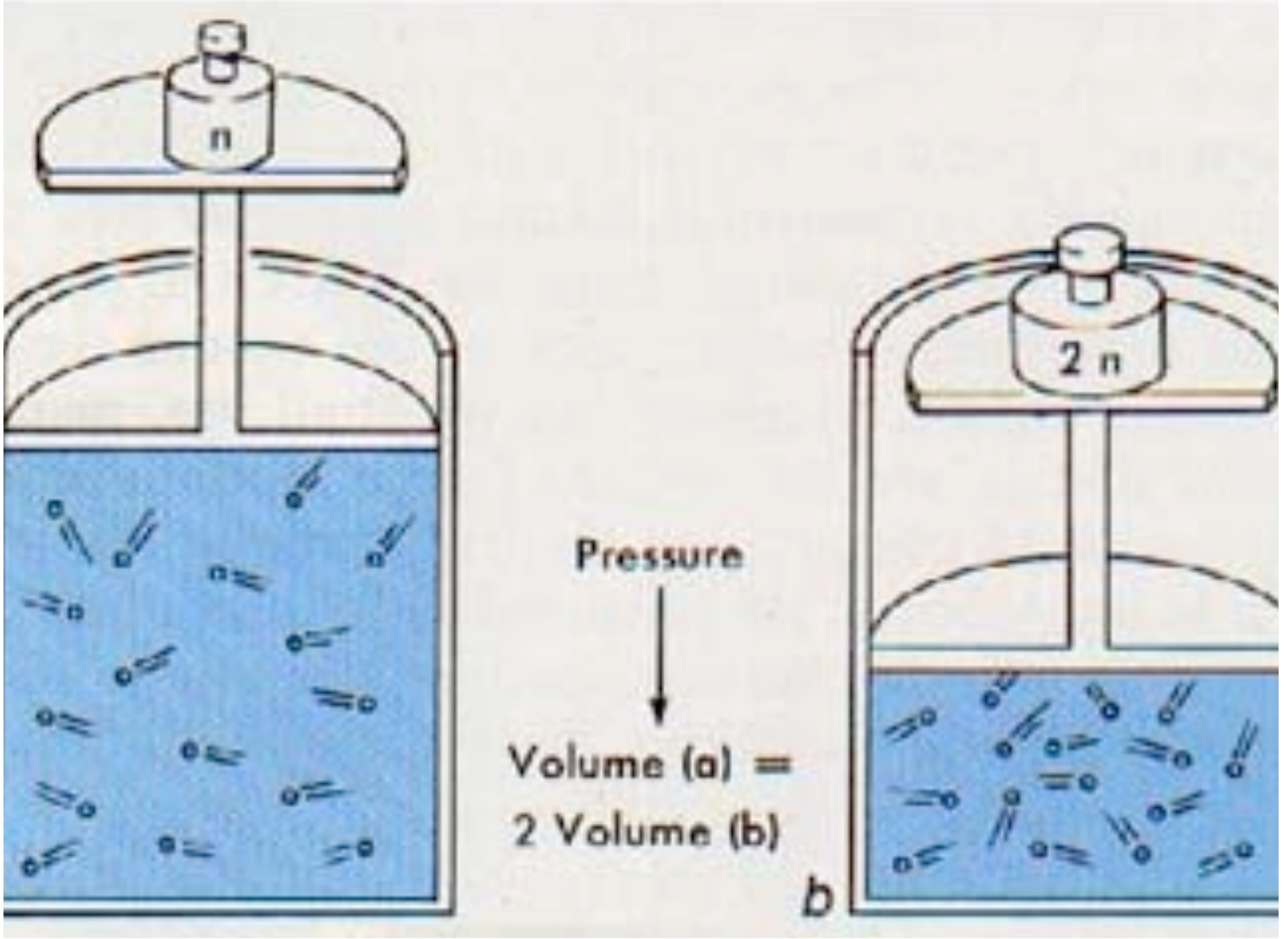


Particle Size

On April 5, 2010, metal mining equipment created a spark as it hit rock along a passage of the Upper Big Branch mine, then owned by Massey Energy Company. That spark ignited a pocket of methane gas, which ignited a large quantity of highly explosive coal dust. Twenty-nine miners died, two were injured and Massey Energy was engulfed in accusations of negligence and willful concealment of unsafe conditions.

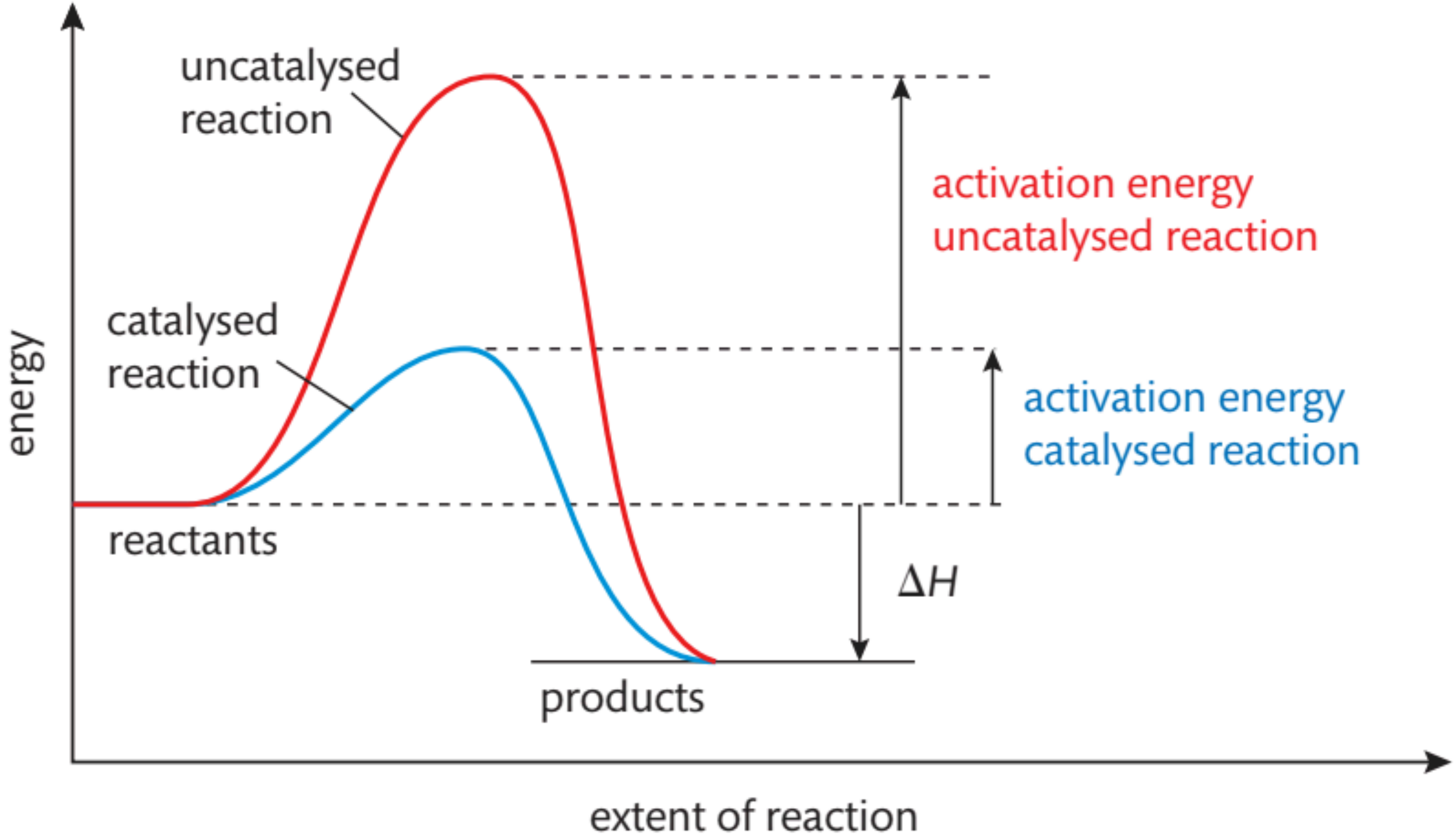
Pressure

- What do you think?



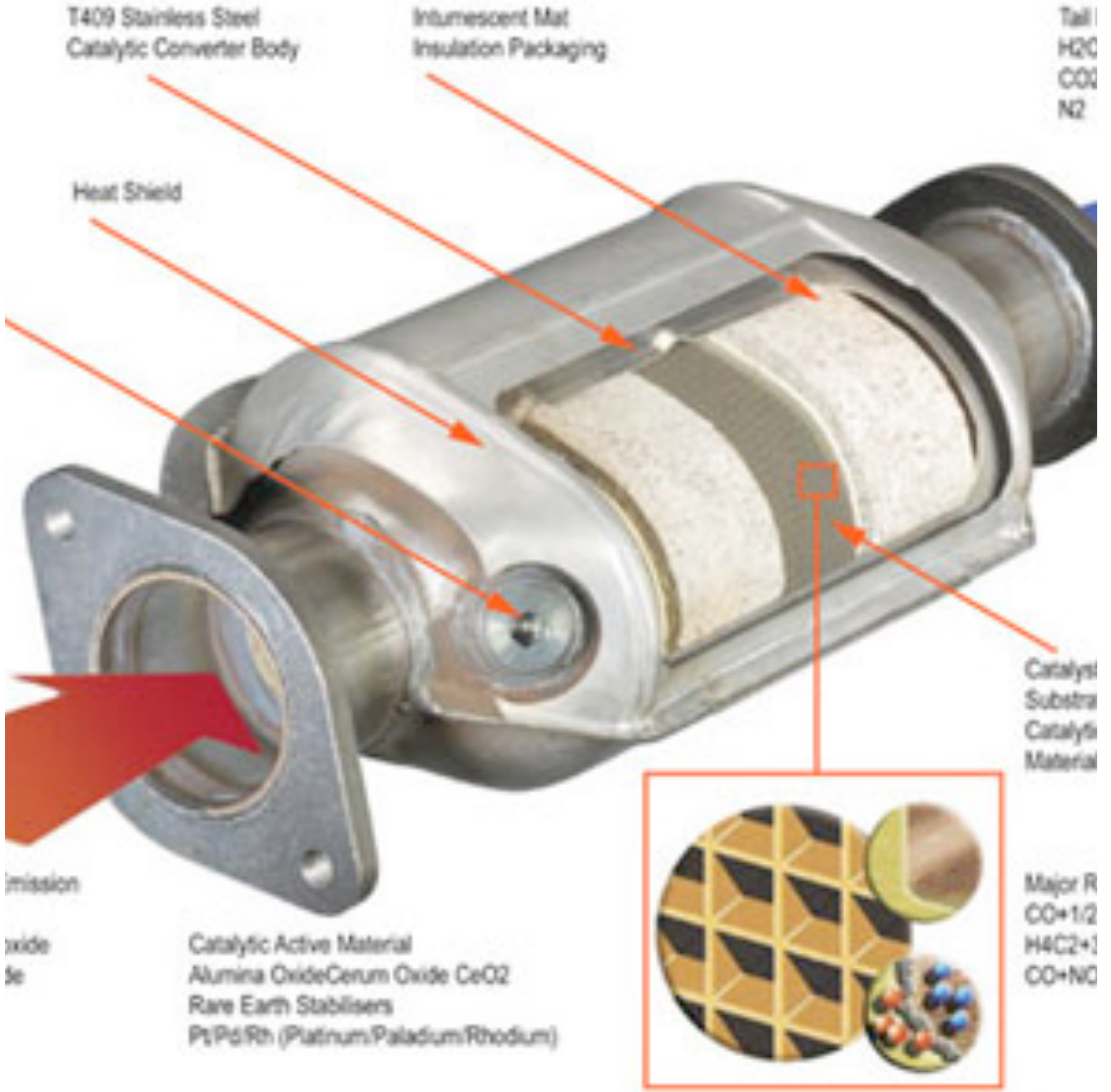
Catalyst

- a substance that increases the rate of a reaction without itself going through a chemical change
- provides an 'alternate route for reaction' - has a lower activation energy



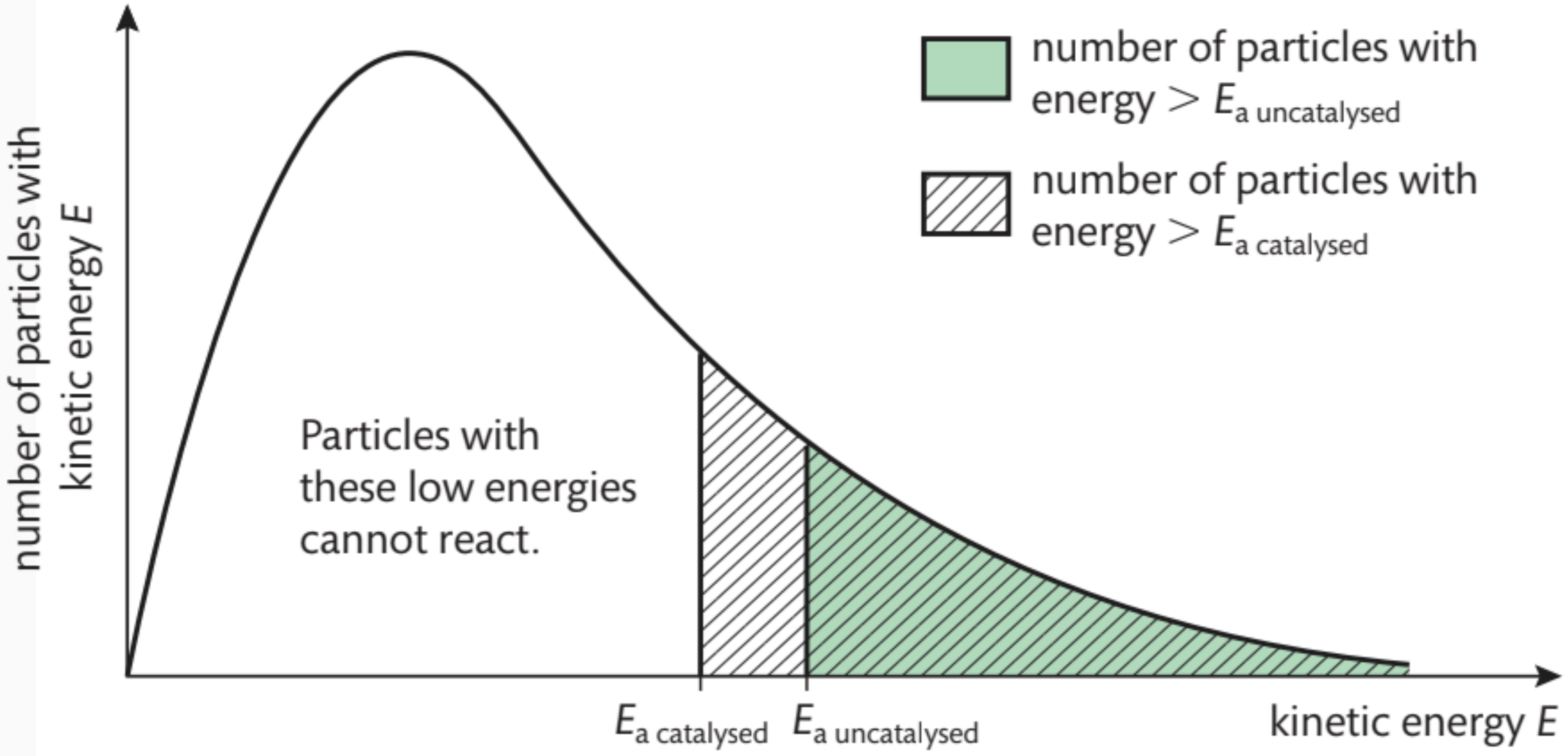
Catalysts

- certain manufacturing processes use catalysts to increase efficiency and yield (many are a closely guarded secret)
- Every biological reaction uses a catalyst…called enzymes
- Used in making cheese
- Field of biotechnology is developing these applications rapidly



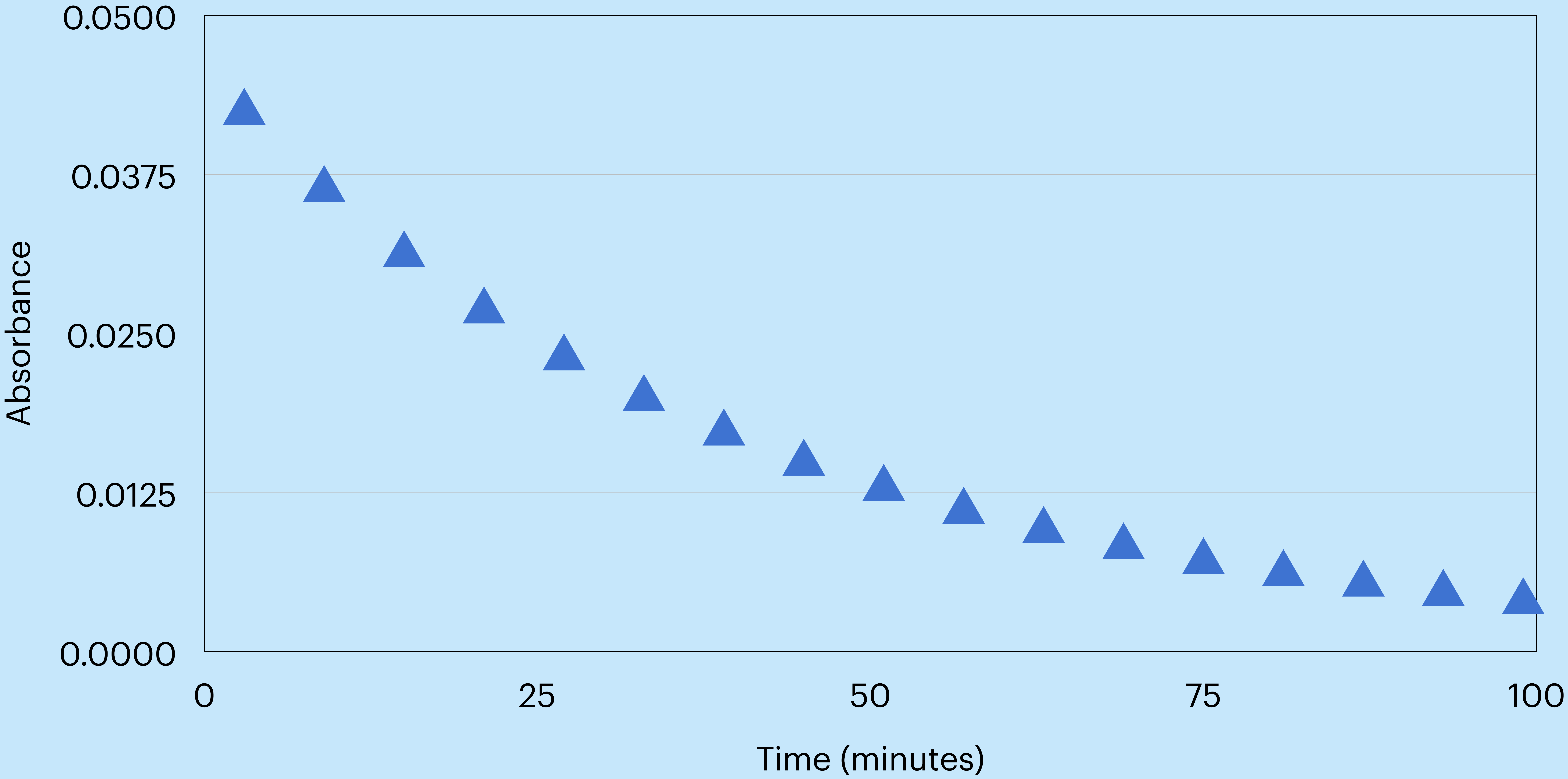
Catalysts

- In review - more particles will have the energy to "get over the hump" (activation energy) due to the fact a catalyst was used



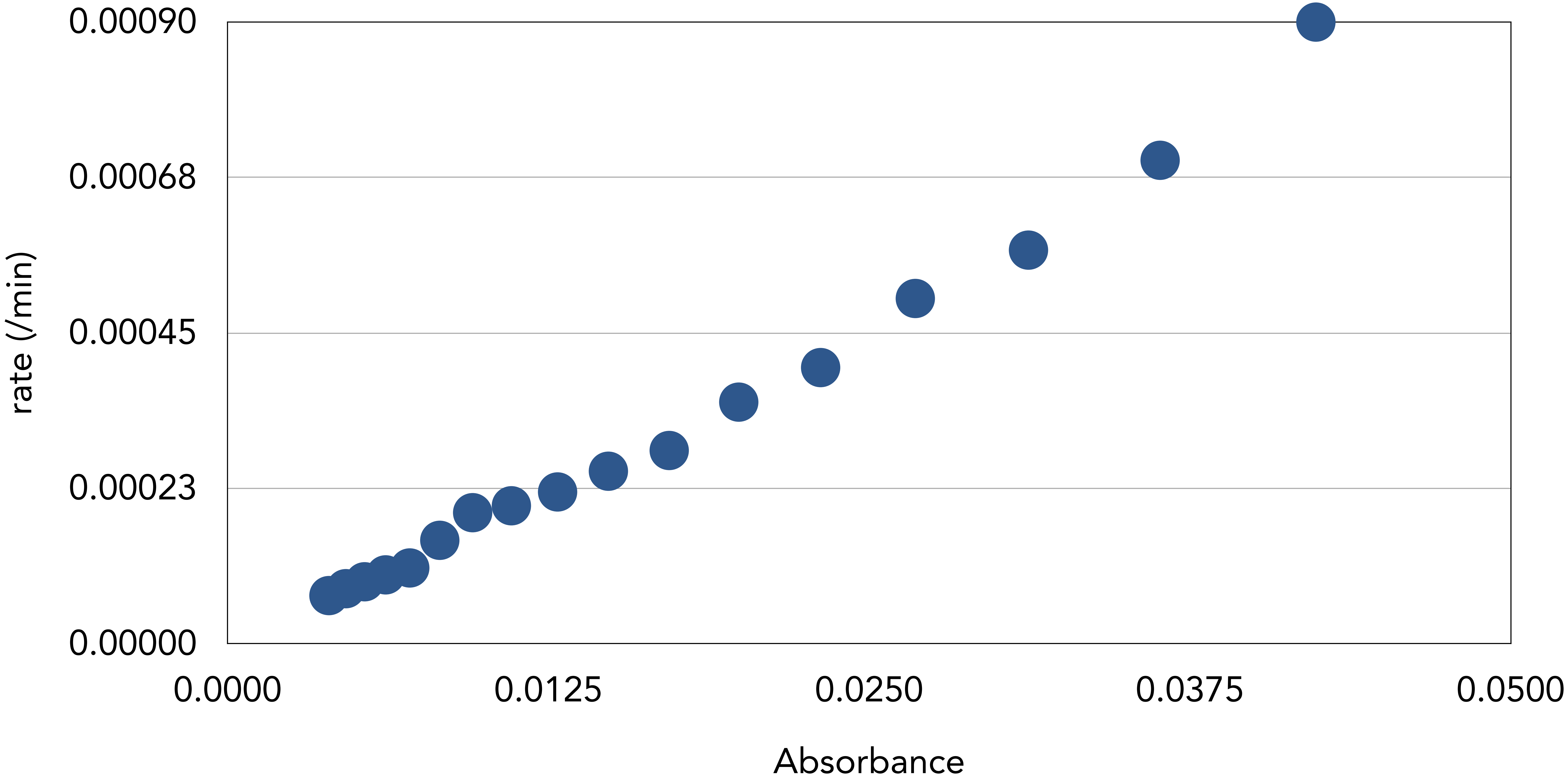
16.1 Rate Expression

- This graph shows the absorbance of the decomposition of $C_{60}O_3$ over time



Rate vs Absorbance

- What's true about this chart?
- Reaction rate is directly proportional to the concentration
  - rate $\propto [C_{60}O_3]$



Rate Constant

- We know: rate $\propto$ $[C_{60}O_3]$
- This can be converted to an equation using a constant
  - reaction rate = k $[C_{60}O_3]$
- This is called the <u>rate expression</u> or the <u>rate law</u>
- It is considered a **<u>first-order</u>** reaction because the concentration of the reactant is raised to the first power

Rate Expression

In general, the rate is proportional to the product of the concentration of the reactants, raised to a power

- A + B → products
- Rate $\propto [A]^m[B]^n$ or rate $= k\,[A]^m[B]^n$
- The powers to which the concentrations are raised in the rate expression, m and n, are known as the orders of reaction
- The overall order for the reaction is $m + n$

Example

- The reaction $2H_{2(g)} + 2NO_{(g)} \rightarrow 2H_2O_{(g)} + N_{2(g)}$ is shown to be the second order with respect to NO and first order with respect to H_2.
  - Give the rate expression for this reaction and its overall order.

Notice…

- The orders of reaction <u>cannot</u> be determined by looking at the coefficients of the reactants.
- Reaction order can only be determined experimentally
- There is no prediction to be made by looking at the coefficients

Another...

- The rate expression for the reaction
  - $NO_{(g)} + O_{3(g)} \rightarrow NO_{2(g)} + O_{2(g)}$

is: $rate = k[NO][O_3]$

  - What is the order with respect to each reactant and what is the overall order of the reaction?

Units of *k*, the Rate Constant

Zero Order

Rate = k

k = units of rate

= **$\text{mol dm}^{-3}\ \text{s}^{-1}$**

First Order

Rate = $k[A]$

to the board...

Second Order

Rate = $k[A]^2$

to the board...

Third Order

Rate = $k[A]^3$

again...

Example

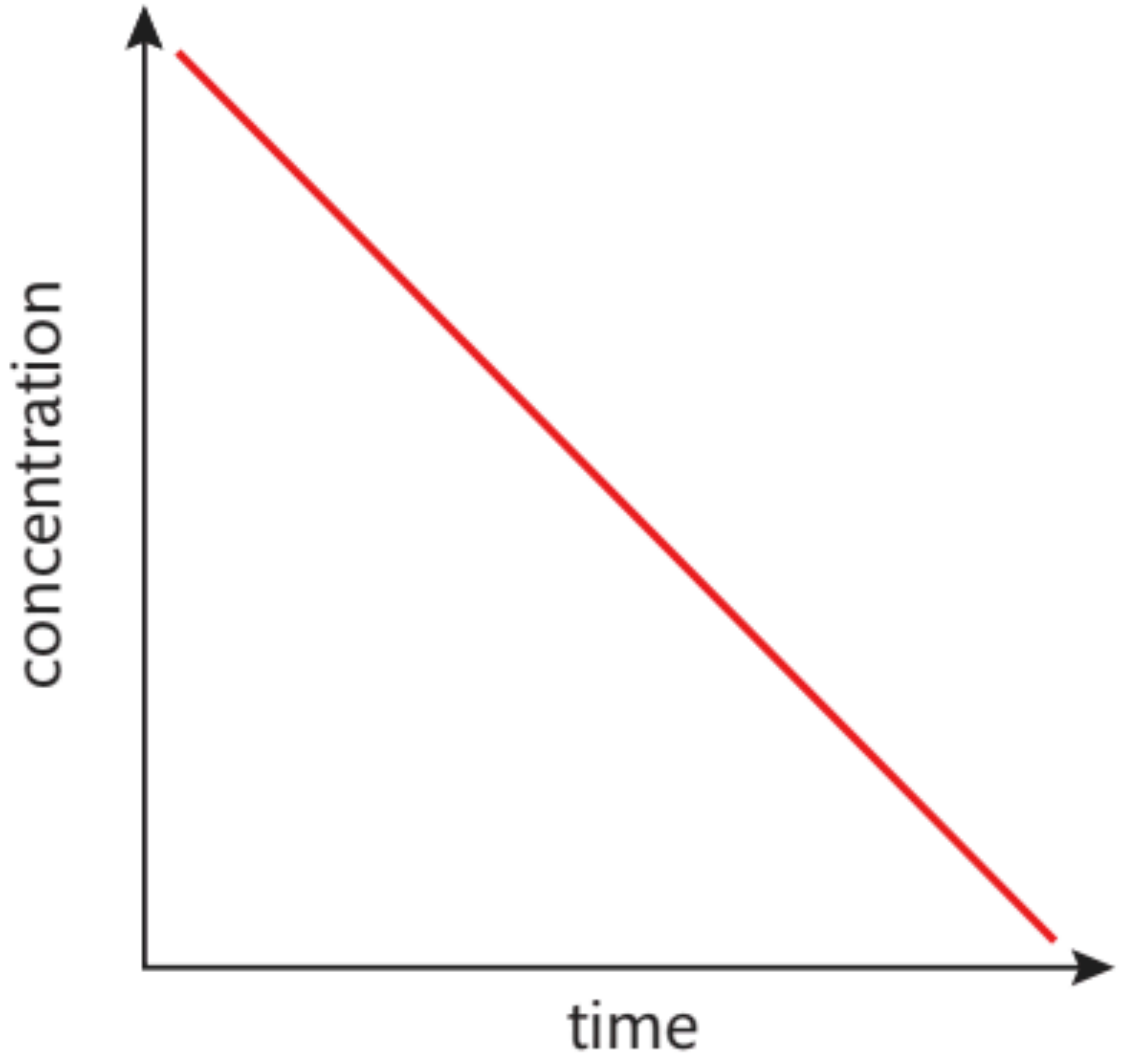
A reaction has the rate expression:

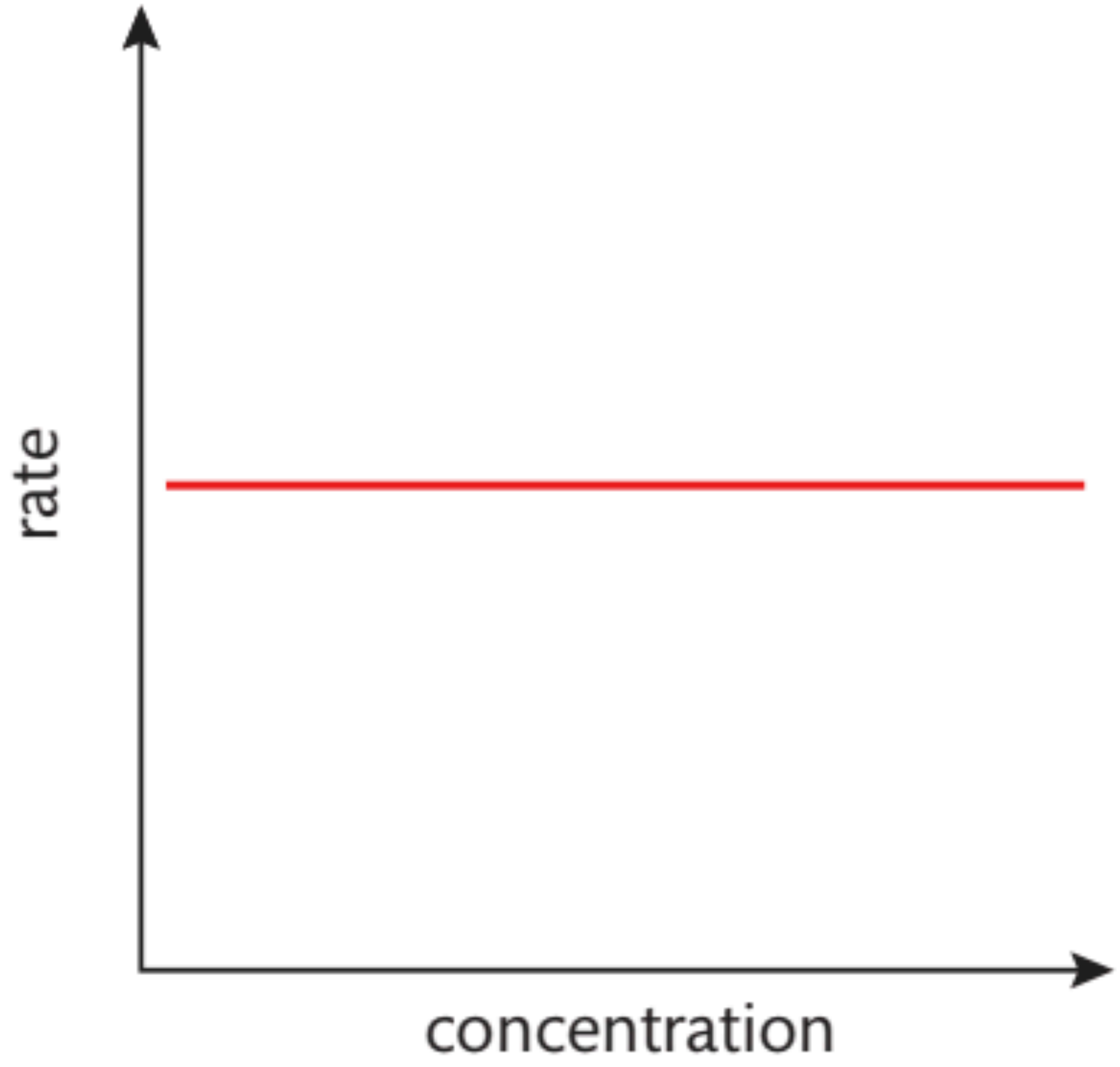
$$\text{rate} = k\,[A]^2[B]$$

Calculate the value of *k*, including units, for the reaction when the concentrations of both A and B are 2.50×10^{-2} mol dm^{-3} and the rate is 7.75×10^{-5} mol dm^{-3} s^{-1}

Zero Order Reactions

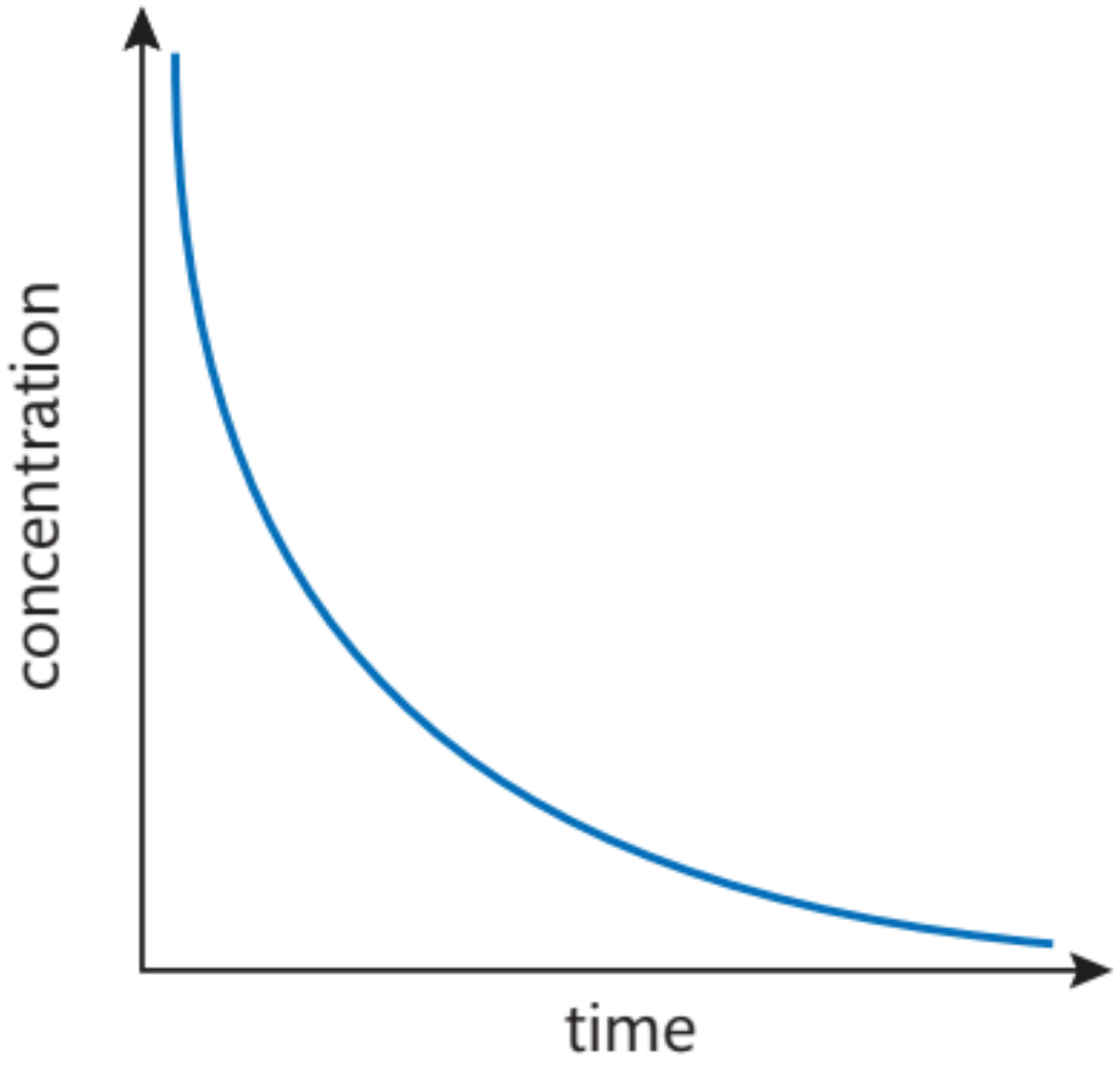
- rate = k $[A]^0$ or rate = k
- concentration does not affect the rate



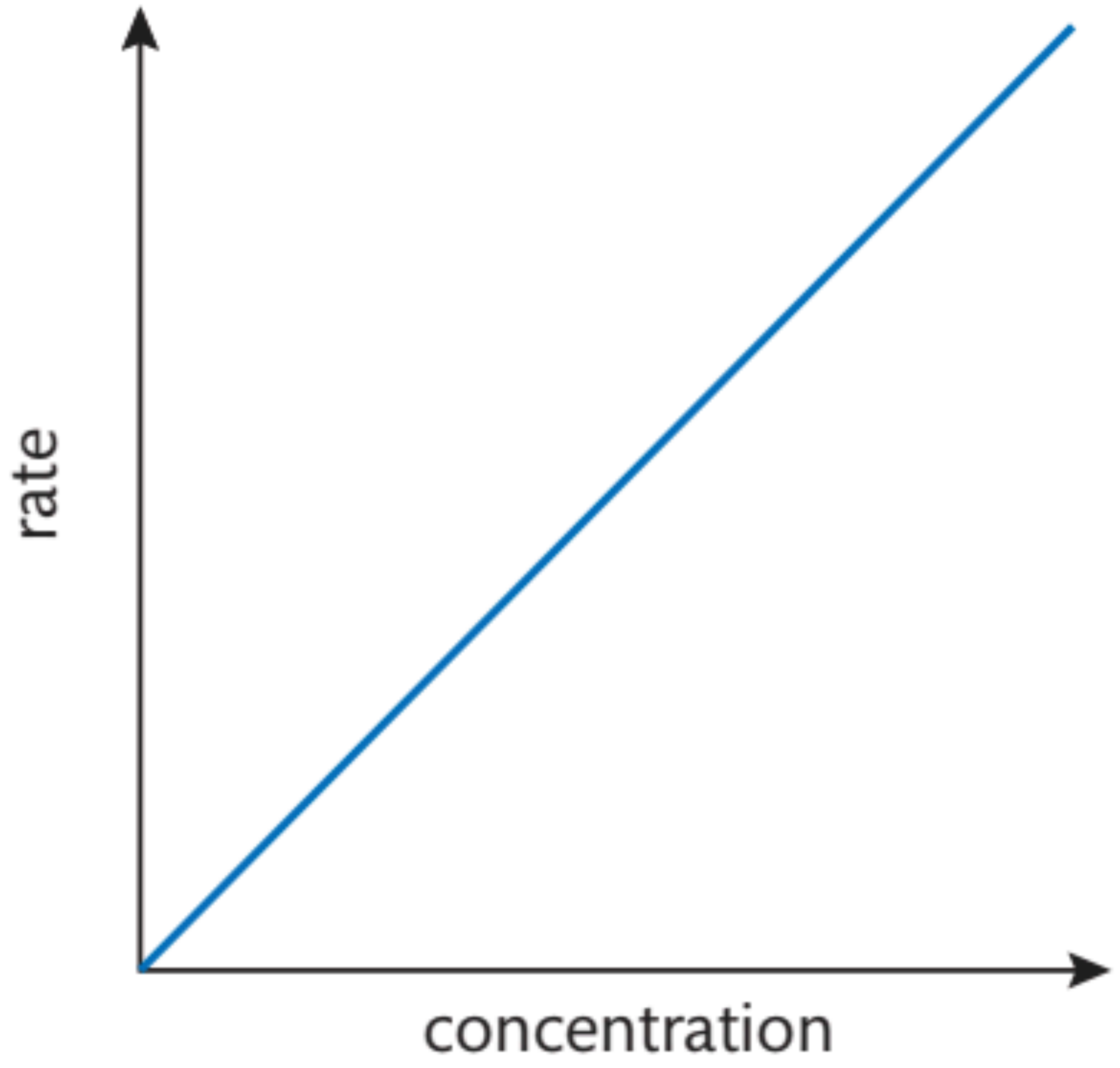


First Order Reactions

- rate = $k[A]$
- concentration is directly proportional to the rate

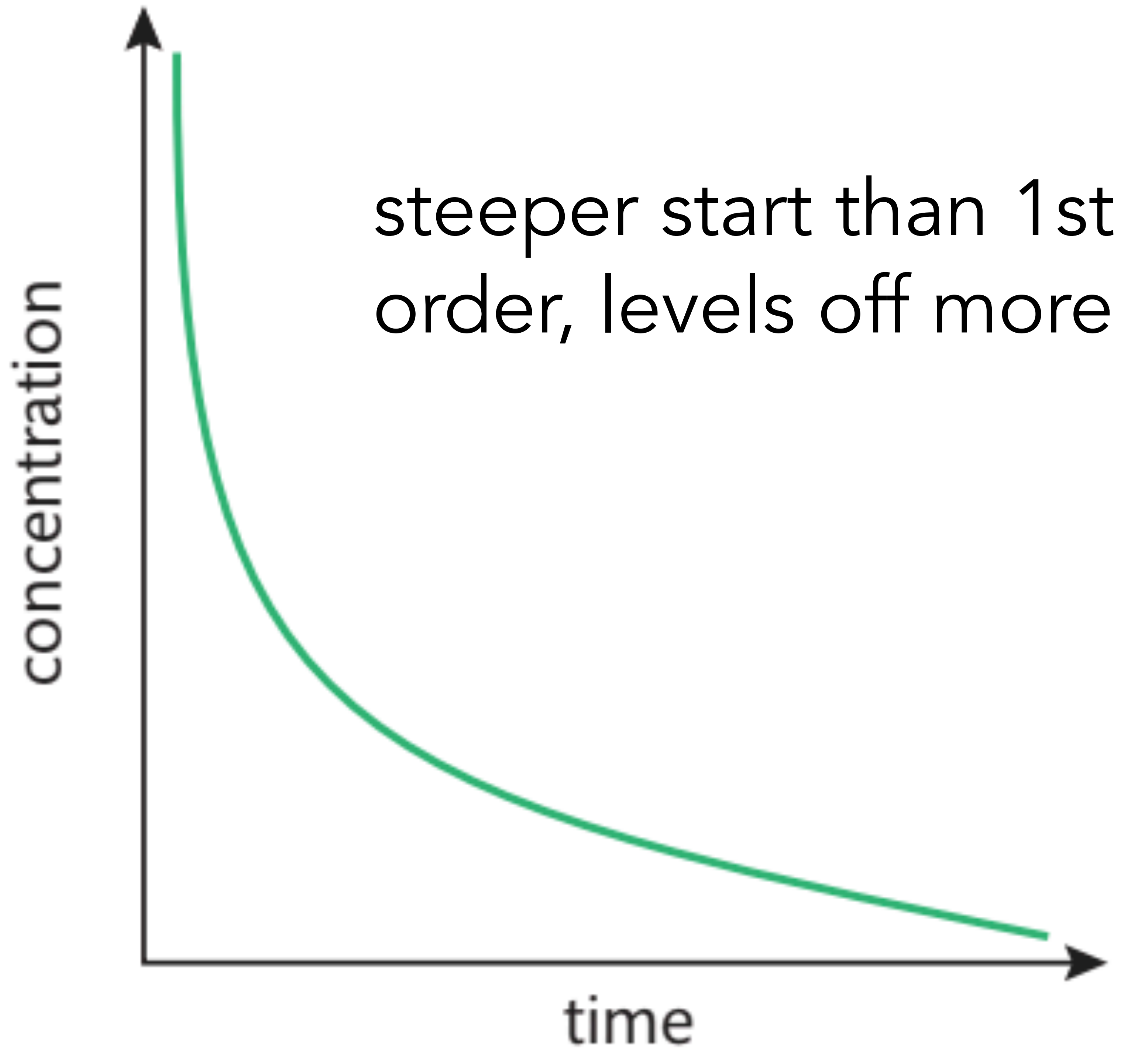


this graph shows a straight line with gradient, k



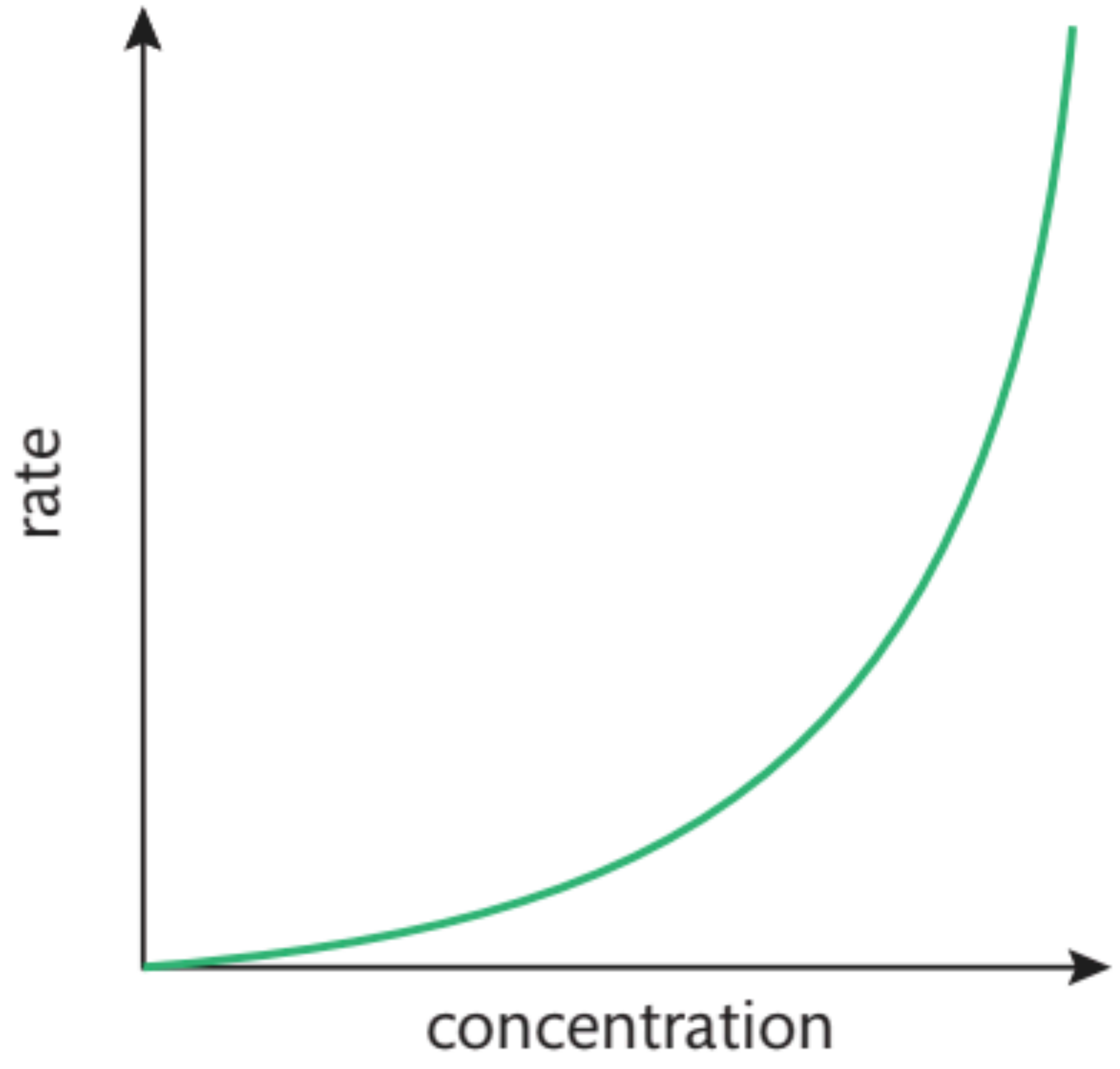
Second Order Reactions

- rate = $k[A]^2$
- rate is proportional to the square of concentration of A

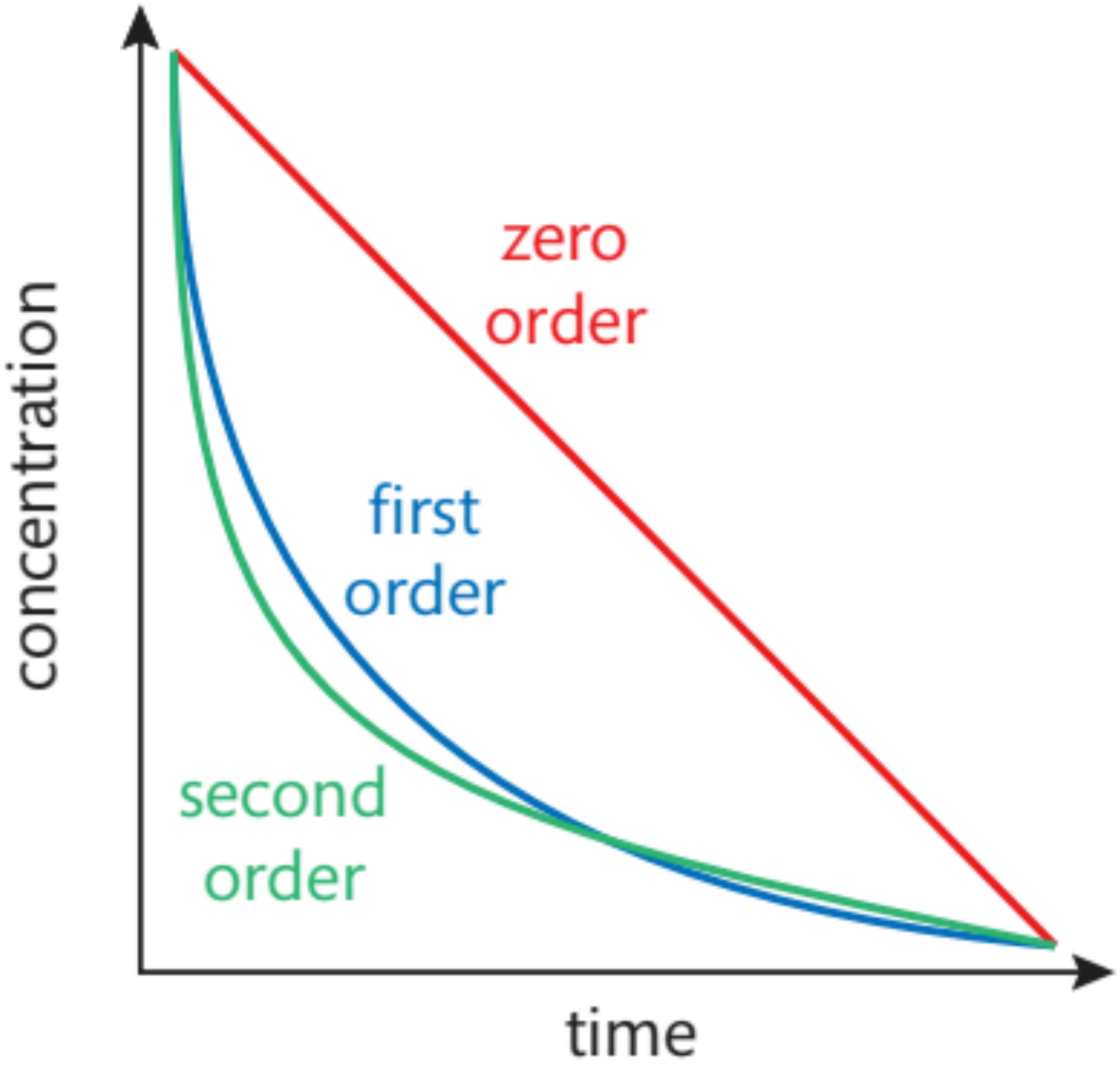


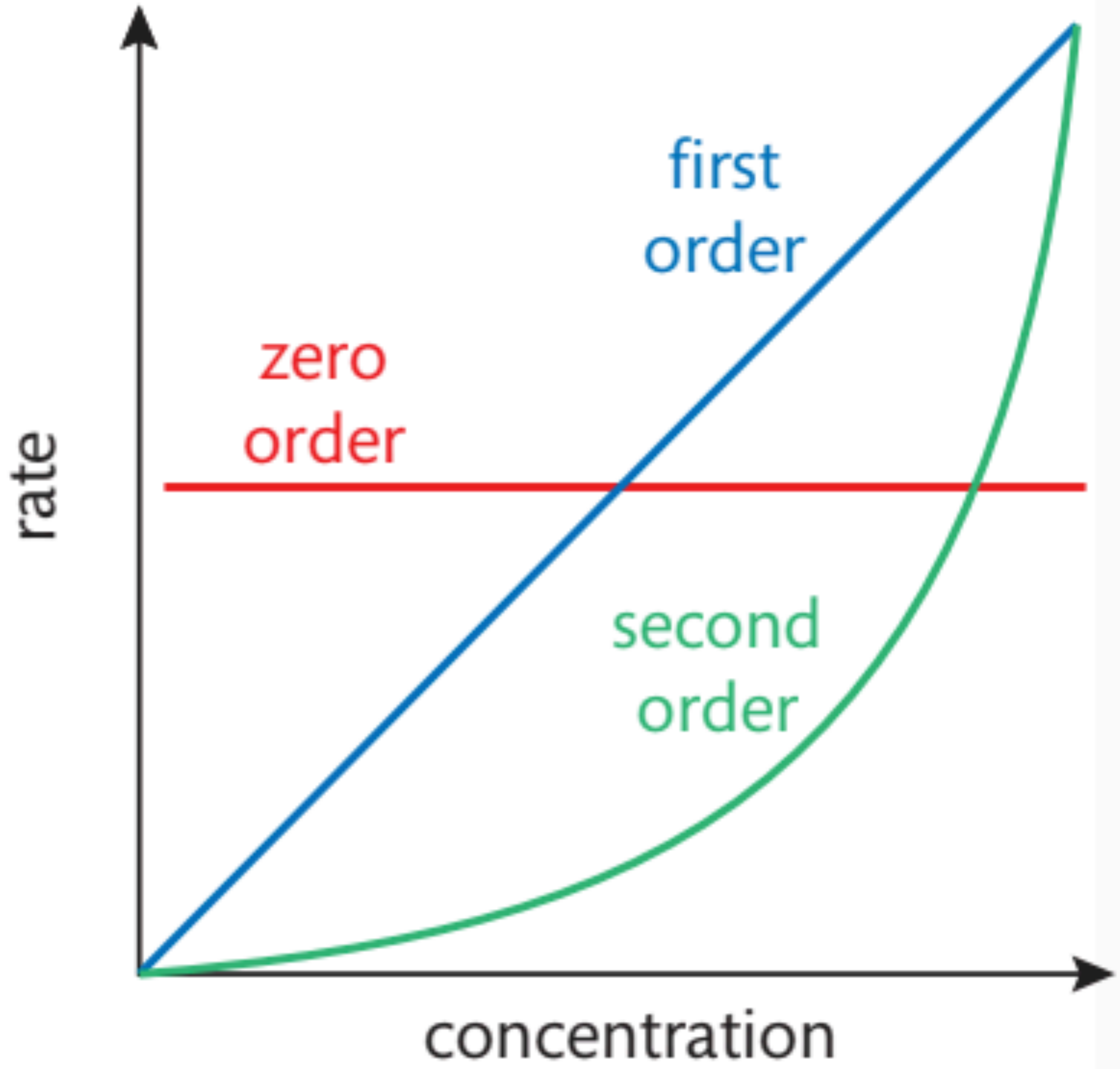
steeper start than 1st order, levels off more

is a parabola, gradient is proportional to concentration and is initially zero



Putting it all Together





Half-life

- First order reactions have a constant half-life
  - if the time is measured to decrease the amount of starting reactant by half, this interval is independent of the initial concentration
  - Only true for 1st order reactions
  - shorter the half life, faster the reaction rate

Determining the Order of a Reaction

Initial Rates Method

Involves carrying out different reactions by changing concentrations while holding others constant

Finding Order of Reaction

1. If changing the concentration of A has no effect on the rate, the rate must be zero order with respect to A
2. If changes in A produce proportional changes in rate, it must be first order with respect to A (doubling concentration doubles the rate)
3. If changes in A leads to an increase equal to the square of the change, the reaction is second order with respect to A (doubling concentration leads to 4-fold increase)

Example

- Use the data in the table below to work out the order of reaction with respect to A and B. Also, decipher the rate expression for the reaction.

Experiment #	Initial Concentrations (mol dm^{-3})		Initial Rate
	[A]	[B]	
1	0.1	0.1	2.0×10^{-4}
2	0.2	0.1	4.0×10^{-4}
3	0.3	0.1	6.0×10^{-4}
4	0.3	0.2	2.4×10^{-3}
5	0.3	0.3	5.4×10^{-3}

Reaction Mechanism

- Most reactions occur at a measurable rate that occur as a “series of steps”
- Usually, the products of a single step are used as a reactant in a subsequent step - exist only as “intermediates”

$$NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$$

This reaction happens in the following steps:

step 1: $NO_{2(g)} + NO_{2(g)} \rightarrow NO_{(g)} + NO_{3(g)}$

step 2: $NO_{3(g)} + CO_{(g)} \rightarrow NO_{2(g)} + CO_{2(g)}$

the overall reaction can be found by canceling the common reactants/products

Molecularity

used in reference to the number of species involved

unimolecular - uses a single reactant particle

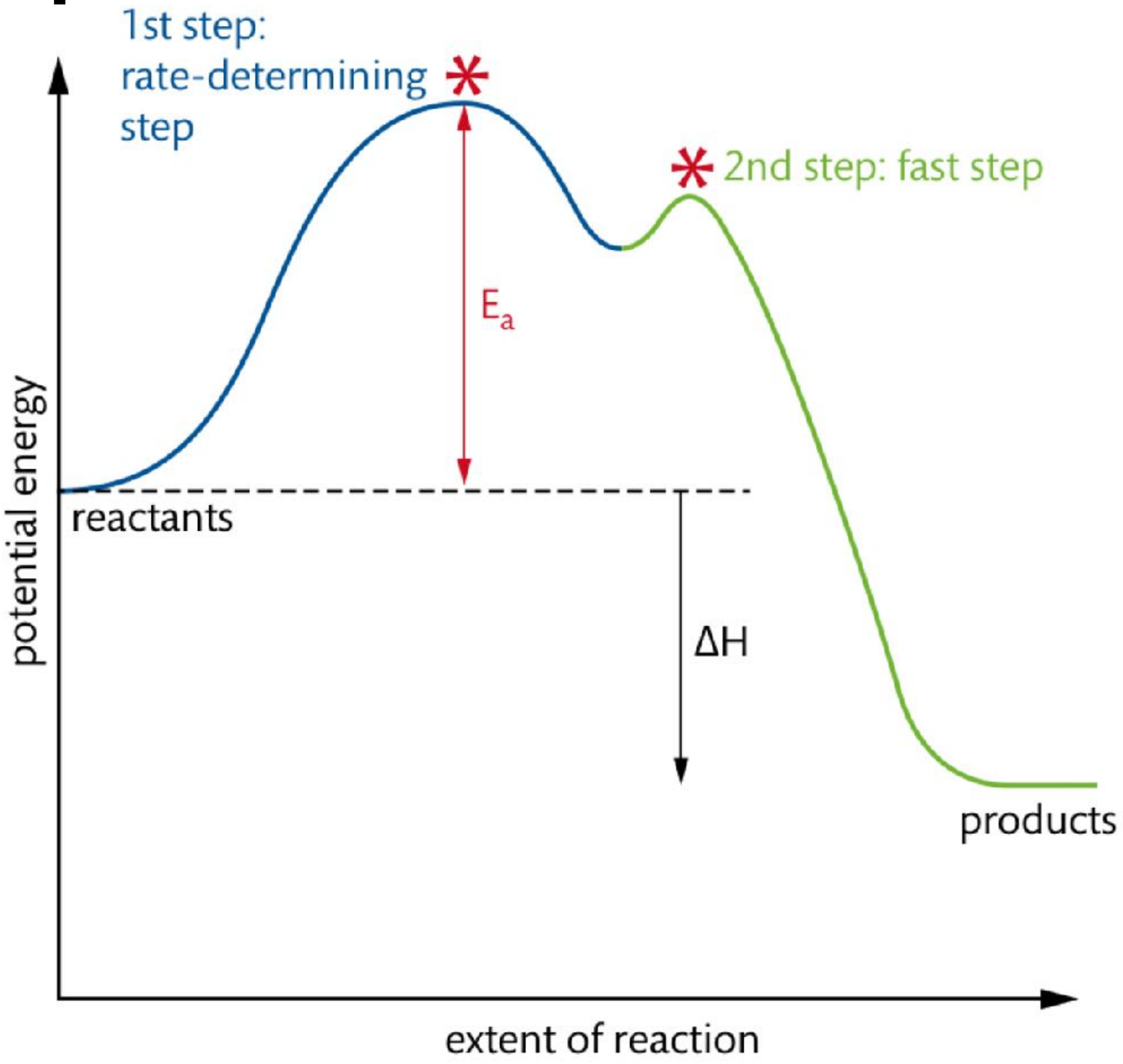
bimolecular - uses two reactant particles

In our reaction, both steps were **bimolecular**

Rate Determining Step

- On your way to school...do you get stuck anywhere?
- The slowest step in a chemical reaction will determine the overall rate - this is the *rate determining step (RDS)*

Rate Determining Step



Rate Expression and Mechanism

- Rate determining step - single molecular event
  - Collision theory - if a species has a concentration in a reaction, it must be a part of the rate law (expression)

Equation for rate determining step	Molecularity	Rate law
A → products	unimolecular	rate = k $[A]$
2A → products	bimolecular	rate = k $[A]^2$
A + B → products	bimolecular	rate = k $[A][B]$

Finding the Rate Law

Rate law is dependent on rate determining step

$$2NO_2Cl_{(g)} \rightarrow 2NO_{2(g)} + Cl_{2(g)}$$

Mechanism:

- step 1: $NO_2Cl_{(g)} \rightarrow NO_{2(g)} + Cl_{(g)}$ *slow - RDS*
- step 2: $NO_2Cl_{(g)} + Cl_{(g)} \rightarrow NO_{2(g)} + Cl_{2(g)}$ ***fast***

- Which step determines the rate of reaction?
- What will the rate expression for that step look like?
  - rate = k $[NO_2Cl]$
  - first order reaction

What happens when the rate determining step doesn't happen 1st?

$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$$

- mechanism:
  - step 1: $NO_{(g)} + NO_{(g)} \rightarrow N_2O_{2(g)}$ *fast*
  - step 2: $N_2O_{2(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$ *slow - RDS*
- So…rate depends on step 2
  - rate = $k\,[N_2O_2][O_2]$

Continued

- rate = k $[N_2O_2][O_2]$
- BUT! - N_2O_2 is a product of the first equation!
- Substitute the rate expression from the first reaction:
  - rate = k $[NO]^2[O_2]$

∴ This is a third order reaction

Example

If the mechanism of a reaction is:

$AB_2 + AB_2 \rightarrow A_2B_4$ slow

$A_2B_4 \rightarrow A_2 + 2B_2$ fast

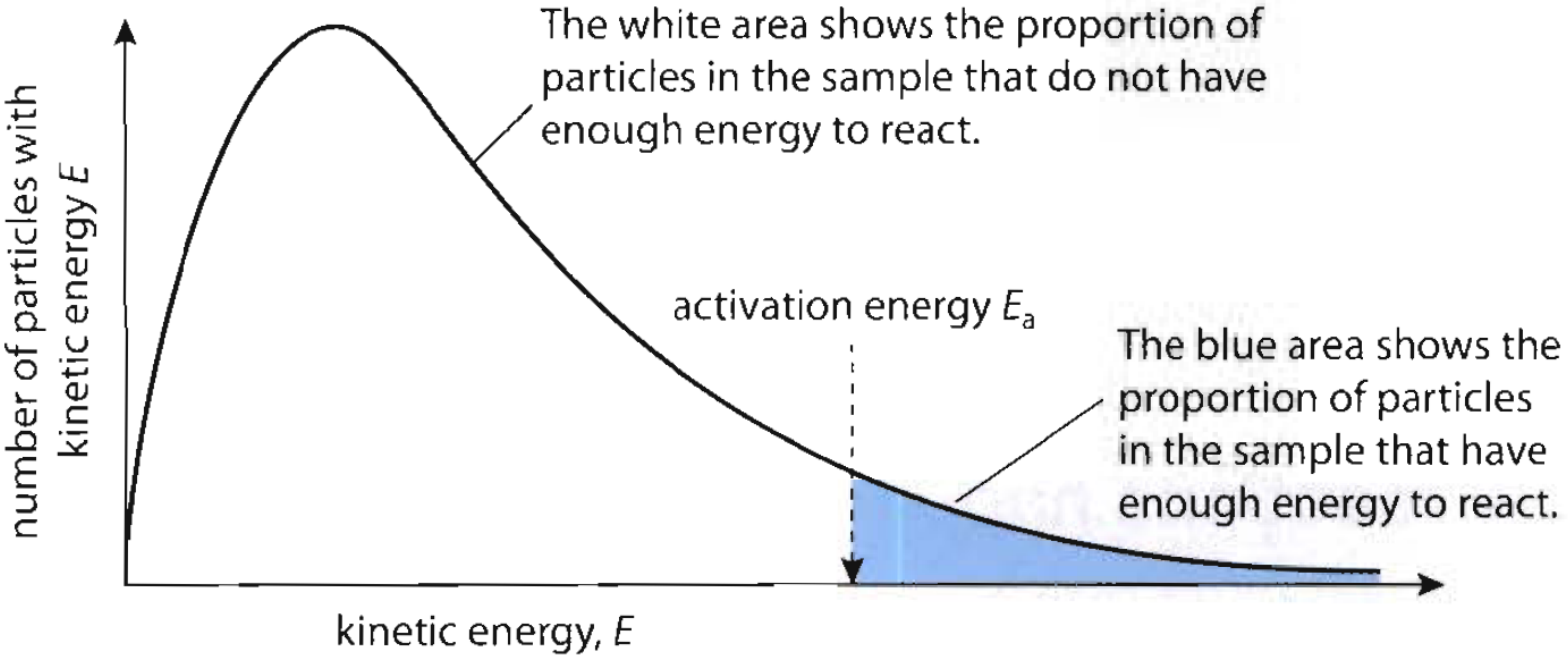
1. *What is the overall equation for this reaction?*
2. *What is the rate expression for this reaction?*
3. *What units will the rate constant have in this reaction?*

16.2 Activation Energy

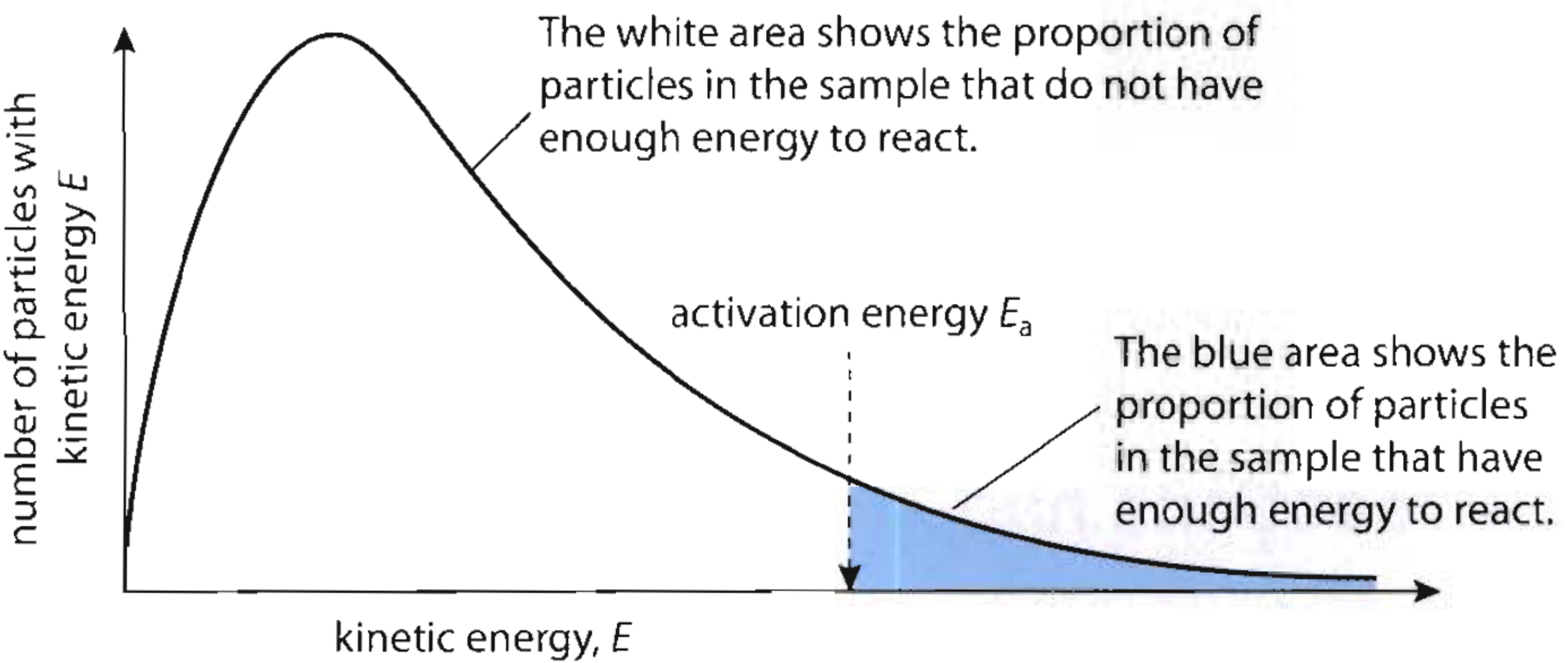
- Rate of reaction depends on:
    - k: the rate constant
    - the concentration of the reactants
- Rate = k [A][B]
- Where does temperature fit in?

Activation Energy

- If activation energy is high, a small temperature change will cause a large increase in the number of particles with sufficient energy to react
- If activation energy is small, a small temperature change will not do much to change the overall rate



- Therefore, the temperature dependance of k depends on the value of the activation energy
- Equation Time!!



The white area shows the proportion of particles in the sample that do not have enough energy to react.

The blue area shows the proportion of particles in the sample that have enough energy to react.

Arrhenius Equation

- The fraction of molecules with enough energy to react (enough Activation energy, E_a) at temperature T is proportional to $e^{-Ea/RT}$
- R = gas constant = 8.31 $J\ K^{-1}\ mol^{-1}$
- T = absolute temperature in Kelvin

$\therefore\ k \propto e^{-Ea/RT}$ or $k = A\ e^{-Ea/RT}$

Arrhenius Equation

$k = A\ e^{-Ea/RT}$

A - the Arrhenius constant

Let’s try to make sense of this…take the natural log of both sides

$\ln k = -E_a/RT + \ln A$

This equation will give a straight line with gradient $-E_a/R$ and y-intercept, ln A (y-axis = ln k , x-axis = 1/T)

Both equations are in IB Data Booklet…yay!

Solving simultaneous equations

Activation energy can also be calculated from values of the rate constant, *k*, at only two temperatures. The formula is derived as follows:

At temperature T_1 where the rate constant is k_1:

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A$$

At temperature T_2 where the rate constant is k_2:

$$\ln k_2 = -\frac{E_a}{RT_2} + \ln A$$

By subtracting the second equation from the first, we can derive the following equation:

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

This equation is also given in section 1 of the IB data booklet.