Welcome to Chemistry 154!

Chemistry for Engineering

Reminders

- **Achieve Assignment 10**
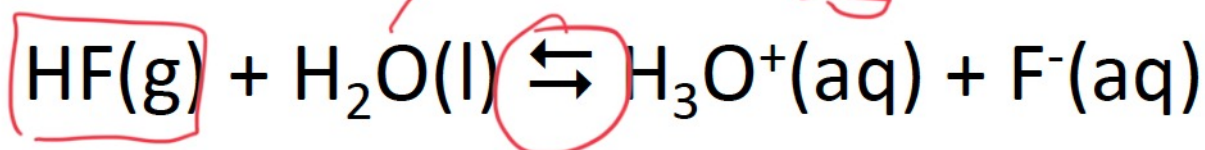- Due Dec. 7th at 11:59pm

- **Unit 10 Worksheet**
- Due Dec. 8th at 11:59pm

Instructor Office Hours
Monday and Friday 7-8pm via Zoom (All Lectures Site)

Clicker Question

In the following equilibrium in a closed system:

$$HF(g) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

How will the equilibrium shift if the volume of the system is reduced?

$$K = \frac{[H_3O^+(aq)][F^-(aq)]}{P_{HF(g)}}$$

	Equilibrium	K
A.	Shifts to the right	No change
B.	Shifts to the right	Changes
C.	No change	No change
D.	Shifts to the left	Changes
E.	Shifts to the left	No change

HF pressure decreases after the equilibrium shifts to the right

This increase is from the volume reduction

Clicker Question

Because $[F^-]\downarrow$ due to precipitation, equilibrium shifts to the Right. As a

In the following equilibrium in a closed system: Result:

$$HF(g) + H_2O(l) \leftrightharpoons H_3O^+(aq) + F^-(aq)$$

$$K = \frac{[H_3O^+]\uparrow[F^-]\uparrow}{P_{HF}\downarrow}$$
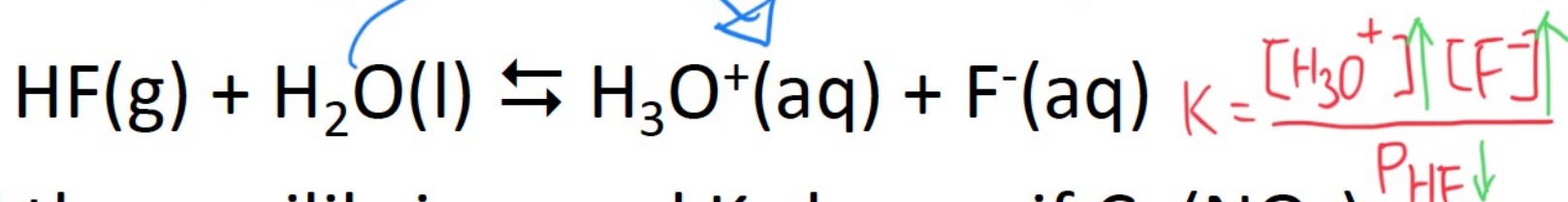
How will the equilibrium and K change if $\underline{Ca(NO_3)_2}$ solid is added, causing $CaF_{2(s)}$ to precipitate?

$$Ca^{2+}_{(aq)} \quad 2NO^-_{3(aq)}$$

Re-establish equilibrium.

	Equilibrium	K
A.	Shifts to the right	No change
B.	Shifts to the right	Changes
C.	No change	No change
D.	Shifts to the left	Changes
E.	Shifts to the left	No change

Solubility equilibria

Solubility: The ability of a compound to dissolve in solution.

Consider:

$Ca(OH)_2(s) \leftrightarrows Ca^{2+}(aq) + 2\ OH^-(aq)$ K = 7.9 x 10^{-6}

K for an ionic solid dissociating into its constituent ions is called K_{sp}
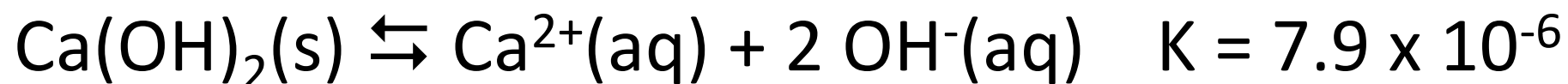
When $[Ca^{2+}]x[OH^-]^2 > 7.9\ x\ 10^{-6}$ the equilibrium will shift to the left and $Ca(OH)_2$ will precipitate.

Exercise

Calculate the solubility of $Ca(OH)_2$.

$$Ca(OH)_2(s) \leftrightarrows Ca^{2+}(aq) + 2\,OH^-(aq) \quad K = 7.9 \times 10^{-6}$$
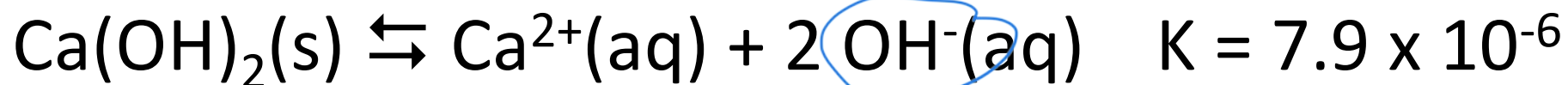
I	—	0	0
C	—	$+x$	$+2x$
E	—	x	$2x$

$$x \cdot (2x)^2 = K_{sp} = 7.9 \times 10^{-6}$$

$$x \cdot 4x^2 = 7.9 \times 10^{-6}$$

$$4x^3 = 7.9 \times 10^{-6}$$

$$x^3 = 0.000001975$$

$$x = (0.000001975)^{\frac{1}{3}}$$

$$= 1.25 \times 10^{-2}\ M$$

solubility of $\uparrow$ $Ca(OH)_2$
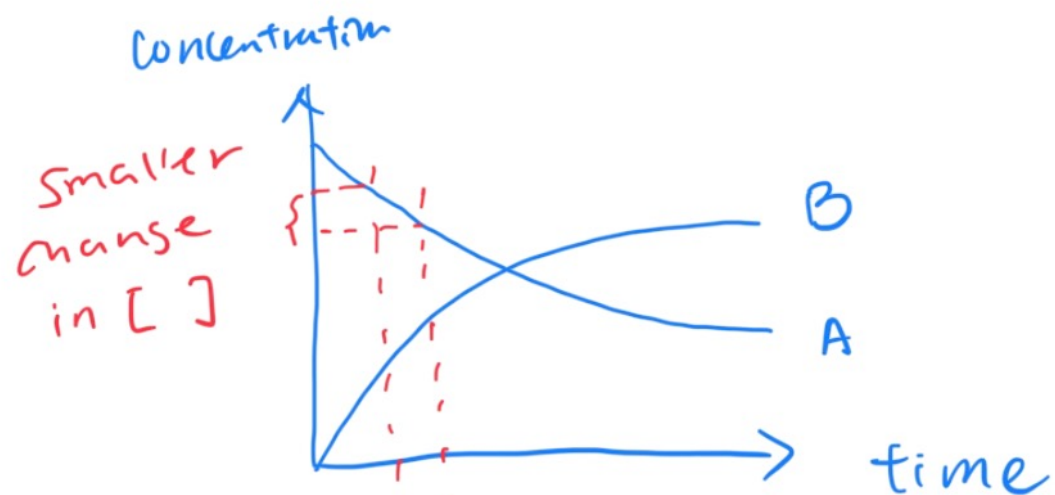
Unit 10
Chemical Kinetics

Reaction rates

$$\text{Rate} = \frac{\text{change in concentration}}{\text{elapsed time}}$$
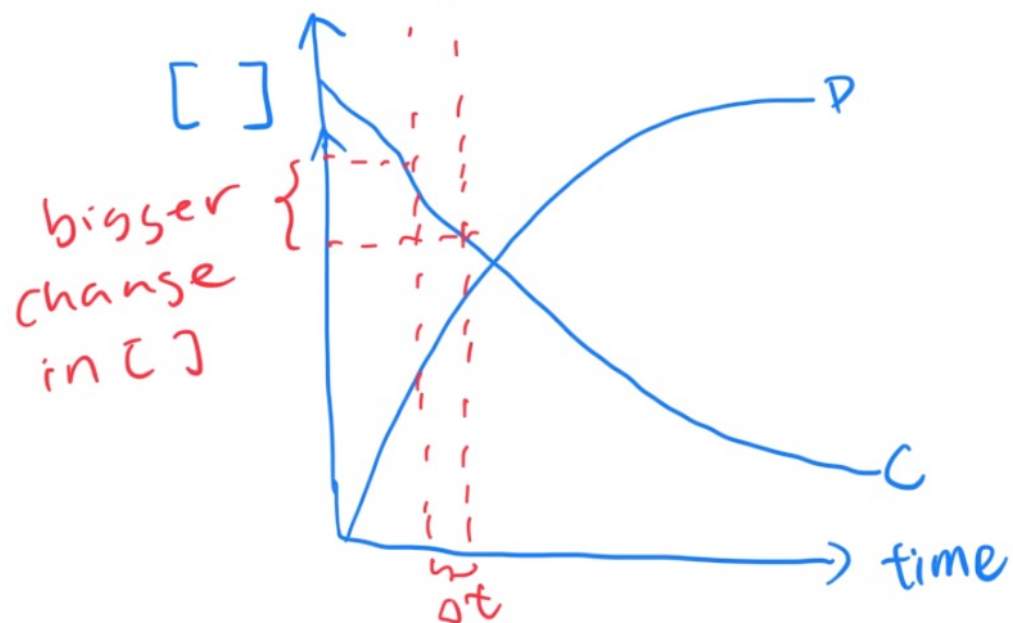
Concentration changes depend on stoichiometry

$$\text{Rate} = \frac{\Delta[\text{product}]}{v_{prod.}\Delta t} = -\frac{\Delta[\text{reactant}]}{v_{react.}\Delta t}$$

A positive rate corresponds with formation of products.

concentration

smaller
change
in [ ]

B

A

time

A → B   ①

slower

[ ]

bigger
change
in [ ]

P

C

time

C → D   ②

faster

δt

Rates

Consider the following reaction:

$$aA + bB \rightarrow cC + dD$$

The rate of the reaction can be determined from the change of any of the chemical species:

$$\text{Rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

$$\text{Rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

$$2 N_2O_5 (g) \rightarrow 4 NO_2 (g) + O_2 (g)$$

Rate = positive value

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{1}{1}\frac{d[O_2]}{dt}$$
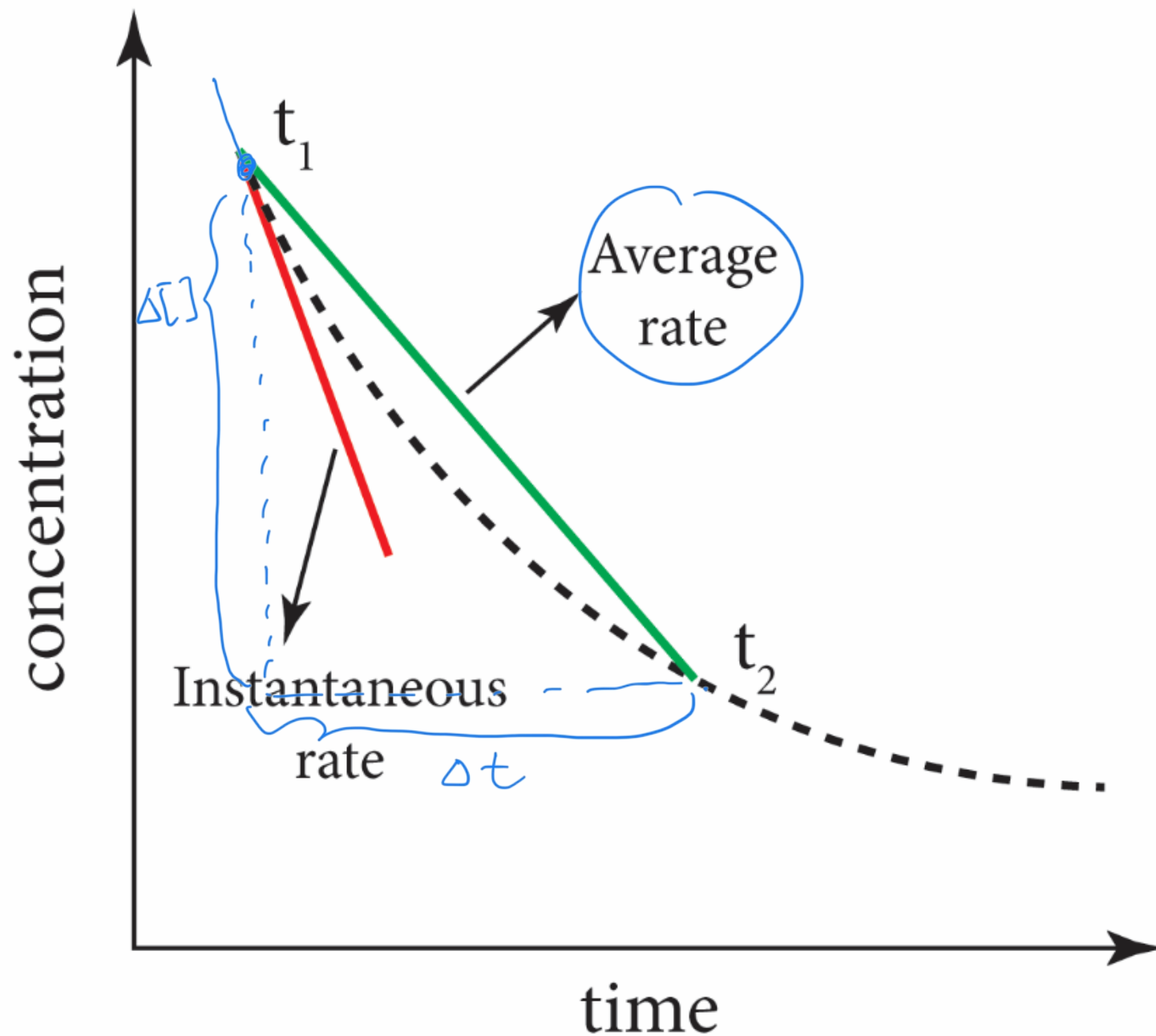
Rate of formation of O_2 is $\frac{1}{4}$ the Rate of formation of NO_2. and $\frac{1}{2}$ the Rate of consumption of N_2O_5.

∴ Rate of formation of NO_2 is quite fast

Average rates and instantaneous rates

Rate law and concentration

The reaction rate depends on the concentration of reactants and a rate constant.

$$A + B \rightarrow C$$

$$Rate = k[A]^n[B]^m$$

Differential rate law

– n and m are referred to as the order of the reaction (need not be integers).
– The rate constant k depends on the reaction, and differs for the forward and reverse directions.
– **k, n, and m are experimentally determined.**

The rate expression for the reaction between nitrogen dioxide and fluorine is experimentally determined to be rate = k [NO$_2$] [F$_2$]. If concentrations are expressed in moles per liter, what are the units of the rate constant (k)?

M

a) s^{-1}

b) mol $L^{-1}s^{-1}$

c) mol L^{-1} s

d) L mol^{-1}s^{-1}

e) None of the above

Rate = (K) (M^2) = M/s

unit ?

$\frac{1}{MS}$

$\left(\frac{1}{M\cdot S}\right)\cdot(M^2) = M/s$

→ this is the same as $\frac{L}{mol\cdot S}$

first Order Reaction:

$$\text{Rate} = \boxed{k}[A]$$

$\uparrow$

M/s

k has unit: $\dfrac{1}{S}$

Second order Reaction: $\text{Rate} = k[A][B]$

$$M s^{-1} = k (M^2)$$

unit of k: $M^{-1} s^{-1}$

Zeroth order reaction: $\text{Rate} = k$

unit of k: $M s^{-1}$

Rate law and concentration

Rate Laws are empirical

Must be experimentally determined

- **k, n, and m are experimentally determined.**

- One method to determine the reaction order and rate constant is **Method of Initial Rates**
  - ❑ **Measure reaction rate at the beginning**

Method of Initial rates

Measure the initial rate of a reaction while adjusting the concentration of the various reactants.
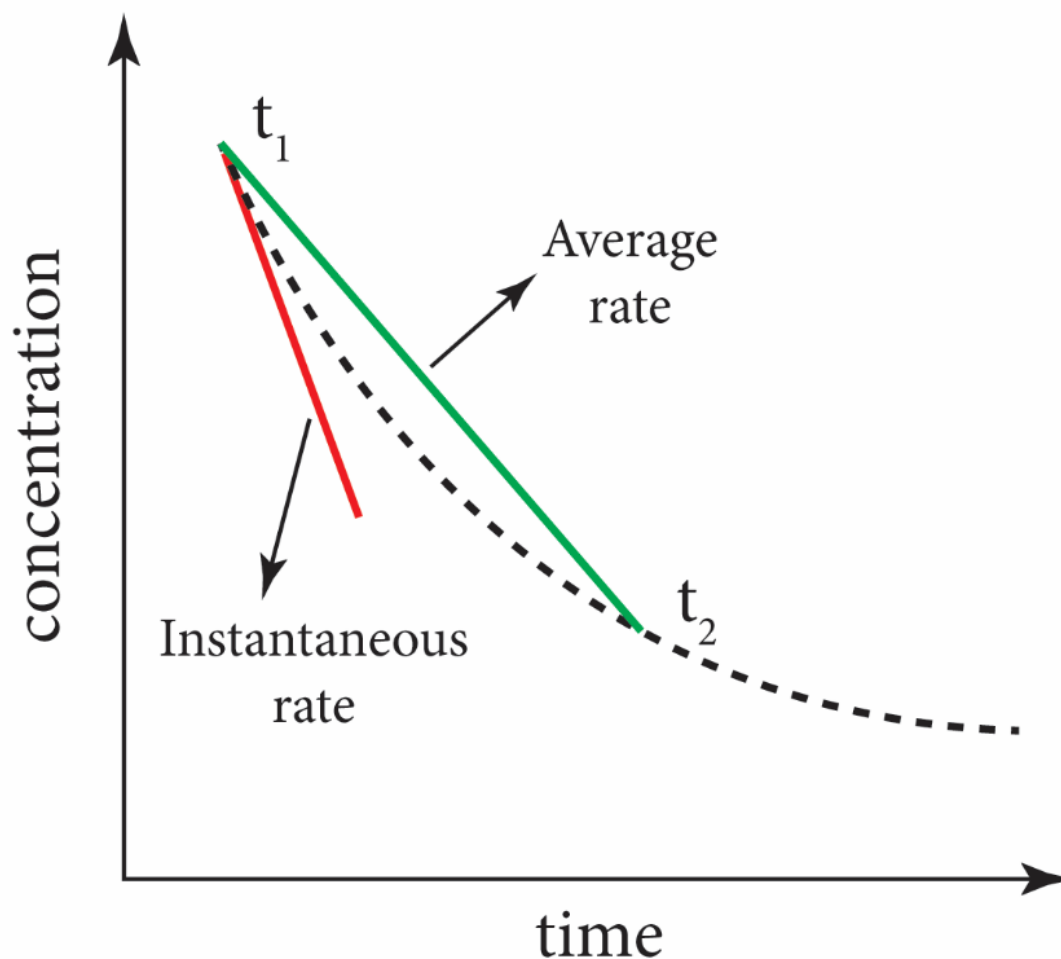
Exercise

Determine the rate law and rate constant for this reaction at the temperature of these experiments. $Rate = k[N_2O_5]^n$

$$2 N_2O_5(g) \rightarrow 4 NO_2(g) + O_2(g)$$

Run	Initial P N_2O_5 (atm)	rate (atm s^{-1})
1	300	8.0 x 10^{-6}
2	150	4.0 x 10^{-6}

1. $8.0 \times 10^{-6} \text{ atm/s} = k (300 \text{ atm})$

2. $4.0 \times 10^{-6} \text{ atm/s} = k (150 \text{ atm})$

Clicker Question

For the reaction $2\ HgCl_2 + C_2O_4^{2-} \rightarrow$ products, data are:

	trial 1	*trial 2*	*trial 3*
[HgCl$_2$] (M)	0.0836	0.0836	0.0418
[C$_2$O$_4^{2-}$] (M)	0.202	0.404	0.404
rate (M/hr)	0.26	1.04	0.53

The rate law is given by Rate = k[HgCl$_2$]^x[C$_2$O$_4^{2-}$]^y. Determine the values of x and y.

$x = 1$

$y = 2$

a) x = 2, y = 1
b) x = 2, y = 2
c) x = 1, y = 2
d) x = 1, y = 1
e) x = 0, y = 2

Integrated rate laws

Integrated rate laws are used to determine the concentration of products at any point during the reaction.

They are obtained by integrating the differential rate laws (for a reactant A, for example).

First order Reaction

$$Rate = -\frac{d[A]}{dt} = k[A]$$

$$\int_{[A]_0}^{[A]} \frac{1}{[A]} \, d[A] = \int_0^t -k \, dt$$
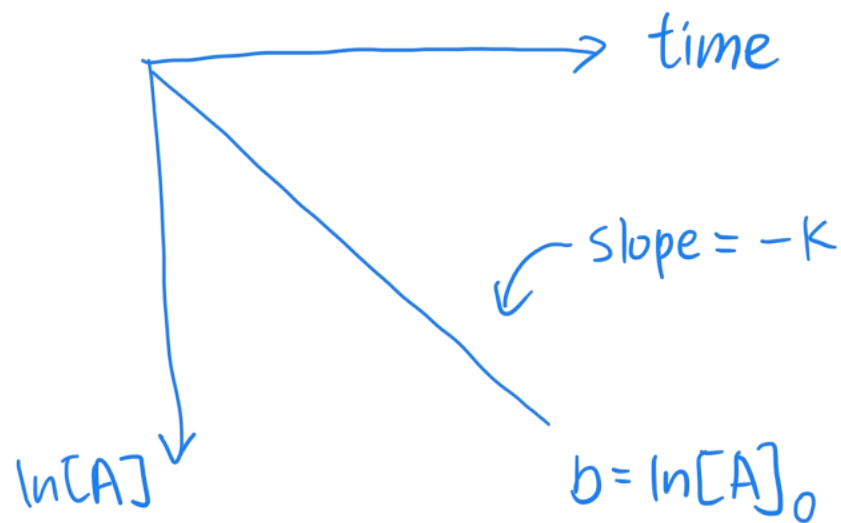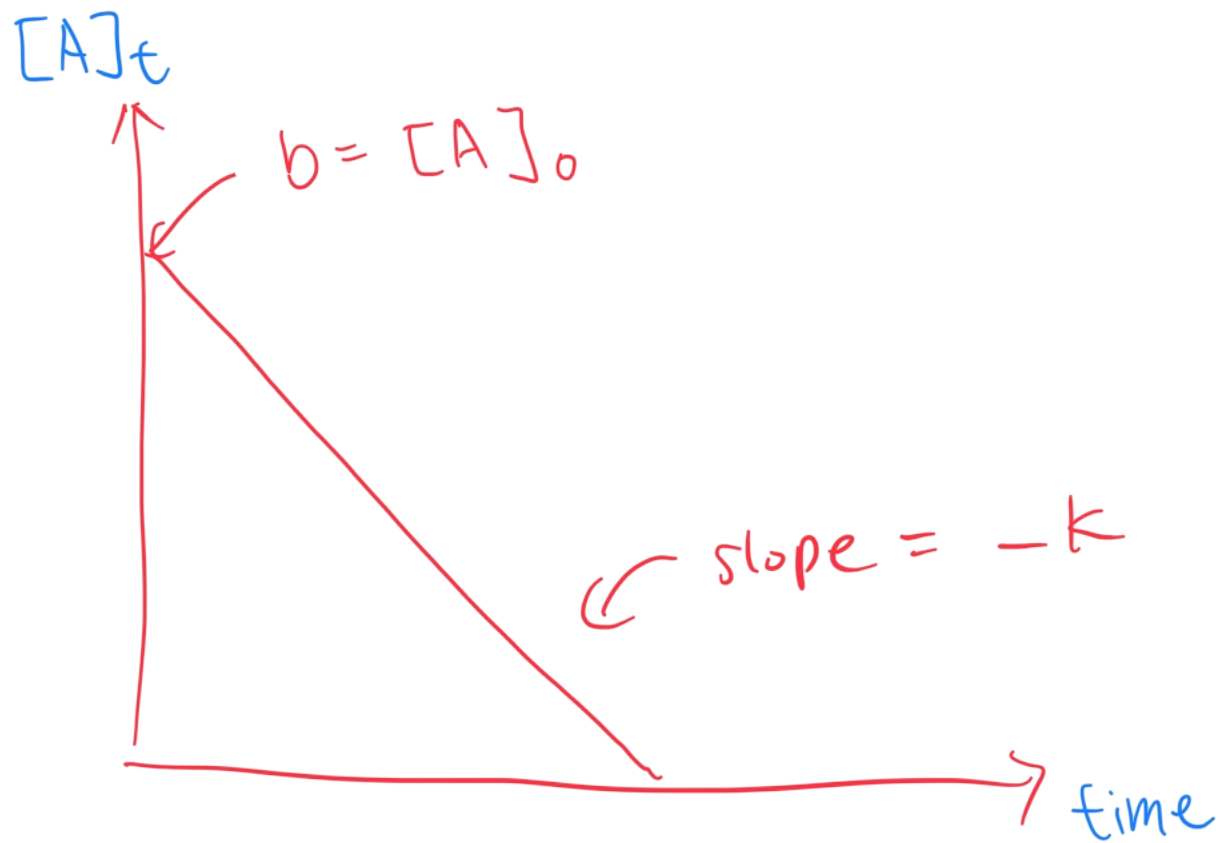
$$\ln[A]_t = -kt + \ln[A]_0$$

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

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

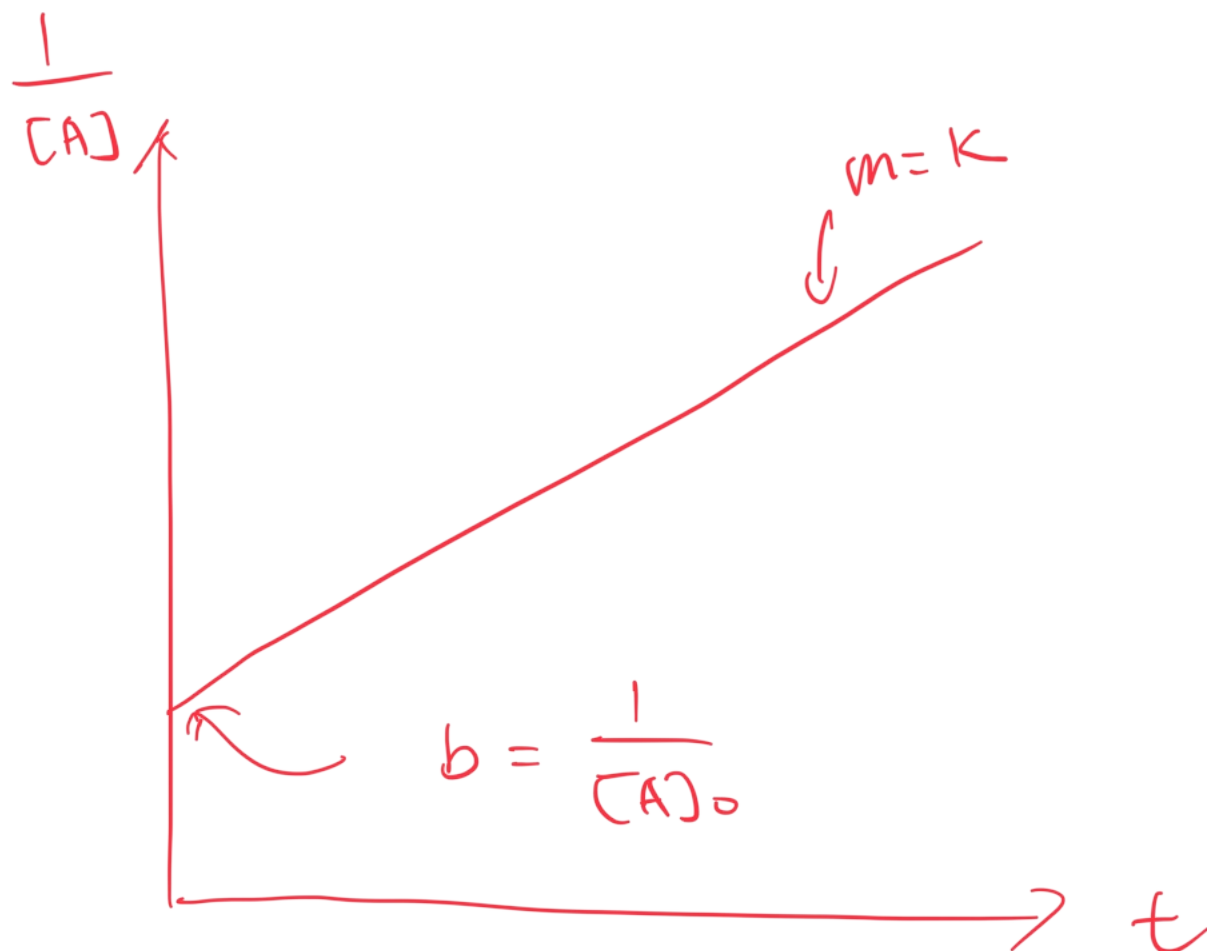$$\frac{[A]_t}{[A]_0} = e^{-kt}$$

$$[A]_t = [A]_0 e^{-kt}$$

time

slope = $-k$

$\ln[A]$

$b = \ln[A]_0$

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

$[A]_t$

$b = [A]_0$

slope $= -k$

time

0th order

$$\frac{1}{[A]_t} = Kt + \frac{1}{[A]_0}$$

Second order

First order integrated rate law

First order reaction: $\boxed{\text{Rate} = -\dfrac{d[A]}{dt} = k[A]}$

Integrating this expression gives

$$\int_{[A]_0}^{[A]_t} \frac{1}{[A]} d[A] = -k \int_0^t dt$$

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

For a first order reaction, $[A]_t = [A]_0 e^{-kt}$ so the concentration decays exponentially with time from the initial value $[A]_0$ to zero.

Zeroth order integrated rate law

Zeroth order reaction: $\boxed{\text{Rate} = -\dfrac{d[A]}{dt} = k[A]^0 = k}$

Integrating this expression gives

$$\int_{[A]_0}^{[A]_t} d[A] = -k \int_0^t dt$$

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

For a zeroth order reaction, $[A]_t$ decays linearly with time from the initial value $[A]_0$ to zero.

Second order integrated rate law

Second order reaction: $\boxed{\text{Rate} = -\dfrac{d[A]}{dt} = k[A]^2}$

Integrating this expression gives

$$\int_{[A]_0}^{[A]_t} \frac{1}{[A]^2}\, d[A] = -k \int_0^t dt$$

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$$

For a second order reaction, $[A]_t = \dfrac{[A]_0}{1+[A]_0 kt}$ so the concentration decays inversely with time from the initial value $[A]_0$ to zero.

Graphical determination of reaction order

$$y = mx + b$$

Zero order rate law:

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

1st order:

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

2nd order:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

Half-life

The half-life of a reactant is the time it takes for its concentration to fall to one-half its original value.

For a 1st order reaction:

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

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$$

1st ORDER

when $[A]_t = \frac{1}{2}[A]_0$

$t_{1/2}$

$$\ln\left(\frac{\frac{1}{2}[A]_0}{[A]_0}\right) = -kt_{1/2}$$

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

Oth ORDER:

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

$$\tfrac{1}{2}[A]_0 - [A]_0 = -kt_{1/2}$$

$$t_{1/2} = \frac{[A]_0}{2k} \qquad \checkmark$$

2nd ORDER.

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$\frac{1}{\tfrac{1}{2}[A]_0} = kt_{1/2} + \frac{1}{[A]_0}$$

$$t_{1/2} = \frac{1}{k[A]_0} \qquad *$$
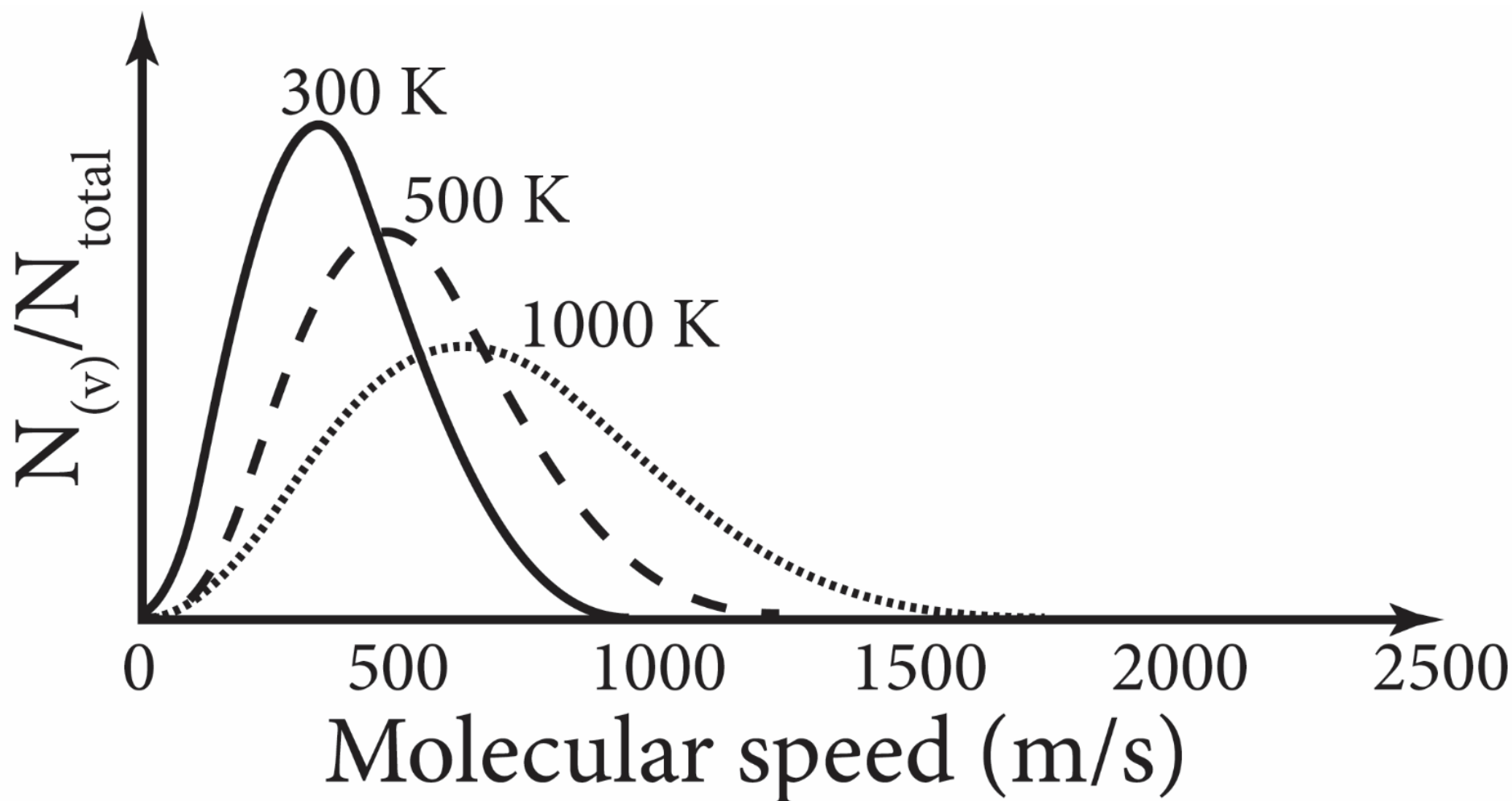
Chemical reactions: a molecular view

Atoms and molecules interact with one another through collisions (remember Kinetic Molecular Theory).

In order for a reaction to occur, collisions between molecules must have :
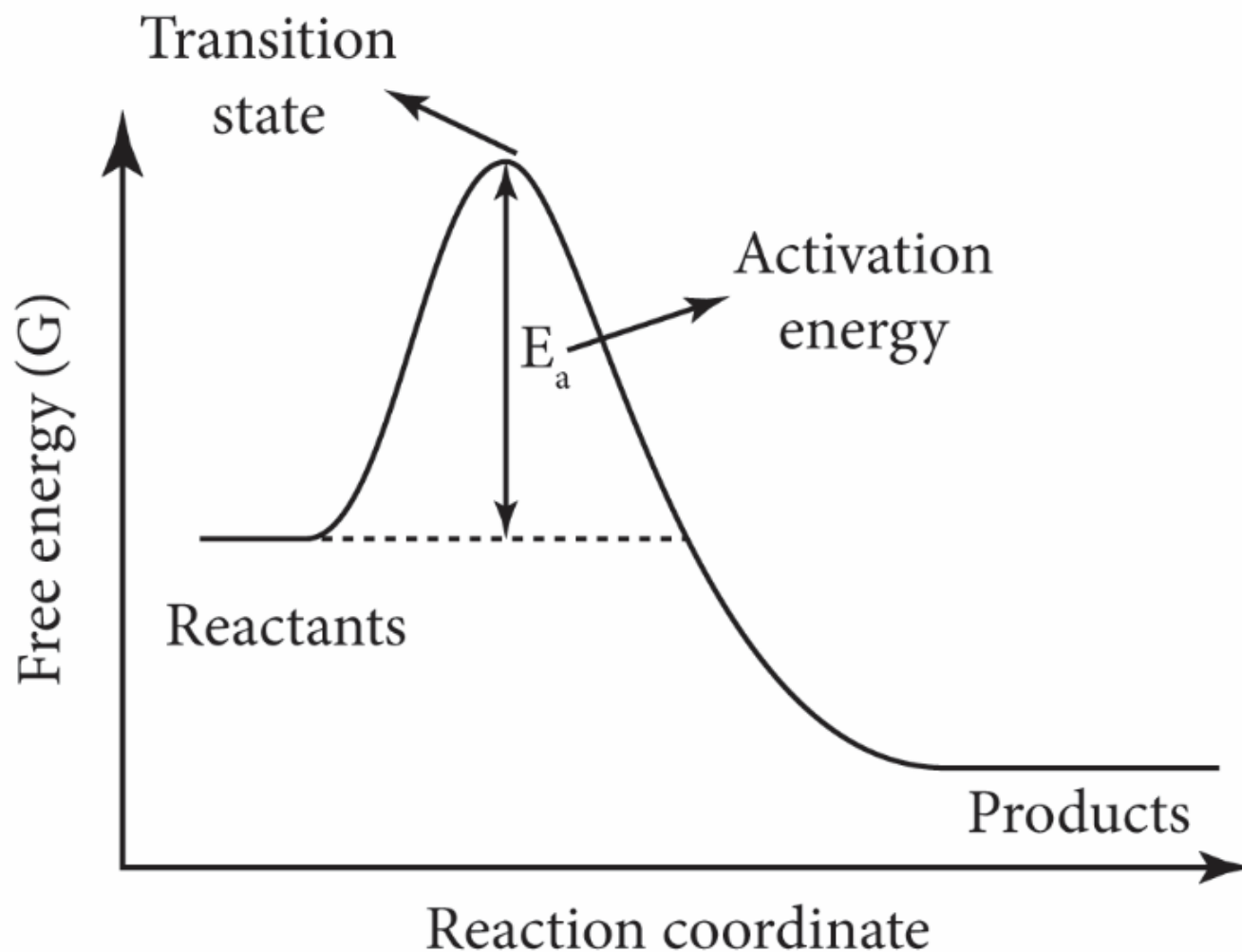– enough energy to break bonds
– appropriate orientation

Temperature and Rates

As temperature increases, more collisions between reactants have the energy necessary for reaction to occur.

Activation Energy (E$_a$)

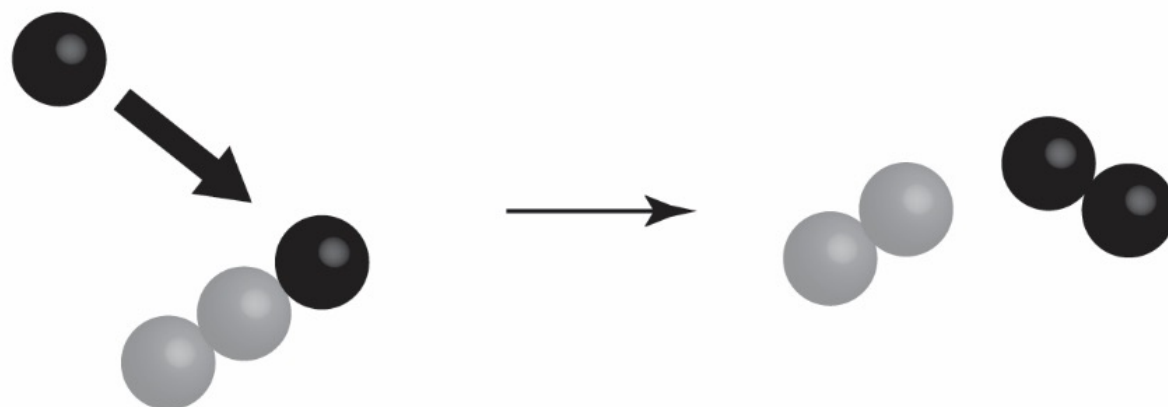Minimum energy that reactant molecules must possess to undergo a particular chemical reaction
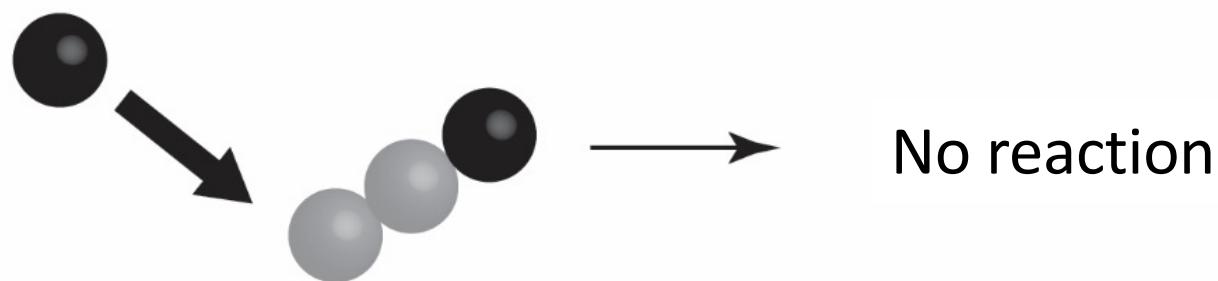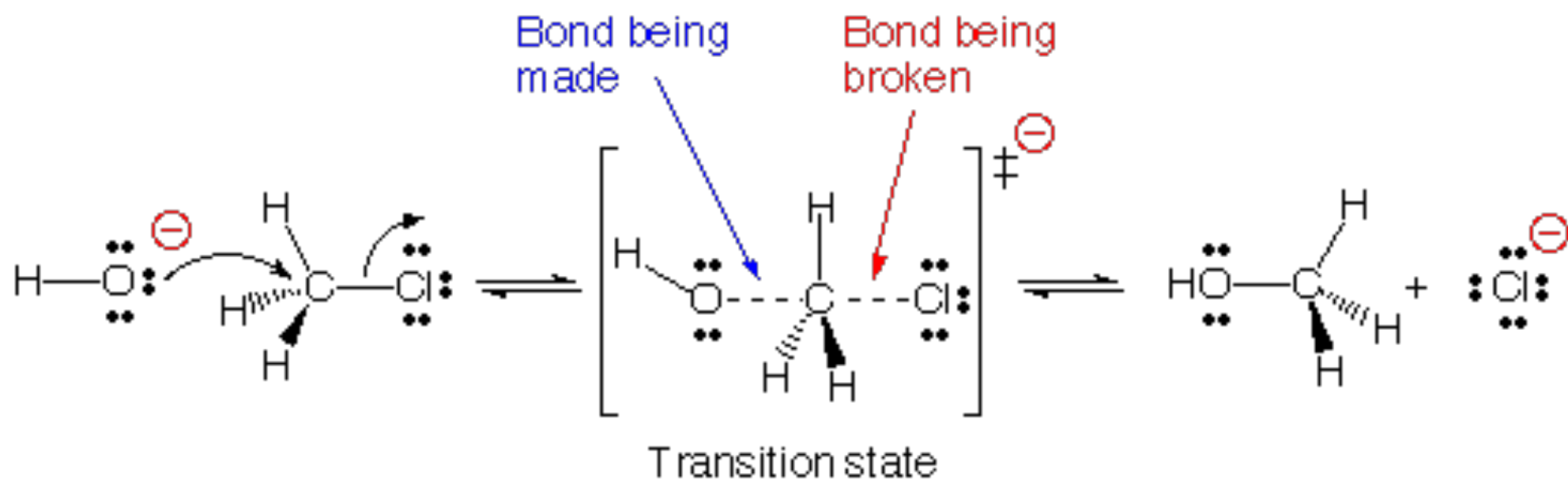
Collision geometry

Some collisions may have enough energy but not the right orientation.

Overall reaction:

Possible pathways:

No reaction

Transition state

Bond being made

Bond being broken

Transition state

Arrhenius Behaviour

The Arrhenius equation describes the relationship between the rate constant (k) and temperature (T).

$$k = Ae^{-E_a/RT}$$

$$\ln k = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

A is called the frequency factor.

Clicker Question

Activation energy is:

a) the difference between the energy of the products and reactants

b) the energy difference between the maximum energy of reaction and the energy of the products

c) the minimum total kinetic energy that molecules must bring to their collisions for a chemical reaction to occur

d) the total kinetic energy of molecules in collisions

e) the total kinetic energy of molecules in a system

Reaction Mechanisms

A reaction mechanism is a collection of one or more elementary steps that account for the way reactants become products.

An elementary step is a reaction describing actual chemical species that react at the molecular level.

The sum of elementary steps in a mechanism gives the overall reaction, which shows the chemical balance of atoms in the reaction but rarely describes how it occurs at the molecular level.

Analogy

boards
tools

overall rxn.
→

finished.

Step 1:

Step 2:

.
'

elementary
steps.

Reaction Mechanisms

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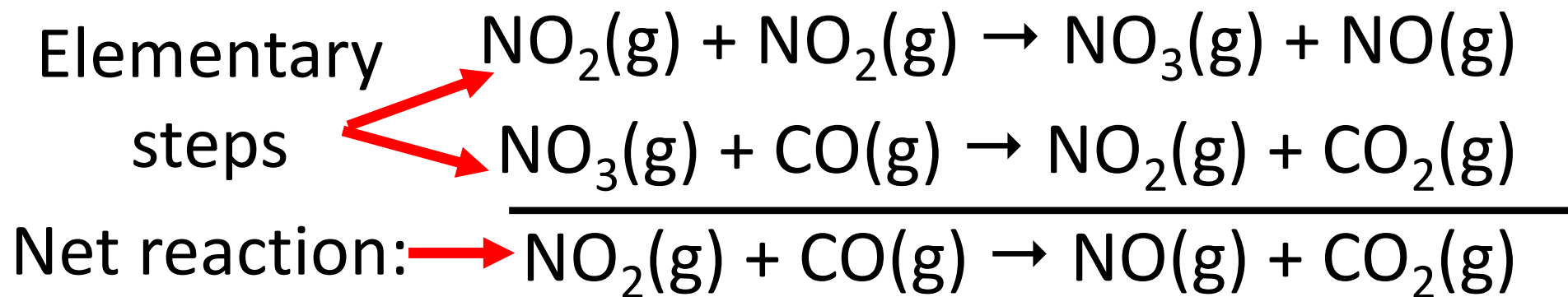
Reaction Mechanism

Consider:

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$
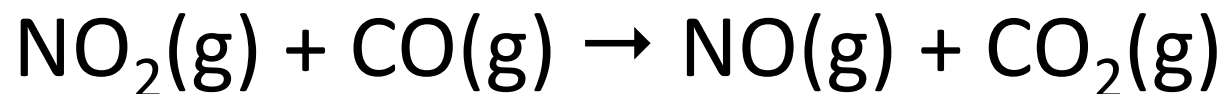
Experimentally determined rate law:

$$Rate = k[NO_2]^2$$

How does this reaction proceed?

Elementary steps

Elementary steps

$$NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$$

$$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$$

Net reaction: $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

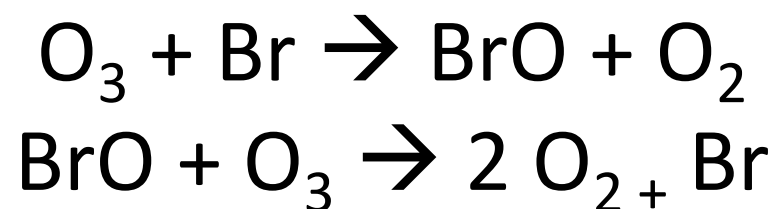NO_3 is an **intermediate**. An intermediate is a species that is not present in the reactants or products but that is formed and consumed during the reaction.

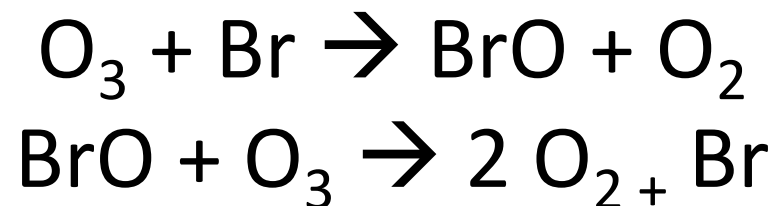For the mechanism shown, which species is a reaction intermediate?

$$O_3 + Br \rightarrow BrO + O_2$$
$$BrO + O_3 \rightarrow 2\ O_2 + Br$$

a) O_3

b) Br

c) BrO

d) O_2

e) $Br + O_2$

Clicker Question

For the mechanism shown, which species is a catalyst?

$$O_3 + Br \rightarrow BrO + O_2$$
$$BrO + O_3 \rightarrow 2\ O_{2\ +}\ Br$$

a) O_3

b) Br

c) BrO

d) O_2

e) $Br + O_2$

Molecularity

The stoichiometric coefficients for reactants in an *elementary step* **DO** provide the order of the reaction.

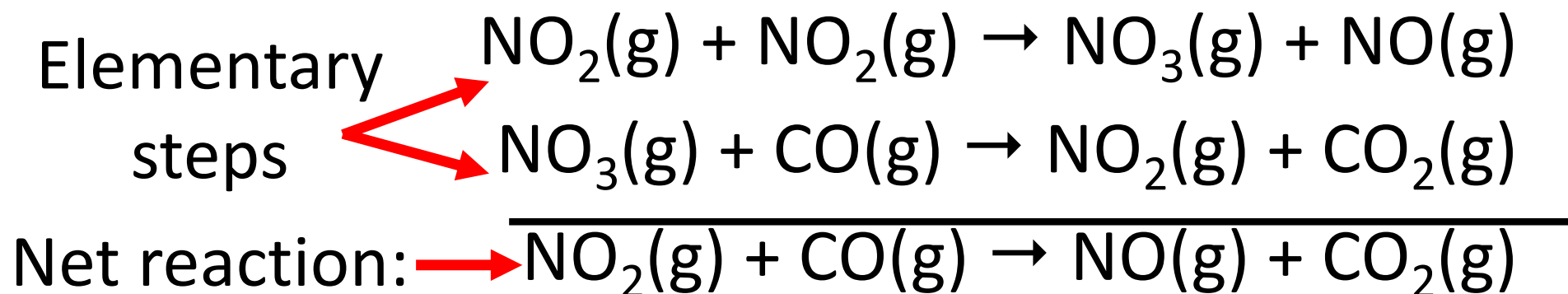| Elementary reaction	Molecularity	Rate law
A → products	Unimolecular	rate = k [A]
A + B → products 2A → products	Bimolecular	rate = k [A] [B] rate = k [A]^2
A + B + C → products 2A + B → products	Termolecular	rate = k [A] [B] [C] rate = k [A]^2 [B]
A + B + C + D → products	Not observed	

Rate-determining step

The slowest step in a reaction mechanism.

The rate-determining step will determine the rate law.

Rate-determining step
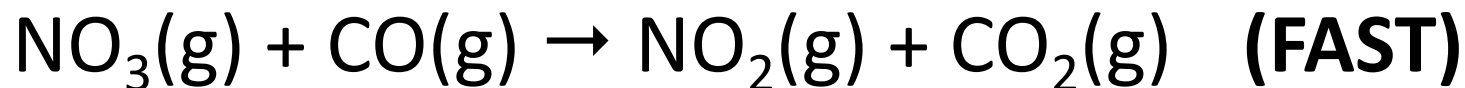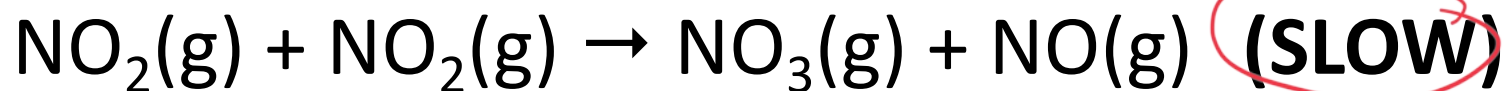
Remember the reaction of NO_2 with CO:

Elementary steps

$$NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$$

$$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$$

Net reaction:

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

The experimentally determined rate law is:

$$Rate = k[NO_2]^2$$

Clicker Question

The reaction $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ proceeds via two elementary steps:

$$NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g) \text{ (SLOW)}$$
$$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g) \text{ (FAST)}$$

Which of the following potential energy diagrams best fits this description?