Rates of Reaction

Some are

FAST

Cosy…

Ooh, aah…

Oh my!

Some are… SLOW!

Ho hum…

Reaction Rate is…

Changes in the amount of chemical substance per unit of time

General equation:

$$\text{Rate} = \frac{\Delta\text{amount}}{\Delta\text{time}}$$

Ways to measure rate…

- Monitor
  - Colour change
  - Mass change
    - Gas formation in an open container
    - Solid made or used
  - Volume (pressure) change
    - gas formation in a closed container
  - Temperature change (up or down)
  - pH change
  - Concentration change…. and many more…

Colour change can be measured using…

a colourimeter

a spectrophotometer

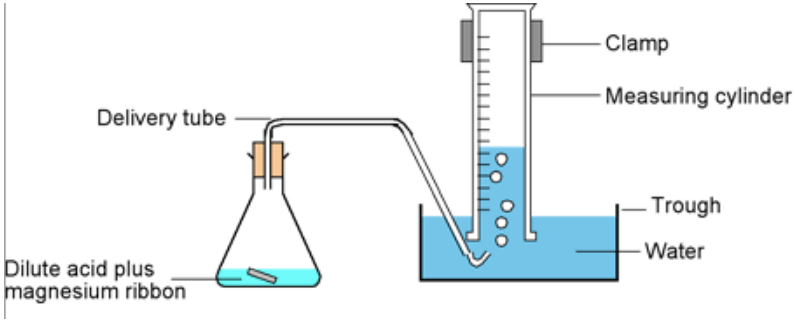
Mass change…

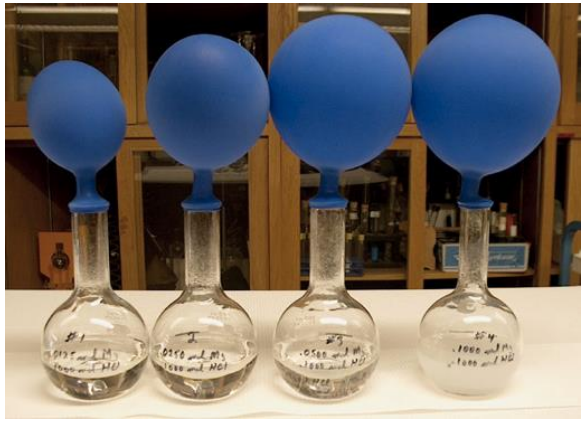
- If a gas is formed in an OPEN container, it can ESCAPE
  - Therefore, mass decreases over time
  - Decrease is due to the LOSS of GAS

Mass change…

A solid may be USED or PRODUCED during a reaction

Volume (pressure) change…

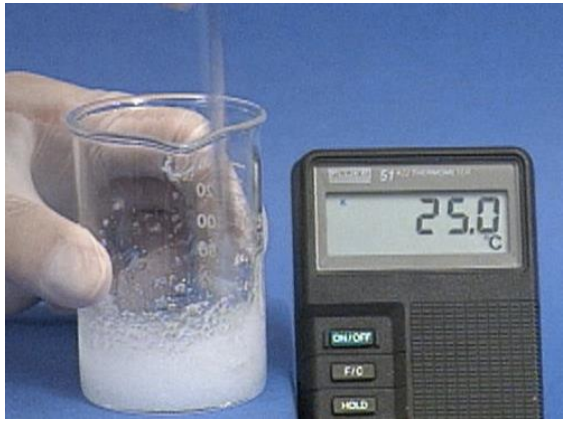


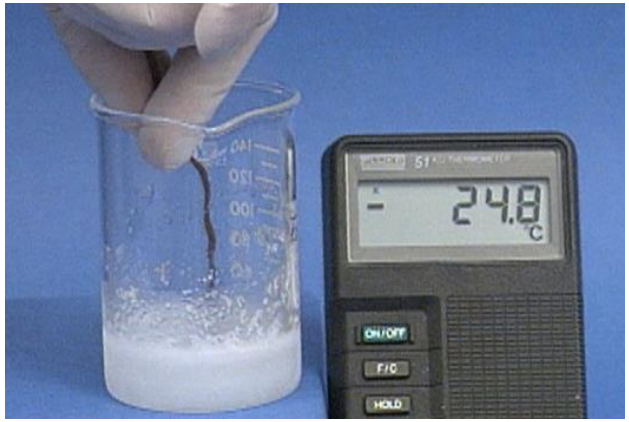


- Gas formed is collected
- Can be measured in 2 ways:
  - Volume produced
  - Pressure change

Temperature change…

- Endothermic
  - Rxn feels cool to touch
  - Energy is absorbed
- Exothermic
  - Rxn feels warm to touch
  - Energy is released





Calculating RATE

- TIME must always be the…

DENOMINATOR

Do not change units, unless you are asked
- could lead to calculation errors

Examples:

If 16g of HCl are used up after 12 min in a reaction, what is the average reaction rate?

$$\text{Rate} = \frac{\Delta\text{mass}}{\Delta\text{time}}$$

$$\text{Rate} = \frac{16\text{ g}}{12\text{ min}}$$

Rate = 1.3 g/min

If a reaction between $CaCO_3$ and HCl produces 245 mL of $CO_{2(g)}$ in 17 s, what is the average rate of the reaction?

Usually, reaction rate is calculated directly…

BUT if a reaction rate is given for one of the species in the reaction you can calculate the reaction rate for the other species in the reaction using…

STOICHIOMETRY

$Mg_{(g)} + 2HCl_{(aq)} \text{--->} MgCl_{2(aq)} + H_{2(g)}$

If the rate production of H_2 is 2.5 mol/min, what is the rate of consumption of HCl?

$$3O_{2(g)} \text{--->} 2O_{3(g)}$$

The forward rate of reaction is 3.0 g/min. What is the reverse reaction rate?

Factors Affecting Rate

- Different reactions occur @ various rates
- The same reaction can be made to have different rates

Rusting in air

vs. rusting in water

Combustion in air

vs. combustion in oxygen

The 5 factors are…

1. Nature of the reactants
2. Surface area
3. Concentration
4. Temperature
5. Other chemicals

Let’s look closely at each….

Website animations…

Nature of Reactants

Some chemicals are naturally more reactive than others

Examples:

Potassium with water	very reactive
Sodium with water	
Iron with water	
Gold with water	very slow

Why?

due to:

- particle size (larger is slower)
- number of bonds (more bonds is slower)

Surface Area

Reactants must touch to react

- easier contact = faster reaction

Therefore:

- bigger surface area = faster rate

Example:

Liquid gas - burns

Vapourized gas - explodes

Coal

Dust is explosive

“lumps” burn

Lighting a fire is much easier with kindling.

Logs will burn once the fire can provide energy for the reaction.

Increasing surface area only works for HETEROGENEOUS reactions, not homogeneous reactions…

HETEROGENEOUS reaction

- reaction that involves 2 or more states

HOMOGENEOUS reaction

- reaction that involves only 1 state

Concentration

Remember…

how the concentrated vs the dilute acid behaved in the lab…

Higher concentration	=	Faster rate
Lower concentration	=	Slower rate

Concentration & Gases…

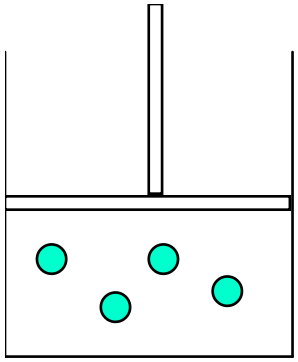
The concentration of a gas is affected by its PRESSURE!

Remember the relationship between pressure & volume…

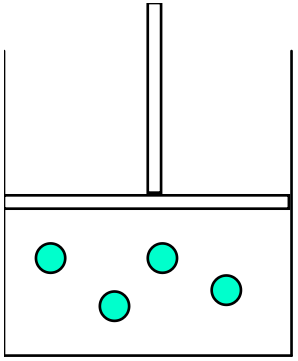
Increase pressure = decrease volume

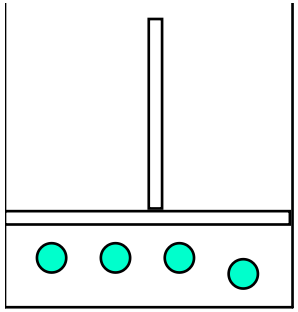
Decrease pressure = increase volume

$$\text{Concentration} = \frac{\text{mol}}{\text{L}}$$



What happens if we compress the container?





What has happened to volume?

… smaller

What has happened to the moles?

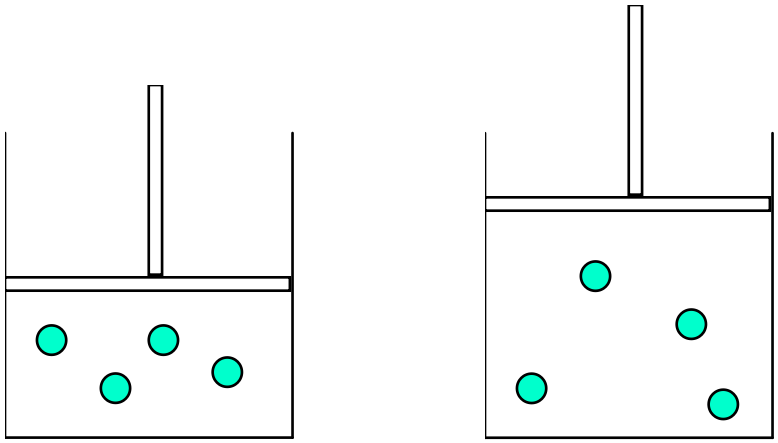
… nothing

What has happened to the concentration?

… BIGGER!!!!

Increase pressure (or decrease volume)
… increases concentration

Let’s decrease pressure…



What has happened to volume? … bigger

What has happened to the moles? … nothing

What has happened to the concentration? … SMALLER!!!!

decrease pressure (or increase volume)
… decreases concentration

Temperature

Increase temperature… FASTER

Decrease temperature… SLOWER

General rule …

Temperature increases by 10° C, rate doubles.

Temperature decreases by 10° C, rate halves.

True for SLOW reactions.

Examples:

1. By what factor does the rate increase if the temperature increases by 30° C?
2. What is the final temperature if a container @ 10° C has a rate increase by a factor of 32?

Other chemicals

- CATALYST

- speeds up the rxn

- enzymes
- catalytic converter

- INHIBITOR

- slows the rxn

To affect reaction rate

- Changes must be made to the REACTANTS only
- Changes that affect reactants only
  - Concentration
  - Nature of the reactants
  - Catalyst (inhibitor)
- Changes that affect the whole container
  - Temperature
  - Pressure (volume)

Reaction speed

- Dependent on REACTANT state

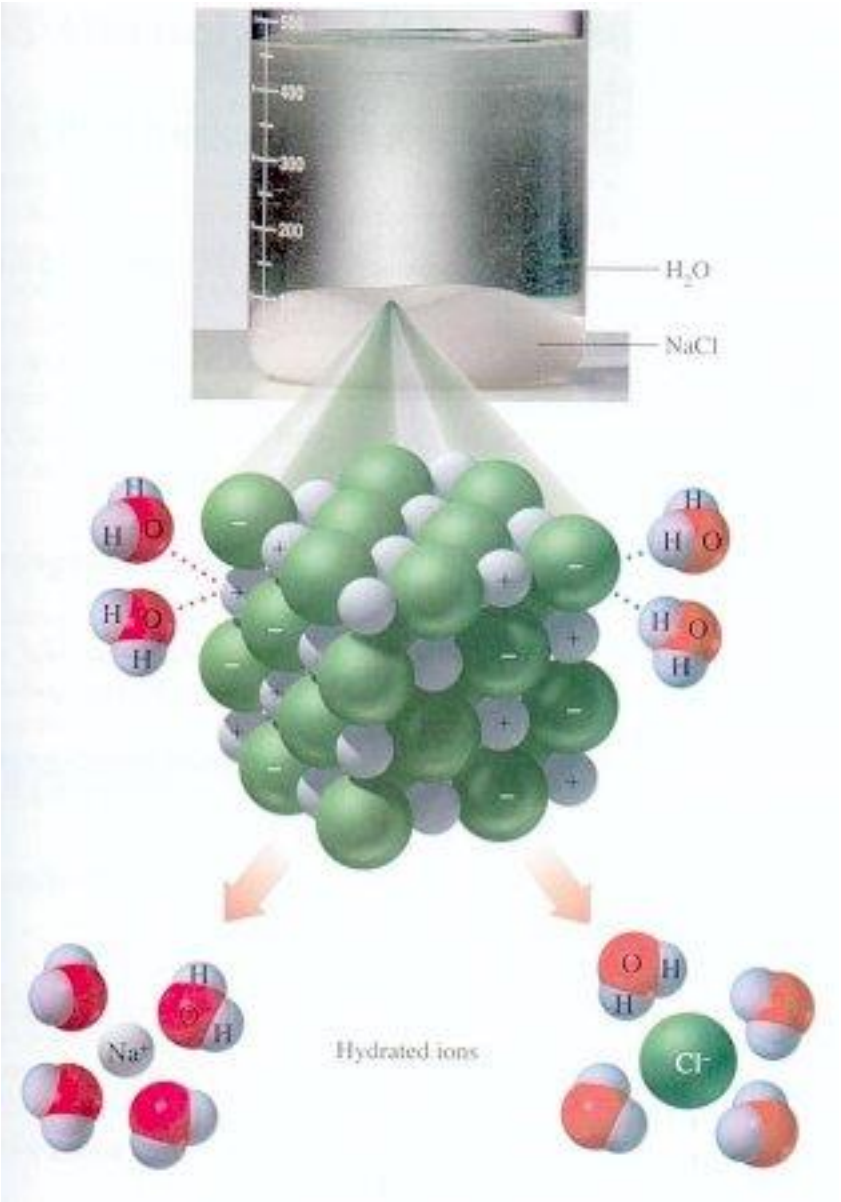
SOLID	SLOW
LIQUID	↓
GAS	
AQUEOUS	FAST

Why are reactions with (aq) reactants instant?

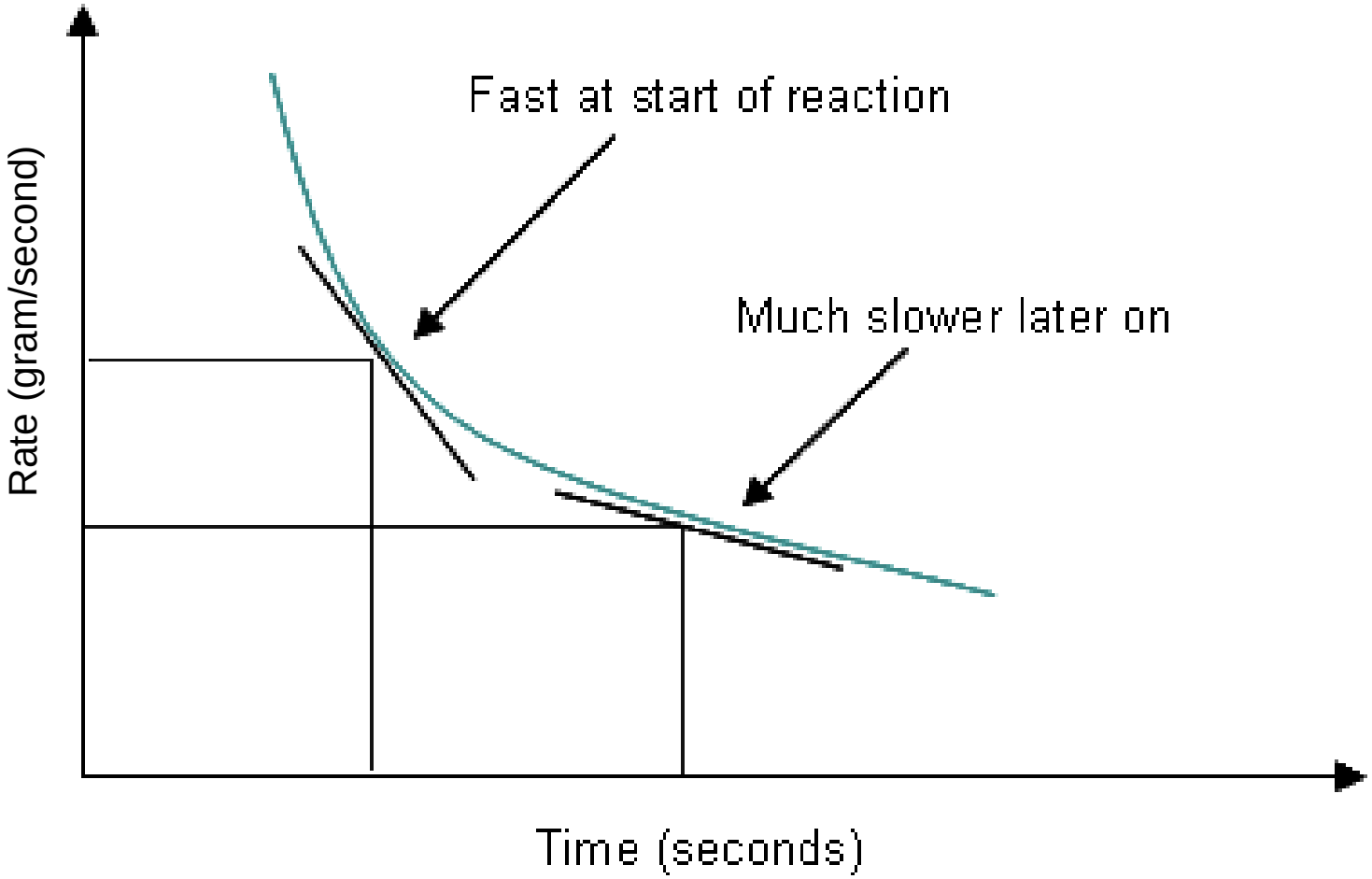
- For a rxn to occur, bonds must be broken
  - Aqueous solutions are really IONS rather than compounds
  - Water has already broken the bonds, therefore, step 1 (breaking bonds) is already complete

Water particles pull apart the sodium & chloride ions from the salt.

Because the bonds are broken, the reaction can be instantaneous



Rxn Rate Change over Time



Collision Theory

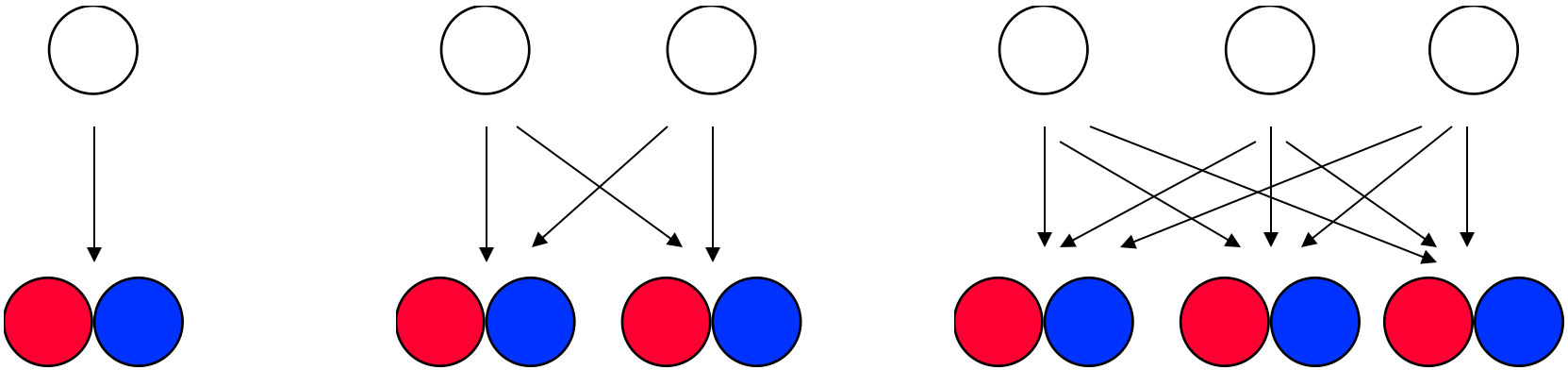
Collision Theory

- A chemcial reaction occurs if there is a SUCCESSFUL COLLISION
- There are 3 parts to the collsion theory

1. Molecules must HIT

- 2 or more particles must hit
  - No hit, no collision
- Increase the number of particles
  - Increase the chance of a successful collision

Possible Collisions



2 particles
- 1 possible collision

4 particles
- 4 possible collisions

6 particles
- 9 possible collisions

- there are also collisions between similar particles but no reaction occurs, so collisions are not counted…

2. Sufficient KINETIC ENERGY

- When molecules collide they must hit with enough force
- Slow moving molecules, too little KE = no reaction

Unsuccessful car accidents happen too…
accidents without damage to the cars

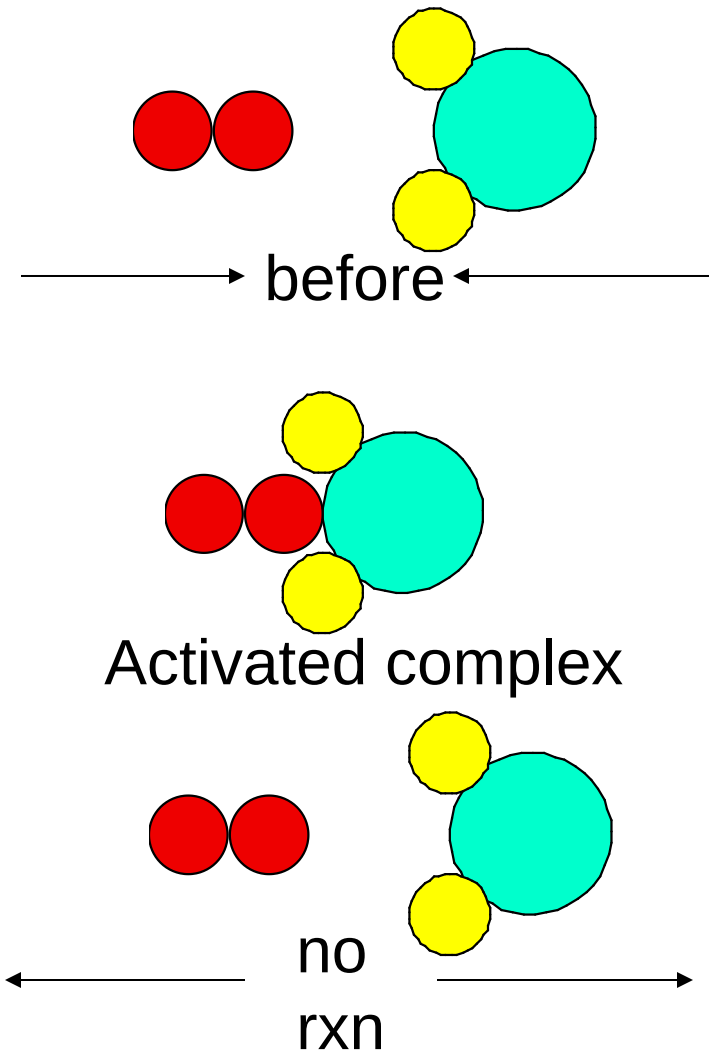
3. FAVOURABLE GEOMETRY

- or PROPER ORIENTATION
- Molecules must hit correctly or the new bonds do not form

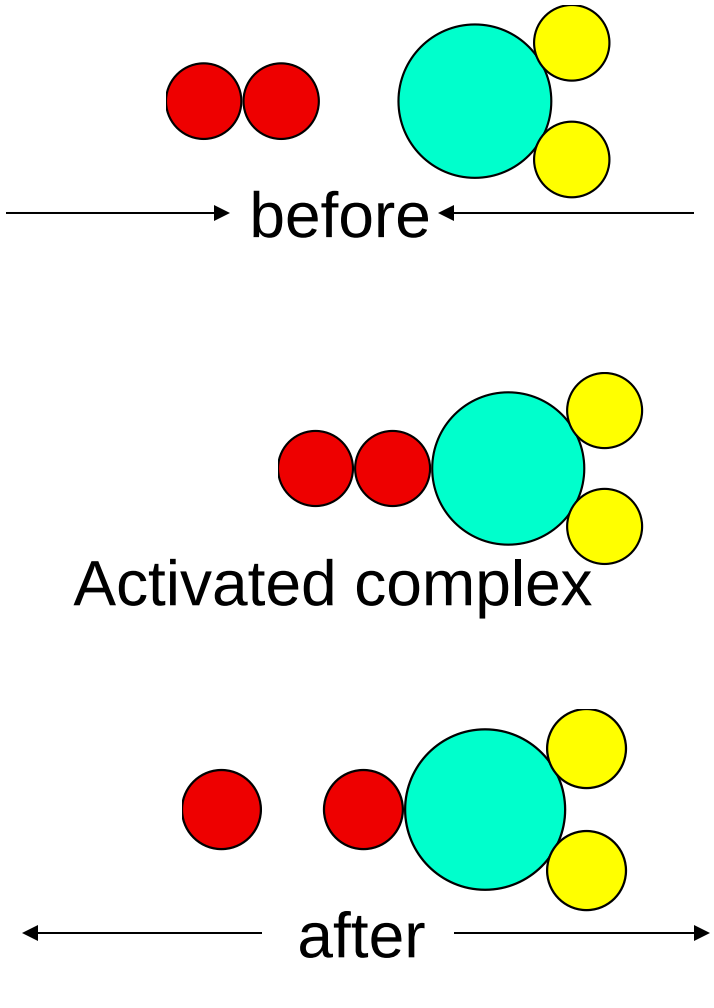
• there are lots of wrong ways to collide…

But only ONE CORRECT way..

WRONG ORIENTATION



PROPER ORIENTATION



Kinetic vs Potential Energy

- Kinetic energy = energy of motion
- Potential energy = stored energy

What happens as particles approach each other?

- they slow down because the electrons in the outer shells begin to repel each other

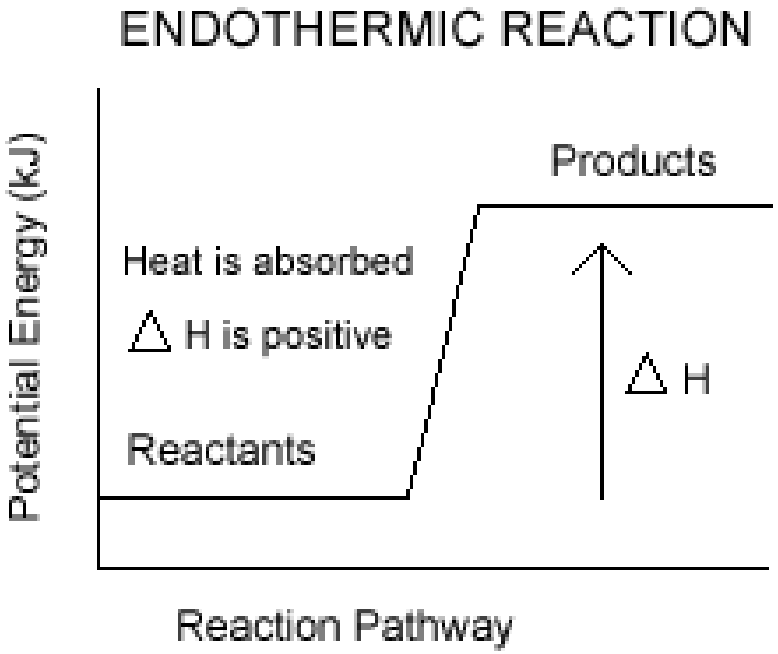
Therefore, the reactants must be moving fast enough (have enough kinetic energy) to overcome this and have a SUCCESSFUL collision

Energy & Reactions

Energy = Heat = Enthalpy

- Energy is required to break & make bonds
- Total energy for the reaction is found by calculating the difference between making & breaking the bonds

Endothermic Reactions



- products feel colder
- $E_p > E_R$

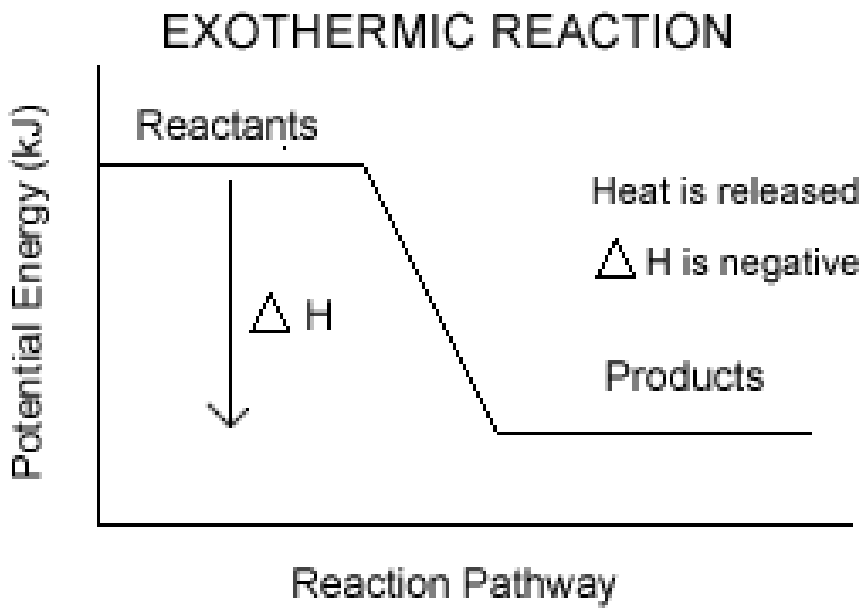
$\Delta H = E_p - E_R$

$H_{2(g)} + 436\ kJ \rightarrow H_{(g)} + H_{(g)}$

or:

$H_{2(g)} \rightarrow H_{(g)} + H_{(g)}$ $\Delta H = 436\ kJ$

Exothermic Reactions



- products feel hotter
- $E_p < E_R$

$\Delta H = E_p - E_R$

$$H_{2(g)} + Br_{2(g)} \rightarrow 2HBr_{(g)} + 362\ kJ$$

or:

$$H_{2(g)} + Br_{2(g)} \rightarrow 2HBr_{(g)} \quad \Delta H = -362\ kJ$$

Kinetic Energy & Reactions

In a typical reaction:

- about 10^{10} collisions per second

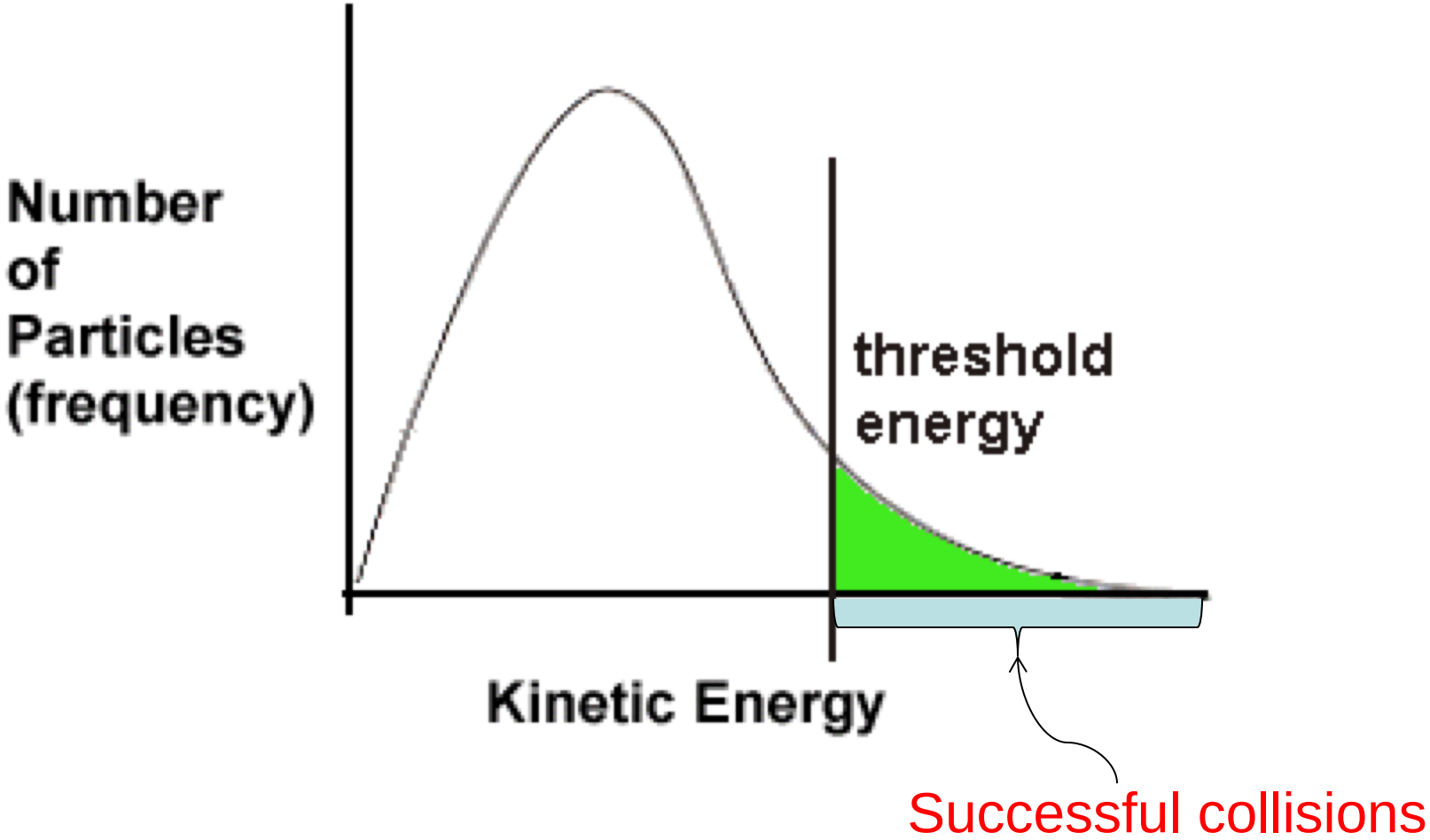
Increase reaction temperature by 10° C…

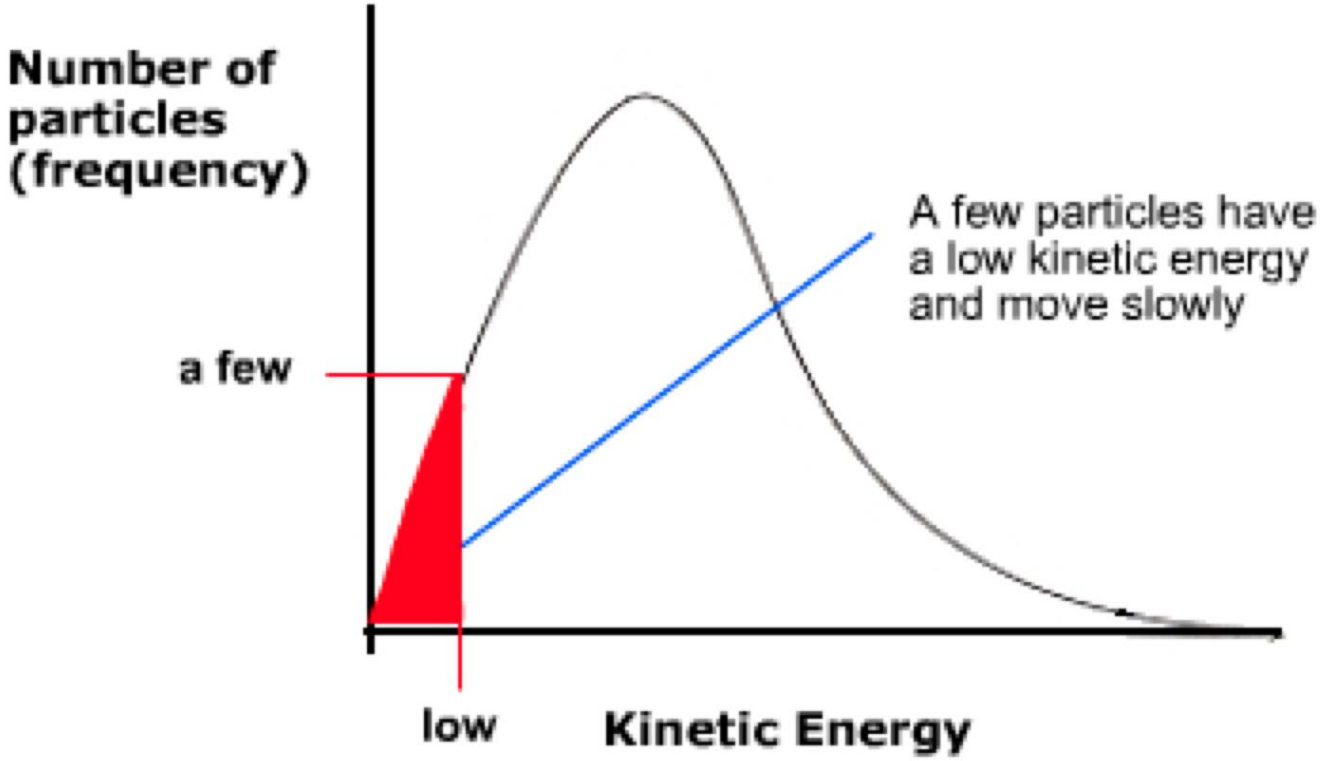
- collisions increase about 1% (hardly @ all)
- rxn rate doubles (large increase)
- why?
  - each molecule gets more energy (moves faster)

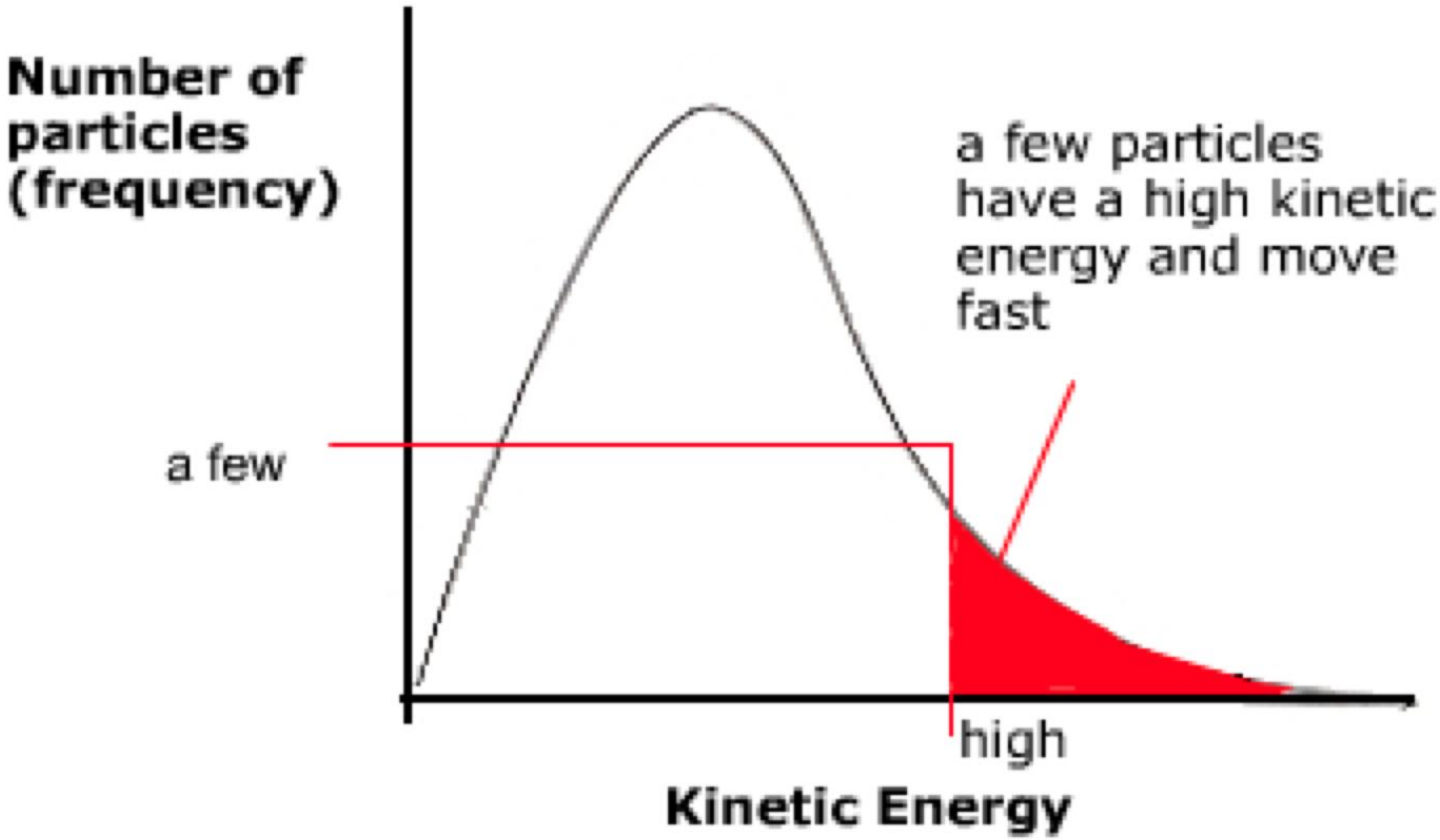
THEREFORE, rate change is due to:

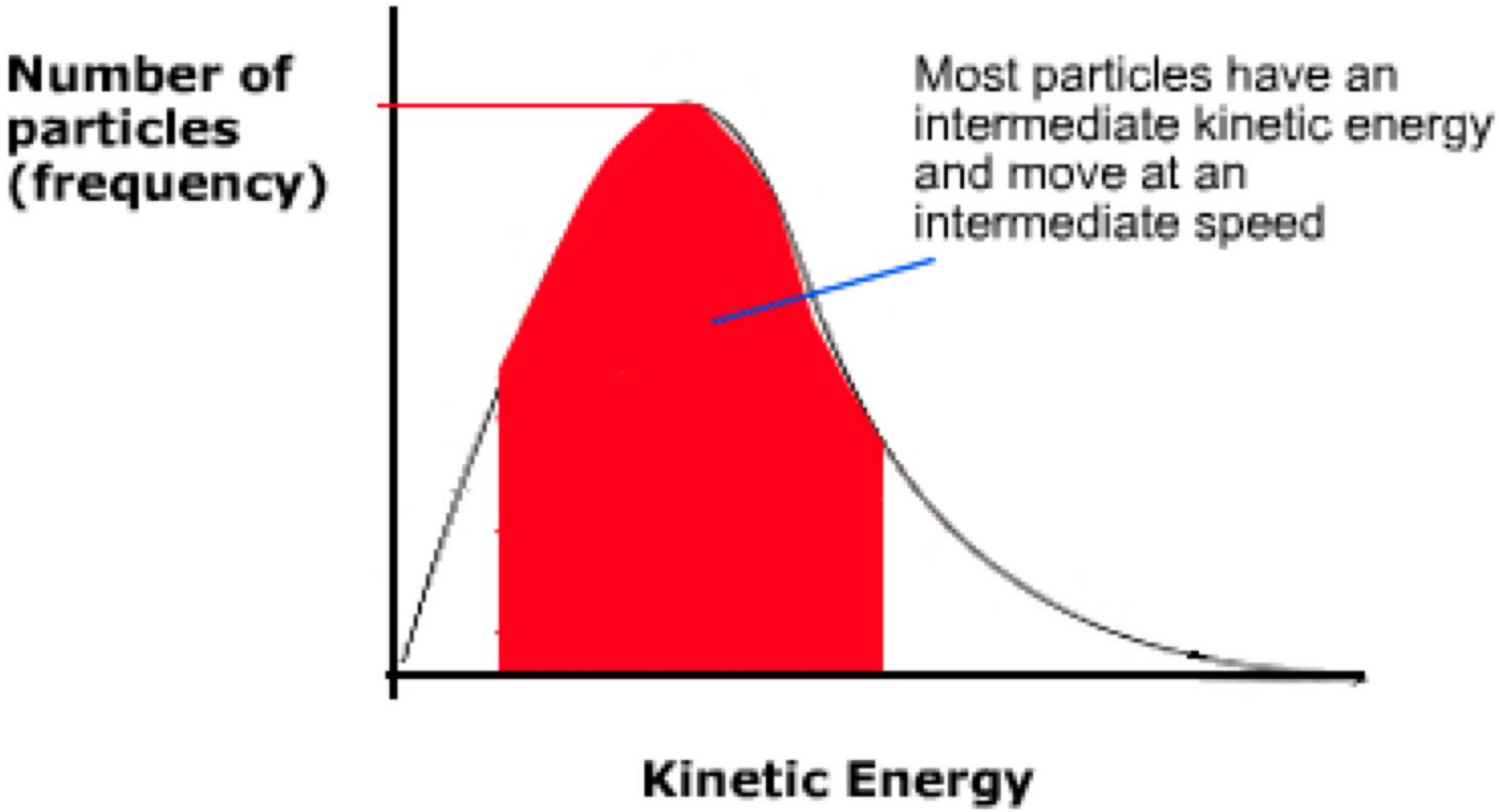
- increase in ENERGY
- NOT increase in collision #

KE Curve

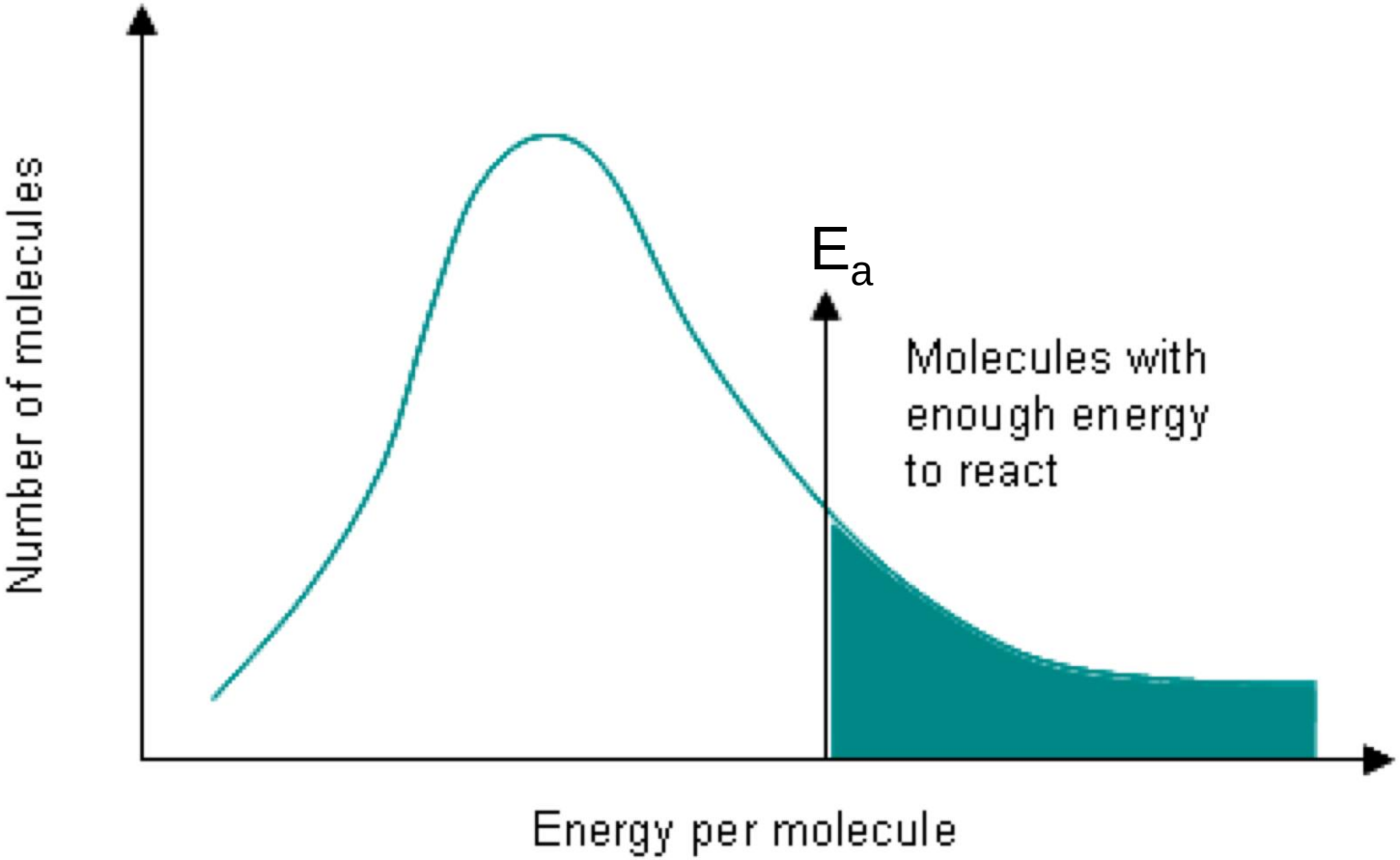

Number of Particles (frequency)
threshold energy
Kinetic Energy
Successful collisions


Number of particles (frequency)
a few
A few particles have a low kinetic energy and move slowly
low
Kinetic Energy


Number of particles (frequency)
a few particles have a high kinetic energy and move fast
a few
high
Kinetic Energy



Not all molecules have the same energy even though they are in the same container!



Only mlcls with energy above the "E_a" can react.

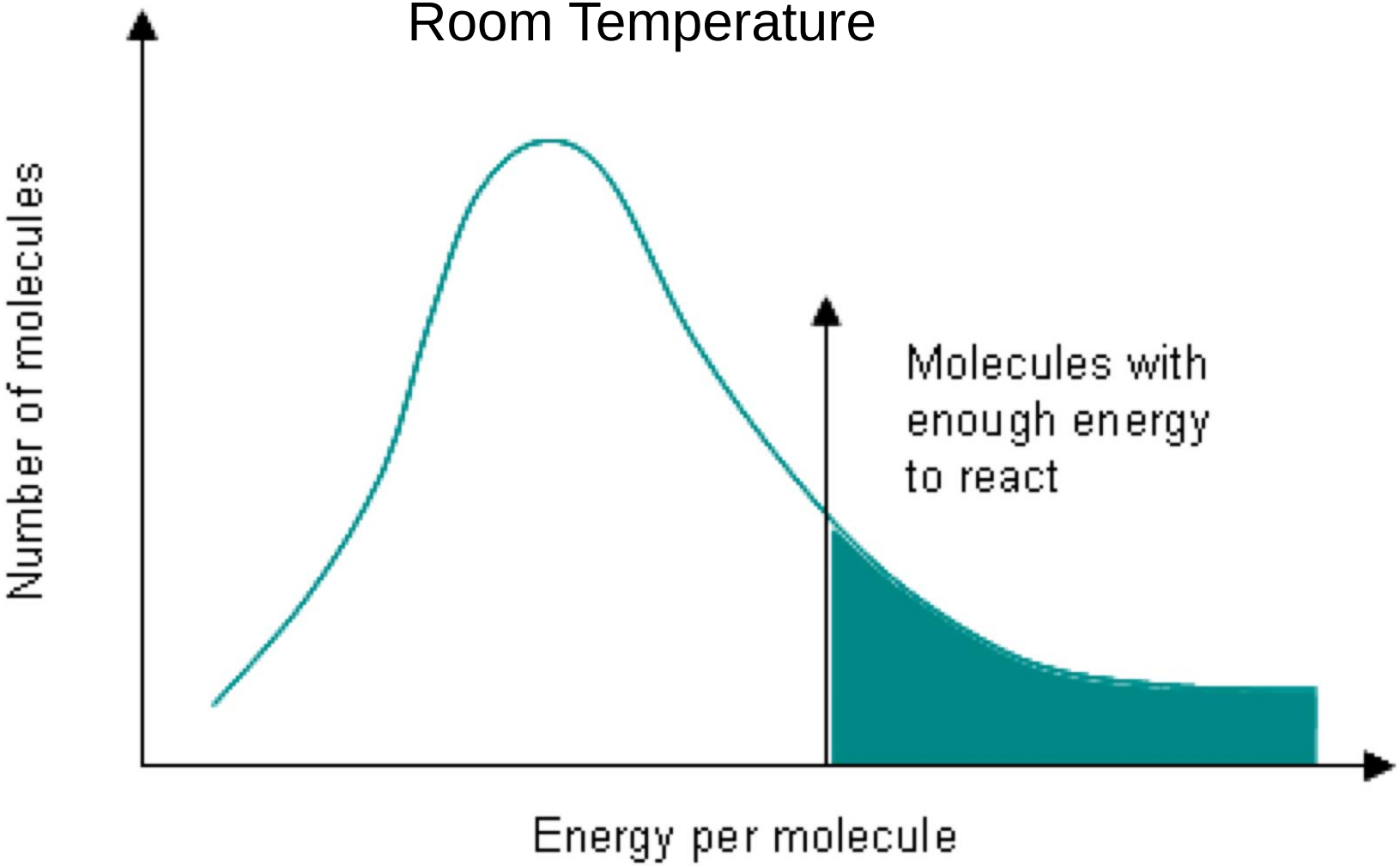
E_a = ACTIVATION ENERGY

- minimum potential energy required for a molecule to react

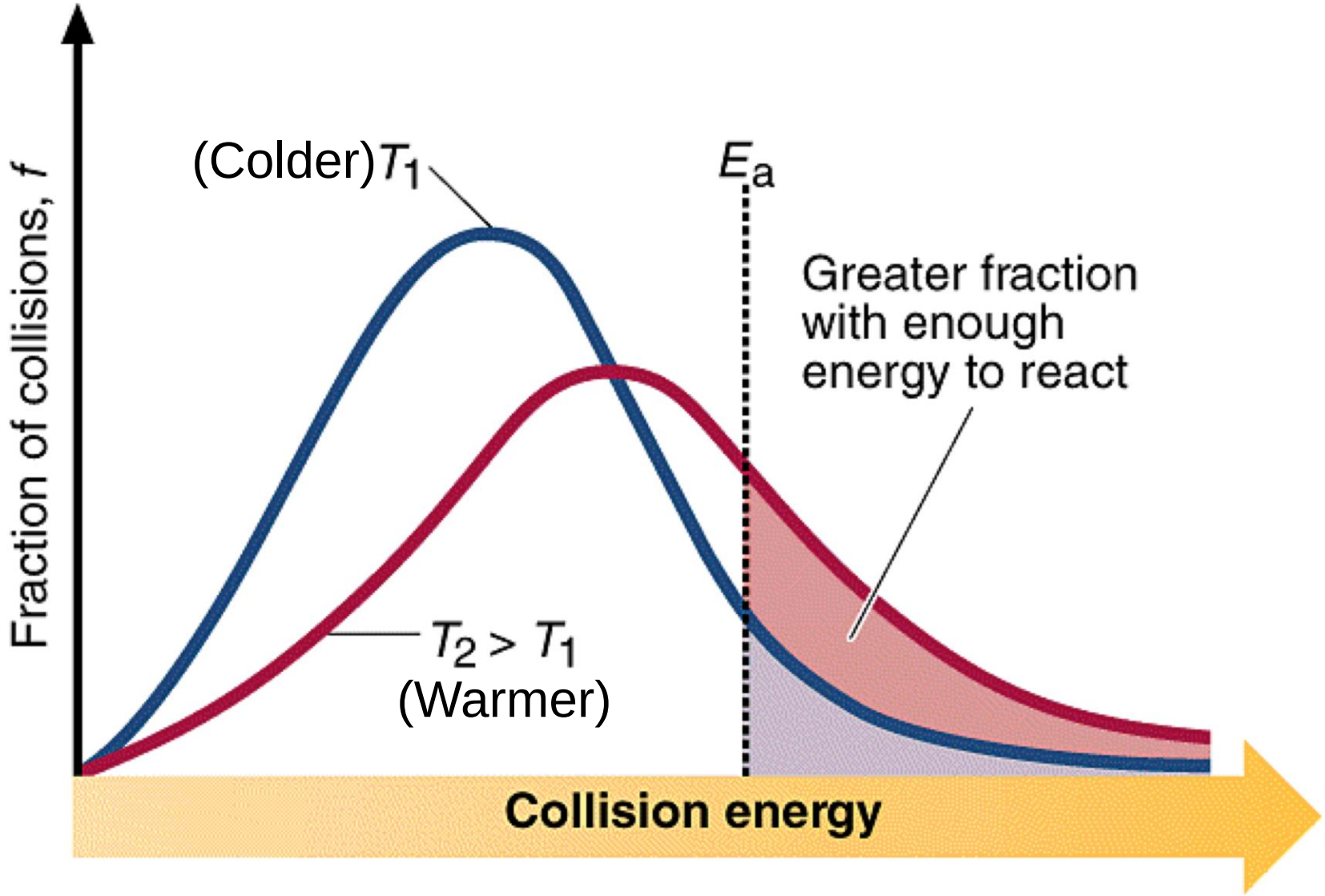
TEMPERATURE

Is the ONLY WAY TO CHANGE the ENERGY of the molecules!

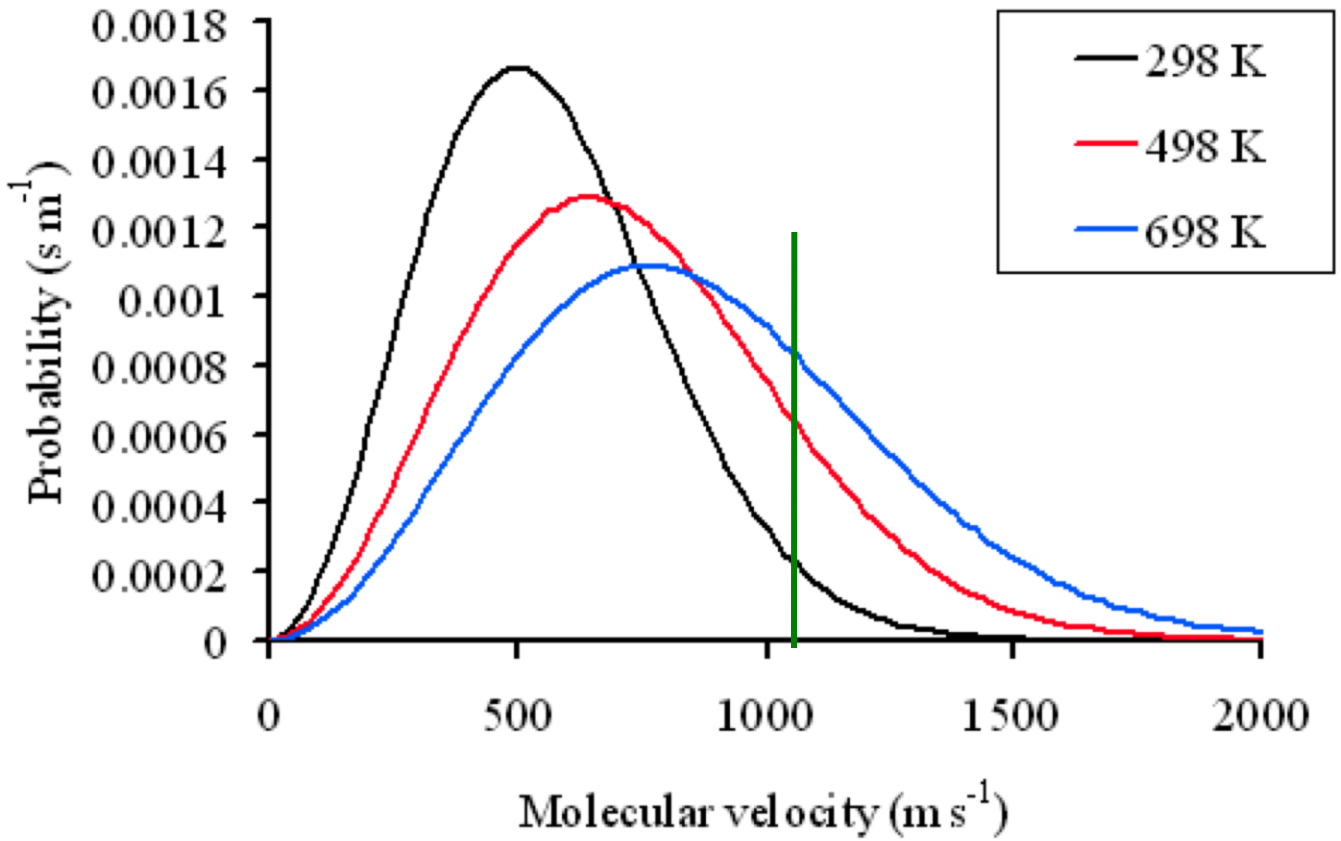
Room Temperature



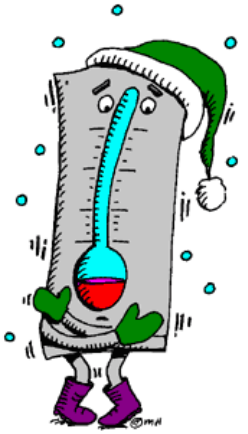
Change the Temperature…



Comparing 3 Temperatures



- very low temperature:
  - only a few mlcls have enough energy to react
  - rate is very slow



- very high temperature:
  - many mlcls have enough energy to react
  - rate is very fast

Energy Changes

remember:

Kinetic Energy ⟷ Potential Energy

- as kinetic energy increases, potential energy decreases (& vice versa)

Energy Terms

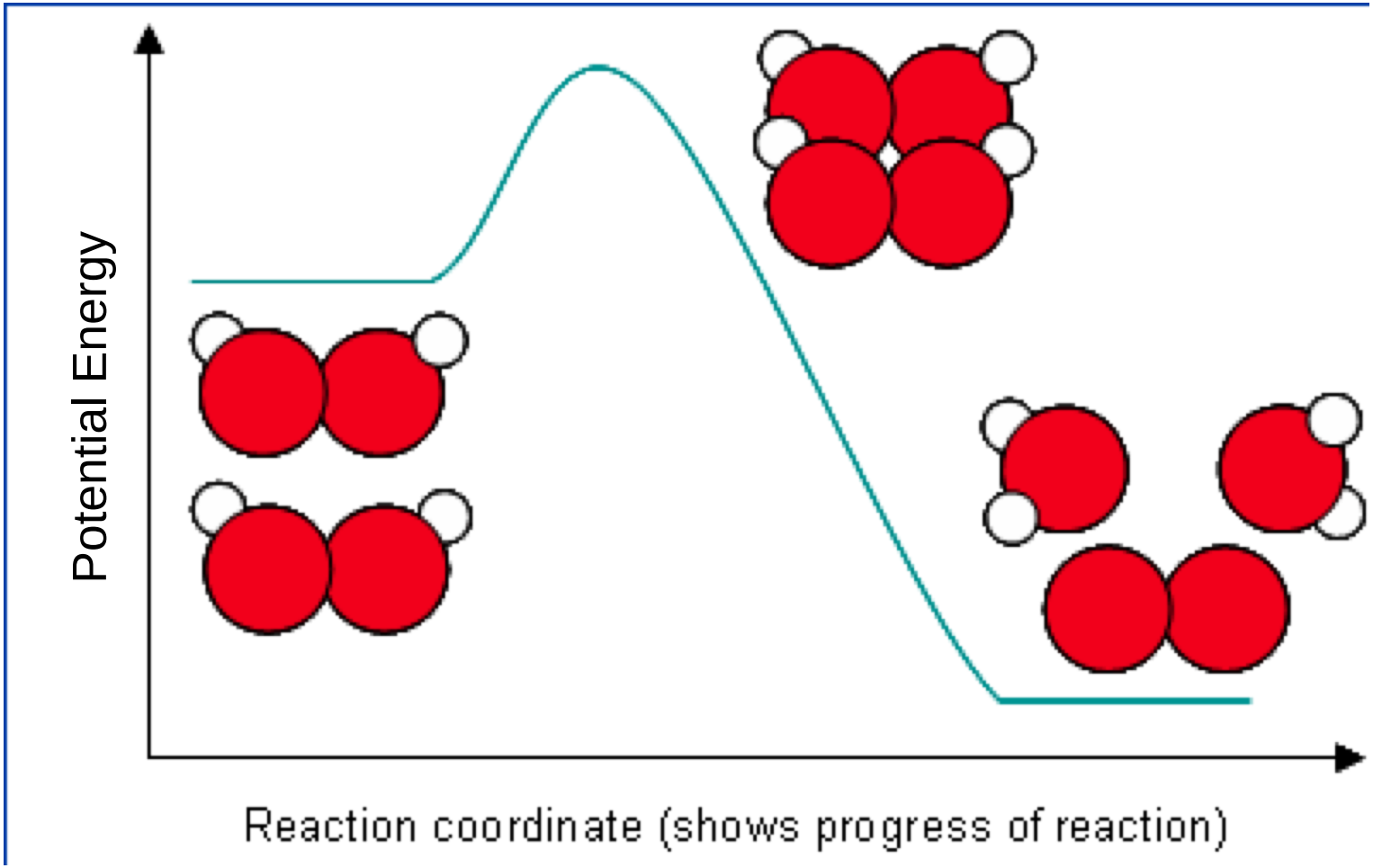
ACTIVATION ENERGY (E_a)

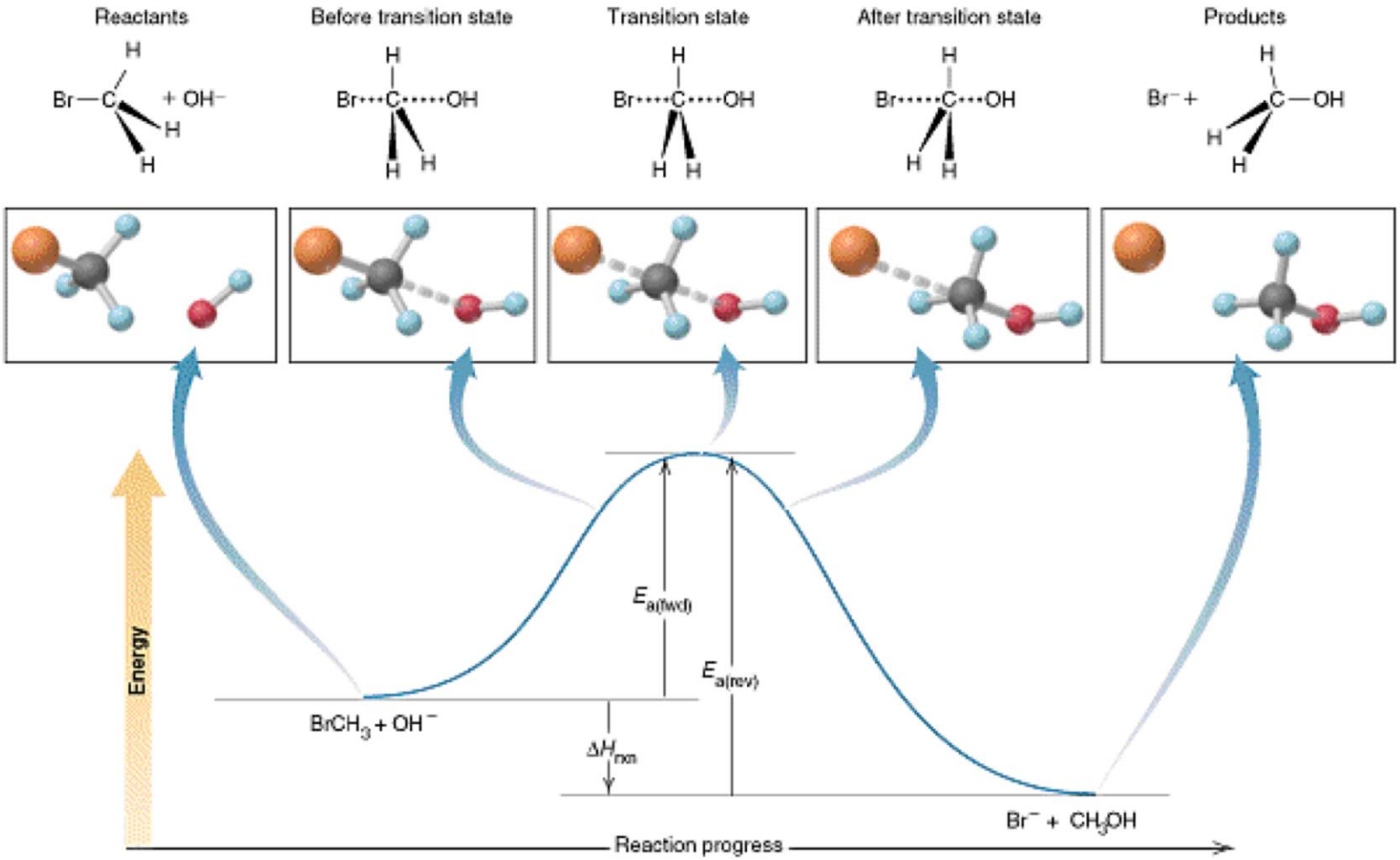
- minimum potential energy required for a successful collision

ACTIVATED COMPLEX (A_c)

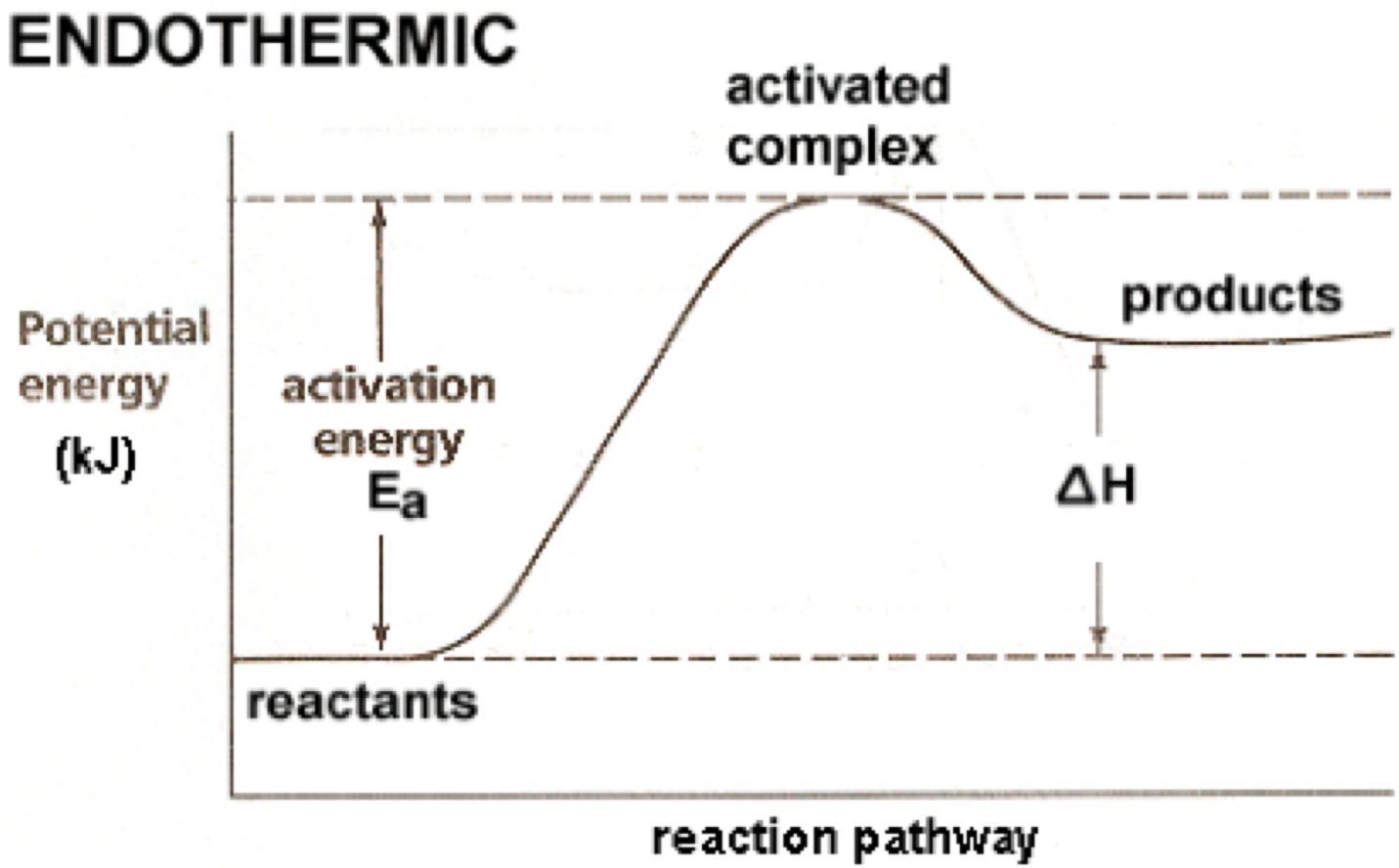
- short-lived transitional (unstable) molecule that is formed when E_a is achieved
- mlcl is made up of ALL reactant particles (elements & charges)
- noun (not a time!)

Activated Complex



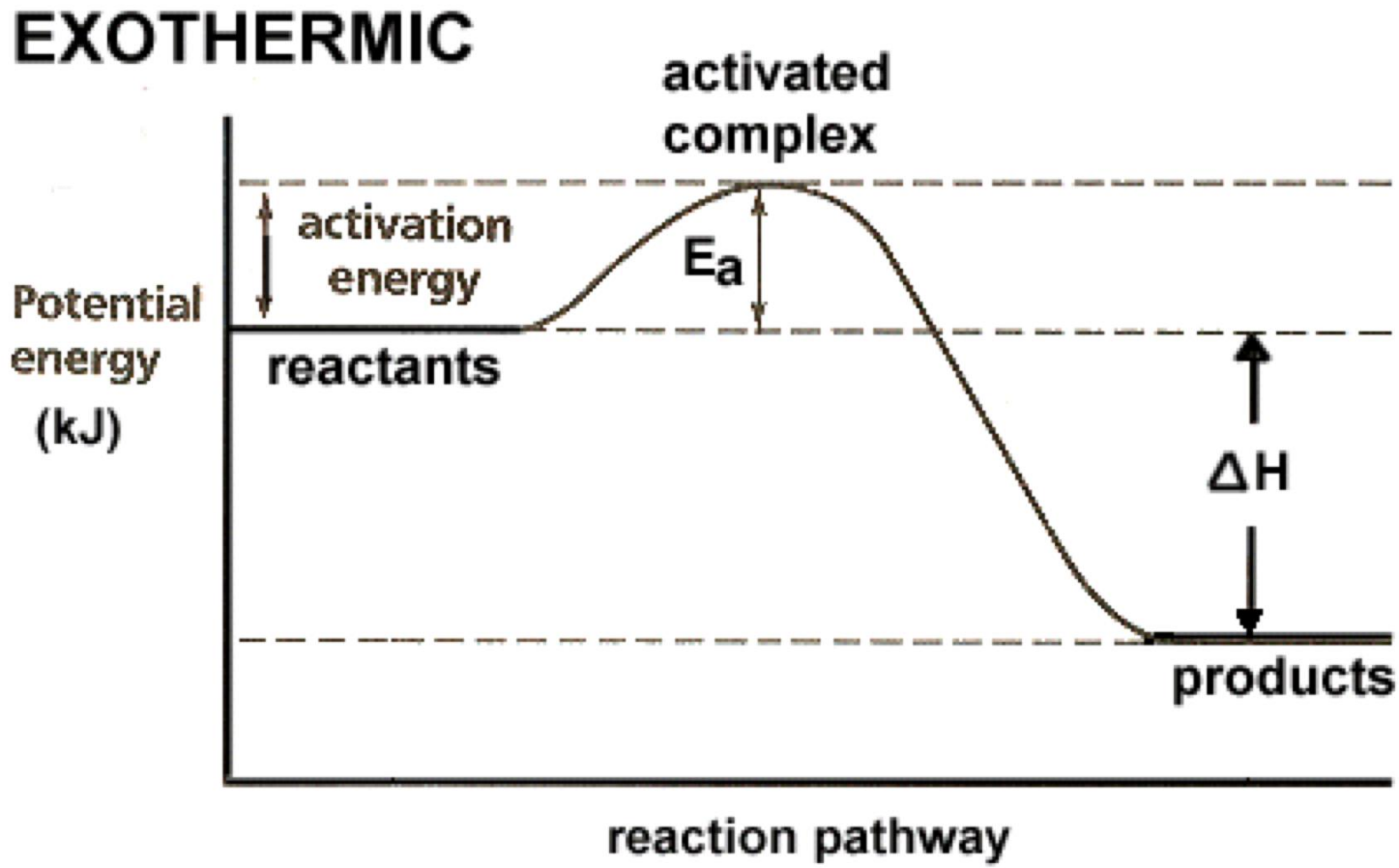

Reactants
Before transition state
Transition state
After transition state
Products
Br—C + OH⁻
Br···C·····OH
Br·····C···OH
Br⁻ +
C—OH
Energy
$E_{a(fwd)}$
$E_{a(rev)}$
$BrCH_3 + OH^-$
ΔH_{rxn}
$Br^- + CH_3OH$
Reaction progress

Rxn Types - Endothermic



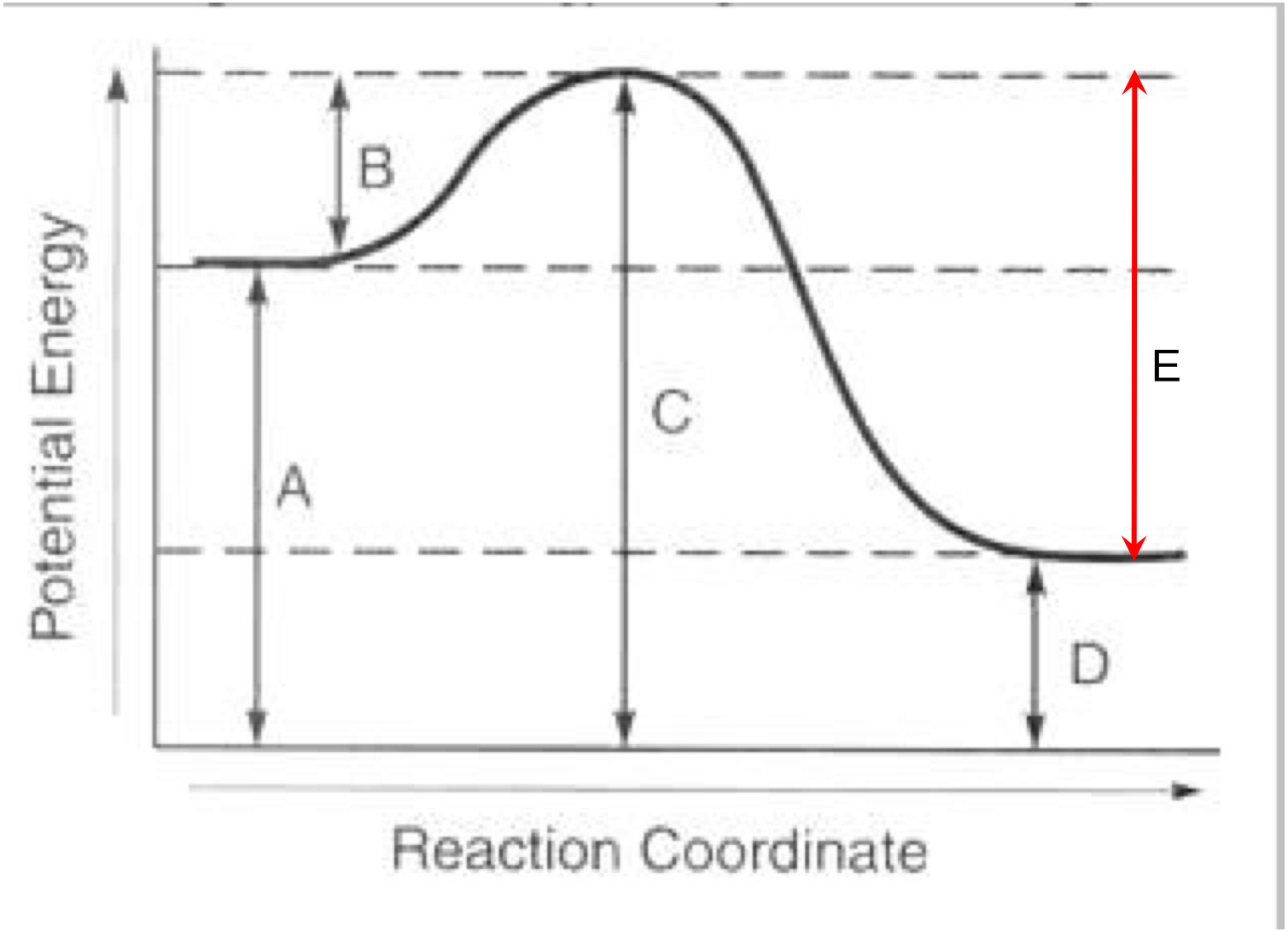
$E_P > E_R$, therefore $\Delta H = +ve$

Rxn Types - Exothermic

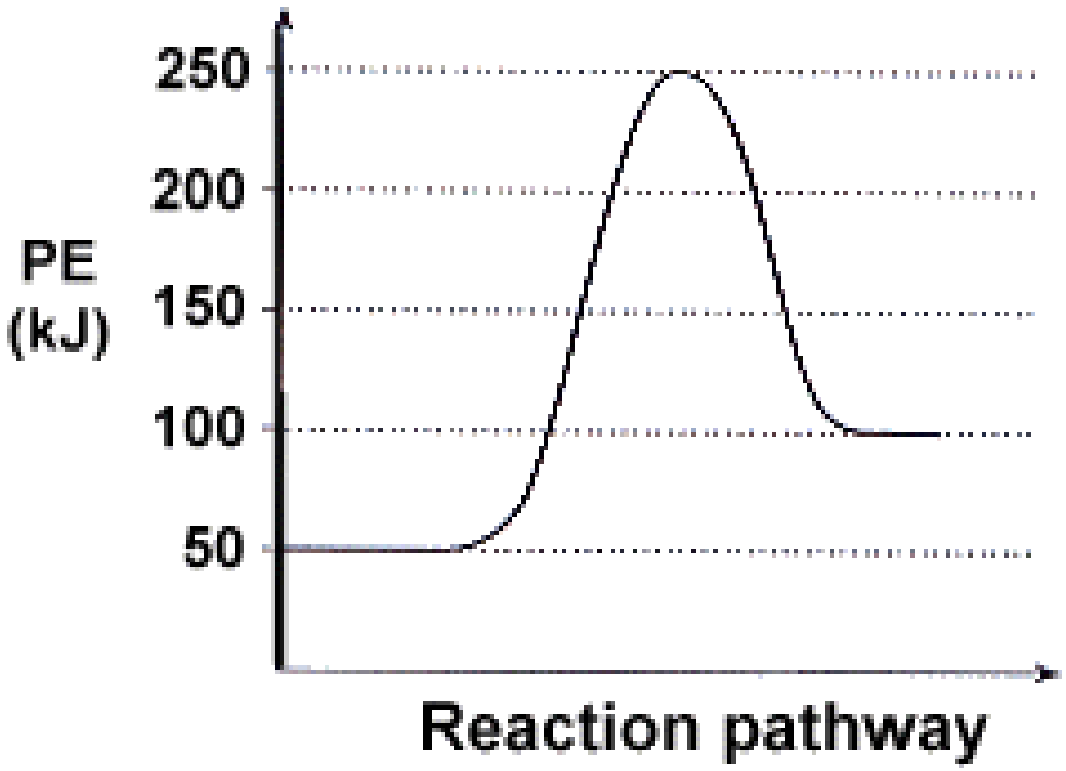


$E_P < E_R$, therefore ΔH = -ve

Reversibility of Reactions

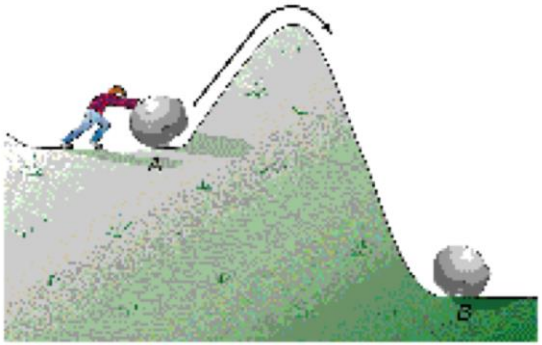


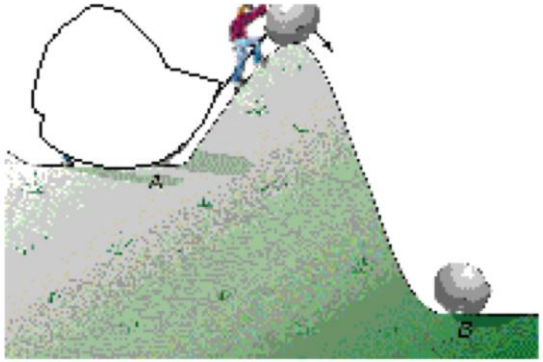
Calculate the values…

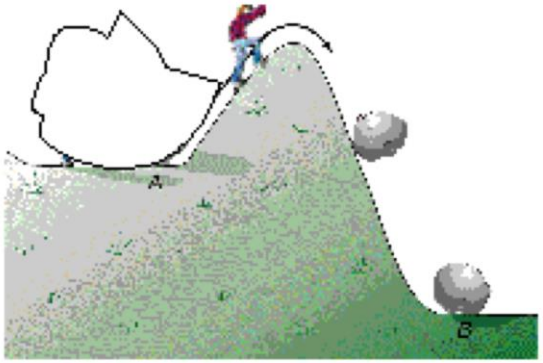


E_R =
E_P =
E_a =
$E_{a(rev)}$ =
energy of A_c =

Thinking of Rxns…







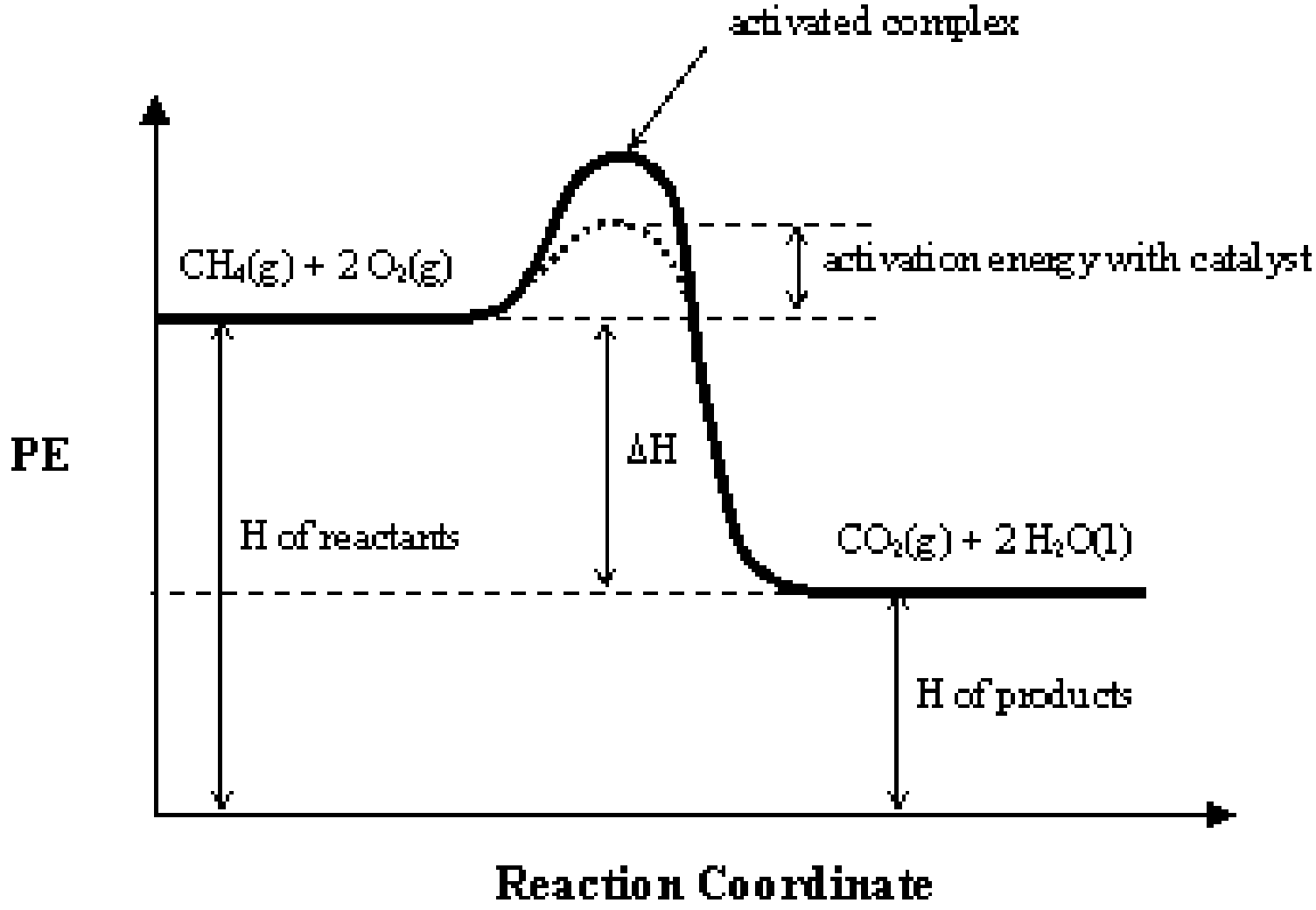
Catalysts & Inhibitors

CATALYST

- increases rxn rate by providing an alternate rxn mechanism requiring a LOWER E_a

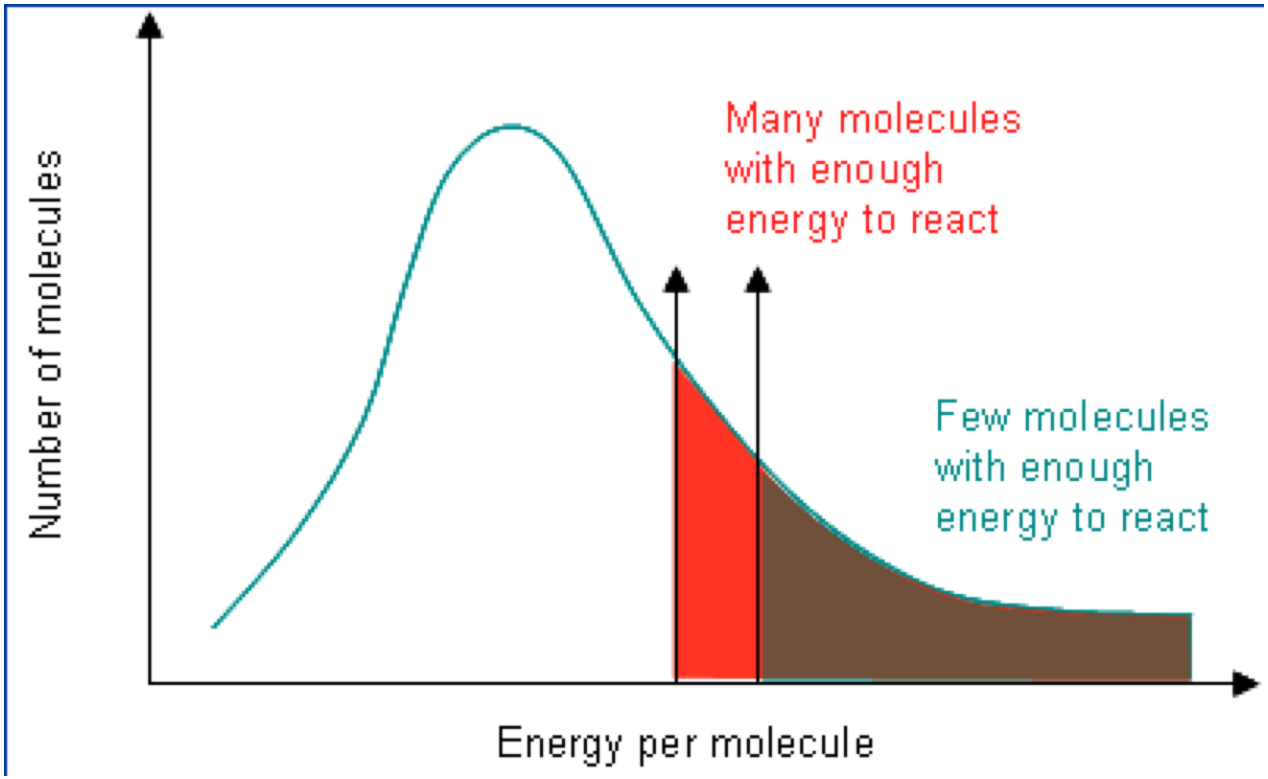
INHIBITOR

- decreases rxn rate by providing an alternate rxn mechanism requiring a HIGHER E_a



note: NO CHANGE in ΔH, E_R, E_P

Catalysts & the KE Curve



- adding a catalyst lowers the “bar”
  - it increases the number of mlcls with sufficient energy for a rxn but does NOT change the energy of the mlcls

Reaction Mechanisms

Most rxns are too complex to occur in 1 step.

WHY? - remember collision theory…

- it is very unlikely that more than 2 particles will have a successful collision, therefore, rxns often require more than one step to occur!

Iodine clock reaction

Halloween Iodine Clock (U-tube)

Ball Demo

A Reaction Mechanism is

the series of steps that lead to the overall observed reaction.

Example Rxn Mechanism

Step 1: $HBr_{(g)} + O_{2(g)} \rightarrow HOOBr_{(g)}$ slow

Step 2: $HOOBr_{(g)} + HBr \rightarrow 2HOBr_{(g)}$ fast

Step 3: $HOBr_{(g)} + HBr_{(g)} \rightarrow H_2O_{(g)} + Br_{2(g)}$ fast

Step 3:(again) $\underline{HOBr_{(g)} + HBr_{(g)} \rightarrow H_2O_{(g)} + Br_{2(g)}}$ fast

Overall Rxn $4HBr_{(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} + Br_{2(g)}$

Reactants: (& Products)

- come from overall rxn only

Reaction Intermediate:

- product of a step, then reactant of a LATER step

Catalyst (Inhibitor)

- reactant of a step, then product of a LATER step

Each elementary process (step)…

has:

- an activated complex
- an activation energy

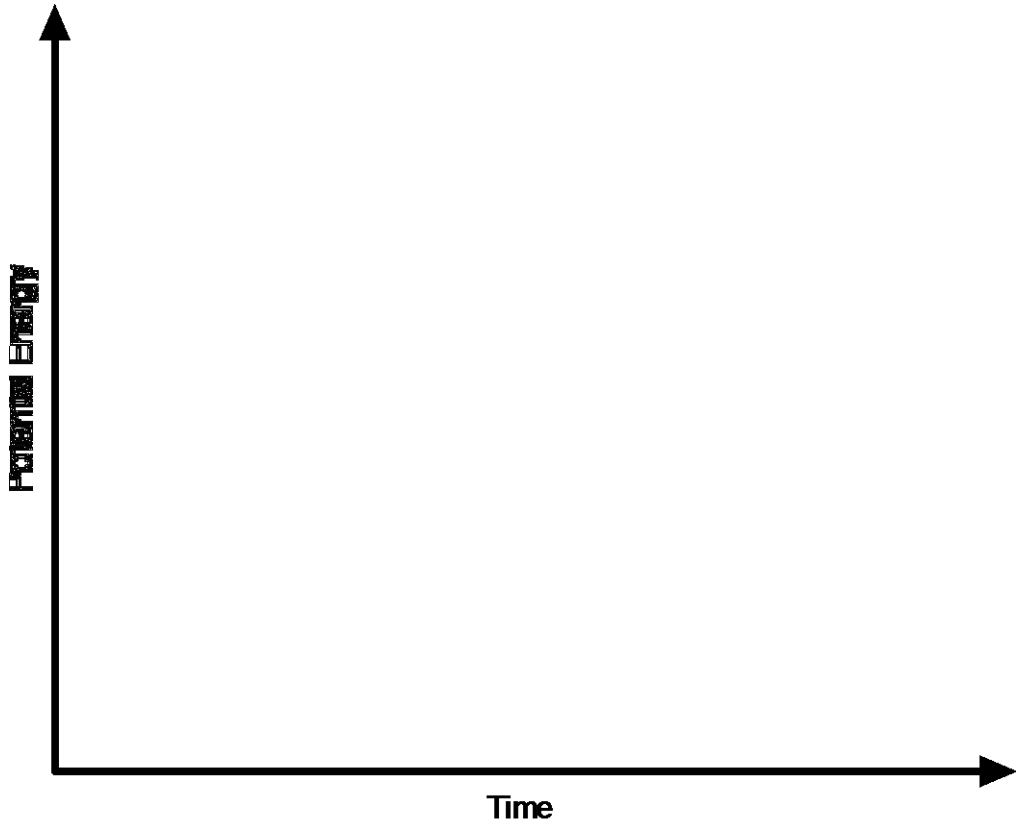
therefore,

- the potential energy curve will have one “bump” for each elementary process of the mechanism

The OVERALL ACTIVATION ENERGY for a rxn mechanism is measured by the RATE DETERMINING STEP (slowest step) ONLY!

- the speed of all steps are compared, there is only ONE slow step per mechanism

Graphing the Mechanism



Rxn Mechanism Examples

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

$NO_{3(g)} \rightarrow NO_{(g)} + O_{2(g)}$ fast

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

Reaction intermediate(s):
Catalyst:
Reactants:
Products:

2) $CO_{(g)} + OH_{(g)} \rightarrow CO_{2(g)} + H_{(g)}$
$H_{(g)} + O_{2(g)} \rightarrow HOO_{(g)}$
$HOO_{(g)} + NO_{(g)} \rightarrow NO_{2(g)} + OH_{(g)}$

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

Reaction intermediate(s):
Catalyst:

3) $CFCl_3 \rightarrow CFCl_2 + Cl$
$Cl + O_3 \rightarrow ClO + O_2$
$ClO + O \rightarrow Cl + O_2$

Overall rxn:
Reaction intermediate(s):
Catalyst:

4) $Cl_2 \rightarrow Cl^{+} + Cl^{-1}$ slow

$Cl^{-1} + H_2S \rightarrow HCl + HS^{-1}$

$Cl^{+} + HS^{-1} \rightarrow HCl + S$ (endothermic)

Overall rxn:

Rxn intermediate(s):

Catalyst:

graph it…

If a step (or parts of a step) are missing…

1. Write the overall rxn (in proper order)
2. Write each step (backwards…products as reactants…)
3. Add the overall & steps (cross off whatever you can)
   - what you have left is the actual step or missing parts written properly (reactants on reactant side…)

Let’s try it…

5) $2NO + ? \rightarrow N_2O + H_2O$ slow

$N_2O + H_2 \rightarrow ? + H_2O$

$2NO + 2H_2 \rightarrow N_2 + 2H_2O$ endothermic

How to solve it?

$2NO + 2H_2 \rightarrow N_2 + 2H_2O$ overall

$+ N_2O + H_2O \rightarrow 2NO$ step 1 reversed

$+ H_2O \rightarrow N_2O + H_2$ step 2 reversed

Cancel like terms & add left over terms

$2NO + 2H_2 \rightarrow N_2 + 2H_2O$

$+ N_2O + H_2O \rightarrow 2NO$

$+ H_2O \rightarrow N_2O + H_2$

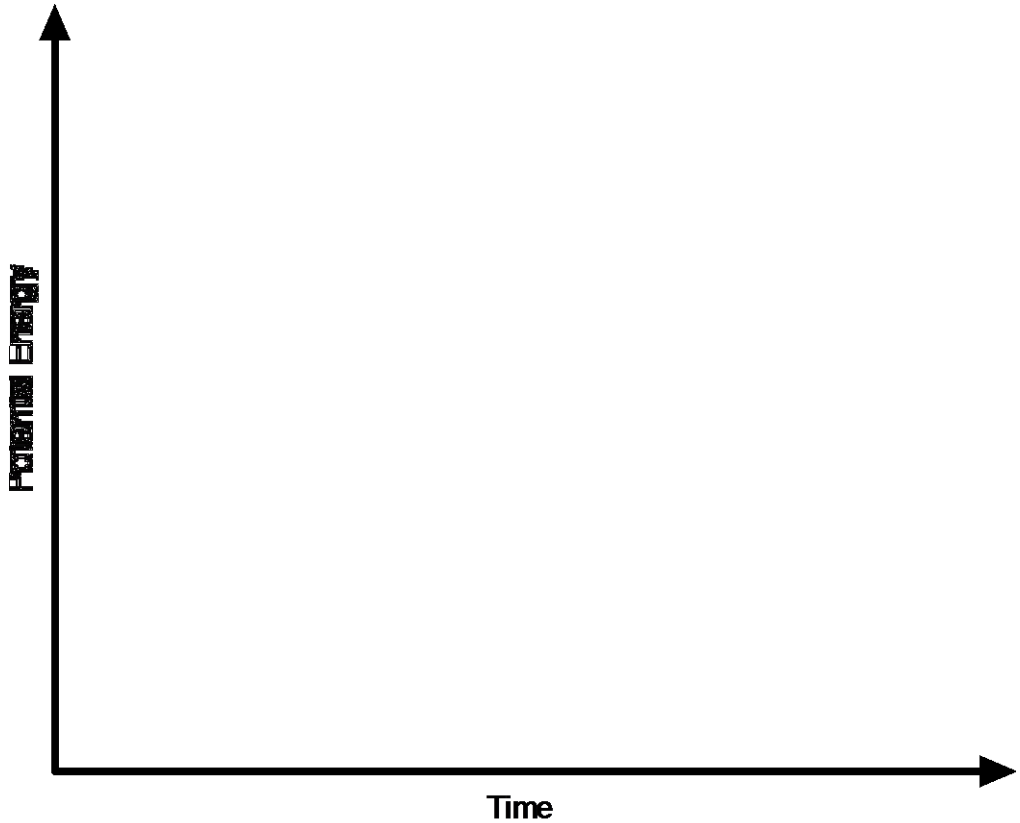
$H_2 \rightarrow N_2$ missing terms

Remember that the "answer" ends up in proper order so the answer is….

$2NO + \underline{H_2} \rightarrow N_2O + H_2O$ slow

$N_2O + H_2 \rightarrow N_2 + H_2O$

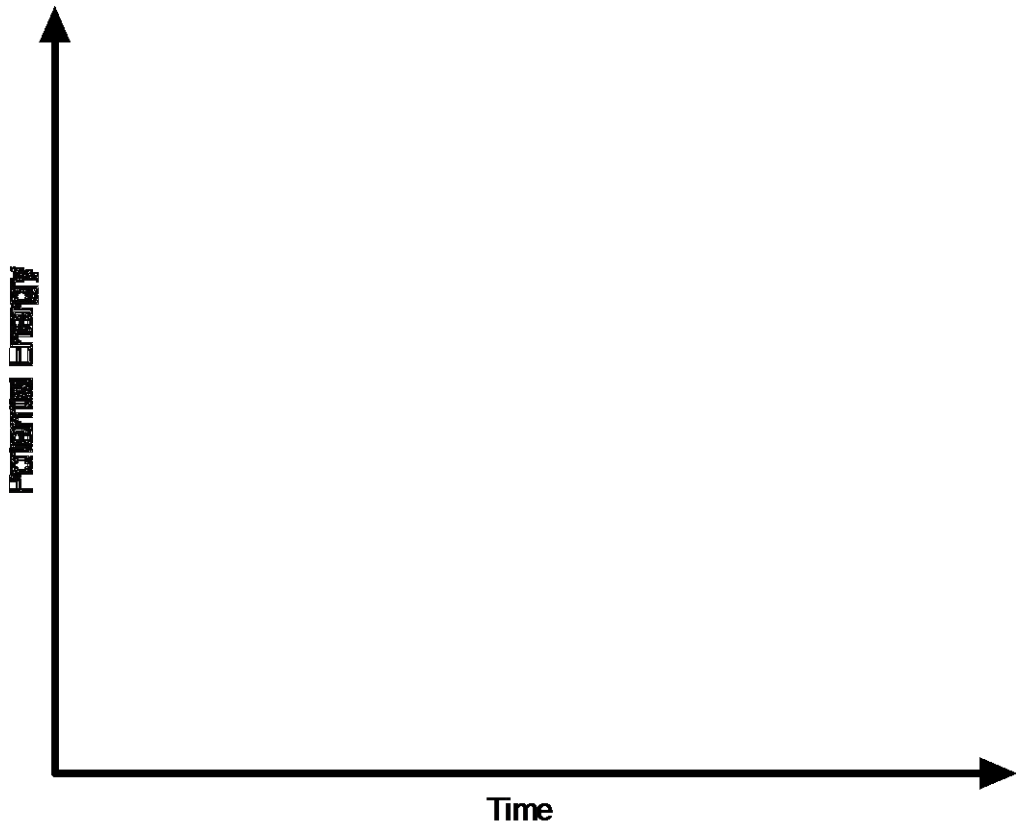
$2NO + 2H_2 \rightarrow N_2 + 2H_2O$ endothermic



6) $2NO \rightarrow N_2O_2$ fast

slow (missing step)

$2NO + O_2 \rightarrow 2NO_2$ overall (exothermic)



7) Step 1:

Step 2: $I + H_2 \rightarrow H_2I$

Step 3: $H_2I + I \rightarrow 2HI$ slow

Rxn $H_2 + I_2 \rightarrow 2HI$ exothermic