REACTION KINETICS

A. REACTION KINETICS AND RATES OF REACTION

1. Reaction kinetics is the study of the **rates of reactions and the factors which affect the rates.**

RATE OF REACTION = **speed at which a reaction occurs**

- Expressed in terms of the **change in amount** of a reactant (consumption/decrease) or product (production/increase) in a **certain interval of time.**

$$\text{Rate} = \frac{\Delta \text{ Amount of reactants or products}}{\Delta \text{ Time}}$$

- The rates of reactants and products are related by their **mole ratios in the balanced equation.**

$$A + 3B \rightarrow 2C + D$$

$$\text{Rate B} = \text{Rate A} \times \frac{3B}{A}$$

$$\text{Rate C} = \text{Rate A} \times \frac{2C}{A}$$

$$\text{Rate D} = \text{Rate A} \times \frac{D}{A}$$

EXAMPLE 1.1 CALCULATING REACTION RATE

a) What is the rate of a reaction if 23.5 g of magnesium is used up after 6 min.

$$\textit{Rate of Using Mg} = \frac{23.5\ g}{6.0\ min} = \mathbf{3.92\ g/min}$$

b) Consider the following reaction:

$$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(g)$$

If the rate of production of $CO_2(g)$ is 2.38×10^{-5} mol/min, what is the rate of consumption of $C_4H_{10}(g)$?

Use mole ratio from balanced equation:

$$\frac{2.38 \times 10^{-5}\ mol\ CO_2}{min} \times \frac{2C_4H_{10}}{8CO_2} = \mathbf{5.95 \times 10^{-6}\ mol\ C_4H_{10}/min}$$

c) What is the rate of production of $H_2O(g)$ in g/min, if the rate of consumption of $C_4H_{10}(g)$ is 7.23×10^{-3} g/min?

Change to moles and use ratio from balanced equation:

$$\frac{7.23 \times 10^{-3}\ g}{min} \times \frac{mol}{58.0\ g} \times \frac{10H_2O}{2C_4H_{10}} \times \frac{18.0\ g}{mol} = \mathbf{1.12 \times 10^{-2}\ g/min}$$

EXAMPLE 1.2 CALCULATING REACTION RATE

Consider the following reaction:

$$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$$

The following data is collected:

Time (min)	Mass of Beaker and Contents (grams)
0.0	256.3
2.0	255.7
4.0	255.1
6.0	254.5

a) What is the rate of production of $H_2(g)$ in mol/s?

The change in mass is a result of $H_2(g)$ escaping and hence H_2 production

$$Rate = \frac{\Delta\ mass\ H_2}{\Delta\ time}$$

$$\frac{1.8\ g\ H_2}{6.0\ min} = 0.30\ g\ H_2/min$$

Convert to mol/s

$$\frac{0.30\ g}{min} \times \frac{mol}{2.0\ g} \times \frac{min}{60\ s} = \mathbf{0.0025\ mol\ H_2/s}$$

b) What is the rate of Al(s) consumption in g/s for the same interval as in (a)?

Use mole ratio to convert from moles of H_2(g) to moles of Al(s) and then molar mass of Al to change from moles to grams.

$$\frac{0.0025\ mol\ H_2}{s} \times \frac{2\ Al}{3\ H_2} \times \frac{27.0\ g}{mol} = \mathbf{0.045\ g/s}$$

2. Consider the following reaction:

$$\underset{\text{brown}}{Cu(s)} + \underset{\text{colourless}}{4HNO_3(aq)} \rightarrow \underset{\text{blue}}{Cu(NO_3)_2(aq)} + \underset{\text{brown}}{2NO_2(g)} + 2H_2O(l) + \text{heat}$$

The reaction rate can be monitored by measuring the following and graphing the change against time:

a) **MASS CHANGE**

- Open system, the $NO_2(g)$ escapes, total mass of system decreases.
- Electronic **balance** and stopwatch.

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

b) **COLOUR CHANGE**

- **Spectrophotometer** and stopwatch.
- Colour intensity increases as more $Cu(NO_3)_2(aq)$ is produced.

$$\text{Rate} = \frac{\Delta \text{ colour intensity}}{\Delta \text{ time}}$$

c) **PRESSURE CHANGE**

- Closed (sealed) container, a **pressure gauge** and stopwatch.
- To measure pressure change, there must be a change in the total number of moles of gas in the reaction.

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

d) **TEMPERATURE CHANGE**

- Exothermic = temperature increases, endothermic = temperature decreases.
- **Thermometer** and stopwatch

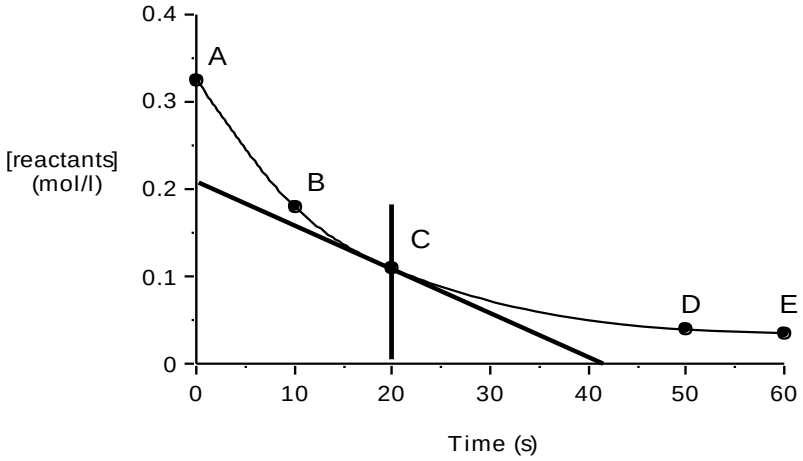
$$\text{Rate} = \frac{\Delta \text{ temperature}}{\Delta \text{ time}}$$

e) **pH CHANGE**

- **pH meter** and stopwatch.
- $HNO_3(aq)$ used up, acidity decreases and pH of the solution increases.

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

3. Rates of reaction do not typically remain constant for the entire duration of a reaction.



- Initially, rates are fast because **[reactants] are high.**
- Rates decrease as reaction proceeds since [reactants] decrease

> The exact rate at any particular time can be obtained by determining the **slope of a line that is tangent** to the concentration–time curve at that point.

4. Some reactions may show an increase in rate after a slow start:
   a) **exothermic** reactions
   b) changes in **surface area**
   c) coatings on reactant surface
   d) **autocatalysis**

B. FACTORS AFFECTING REACTION RATES

1. The factors that affect the rate of a reaction are as follows:

a) **TEMPERATURE**

- When temperature is increased, the time required for a reaction decreases.

$$\text{Rate} = \frac{\Delta \text{ Amount of reactant or product}}{\Delta \text{ time}}$$

- **Increasing temperature increases rate.**

In general, for slow reactions, a **10°C increase in temperature doubles reaction rate.**

EXAMPLE 1.3 PREDICTING CHANGES IN RATE DUE TO TEMPERATURE CHANGE

If the rate of a slow reaction is 7.34×10^{-3} mol/min at 20°C, what would the rate be at 60°C and at 0°C?

Rate (60°C) = (7.34 × 10^{-3} mol/min) × 2 × 2 × 2 × 2 = ***0.117 mol/min***

(7.34 × 10^{-3} mol/min) × ***2^4*** *=* ***0.117 mol/min***

Rate (0°C) = (7.34 × 10^{-3} mol/min) × ½ × ½ = ***1.84 × 10^{-3} mol/min***

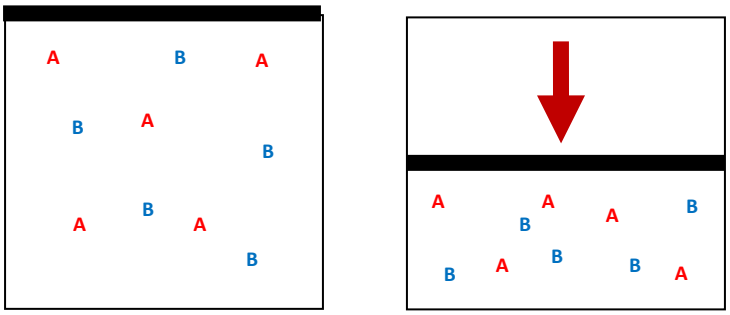
(7.34 × 10^{-3} mol/min) × ***2^{-2}*** *=* ***1.84 × 10^{-3} mol/min***

b) **CONCENTRATION**

- **Increasing reactant concentration increases rate.**

c) **PRESSURE**

- Partial pressure of a gas is proportional to the moles of a gas when temperature is constant.
- **Increasing partial pressure of a gas** is equivalent to increase concentration; therefore, **increases rate.**



d) **NATURE OF REACTANTS**

- Some reactions are naturally faster than others.
- Reactions that involve **breaking weak bonds or transferring electrons** that are weakly held are faster than those in which bonds are strong and electrons are held strongly.
- These are **fundamental differences in the chemical reactivity** of different substances which we have no control.

EXAMPLE 1.5 NATURE OF REACTANTS

a) Consider the reaction of alkali metals with water:

$$2Li(s) + 2H_2O(l) \rightarrow 2Li^+(aq) + 2OH^-(aq) + H_2(g) + Energy$$
$$2Na(s) + 2H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq) + H_2(g) + Energy$$

Reaction with Na occurs faster because Na's $3s^1$ electron is more weakly held than Li's $2s^1$ electron.

b) Consider the oxidation of the iron (II) ion and oxalate ions by the permanganate ion:

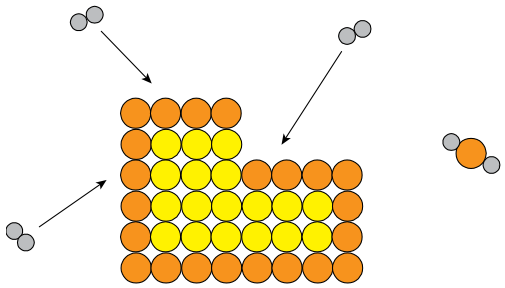
$$\underset{\text{purple}}{5Fe^{2+} + MnO_4^- + 8H^+} \rightarrow \underset{\text{colourless}}{5Fe^{3+} + Mn^{2+}} + 4H_2O$$

$$\underset{\text{purple}}{5C_2O_4^{2-} + 2MnO_4^- + 16H^+} \rightarrow \underset{\text{colourless}}{10CO_2 + 2Mn^{2+}} + 8H_2O$$

First reaction only involves electron transfer, second reaction involves bond breakage; therefore, first reaction will have higher rate.

e) **SURFACE AREA**

- **HETEROGENEOUS** reactions = reactants are in different phases (i.e., solid and liquid or solution).
- **Increasing exposed area (surface area) increases rate.**
- Crushing, powdering, grinding, etc.



Surface area is the one factor that **will affect the rate of heterogeneous reactions (different phases) but not homogeneous reactions (same phase).**

f) **CATALYSTS AND INHIBITORS**

- **CATALYST** = chemical which increase reaction rate but is **regenerated in its original form at the end of a reaction.**
- **INHIBITOR** = chemical substance that reduces reaction rate by combining with a catalyst or one of the reactants in such a way that it prevents the reaction from occurring.

2. The phase of the reactants is also an important consideration that will affect reaction rates. In general, reactions that have reactants:

i) with **oppositely charged aqueous ions** are very fast;

Aqueous Ions > Gases or Liquids > Solids

ii) with **few bonds or weak bonds** are faster than those with many bonds or strong bonds;

iii) in **homogeneous** phases are faster than those in **heterogeneous** phases;

iv) undergoing a **2 particle collision** are faster than those involving 3 or more particles.

EXAMPLE 1.6 PREDICTIING REACTION RATES

Which of the following reactions would you expect to be the (a) fastest and (b) slowest?

a) $2Fe(s) + O_2(g) \rightarrow 2FeO(s)$

b) $CaO(s) + 3C(s) \rightarrow CaC(s) + CO_2(g)$

c) $SnO_2(s) + 2CO(g) \rightarrow Sn(s) + 2CO_2(g)$

d) $2AgNO_3(aq) + Na_2CrO_4(aq) \rightarrow Ag_2CrO_4(s) + 2NaNO_3(aq)$

a) heterogeneous reaction

b) both reactants solid, molecules not free to move about → ***SLOWEST***

c) heterogeneous reaction

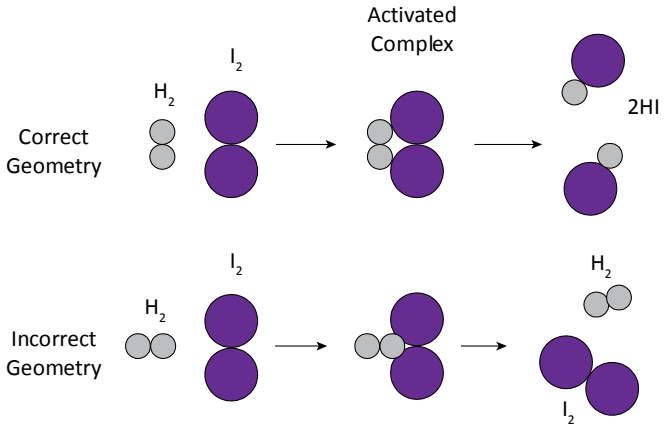
d) aqueous ions can mix freely → ***FASTEST***

C. REACTION RATES AND COLLISION THEORY

1. The **COLLISION THEORY** (or **Kinetic Molecular Theory**) states that reactions depend on collisions between reactant molecules; however,
   - **not all collisions lead to a reaction.** Successful or effective collisions lead to the formation of products while those that don't are ineffective or unsuccessful.
   - The effectiveness of a collision is determined by two general factors:

   a) **ORIENTATION OR GEOMETRY**
   - Colliding reactant molecules must be oriented in a **favourable position to allow bonds to break and atoms to rearrange.**

   Consider the reaction: $H_2 + I_2 \rightarrow 2HI$



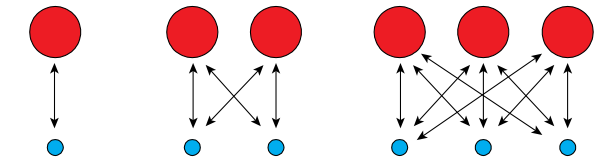
   b) **ACTIVATION ENERGY**
   - For a reaction to occur, molecules need to collide with **sufficient energy to break bonds so that atoms can rearrange and form new bonds.**

ACTIVATION ENERGY = **MINIMUM amount of energy needed for a reaction to occur.**

2. Collision theory explains why increasing concentration and temperature increase reaction rate.

a) **Effect of Increasing Concentration**

- Increasing the concentration of reactants (or partial pressure if gases) increases the **frequency** of possible collisions and hence increases the rate.
- The **percentage or fraction** of collisions that are effective **remains the same.**



- Rate law states:

$$\text{Rate } \alpha\ [A]^a[B]^b[C]^c$$

b) **Effect of Increasing Temperature**

- Increasing temperature increases the **average kinetic energy** of the molecules (i.e., increases the speed at which the molecules are moving).
- Two effects: **(i) molecules collide more often; and (ii) molecules collide with more energy.**
- Increasing temperature **increases the percentage or fraction of effective collisions.**
- Increase in rate that accompanies and increase in temperature is **primarily due to the increase energy of collisions.**

D. ENERGY CHANGES IN CHEMICAL REACTIONS

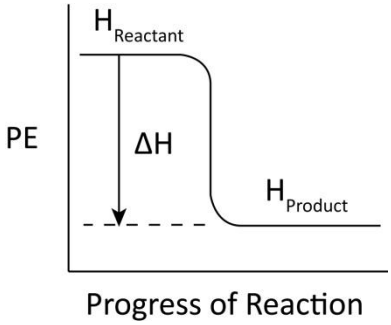
1. **POTENTIAL ENERGY** = stored energy
   - Related the energy of the **electrons in the chemical bonds, as well as the number and types of atoms in the molecule.**
   - Potential energy increases when bonds are broken and decreases when new bonds are formed.

   KINETIC ENERGY = energy of motion
   - Energy exists as a result of **movement of molecules within a system.**
   - Kinetic energy can be related to the **temperature** of the system.

   ENTHALPY (H) = heat of reaction
   - **TOTAL kinetic and potential energy** which exists in a system at constant pressure.

$\Delta H = H_{products} - H_{reactants}$
Pronounced "delta H"

2. During a chemical reaction, the bonds of the reactant molecules are broken, the atoms are re–arranged and new bonds are formed.
   - Heat may be transferred into or out of a system and as a result, the **enthalpy of the reactants and products will be different.**
   - The changes in potential energy that occur during a chemical reaction can be expressed graphically in terms of a **potential energy diagram.**



   - When the products have less enthalpy than the reactants, **heat is GIVEN OFF to the surroundings and it is said to be EXOTHERMIC.**

$\Delta H = H_{products} - H_{reactants}$ (the value of **$\Delta H < 0$**)

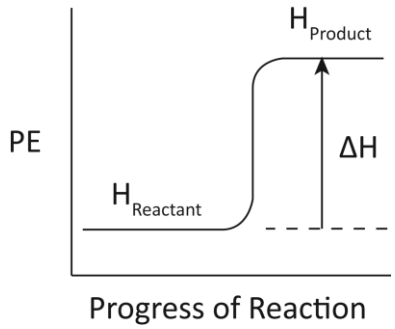
- An exothermic reaction can be expressed as an equation in two ways:

$$H_2 + Cl_2 \rightarrow 2HCl + \mathbf{184\ kJ}$$

or

$$H_2 + Cl_2 \rightarrow 2HCl \qquad \mathbf{\Delta H = -184\ kJ}$$

3. Contrasting PE diagram:



- When the products have more enthalpy than the reactants, **heat is ABSORBED from the surroundings and it is said to be ENDOTHERMIC.**

$$\Delta H = H_{products} - H_{reactants} \qquad \text{(the value of } \mathbf{\Delta H > 0}\text{)}$$

- An endothermic reaction can be expressed as an equation in two ways:

$$2N_2 + O_2 + \mathbf{164\ kJ} \rightarrow 2N_2O$$

or

$$2N_2 + O_2 \rightarrow 2N_2O \qquad \mathbf{\Delta H = +164\ kJ}$$

EXOTHERMIC $\rightarrow$ $H_{products} < H_{reactants}$ $\rightarrow$ ΔH is negative

ENDOTHERMIC $\rightarrow$ $H_{products} > H_{reactants}$ $\rightarrow$ ΔH is positive

E. KINETIC ENERGY DISTRIBUTIONS

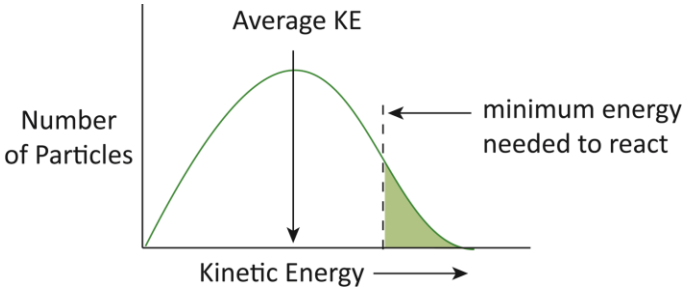
1. Consider the reaction:

$$C_2H_5OH \rightarrow C_2H_4 + H_2O$$

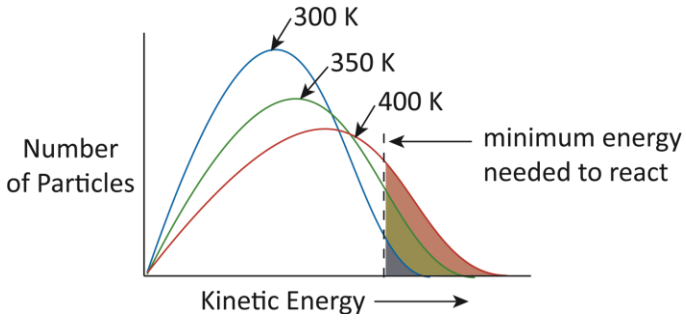
At room temperature this reaction is very slow and the rate is not detectable; however molecules at room temperature and pressure undergo about 10^{10} collisions/second so the **lack of reactivity is not due to lack of collisions.**

2. When the temperature is increased, the reaction rate increases. This occurs because the **molecules have more energy.**

- At a given temperature the energy of the molecules can be shown as a **distribution.**



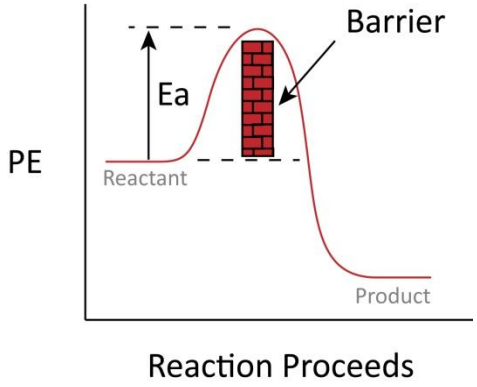
- Some molecules have high KE while others have low KE (distribution).
- Increasing temperature increases the **average energy of the system.**
- Only the molecules with **KE ≥ minimum energy will react.**



- Although more collisions may occur when the temperature is increased, the increased reaction rate due to an increase in temperature is **PRIMARILY DUE to the increased number of molecules with sufficient energy to react.**

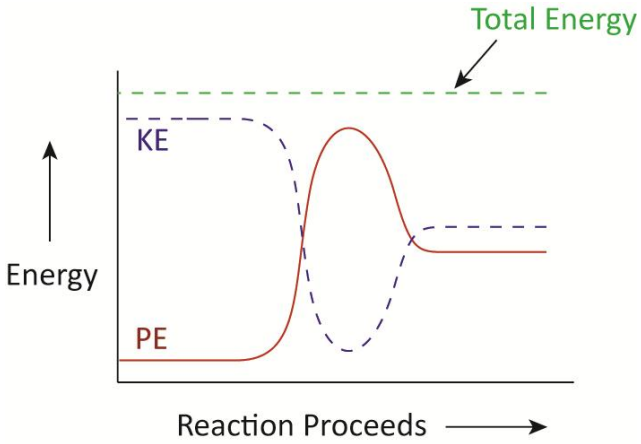
F. ACTIVATION ENERGIES

1. The existence of a **minimum energy requirement** before a molecule can react means that there is a "barrier" to overcome.



ACTIVATION ENERGY (E_a) = the MINIMUM amount of energy required for reactants to form the activated complex.

2. When reactant molecules approach each other during a chemical reaction, they slow down and their **kinetic energy is converted to potential energy.**

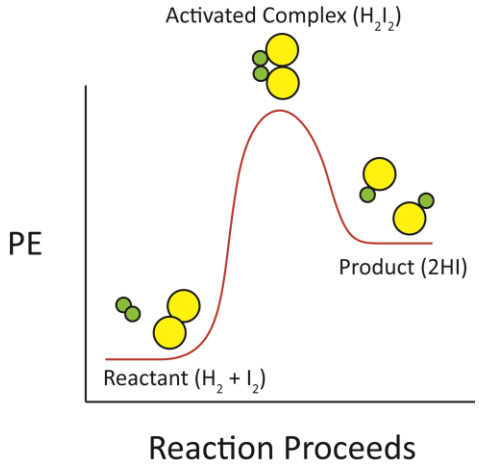


- If the molecules can gain enough PE, bonds can be broken and new bond made and an **ACTIVATED COMPLEX** is formed.

ACTIVATED COMPLEX = high energy, unstable arrangement of atoms which occurs when reactants are in the process of rearranging to form products (reaction intermediate)

- After the reaction occurs, the newly formed molecules repel each other and speed up. PE is then converted to KE as the product molecules move away from each other.

Total Energy = Potential Energy + Kinetic Energy

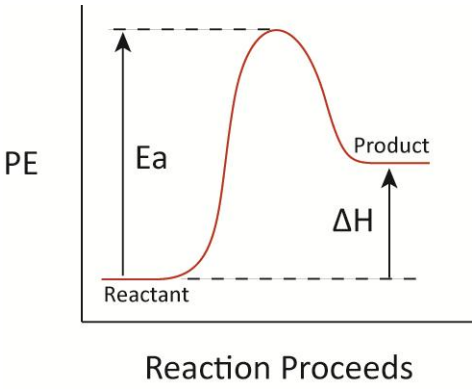


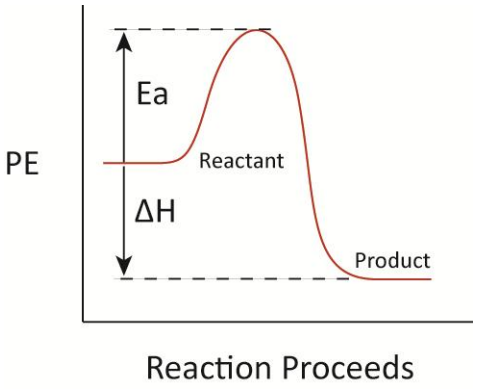
- On the PE diagram, the reactants are assumed to collide with **ideal geometry.**
- If the molecules do not have ideal geometry, a reaction can still take place but it is reflected as an **increase in activation energy.**

2. Consider the PE diagrams for and exothermic and endothermic reaction:

i) Activation Energy (E_a) is the energy **difference between reactant and activated complex**

ii) Change in Enthalpy (ΔH) is the **difference between reactant and product**

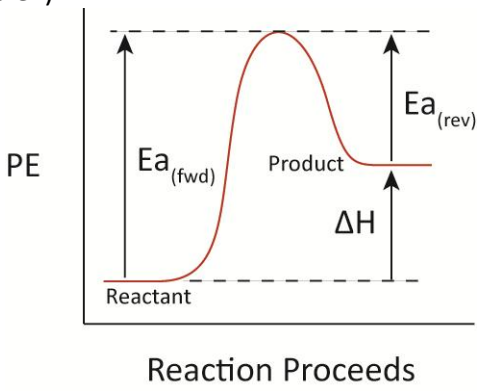




iii) For a reversible reaction,

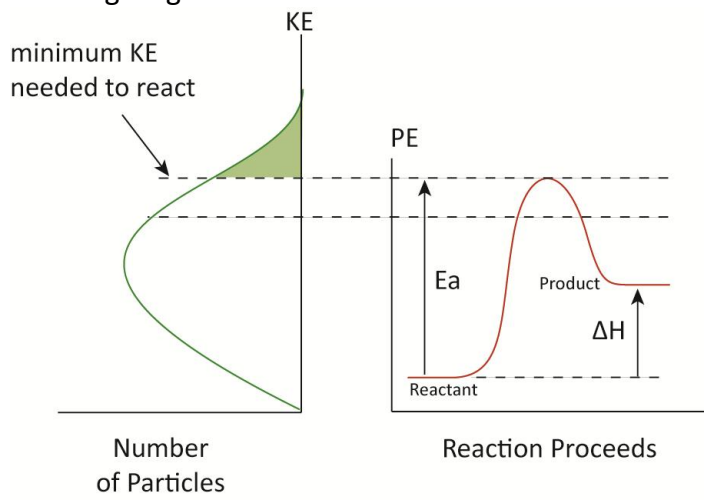
$$\text{Reactant} \rightleftarrows \text{Product}$$

- E_a(fwd) refers to the activation energy for the forward reaction (reactant to activated complex)
- E_a(rev) refers to the activation energy for the reverse reaction (products to activated complex).



3. The rate of a reaction can be related to the activation energy of the reaction.

Consider the following diagram:



A relationship can be seen when we compare the KE distribution to a PE diagram:

- **E_a very high**, few molecules will have enough energy to react, **REACTION RATE will be low.**
- **E_a low**, more molecules will have enough energy to react, **REACTION RATE will be high.**

The higher the activation energy, the slower the reaction rate and vice versa.

G. REACTION MECHANISMS

1. Most reactions do not occur in one step:
   - Unlikely that **several particles would collide simultaneously with sufficient energy and correct orientation**
   - Reactions often occur as a result of **several steps**

> **ELEMENTARY PROCESSES = collisions involving only 2 particles**

2. Consider the following reaction:

$$4HBr(g) + O_2(g) \rightarrow 2H_2O(g) + 2Br_2(g)$$

- Unlikely 4 HBr molecules and 1 O_2 molecule will collide simultaneously to undergo a chemical change. Instead, the reaction occurs in more than one step.

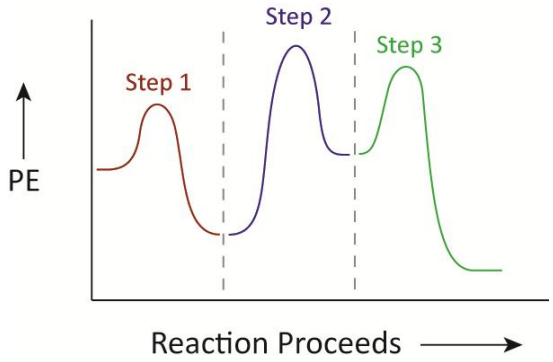
$HBr(g) + O_2(g) \rightarrow HOOBr(g)$	slow
$HOOBr(g) + HBr(g) \rightarrow 2HOBr(g)$	fast
$2HOBr(g) + 2HBr(g) \rightarrow 2H_2O(g) + 2Br_2(g)$	fast

$$4HBr(g) + O_2(g) \rightarrow 2H_2O(g) + 2Br_2(g)$$

- Overall equation can be found by **adding up all the chemical species on the left and the right and canceling out similar species.**

> **REACTION MECHANISM = sequence of steps which makes up an overall reaction**

3. PE diagram of a reaction mechanism:



- **Each step will have its own peak** (a 3 step mechanism will have three peaks, a 4 step mechanism will have 4 peaks etc.)
- Overall activation energy is the **difference between reactants and highest peak.**

- The activation energy for each step is the PE difference between the activated complex and the reactants involved in that step.
- The step with the **highest E_a** in the PE diagram is called the **rate determining step.**

RATE DETERMINING STEP = the slowest step in a mechanism (acts as a "bottle–neck")

EXAMPLE 1.7 DETERMINING THE OVERALL REACTION FROM A MECHANISM

What is the overall reaction for the following reaction mechanism?

$$A + B_2 \rightarrow AB_2$$
$$AB_2 + A \rightarrow A_2B_2$$
$$A_2B_2 + C_2 \rightarrow 2AC + B_2$$

$$2A + 2C \rightarrow 2AC$$

EXAMPLE 1.8 IDENTIFYING REACTION INTERMEDIATES

What is the missing species?

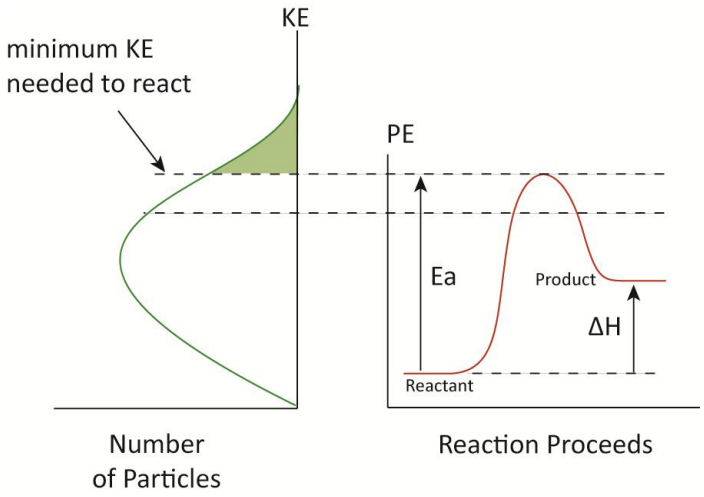
$$NO + H_2 \rightarrow H_2O + N$$
$$NO + H_2 \rightarrow H_2O + N$$
$$?$$

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

$$N + N \rightarrow N_2$$

H. THE EFFECTS OF CATALYSTS ON THE ACTIVATION ENERGY

1. We know that catalysts are chemical substance that speed up a chemical reaction. The problem however, is how does this increase occur?



- Catalysts do not change the energy difference between reactants and products and hence **ΔH for the reaction does not change.**
- A catalyst **lowers the activation energy of a reaction.** As a result, more molecules have enough energy to react and hence the reaction rate increases.
- A catalyst will **decrease the E_a for both the forward and reverse reaction.**

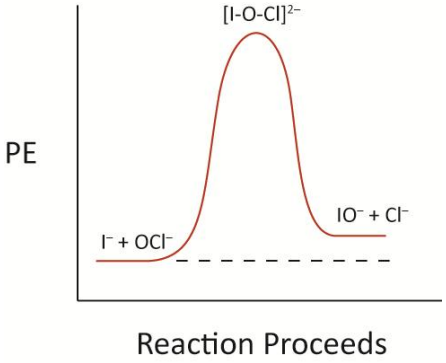
Catalyst work by providing an alternative mechanism having a lower activation energy.

- It is important to note that although the catalyzed reaction has a lower activation energy, the original pathway is still available; however very few reactants will go over the higher "energy hump", relative to the numbers that go over the lower, catalyzed hump.

2. Consider the following reaction:

$$OCl^- + I^- \rightarrow OI^- + Cl^-$$

- The uncatalyzed reaction has a very high activation energy because it requires two negatively charged ions to approach each other and react.



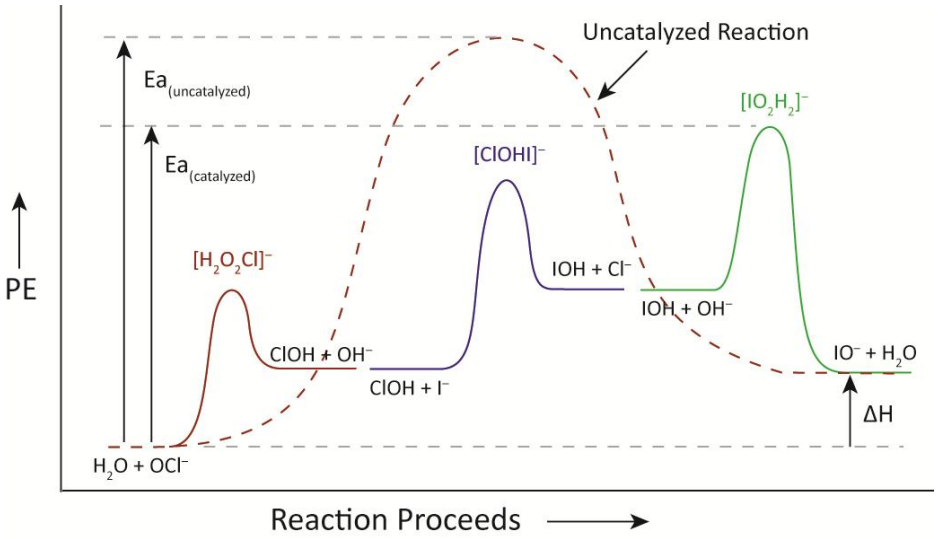
- With water acting as a catalyst, an alternate mechanism with a lower overall activation energy is available.

Step 1: $OCl^- + \mathbf{H_2O} \rightarrow [Cl–O–\mathbf{H}–\mathbf{O}–\mathbf{H}]^- \rightarrow ClOH + OH^-$

Step 2: $I^- + ClOH \rightarrow [I–\mathbf{O}–Cl]^- \rightarrow IOH + Cl^-$

$\quad\quad\quad

- The PE diagram below represents the situation when a catalyst is added.



i) The catalyst **(H_2O)** is an active participant in the reaction which is **REGENERATED** in a later step of the reaction mechanism.

ii) The change in enthalpy, ΔH, for the overall reaction **remains the same; only the intermediate reaction details differ.**

iii) Both **intermediate** species and **catalyst** cancel out when the individual steps are added to get the overall reaction.

iv) Intermediate species **(ClOH, IOH, and OH^-)** do not appear in the overall reaction because they are first produced and then used up as reactants in subsequent steps. The catalyst, H_2O, is initially used up as a reactant and then subsequently produced in a later step.

REACTION INTERMEDIATE → **Product then reactant**

CATALYST → **Reactant then product**

3. Some common catalysts:

a) Most biological reactions are initiated or aided by catalysts called **ENZYMES**. Enzymes are protein molecules which have a particular shape and composition to catalyze a specific reaction. The molecule that the enzyme acts on is called the **"SUBSTRATE".**

e.g. malt***ase***, ethanol dehydrogen***ase***

b) **Platinum** is a common catalyst used in many industrial process such as the production of sulphuric acid, H_2SO_4.

c) The **catalytic converter** in automobiles contain particles of platinum, palladium, and rhodium which convert CO and unburned hydrocarbons to CO_2 and H_2O.

d) One of the most commonly used catalysts in chemistry is **H^+(aq), found in solutions of acids.**