# Unit 4, Lesson 03: Collision Theory and the Rates of Chemical Reactions

<u>Collision theory</u> states that in order for a chemical reaction to occur, the reactant atoms or molecules must collide with each other.

- when molecules approach one another, the valence electrons from one molecule repel the valence electrons in the other molecule and distort the existing bonds
- if the reactant molecules collide with sufficient energy and in the correct orientation, the repulsion between valence electrons will break the existing bonds, allowing new (lower energy) bonds to form. This is called an "effective collision"



• if the reactant molecules do not collide with sufficient energy or collide in the wrong orientation, the existing bonds are not broken and no reaction occurs. This is called an "ineffective collision"



- the minimum amount of energy required for a successful collision is called "activation energy", Ea
- the "activated complex" is a theoretical high energy particle that exists for a fraction of a second at the instant the particles collide. The activated complex can break down into either the reactants in an ineffective collision or the products in an effective collision
- by controlling the collisions of the reactants, we can control the rate at which chemical reactions occur

# H-S + CH<sub>3</sub>Br $\rightarrow$ H-S-CH<sub>3</sub>-Br $\rightarrow$ HSCH<sub>3</sub> + Br (atom)

### **Potential Energy Changes During Chemical Reactions**

The energy changes during a chemical reaction can be graphed as a "reaction pathway":

Reaction Progress

Reaction pathways show:

- 1. <u>Activation Energy ( $E_a$ )</u>: the minimum amount of energy that is required for a reaction to occur.
- if the activation energy is low, the reaction will occur relatively easily
- if the activation energy is high, it is much less likely that the reaction will occur (the bonds in the reactants are too difficult to break for the reaction to proceed)
- in general, the lower the activation energy, the faster the reaction rate
- 2.  $\Delta$ **H**: the net change in enthalpy between the reactants and products if a reaction does occur.
- if  $\Delta H$  is negative, the products are lower energy than the reactants. The reaction is exothermic and will likely occur if the activation energy can be reached
- if  $\Delta H$  is positive, the products of the reaction are higher energy than the reactants. The reaction is endothermic and energy must be put into the system in order for the reaction to occur

A model may help you to visualize the energy changes during a reaction:

- a) Activation energy:
- the man must roll the rock to the top of the hill before the reaction will proceed
- the bigger the hill, the greater the Ea
- b) Activated complex:
- at the top of the hill, the rock is very high energy and can roll either way
- c)  $\Delta \mathbf{H}$ :
- after the "reaction", the rock has lower potential energy than before, so the reaction from  $A \rightarrow B$  is exothermic
- if the rock rolled to position "C", it would have higher potential energy than before the reaction, so the reaction from  $A \rightarrow C$  is endothermic



The model also shows that the reaction is **reversible**.

If the rock is in position B, it is entirely possible to push it back into position A, but it will take a great deal of energy to roll the rock back up the hill in the reverse direction.

- the activation energy for the reverse reaction is so high, it is very unlikely that the reaction can be made to occur without a huge input of energy
- the reverse reaction from  $B \rightarrow A$  is also endothermic
- the fact that the E<sub>a</sub> for the reverse reaction is so large, and the reverse reaction is endothermic means that the reverse reaction, while possible, is unlikely

### **Summary:**

Many reactions are reversible and can occur in both directions. Which direction is favoured depends on two factors: the activation energy and  $\Delta H$ .

Activation energy  $(E_a)$  determines the rate of the forward and reverse reactions. The lower the Ea, the faster the rate.

Enthalpy change ( $\Delta H$ ) determines whether the reaction will proceed once it gets going. Exothermic reactions will proceed because they produce lower energy products. Endothermic reactions need energy to be put in before the reaction will proceed.

There is no direct relationship between  $E_a$  and  $\Delta H$ .

### **Examples:**



reaction progress



- the forward reaction is exothermic with a small  $E_a$
- the forward reaction is very likely to proceed and will occur rapidly
- the reverse reaction is endothermic with a large  $E_a$
- the reverse reaction is less likely to proceed, and the rate of the reaction will be slow
- the rate of the forward reaction will be faster than the rate of the reverse reaction

- the forward reaction is endothermic with a large  $E_a$
- the forward reaction is unlikely to proceed and will occur slowly
- the reverse reaction is exothermic with a lower E<sub>a</sub>
- the reverse reaction will be more likely to proceed, but the E<sub>a</sub> is still large and the rate of the reaction will be slow
- the rate of the reverse reaction will be faster than the forward reaction

**Note**: there is no direct relationship between  $E_a$  and  $\Delta H$ 

Factors that affect the rate of a chemical reaction:

- 1. <u>**Temperature**</u>: temperature is a measure of the *average* kinetic energy of the particles in a substance (how fast the particles in a substance, on average, are moving). Some particles are moving faster than the average temperature and some are moving slower
- if temperature is increased, the particles will move faster on average
- the graph below is called a Maxwell-Boltzmann distribution which shows the relative proportions of particles that have enough energy to meet the activation energy at two temperatures: a lower temperature, T<sub>1</sub> and a higher temperature T<sub>2</sub>. As the temperature (the average kinetic energy) increases, a larger proportion of particles have sufficient energy to achieve the activation energy and complete the reaction:



- also, when temperature is increased, because the particles are moving faster, there will be more collisions between reactants. If there are more collisions, the reaction will happen more quickly and the reaction rate will increase
- so, increasing the temperature increases the reaction rate for two reasons: more collisions and harder collisions
- on average, for every 10°C the temperature of a system increases, the reaction rate doubles
- 2. <u>Concentration</u>: concentration refers to the number of particles in a given volume. Concentration can refer to the number of gas particles in a certain volume (gas pressure) or the amount of solute in a solution (mol/L).
- the more concentrated the particles, the more "crowded" they are and the more frequently they will collide
- if there are more collisions, the rate of the reaction will increase
- as concentration of the reactants increases, the rate of the reaction will also (usually) increase

- 3. <u>Surface Area</u>: surface area refers to the amount of exposed surface of a reactant that is available for a collision.
- if the reactants are gases, the particles are free to move and collide, so there is a huge surface area that is exposed to react. As a rule, gas systems react very quickly.
- if one of the reactants is a solid or a liquid- the only particles that can react are the particles on the surface where the other reactants can collide with them. The particles inside a lump of solid are covered up and can not be hit by the other reactants. So, if we can spread the solid or liquid reactant out, it will increase the surface area so that more of the molecules are exposed to the other reactants, then there will be more collisions and a faster reaction rate
- for example, if we take a solid chunk of a chemical and grind it into a fine powder, there will be more surface area exposed and a faster reaction rate. Similarly, if we take a lump of metal and pound it out into a flat sheet, there will be more surface area and the reaction rate will increase.
- 4. <u>The Nature of the Reactants</u>: small, simple ions and molecules move through gases or solutions much more easily than larger "clumsy" molecules
- as a rule, the smaller the reactant particles, the faster the reaction rate
- ions in solution react particularly quickly because the charges on the ions attract each other and help to arrange the particles in the correct orientation. Precipitation reactions are almost instantaneous

# 5. The Presence of a Catalyst

- a <u>catalyst</u> is a substance that increases or decreases the rate of a reaction without being consumed itself
- often a catalyst works by holding reactant molecules in a certain orientation that puts stress on the bonds and makes the collisions with the other reactants more effective
- a catalyst does not change the overall reaction- it just makes it easier for the reaction to occur so the rate increases
- enzymes are protein molecules that act as catalysts in living systems. Enzymes bind onto reactant molecules and put stress on their bonds. When another reactant collides with the first reactant, then it is much easier to break the bonds and allow the reaction to move forward. So enzymes allow chemical reactions to occur at body temperature

Catalysts change the reaction rate by providing an alternative pathway for a reaction (a different activated complex is formed). Catalysts can be used to control the rate of a reaction:

- if E<sub>a</sub> is lowered, reaction rate will increase (a positive catalyst)
- if  $E_a$  is raised, reaction rate will decrease (a negative catalyst)



**Note**: a catalyst lowers the activation energy for both the forward and reverse reactions, but overall enthalpy change ( $\Delta$ H) is not changed

**Reaction Progress** 

### Unit 4, Lesson 03: Collision Theory and the Rates of Chemical Reactions

## Homework:

- 1. Read pages 289 to 294
- 2. On page 294, answer questions 13 16
- 3. On page 296, answer questions 2, 3, 4, 6, 7
- 4. Define: activation energy and activated complex (aka transition state).
- 5. Why, in general, does a reaction with a high activation energy have a low rate?
- 6. Why, in general, does a reaction with a low activation energy have a high rate?
- 7. A certain reaction has a **very** high activation energy and is slightly endothermic.
  - a) Sketch a possible potential energy diagram (reaction pathway) for the reaction.
  - b) On the diagram label the reactants, products, activated complex, heat of reaction ( $\Delta H$ ) and the activation energy ( $E_a$ ).
- 8. A certain reaction has a **very** low activation energy and is highly exothermic.
  - a) Sketch a possible potential energy diagram (reaction pathway) for the reaction.
  - b) On the diagram label the reactants, products, activated complex, heat of reaction ( $\Delta H$ ) and the activation energy ( $E_a$ ).
- 9. Many exothermic reactions (such as burning paper) require energy to get the reaction started, but they are able to sustain themselves one they start to burn. Explain why.
- 10. With regard to reaction rates, how might you:
- a) slow food spoilage
- b) slow the rusting of a car
- c) increase the rate of combustion for a campfire?