

CHEMICAL EQUILIBRIUM



Topics covered in this chapter:

- 1.1 Reaction Rate
- 1.2 Collision Theory
- 1.3 Changing Reaction Rate
- 1.4 Equilibrium
- 1.5 Equilibrium Constant
- 1.6 Le Chatelier's Principle

1.1 Reaction Rate

- Some chemical reactions can be very slow (such as the rusting of nails) while others (like the formation of precipitates) are extremely fast.
- Chemists are particularly keen to know what makes some reactions go faster than others, as this would allow them to favourably control important chemical reactions.
- For example, it would be an advantage to slow down reactions such as the formation of rust and speed up reactions such as the setting of glue.
- Hence it is particularly important for chemists to understand the factors, which influence reaction rate.

Measuring Reaction Rate

Several changes occur during a chemical reaction and any of them can be used to measure reaction rate.

Consider the reaction illustrated at below where hydrochloric acid has been added to granulated zinc:





Changes that take place during this reaction

- The mass of zinc decreases;
- The H^+ concentration decreases;
- The Zn^{2+} concentration increases;
- The volume of $\text{H}_{2(g)}$ increases.

The rate of reaction in the above situation can be determined by observing the rate of any of the changes described above.

In general, we can say:

The rate of reaction, at some instant, is the rate at which reactants are used up or, alternatively, the rate at which products are formed.

Factors Affecting Reaction Rate

The rate of a chemical reaction is affected by the:

1. nature of the reactants
2. concentration of the reactants
3. state of subdivision of the reactants
4. temperature
5. presence of a catalyst.

1.2 Collision Theory

In order to explain why these five factors affect reaction rate it is best to look at what happens at a molecular level and consider collision theory.

In order for a reaction to take place there must be successful collisions between reacting particles.

The success of any collision is improved if:

- the reacting particles have an appropriate collision orientation
- the reacting particles collide with sufficient energy.

Ultimately the greater the rate of successful collisions, the faster the reaction rate.

1.3 Changing Reaction Rate

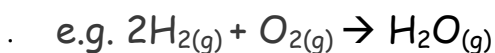
The Nature of Reactants

- **Ionic reactions** are rapid, as they do not involve the breaking of bonds



- The reaction is almost instantaneous as no reactant bonds have to break and there is a strong electrostatic attraction between oppositely charged ions.

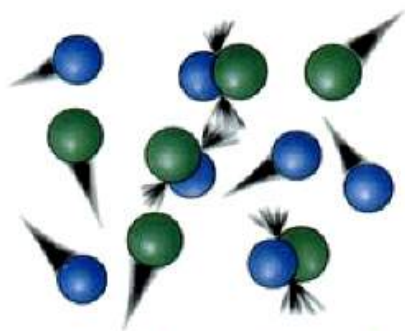
- **Molecular reactions** are slow since they involve bond breaking and bond formation. Collisions are often unsuccessful at room temperature as there is insufficient activation energy.



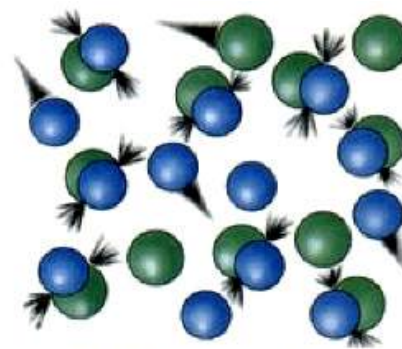
- The reaction is very slow (almost undetectable) at room temperature as they involve the breaking of strong covalent bonds.

Concentration

- Reaction rate is affected by the concentration of reactants in either the solution or gaseous phase (Not solid phase).
- Collision theory tells us that for a reaction to take place the reacting particles must collide.
- So if the number of particles per unit volume is increased the number of collisions will also increase.



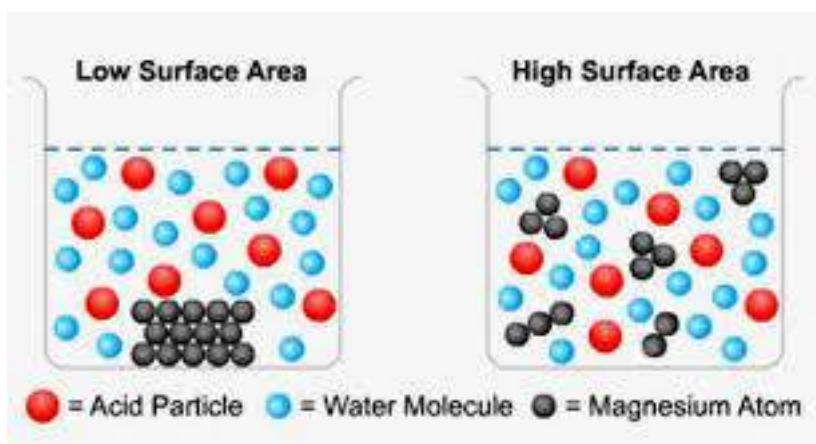
Low concentration = Few collisions



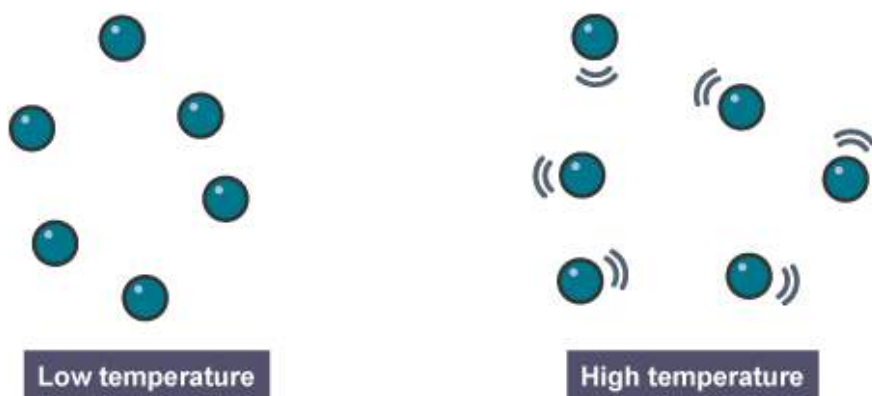
High concentration = More collisions

Surface Area

- The greater the surface area of reactants, the more exposed the reactant particles are. Hence increased frequency of successful collisions which results in a faster rate of reaction.
- Hence fine grained sugar would dissolve faster in a cup of coffee than a lump of sugar.



Temperature



As temperature increases so does the velocity of the reacting particles. This has a two fold effect on reaction rate.

- The number of collisions per unit time increases. This increases the number of successful collisions and hence reaction rate.
- The force, and therefore likely success, of each collision increases. More importantly, the proportion of particles with sufficient activation energy increases with temperature and hence the reaction rate increases markedly.

Kinetic Energy Distribution and Temperature

- The temperature of any substance is related to the average kinetic energy of all its particles.
- However not all the particles (at any particular instant) are travelling at the same speed.

- *If we consider a reaction with a fairly high activation energy then very few particles have sufficient energy to undergo a reaction (shaded area).*
- A small change in temperature however, can markedly increase the proportion of particles with energy greater than activation energy (E_a) as can be seen by a large increase in total area to the right of E_a .

Catalyst

- The presence of a catalysts helps to speed up a reaction.
- Catalyst are not consumed in the reaction.
- Catalysts provide an alternate and easier reaction pathway of lower activation energy.

Catalysts are involved in many important chemical reactions (e.g. Iron in the Haber process).

1.3 Summary Questions

1. What is meant by a successful collision between reacting particles?
2. A reaction between zinc and HCl was fastest at the beginning. Use collision theory to explain why
3. Catalyst are usually in the form of powders or fine wire mesh. Why is this?

4. An increase in temperature of only $10\text{ }^{\circ}\text{C}$ can distinctly increase reaction rate. Explain the main reason for this using the appropriate diagram.

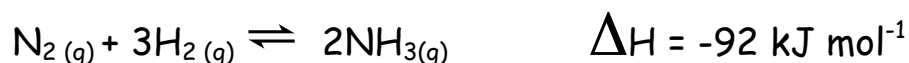
1.4 Equilibrium

- It is sometimes assumed that a chemical reaction can only go in one direction. However, this is not the case.
- Theoretically all reactions are reversible although one direction may be highly favoured.
- Where a single arrow (\rightarrow) is used in an equation it indicates that the forward reaction is highly favoured.
- Where a double arrow (\rightleftharpoons) is used it indicates that the reaction can occur readily in either direction.
- The extent to which the reaction proceeds depends on the nature of the reactants and reaction conditions.
- Within a closed system an equilibrium will always occur between reactants and products.
- A closed system is one which allows energy, but not matter, to be exchanged with the surroundings.

At equilibrium:

- the forward reaction rate is equal to the reverse reaction rate
- there is no change in macroscopic properties such as concentration, pressure or colour. (This is how we recognise that equilibrium has been reached.)

A important equilibrium reactions occurs in the production of ammonia using the Haber process. This reaction is represented as follows:



The progress of this reaction to equilibrium can be represented graphically

- the variation of reaction rate with time
- the variation of concentration with time.

1.4 Summary Questions

1. The concentration of the N_2 and H_2 decreases most rapidly at first. Why?
2. The concentration of H_2 drops off much more quickly than N_2 . Why?

1.5 Equilibrium Constant (K)

- For any equilibrium reaction there is an equilibrium constant (K).
- This constant, which is always a positive number, allows us to predict how far an equilibrium reaction will go in one direction.

$K > 1$	Reaction favours product (favours the right hand of the equilibrium reaction).
$K < 1$	Reaction favours reactants (favours the left hand of the equilibrium reaction).

The equilibrium constant is derived from a mathematical relationship involving the concentration of reactants and products at equilibrium.



$$\text{Then } K = \frac{[C]^c[D]^d}{[A]^b[B]^a}$$

where: $[] = \text{equilibrium concentration in mol L}^{-1}$

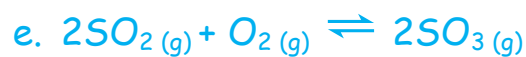
Worked Examples:

It is important to note that:

- Solids and liquids are NOT included in the K expression.
 - This is because the concentration of a solid does NOT vary, nor does the concentration of water in an aqueous solution (*only gases and aqueous solutions are included*)
- The value of K does not change if you change the concentration, pressure or volume.
- However, K varies with temperature. If temperature is increased the value of K increases for endothermic reactions (products favoured) and decreases for exothermic reactions (reactants favoured).
- The value of K refers only to the equilibrium position.

1.5 Summary Questions

1. Write equilibrium constant expressions for the following:



1.6 Le Chatelier's Principle

- Chemical systems that are in equilibrium can be easily affected by a change in conditions such as pressure, concentration or temperature.
- Le Chatelier's principle helps us predict the direction of the change. It can be stated simply as follows:
 - **If a change in conditions is made to a chemical system in equilibrium, then the system will adjust in such a way as to partially counteract the imposed change.**

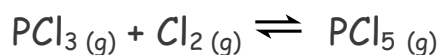
For a system at equilibrium this means that

- increasing the concentration of a substance will favour the reaction which uses up that substance
- increasing the pressure of a gas will favour the reaction which decreases the pressure
- increasing the temperature of the system will favour the reaction which will lower the temperature.

A. Effect of changing concentration

- Suppose that for a system at equilibrium, more of one particular substance is added.
- This will increase the concentration of that substance and hence the rate of the reaction that consumes it.

Consider the following system at equilibrium:



Suppose that further $\text{Cl}_2(g)$ is added. Then:

- the forward reaction rate would increase while the reverse reaction rate would not initially be affected (Since the concentration of the $\text{PCl}_5(g)$ has not changed)
- as more $\text{PCl}_5(g)$ is produced, the reverse reaction rate also begins to increase.
- a new equilibrium would eventually be reached with identical new forward and reverse reaction rates.

The changes in concentration can be shown graphically

1.6A Summary Questions

Predict the *initial* change to the reaction rate and the favoured reaction direction for the following systems, initially at equilibrium.

System at equilibrium	Imposed change	Initial change in Forward R/ R	Initial change in Reverse R/R	Direction Favoured.
$\text{H}_{2(g)} + \text{I}_{2(g)} \rightleftharpoons 2\text{HI}_{(g)}$	Increase $\text{I}_{2(g)}$			
$\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$	Increase $\text{NH}_{3(g)}$			
$\text{Ba}(\text{OH})_{2(s)} \rightleftharpoons \text{Ba}^{2+}_{(aq)} + 2\text{OH}^{-}_{(aq)}$	Increase $\text{Ba}^{2+}_{(aq)}$			
$\text{HCN}_{(aq)} \rightleftharpoons \text{H}^{+}_{(aq)} + \text{CN}^{-}_{(aq)}$	Increase $\text{HCN}_{(aq)}$			
$\text{MgCO}_{3(s)} \rightleftharpoons \text{MgO}_{(s)} + \text{CO}_{2(g)}$	Decrease $\text{CO}_{2(g)}$			
$\text{MgCO}_{3(s)} \rightleftharpoons \text{MgO}_{(s)} + \text{CO}_{2(g)}$	Decrease $\text{MgCO}_{3(s)}$			

B. Effect of changing pressure or volume of a gas

- In equilibrium systems involving gases, changing the volume can alter the pressure and hence the concentration of all species.
- This will cause a change in both the forward and reverse reaction rates.
- The favoured reaction direction will depend on the number of gas particles present in the reactants and products.

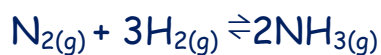
Consider the following where the systems are initially at equilibrium:

Example 1



- An increase in pressure will have no effect on the equilibrium position of this reaction.
- In this example above both forward and reverse reactions increase equally since the number of gas particles are the same.
- Hence there is no change in equilibrium position, just a change in reaction rate.

Example 2



- An increase in pressure will favour the side with the least number of molecules.
- This is in accordance with Le Chatelier's Principle.
- When the pressure is increased (by reducing the volume), the number of gas particles in a given volume increases.
- The system will oppose this change by favouring the reaction which produces the least number of particles.
- In the example above the favoured reaction direction would be to the right.

1.6B Summary Questions

Question 1

Predict the favoured reaction directing the following cases.

System at equilibrium	Imposed volume change	Consequent pressure change	Direction favoured
$\text{CO}_{2(g)} + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g)$	decrease		
$\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$	increase		
$\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$	increase		
$2\text{HgO}(s) \rightleftharpoons 2\text{Hg}(l) + \text{O}_2(g)$	decrease		
$6\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \rightleftharpoons \text{C}_6\text{H}_{12}\text{O}_6(g) + 6\text{O}_2(g)$	increase		
$2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$	decrease		

Question 2

The graph below indicates the concentration of $\text{NO}_{2(g)}$ and $\text{N}_2\text{O}_{4(g)}$ in a closed system during the first 4 minutes of an experiment.

- Write an equation for the reaction
- Write an equilibrium constant expression for the reaction
- What substances were initially present in this closed system?
- At what time was equilibrium reached?
- What happened to the pressure of the gases at $t = 4$ minutes?
How was this achieved?

f. Indicate on the graph the likely changes to the concentration of $\text{NO}_{2(g)}$ and $\text{N}_2\text{O}_{4(g)}$ as a new equilibrium is established?

1.6C Effect of changing temperature

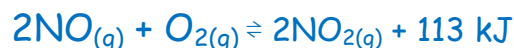
In considering the effect of a temperature change it is best to include the heat of reaction as part of the equation.

In this way heat can be considered as one of the reactants.

Consider:



This exothermic reaction can be rewritten as:



- If heat is added to this system at equilibrium the system reaction will move in the direction that uses up heat. In this case the reverse reaction is favoured.
- Note that both the forward and reverse reaction rates increase except that the reverse reaction rate increases to a greater extent initially.

1.6C Summary Questions

Question 1

Predict the favoured reaction directing the following cases.

System at equilibrium	Temperature change	Direction favoured
$\text{N}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) + 92\text{kJ}$	decrease	
$\text{N}_2\text{O}_4(\text{g}) + 54\text{kJ} \rightleftharpoons 2\text{NO}_2(\text{g})$	increase	
$\text{CH}_3\text{OH}(\text{g}) + 91\text{kJ} \rightleftharpoons 2\text{H}_2(\text{g}) + \text{CO}(\text{g})$	decrease	
$\text{S}(\text{s}) + \text{O}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + 297\text{kJ}$	increase	
$\text{CO}(\text{s}) + \text{H}_2\text{O}(\text{l}) + 131\text{kJ} \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2(\text{g})$	decrease	

1.6D Effect of using catalysts

Catalysts provide a lower activation energy pathway for a reaction and hence help increase both the forward and reverse reaction rates.

Hence catalysts do not affect equilibrium position but are useful in helping reactions achieve equilibrium more quickly.

Reaction Rate and Equilibrium Position

These two aspects should be treated **independently** when predicting changes to a system.

It is important to remember an increase in reaction rate does not necessary favour products.

1.6D Summary Questions

Question 1

The following reaction is at equilibrium:



Determine the effect of imposing the changes indicated in the table below.

Imposed change	Initial change to		Final change to			New equilibrium position
	Forward R/R	Reverse R/R	[NO]	[Br ₂]	[NOBr]	
Adding NO						
Removing some NOBr						
Decreasing the volume of system						

Question 2

Complete the following table which relates to the reaction shown:



Imposed changed	Initial change to		Final change to			New equilibrium position
	Forward R/R	Reverse R/R	[H ₂ O]	[CO]	[H ₂]	
Removing some H ₂						
Adding a catalyst						
Increasing the temperature						
Increasing the pressure						