Kinetics

- Basic Concepts of Kinetics: In order for a reaction to occur, reactant particles must collide- Collision Theory
- Collisions between particles can produce a reaction if both the spatial orientation and energy of the colliding particles are conductive to a reaction

Factors Affecting Rate of Reaction: Dependent on factors such as: Nature of the reactants, concentration, surface area, presence of a catalyst, and temperature

- All these factors affect rate of reaction by changing the number of effective collisions that take place between particles. Pressure can be a factor that affects the rate of reactions involving gases

Nature of Reactants: Covalent bonds are slower to react than ionic substances due to the greater number of bonds that must be broken before a reaction can occur

- Breaking more bonds requires that the particles must have more energy when they collide

Concentration: Most chemical reactions will proceed at a factor rate if the concentration of one or more reactants is increased

Surface Area: More surface area of a substance is exposed, there are more chances of reactant particles to collide, increasing the reaction rate

- A finely divided powder will react more rapidly than a single chunk of the same mass

Pressure: Little or no effect on the rate of reaction between solids or liquids, it has an effect on gases

- An increase in pressure increases the concentration of gaseous particles. It increases the rate of a reaction that involves gases

Presence of a Catalyst: Catalysts are substances that increase the rate of reaction by providing a different and easier pathway for a reaction

- Catalysts take part in a reaction, but are unchanged when the reaction is complete

Temperature: The greater the temperature of a substance, the faster the molecules move. The kinetic molecular theory states that collisions must occur in order for a reaction to take place

- Greater the temperature, greater chances for a reaction to occur

Factors	**Increases Rate**
Nature of Reactants	Ionic more than covalent
Concentration	Increased Concentration
Pressure	Increased pressure for gases
Temperature	Increased Temperature
Surface Area	Increased Surface Area
Catalyst	Presence of a Catalyst

Equilibrium

- Each potential energy diagram show a forward reaction and reverse reaction and even at the same time. When both the forward and reverse reaction occur at the same rate, the condition is called equilibrium. An equation representing equilibrium uses a double arrow instead of a single arrow to show that reaction ar proceeding in both directions
- Equilibrium is a state of balance between the rates of 2 opposite processes that are taking place at the same rate. Equilibrium can only occur in a system in which neither reactants nor products can leave the system
- Equilibrium is a dynamic process, it implies motion in which the interactions of reactant particles are balanced by the interactions of product particles. Equilibrium is an important concept because many chemical reactions and physical processes are reversible, they are able to proceed in both directions
- Quantities of reactants and products are not necessarily equal at equilibrium.

Physical Equilibrium: Equilibrium occurs during physical processes such as change of state or dissolving

Phase Equilibrium: Can exist between the solid and liquid phases of a substance, the melting point of the solid phase or the freezing point of the liquid phase.

Solution Equilibrium: Solids in liquids exist in equilibrium in a saturated solution. Equilibrium may also be attained in a closed system between a gas dissolved in a liquid and the undissolved gas.

- The equilibrium can be disturbed by a change in temperature. If the temperature is raised, a solid generally becomes more soluble in a liquid.
- As the temperature increases, the rate of the gas escaping from the liquid increases, while the rate at which gas particles dissolve decreases. THis decreases the solubility of the gas in the liquid. As the temperature rises, the solubility of all gases decreases in a liquid

Chemical Equilibrium: Condition which occurs when the concentration of reactants and products participating in a chemical reaction exhibit no net change over time. Chemical equilibrium may also be called a "steady state reaction." This does not mean the chemical reaction has necessarily stopped occurring, but that the consumption and formation of substances has reached a balanced condition. The quantities of reactants and products have achieved a constant ratio, but they are almost never equal. There may be much more product or much more reactant.

Le Chatelier’s Principle: Any change in temperature, concentration or pressure or an equilibrium system is called a stress. Le Chatelier’s principle explains how a system at equilibrium responds to relieve any stress on the system

Using Le Chatelier's Principle with a change of concentration

Suppose you have an equilibrium established between four substances A, B, C and D.

$$A + 2B \rightleftharpoons C + D$$

If you changed the conditions by increasing the concentration of A, according to Le Chatelier, the position of equilibrium will move in such a way as to counteract the change. That means that the position of equilibrium will move so that the concentration of A decreases again - by reacting it with B and turning it into C + D. The position of equilibrium moves to the right.

$$A + 2B \rightleftharpoons C + D$$

The position of equilibrium moves to the right if you increase the concentration of A.

What would happen if you changed the conditions by decreasing the concentration of A?
According to Le Chatelier, the position of equilibrium will move so that the concentration of A increases again. That means that more C and D will react to replace the A that has been removed. The position of equilibrium moves to the left.

$$A + 2B \rightleftharpoons C + D$$

The position of equilibrium moves to the left if you decrease the concentration of A.

This is essentially what happens if you remove one of the products of the reaction as soon as it is formed. If, for example, you removed C as soon as it was formed, the position of equilibrium would move to the right to replace it. If you kept on removing it, the equilibrium position would keep on moving rightwards - turning this into a one-way reaction.

Using Le Chatelier's Principle with a change of pressure
This only applies to reactions involving gases:

$$A_{(g)} + 2B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$$

What would happen if you changed the conditions by increasing the pressure?
According to Le Chatelier, the position of equilibrium will move in such a way as to counteract the change. The position of equilibrium will move so that the pressure is reduced again.
Pressure is caused by gas molecules hitting the sides of their container. More molecules you have in the container, higher the pressure will be. The system can reduce the pressure by reacting in such a way as to produce fewer molecules.
In this case, there are 3 molecules on the left-hand side of the equation, but only 2 on the right. By forming more C and D, the system causes the pressure to reduce.

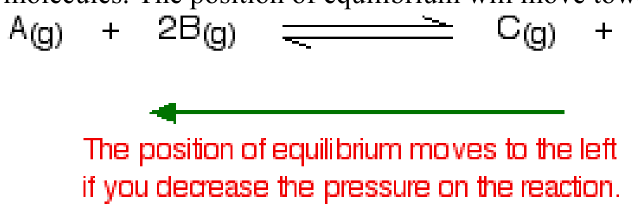
$$A_{(g)} + 2B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$$

The position of equilibrium moves to the right if you increase the pressure on the reaction.

Increasing the pressure on a gas reaction shifts the position of equilibrium towards the side with fewer molecules.

What would happen if you changed the conditions by decreasing the pressure?

Equilibrium will move in a way that pressure increases again. It can do that by producing more molecules. The position of equilibrium will move towards the left-hand side of the reaction.

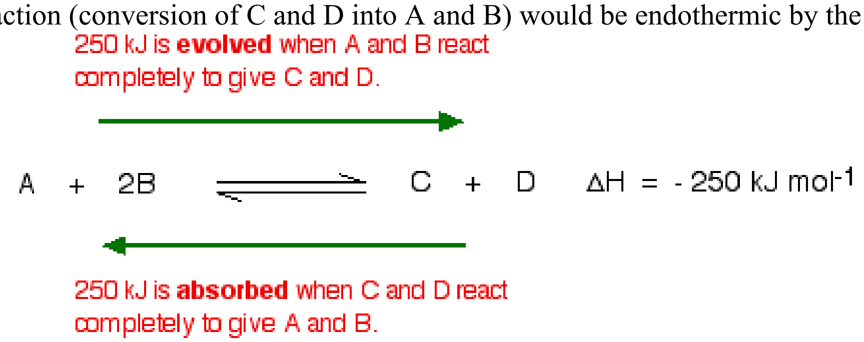


What happens if the same number of molecules are on both sides of the equilibrium reaction?
In this case, increasing the pressure has no effect whatsoever on the position of the equilibrium. Because you have the same numbers of molecules on both sides, the equilibrium can't move in any way that will reduce the pressure again.

Using Le Chatelier's Principle with a change of temperature
For this, you need to know whether heat is given out or absorbed during the reaction. Assume that our forward reaction is exothermic (heat is evolved):

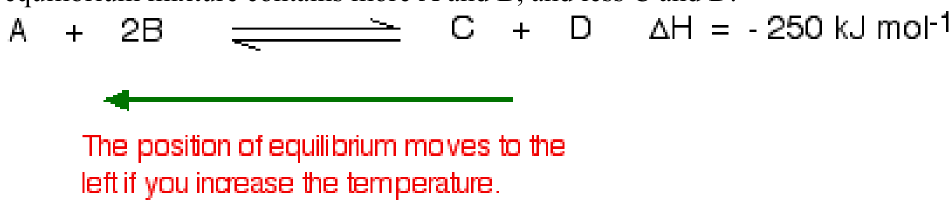
$$A + 2B \rightleftharpoons C + D \quad \Delta H = -250 \text{ kJ mol}^{-1}$$

This shows that 250 kJ is evolved (hence the negative sign) when 1 mole of A reacts completely with 2 moles of B. For reversible reactions, the value is always given as if the reaction was one-way in the forward direction.
Back reaction (conversion of C and D into A and B) would be endothermic by the same amount.

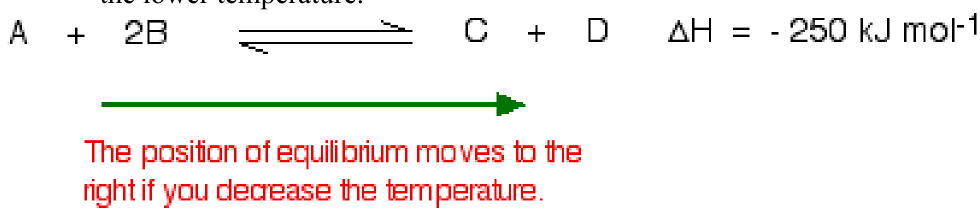


What would happen if you changed the conditions by increasing the temperature?

According to Le Chatelier, position of equilibrium will move in such a way as to counteract the change. That means that the position of equilibrium will move so the temperature is reduced again.
Suppose the system is in equilibrium at 300°C, and you increase the temperature to 500°C. **How can the reaction counteract the change you have made? How can it cool itself down again?**
To cool down, it needs to absorb the extra heat that you have just put in. In the case we are looking at, the back reaction absorbs heat. The position of equilibrium therefore moves to the left. The new equilibrium mixture contains more A and B, and less C and D.



- If you were aiming to make as much C and D as possible, increasing the temperature on a reversible reaction where the forward reaction is exothermic isn't a good idea!
- What would happen if you changed the conditions by decreasing the temperature?
- The equilibrium will move in such a way that the temperature increases again.
- Suppose the system is in equilibrium at 500°C and you reduce the temperature to 400°C. The reaction will tend to heat itself up again to return to the original temperature. It can do that by favouring the exothermic reaction.
- The position of equilibrium will move to the right. More A and B are converted into C and D at the lower temperature.



Summary
- Increasing the temperature of a system in dynamic equilibrium favours the endothermic reaction. The system counteracts the change you have made by absorbing the extra heat.
- Decreasing the temperature of a system in dynamic equilibrium favours the exothermic reaction. The system counteracts the change you have made by producing more heat.

Le Chatelier's Principle and catalysts
Adding a catalyst makes absolutely no difference to the position of equilibrium, and Le Chatelier's Principle doesn't apply to them.
This is because a catalyst speeds up the forward and back reaction to the same extent. Because adding a catalyst doesn't affect the relative rates of the two reactions, it can't affect the position of equilibrium. So why use a catalyst?
For a dynamic equilibrium to be set up, the rates of the forward reaction and the back reaction have to become equal. This doesn't happen instantly. For a very slow reaction, it could take years! A catalyst speeds up the rate at which a reaction reaches dynamic equilibrium.

Enthalpy: Tendency in nature to change to a state of lower energy. Exothermic reactions move toward a lower energy state as some of the energy contained in the reactants is released. THe products have less potential energy than the reactants Drive toward lower energy is also the drive toward lower enthalpy

Entropy: Measure of the disorder or randomness of a system. Greater the disorder, the higher the entropy.

- Examples of entropy change are physical changes from the solid, crystalline phase (great order, low entropy), to the liquid phase (more randomness, higher entropy), to the gaseous phase (maximum randomness, highest entropy). FOr chemical changes, compounds represent a state of greater order and lower entropy than the free elements of which they are composed

To identify whether reactants or products have the greater amount of entropy consider:

1. The solid phase has less entropy than the liquid phase, which has less entropy than the gaseous phase
2. Generally, the side of the equation with the greater number of molecules has the greater amount of entropy

Equilibrium Expression: The mathematical expression that shows the relationship of reactants and products in a system at equilibrium. It is a fraction with the concentrations of reactants and products expressed in moles per liter. Each concentration is then raised to the power of its coefficients in a balanced equation. This expression equals a value called the equilibrium constant (Keq), which remains the same for a particular reaction at a specified temperature

Writing the Equilibrium Expression

The equilibrium expression for a chemical reaction may be expressed in terms of the concentration of the products and reactants. Only chemical species in the aqueous and gaseous phases are included in the equilibrium expression because the concentrations of liquids and solids does not change. For the chemical reaction:

$jA + kB \rightarrow lC + mD$

The equilibrium expression is

$K = ([C]l[D]m) / ([A]j[B]k)$

K is the equilibrium constant

[A], [B], [C], [D] etc. are the molar concentrations of A, B, C, D etc.

j,k, l, m etc. are coefficients in a balanced chemical equation