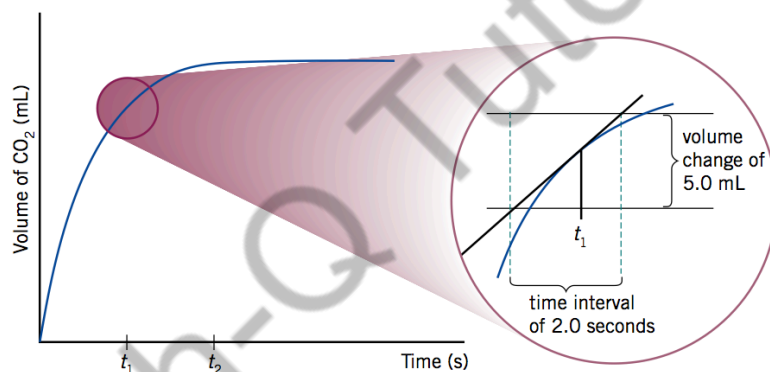


- The **reaction rate** (rate of reaction) in a particular reaction is defined as how fast or slow a reaction takes place

Measurement of Reaction Rate

- The reaction rate can be measured by observing the:
 - o Rate of disappearance of reactants
 - o Rate of appearance of products
- E.g. in the reaction of hydrochloric acid with marble chips: $\text{CaCO}_3(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Ca}^{2+}(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
 - o The rate of reaction may be calculated by either observing:
 - The rate of mass of CaCO_3 being consumed (i.e. decreasing mass)
 - The rate of H^+ being diluted (i.e. decreasing concentration)
 - The rate of Ca^{2+} being concentrated (i.e. increasing concentration)
 - The rate of volume of CO_2 gas being produced (i.e. increasing volume)
 - o Any of these rates can be inferred by calculating the gradient of a graph where:
 - Time is graphed on the x axis
 - The quantity of reactant/product on the y axis
 - The graph below measures the volume of CO_2 produced in the aforementioned reaction of acid with marble chips



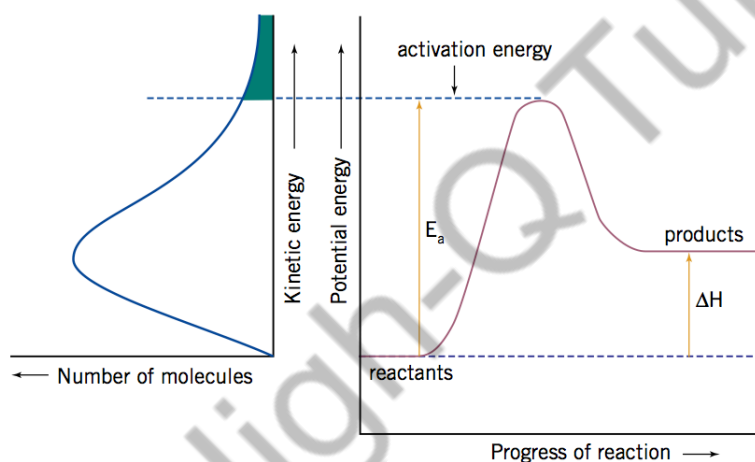
- The **average reaction rate** is calculated by measuring the straight line gradient over that time interval
- The **instantaneous reaction rate** is calculated by measuring the gradient of the tangent at that exact point in time
- The steeper the slope of the graph, the faster the reaction rate
 - o The rate of this reaction is quickest at the beginning of the reaction, as shown by the steepness of the slope of the graph
 - o However, as the reaction proceeds, the rate decreases, until at time t_2 , it is complete (i.e. one of the reactants will have been consumed completely at this time)

Collision Theory and Activation Energy

- The collision theory requires that for a collision between reactant particles to lead to a chemical reaction, two conditions must be met:
 - o The molecules must collide with a sufficient energy to disrupt the bonds of the reactant molecules. This minimum energy that is required is the activation energy (E_a) of the reaction
 - o The molecules must collide with an orientation that is suitable for the breaking of some bonds and the formation of others

Energy Profile Diagrams

- Energy profile diagrams can be used to show the potential energy changes during the course of a chemical reaction
 - o The activation energy for the reaction is the difference in the potential energies of the reactants and the transition states
 - o The transition state, or activated complex represents the highest energy state for the reacting system and corresponds to the stage in the reaction where bond-breaking and bond-forming processes are taking place
 - However, the transition state is an unstable state, and only has a temporary existence. Once formed, it will quickly either convert to products or return to reactants
- The energy profile diagram can be related to kinetic energy distribution for a reaction at a particular temperature



- When reactant molecules collide, a reaction will only occur if the energy of the collision is sufficient to supply the activation energy required for the reactants to reach the transition state
 - o Above, only the small shaded proportion of molecules have energies greater than that of the activation energy barrier

Factors Affecting Reaction Rate

Nature of Reactants

- Slower reactions will have higher activation energy than faster reactions
- The different activation energies for different reactions are related to the ease with which bond breaking and reforming processes occur. This will depend on the nature of the reactants
- High activation energies are often associated with reactions in which:
 - o Strong bonds are required to be broken; and/or
 - o The bond breaking and forming processes are complex
- E.g. The low reactivity for N_2 gas can be attributed to the high activation energy required to break the triple bond between the N atoms
- E.g. In the reaction between natural gas and oxygen gas: $CH_4(g) + O_2(g) \rightarrow CO_2(g) + H_2O(l)$
 - o The reaction occurs to almost no extent at room temperature due to the high activation energy associated with the complex bond rearrangement processes
- E.g. In the reaction between silver and chloride ions: $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$
 - o The reaction rate is high due to the low activation energy associated with the simple collision between two ions

Concentration (of solutions) or Partial Pressure (of gases)

- The effect of increasing the concentration of a reactant in solution is that reactant molecules collide with each other more often
 - o If a greater number of collisions occur per unit of time, this will result in a greater rate of successful collisions per unit time (i.e. the reaction rate will increase)
 - o E.g. In the reaction between hydrochloric acid and $CaCO_3$, using a more concentrated solution of HCl will allow the reaction rate to increase
- This same theory can be applied to gases, where increasing the partial pressure of gaseous reactants increase the rate of collision between molecules and hence the rate of reaction
 - o E.g. For example, in the production of hydrogen iodide gas: $H_2(g) + I_2(g) \rightarrow 2HI(g)$, increasing the partial pressure of either/both gases will cause an increase in the reaction rate

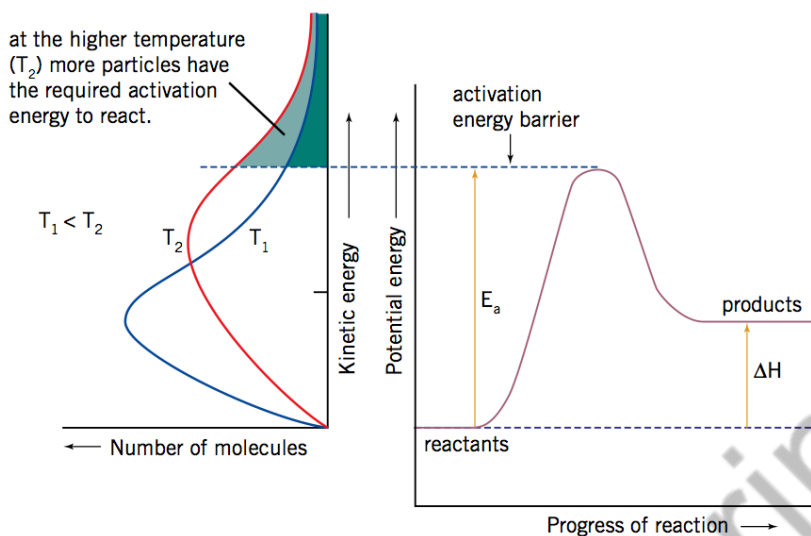
State of Subdivision

- If the surface area of a solid or liquid reactant is increased, more of the reactant molecules are exposed to collisions, thereby increasing the reaction rate
- E.g. A log of wood cut into smaller pieces burns far more rapidly than if it were in one piece. The effect of cutting the wood into more pieces is to expose more of the wood to the oxygen that it needs for combustion
- An increase in surface area can be achieved when:
 - o Solid reactants are ground/powdered
 - o Liquid reactants are sprayed

Temperature

- The temperature of a reacting system has a significant effect on the rate of a reaction. An increase in temperature will cause an increase in reaction rate due to two reasons:

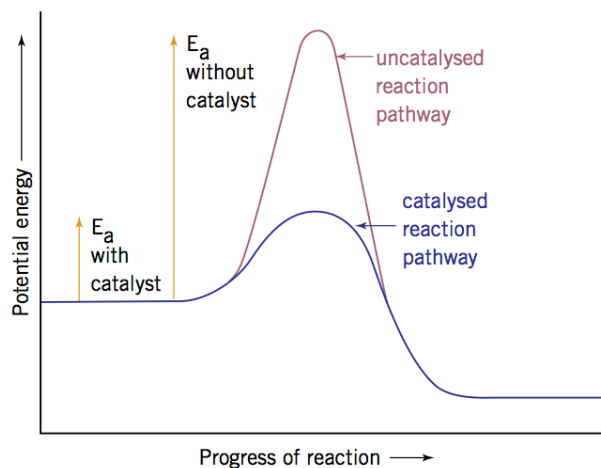
- o An increase in temperature causes the distribution of molecular energies to change



- As the temperature is raised, a greater proportion of reactant molecules have sufficient kinetic energy to supply the activation energy required for the reaction
 - This means a greater proportion of molecular collisions will be successful collisions, and as a result, produces an increase in reaction rate
- o An increase in temperature causes the average kinetic energy of every molecule to increase
 - As $E_k = \frac{1}{2}mv^2$ (and the mass m , remains constant), an increased kinetic energy corresponds to an increase in the molecular velocities of reactant molecules v
 - The increased velocities lead to a greater amount of collisions within the same time period, again resulting in an increase in reaction rate

Catalysts

- A catalyst is a substance, or mixture of substances that increases the rate of a chemical reaction without being permanently consumed in the reaction
- Catalysts increase reaction rate by providing an alternative reaction pathway with lower activation energy

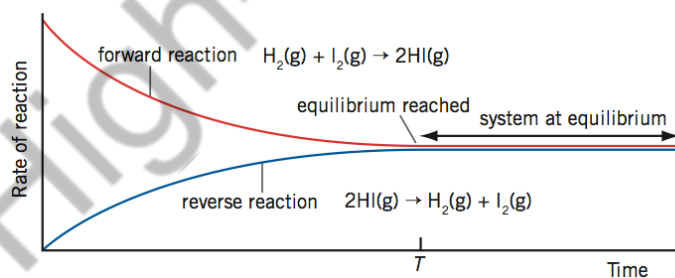


- Catalysts generally operate by forming intermediate compounds in which the bond breaking and rearrangement process requires less energy than if the reaction alone were involved. Reactant molecules in metal catalysts collide with the metal surface and become attached to the metal. The molecular rearrangements that occur during this process make it more likely that subsequent reactant collisions will be successful
 - o E.g. In the manufacture of ammonia using an iron catalyst, N_2 and H_2 are bound to the iron surface as separate atoms, where these atoms are now reactive and combine to form NH_3 molecules
- A decrease in activation energy means a greater proportion of molecular collisions will be successful collisions, and as a result, a catalyst produces an increase in reaction rate

- Not all reactions go to completion. Even after a long reaction time, some reaction systems remain a mixture of reactants and products
 - o This is explained by the fact that reactions are reversible (i.e. the products in a reaction are able to react to reform the reactants)
 - o E.g. The reaction of hydrogen with iodine to form hydrogen iodide: $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
 - If some hydrogen and iodine gas are mixed and allowed to react (for infinite time), the entire system will not consist of only hydrogen iodide (but also some hydrogen and iodine)
 - This because, as hydrogen iodide forms, it can react via the reverse reaction, to re-form hydrogen and iodine
 - o To indicate that both forward and reverse reactions are occurring, a double arrow is used, instead of a single arrow where only the forward or reverse reaction occurs

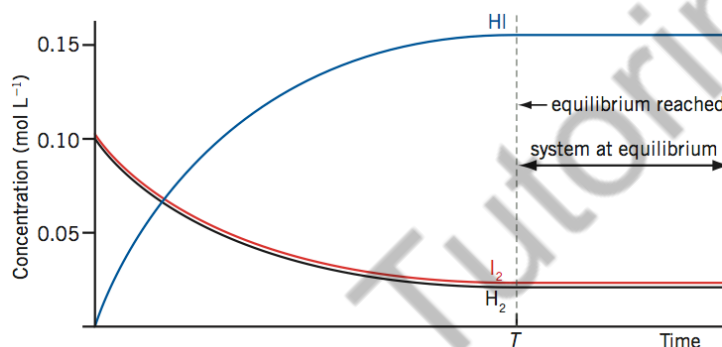
Equilibrium

- Let us consider equilibrium in the reaction of hydrogen with nitrogen to form ammonia by considering:
 - o Reaction rates vs Time
 - The forward reaction rate is initially fast
 - As the concentrations of the reactants decrease, the forward reaction rate (i.e. rate of consumption of hydrogen and iodine, and production of hydrogen iodide) decreases
 - The rate of this reverse reaction is initially zero
 - As the concentration of the product increases, the reverse reaction rate (i.e. rate of consumption of hydrogen iodide, and production of hydrogen and iodine) increases
 - At some time T , a stage is finally reached where the rate of the forward reaction is equal to the rate of the reverse reaction. This means ammonia is being formed as quickly as it is decomposing to re-form hydrogen and nitrogen



- As the forward and reverse reactions continue to proceed (i.e. both reactions continue to proceed at a microscopic level), the system is said to be in **dynamic equilibrium** as the substances continue to switch between reactants and products

- Concentrations vs Time
 - Assume that the reaction mixture at the beginning of the experiment is composed of:
 - Only H_2 and N_2
 - No HI
 - As the reaction begins, the concentrations of H_2 and I_2 decrease as they react with one another
 - They decrease by the same amount, at the same rate, because these two reactants react in a 1:1 stoichiometric ratio
 - Over time, the concentration of HI increases as more is produced in the forward reaction
 - Because the stoichiometric ratio between each of the reactants and HI is 1:2, the concentration of HI will increase by twice as much as the reactant concentrations decrease
 - Finally, at some time, when the forward and reverse reaction rates become equal, there is no net change in the concentrations (i.e. they remain constant over time). This is when the system is at equilibrium
 - The system will remain at equilibrium until a change is made to it



- As the net reaction rate is zero, and the concentrations of the substances remains constant, the macroscopic properties of the system at equilibrium are constant
- Note the following aspects of the two graphs aforementioned:
 - Reaction rates vs Time
 - There are two lines only
 - The two lines meet and plateau, as the two rates are constant
 - Concentration vs Time
 - There may be any number of lines, depending on the number of reactants and products
 - All lines plateau as the concentrations are constant, but they do not need to be of equal value
 - Equilibrium can only be reached in a **closed system**
 - A closed system is a system that does not allow the input or escape of any matter
 - An **open system** is a system that does allow the input or escape of matter
 - In both closed and open situations, energy is able to enter and leave the system

Equilibrium in Physical Systems

- Dynamic equilibrium are not limited to chemical changes, but can also be established in physical changes:
 - o **Equilibrium Vapour Pressure**
 - When a liquid is placed in a closed container, some of the liquid evaporates to produce a vapour above the liquid. Some of this vapour also condenses to re-form the liquid
 - If left long enough, equilibrium will be established between the liquid and the vapour
 - At this stage, the rate at which the liquid is evaporating will equal the rate at which the vapour is condensing (i.e. molecules will be escaping from the liquid at the same rate as they are re-entering the liquid phase)
 - The amount of liquid and vapour present will remain constant with time
 - o At this stage, the pressure exerted by the vapour (the equilibrium vapour pressure) will be a constant
 - o **Solution Equilibrium**
 - When a solid is placed in a liquid, some of the solid begins to dissolve as the particles of the solid break away from the lattice and mix with the solvent's particles. These dissolved particles can also crystallise out of solution to re-form the solid
 - If sufficient solid is present, equilibrium will be established between the solid and the dissolved particles when the particles are dissolving at the same rate at which they are crystallising
 - At this stage, the amount of solid present will remain constant, and the amount of dissolved substance will also be constant

Equilibrium Constant

- It has been found experimentally, that for any reaction at equilibrium, with the general reaction $aA + bB \rightleftharpoons cC + dD$, the fraction $\frac{[C]^c[D]^d}{[A]^a[B]^b}$ remains constant (at a particular temperature)
 - o [A], [B], [C] and [D] represent the concentrations of A-D in mol L^{-1} , and the lower-case letters a , b , c and d represent the balancing coefficients of these reactant/products, in the equation
 - o This fraction value is called **the equilibrium constant K** and is given by the **equilibrium expression**
$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$
- The value of the ratio $\frac{[C]^c[D]^d}{[A]^a[B]^b}$ will only equal the equilibrium constant K when the system is at equilibrium
- The **reaction quotient Q** is also calculated from the same ratio
 - o If $Q = K$, then the system is at equilibrium
 - o If $Q < K$, then there are less products and more reactants than at equilibrium. This means that the forward reaction will be favoured for the system to reach equilibrium
 - o If $Q > K$, then there are more products and less reactants than at equilibrium. This means that the reverse reaction will be favoured for the system to reach equilibrium
- When writing these equilibrium expressions:
 - o The concentrations of the products are written on the top line of the fraction, and the concentrations of the reactants are written on the bottom line
 - o If there are two or more reactants or products, their concentrations are multiplied together
 - o The power to which the concentration of a particular substance is raised is the same as its balancing coefficient for that same substance, in the equation
 - o The equilibrium law expression does not include substances that are solids or pure liquids, because their concentrations do not vary from one reaction to the next (i.e. they are pure substances with a concentration of 1)
 - The exception to this is when in a homogenous system, all substances are in same phase. In this case solids and liquids are included because the relative proportion is important
- An equilibrium constant has the following characteristics:
 - o It is a constant value for a particular equation representing a reaction at a given temperature
 - o If the temperature of a reaction is changed, then the value of the equilibrium constant also changes
 - o It indicates the relative proportions of reactants and products in an equilibrium mixture (i.e. it gives an indication of the extent of the reaction)
 - If the equilibrium constant has a very large value ($\gg 1$), it means large concentrations of products and very small concentrations of reactants are present. We say that equilibrium lies to the right
 - If the equilibrium constant is very small ($\ll 1$), then the concentrations of reactants must be very large and the concentrations of products very small. We say that equilibrium lies to the left
 - If the equilibrium constant is close to 1, there are similar concentrations of reactants and products
 - o The size of the equilibrium constant provides no indication of the rate of the reaction (i.e. it does not indicate how quickly a particular reaction reaches equilibrium)

Changes to Equilibrium

- The effect of various changes on a system at equilibrium can be predicted using:
 - o An understanding of reaction rates and collision theory
 - o **Le Châtelier's principle:** If a system at equilibrium is subjected to a change in conditions, the system will adjust to re-establish equilibrium in such a way as to partially counteract the imposed change
 - o The equilibrium constant

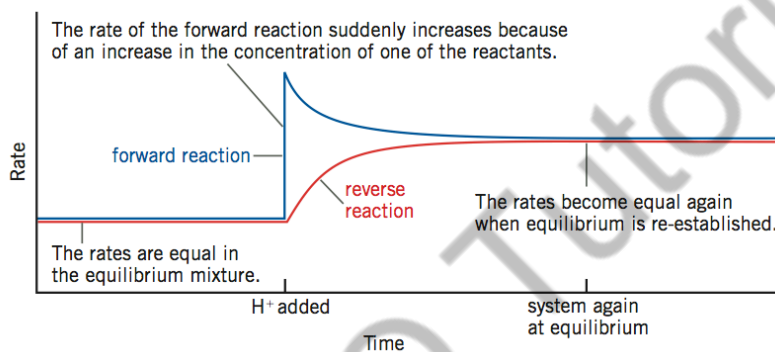
Changes in Concentration

- If the concentration of one of the reactants in an equilibrium mixture is increased (e.g. by adding more of the substance), the mixture will no longer be at equilibrium

- E.g. The following equilibrium system exists between chromate and dichromate ions in an acidic solution:

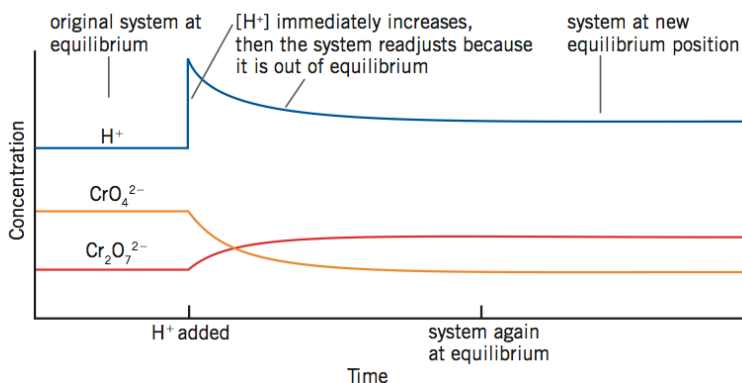
$2\text{CrO}_4^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \rightleftharpoons \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$. Let us consider the effect of adding some hydrochloric acid in terms of:

- o Reaction rates and collision theory:



- As soon as the acid is added, the concentration of H^+ ions increases, causing an immediate increase in the rate of the forward reaction. This means that the system is no longer at equilibrium
- As the forward reaction rate is proceeding at a greater rate than reverse reaction rate:
 - The concentrations of reactants begins to decrease
 - o This results in a gradual decrease in the rate of the forward reaction
 - The concentration of products begins to increase
 - o This results in a gradual increase in the rate of forward reaction
- Finally, the forward and reverse reaction rates are again equal and equilibrium is re-established
- The forward and reverse reaction rates in the new equilibrium mixture is greater than the rates in the initial equilibrium mixture

○ Le Châtelier's Principle:



- When the acid is added, the concentration of the H^+ ions immediately increases
- According to Le Châtelier's principle, to oppose the change, some of the added H^+ needs to be 'removed'. For this to happen, the equilibrium position shifts towards the products (i.e. a net reaction occurs towards the right, or the forward reaction is favoured)
 - This was shown before, where the rate of the forward reaction was greater than the rate of the reverse reaction until equilibrium was re-established
- In the net reaction that occurs to get back to equilibrium, some of the CrO_4^{2-} and H^+ reacts to produce more $\text{Cr}_2\text{O}_7^{2-}$ and H_2O . As a result, at the new equilibrium position:
 - The concentration of CrO_4^{2-} is smaller, and the concentration of the $\text{Cr}_2\text{O}_7^{2-}$ is greater than before the change was made
 - The concentration of the H^+ is greater than it was before the acid was added to the original mixture because even though some of it reacted in getting back to equilibrium, the total amount added is not completely consumed
- According to the stoichiometric ratios shown in the balanced equation:
 - The reactants react in a 1:1 ratio, thus in getting back to equilibrium, the H^+ and CrO_4^{2-} concentration decreases by the same amount
 - The ratio between CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ is 2:1, so the concentration of $\text{Cr}_2\text{O}_7^{2-}$ increases by only half of that compared to the decrease in concentration of the reactants

○ Equilibrium Expression:

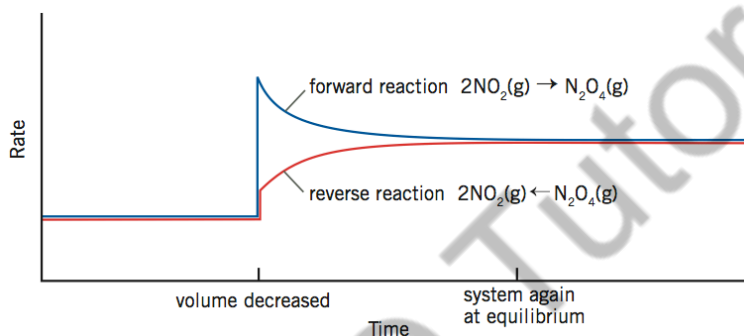
$$K = \frac{[\text{Cr}_2\text{O}_7^{2-}]}{[\text{CrO}_4^{2-}]^2[\text{H}^+]^2}, \quad Q = \frac{[\text{Cr}_2\text{O}_7^{2-}]}{[\text{CrO}_4^{2-}]^2[\text{H}^+]^2}$$

- When acid is added to the mixture, the concentration of H^+ is increased, which means that the value of the reaction quotient Q is now smaller than that of the equilibrium constant K
- For Q to again equal to K , the numerator needs to be increased and/or the denominator decreased. This can be achieved if the net reaction proceeds towards the right, to form more products and reduce the amount of reactants

- If an equilibrium system involves a solid or liquid, then a change in the mass of this solid or liquid will not put the system out of equilibrium, as there has been no changes to the concentration of any of the species
- If an inert ion is added to an aqueous system in equilibrium, the concentrations of the original ions that represent the equilibrium do not change, thus there is no effect on the position of equilibrium

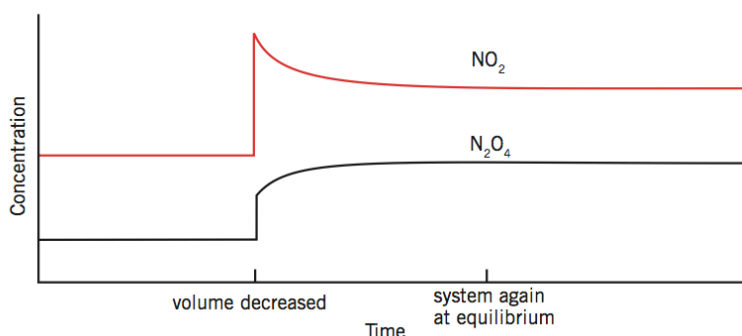
Changes in Volume (or Pressure) of a Gaseous System

- If the volume of a gaseous equilibrium system, or pressure of the system is changed, then the partial pressures (i.e. concentration of the gas) of all the gaseous substances making up that system will also be changed
 - o As $P \propto \frac{1}{V}$:
 - An increase in volume (or decrease in total pressure) will cause a decrease in the concentrations of all gaseous substances
 - A decrease in volume (or increase in total pressure) will cause an increase in the concentrations of all gaseous substances
- It is the relative number of reactant and product gaseous particles in the balanced chemical equation involved in the reaction, that influences whether these changes in concentrations put the system out of equilibrium depends on the relative number of reactant and product particles (not including solids or pure liquids) involved in the reaction
- E.g. The following equilibrium system exists between two gases: $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$. Let us consider the effect of decreasing the volume of the reaction vessel in terms of:
 - o Reaction rates and collision theory:



- The partial pressures of both gases increases, hence there is an immediate increase in both the forward and reverse reaction rate. As there is a greater number of reactant gaseous molecules than product gaseous molecules, the forward reaction rate increases more than the reverse reaction rate
- As the forward reaction rate is proceeding at a greater rate than reverse reaction rate:
 - The concentrations of reactants begins to decrease
 - o This results in a gradual decrease in the rate of the forward reaction
 - The concentration of products begins to increase
 - o This results in a gradual increase in the rate of forward reaction
- Finally, the forward and reverse reaction rates are again equal and equilibrium is re-established
- The forward and reverse reaction rates in the new equilibrium mixture is greater than the rates in the initial equilibrium mixture

- o Le Châtelier's Principle:



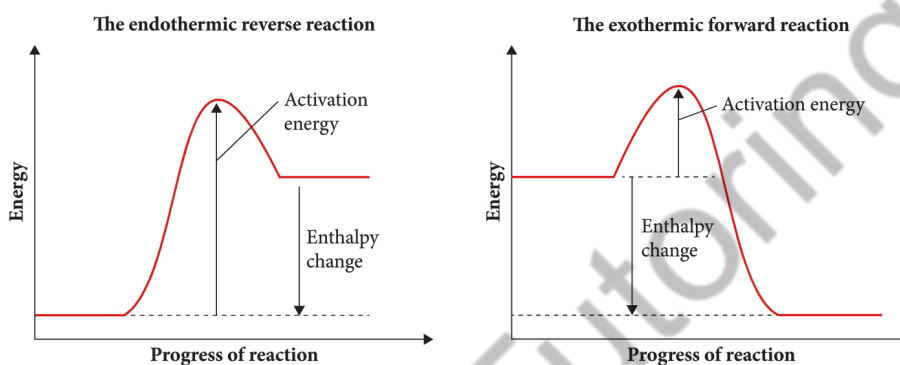
- When the volume is decreased, the partial pressure of both gases immediately increases
 - According to Le Châtelier's principle, to oppose the change, the total pressure needs to be decreased. For this to happen, the equilibrium position shifts towards the side with less particles, which in this case is a shift towards the products, hence converting two molecules into one
 - This was shown before, where the rate of the forward reaction was greater than the rate of the reverse reaction until equilibrium was re-established
 - As a result, at the new equilibrium position:
 - The partial pressure of N_2O_4 is greater than before the change was made, as well as greater than immediately after the change was made
 - o The amount of N_2O_4 is more than before the change was made as the equilibrium yield shifts to the right
 - The partial pressure of NO_2 is smaller than before the change was made, but greater than immediately after the change was made
 - o The amount of NO_2 is less than before the change was made
 - According to the stoichiometric ratios shown in the balanced equation:
 - The ratio between NO_2 and N_2O_4 is 2:1, so the concentration of N_2O_4 increases by only half of that compared to the decrease in concentration of NO_2
- o Equilibrium Expression: Let us assume that the volume of the reaction vessel was halved, and so the partial pressure of both gases doubles
 - $$K = \frac{[N_2O_4]}{[NO_2]^2}, Q = \frac{[2N_2O_4]}{[2NO_2]^2} = \frac{2[N_2O_4]}{4[NO_2]^2} = \frac{1}{2} \frac{[N_2O_4]}{[NO_2]^2}$$
 - When the volume of the reaction vessel is halved, the value of the reaction quotient Q is now smaller than that of the equilibrium constant K
 - For Q to again equal to K , the numerator needs to be increased and/or the denominator decreased. This can be achieved if the net reaction proceeds towards the right, to form more products and reduce the amount of reactants
- If a reaction contains equal numbers of gaseous particles on both sides of the equation, the system is not put out of equilibrium by a change in volume or pressure
- If an inert gas is added to a gaseous system in equilibrium at constant volume, the total pressure increases (due to the additional partial pressure of the new gas). However, the partial pressures of the original gases that represent the equilibrium do no change
 - o Thus when an inert gas is added to the system in equilibrium at constant volume there will be no effect on the position of equilibrium

Changes in Solvent Volume of an Aqueous System

- The effect of adding water to an aqueous system can be modelled in a similar way to increasing the volume of a gaseous system
 - o This is because the dilution of an aqueous system reduces the concentration of all the aqueous substances, proportional to the molar amount initially present

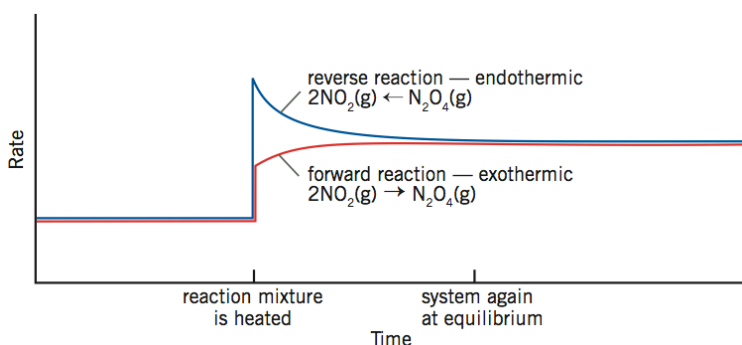
Changes in Temperature

- In a reversible reaction, the reaction in one direction will be endothermic, while the reaction in the opposite direction will be exothermic. In both reactions, the activation energy is the difference between the enthalpy of the activated complex and the reactants
 - o The lower enthalpy of the reactants in an endothermic diagram means that the endothermic reaction will always have a greater activation energy than the exothermic reaction for the same reversible reaction

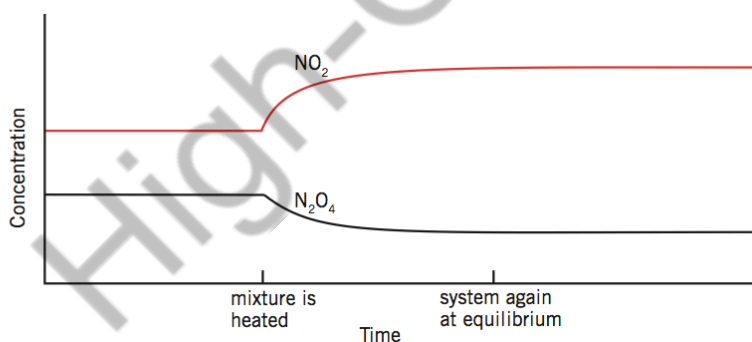


- o Therefore:
 - If the temperature of an endothermic reaction a system is increased, both the forward and reverse reaction rates increase. However the endothermic reaction increases by more, as it increases the proportion of particles able to participate in the endothermic reaction more than it will increase for the exothermic reaction (because the endothermic reaction has a higher activation energy)
 - If the temperature of an endothermic reaction a system is decreased, both the forward and reverse reaction rates decrease. However the endothermic reaction decreases by more, as it reduces the proportion of particles able to participate in the endothermic reaction more than it will reduce for the exothermic reaction
- The impartial effect on reaction rate of a temperature change confirms that a change in the temperature of an equilibrium system will the force the system out of equilibrium
 - o This is consistent with our knowledge that the equilibrium constant value for any reaction remains constant at a particular temperature only. Thus a change in temperature should change the equilibrium constant value, yet at the same time, there is no immediate effect on the concentration of any of the substances (i.e. the previous K value is now a Q value). Hence the system will be forced out of equilibrium

- E.g. The following equilibrium system exists between two gases: $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g}) + 57 \text{ kJ}(\text{g})$. Let us consider the effect of increasing the temperature in terms of:
- o Reaction rates and collision theory:



- The forward reaction is exothermic, thus the reverse reaction is endothermic
- When the temperature of the system is increased, both the forward and reverse reaction rates immediately increase, however the reverse reaction increases by more as it is the endothermic reaction
- As the reverse reaction rate is proceeding at a greater rate than forward reaction rate:
 - The concentration/pressure of the products begins to decrease
 - o This results in a gradual decrease in the rate of the reverse reaction
 - The concentration/pressure of the reactants begins to increase
 - o This results in a gradual decrease in the rate of forward reaction
- Finally, the forward and reverse reaction rates are again equal and equilibrium is re-established
- The forward and reverse reaction rates in the new equilibrium mixture is greater than the rates in the initial equilibrium mixture
- o Le Châtelier's Principle:



- When the temperature of the system is increased, the reverse reaction, the endothermic reaction, would be favoured in an attempt to remove the added heat
- According to the stoichiometric ratios shown in the balanced equation:
 - The pressure/amount of NO_2 increases and the pressure/amount of N_2O_4 decreases in a 2:1 ratio, until the new equilibrium position is reached

Addition of a Catalyst

- When a catalyst is added to a reversible reaction, it lowers the activation energy for both the forward and reverse reactions by the same amount. This results in an increase in the rate of both the forward and reverse reactions by the same amount
 - o As a result, a catalyst does not affect the extent of the reaction (i.e. the relative proportions of reactants or products obtained in the equilibrium mixture) but it does allow the equilibrium position to be reached more quickly
- Note the following aspects of the concentration vs time graphs previously considered:
 - o If the change to the system is an increase/decrease in the concentration/partial pressure of one substance, there is a sudden increase/decrease in one substance only
 - o If the change is an increase/decrease in volume/pressure of a gaseous system, or an increase in the solvent volume of an aqueous system, there is a sudden increase/decrease in the concentration/partial pressure all of the substances
 - o If the change is an increase/decrease in temperature, there is no sudden changes in the concentration/partial pressure of any of the substances

Reaction Rate vs Equilibrium Considerations

- In industrial chemical processes, the maximum yield of product for the minimum cost is sought
 - o Factors affecting reaction rates and equilibrium (and economics/safety) have to be considered in planning industrial processes and chemical plants
 - o Because factors affecting reaction rates and equilibrium are sometimes in conflict, a compromised set of conditions may be needed in which a reasonable yield is obtained at a satisfactory rate
- E.g. The Haber Process (i.e. production of ammonia gas): $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}); \Delta H = -92 \text{ kJ}$
 - o According to Le Châtelier's principle, the following conclusions can be reached:
 - Increasing the pressure exerted on an equilibrium system will cause the concentrations of all the substances to increase. To oppose this change, there is a shift of the position of equilibrium to the right (i.e. 4 reactant particles converted to 2 product particles). Thus favouring the forward reaction reduces the overall number of particles, thereby partially counteracting the initial increase in pressure
 - Thus an increase in pressure will favour the production of a higher yield of ammonia
 - Decreasing the temperature can be partially counteracted by favouring the exothermic reaction (i.e. increased temperature of surroundings). Thus a decrease in temperature will favour the forward reaction
 - Thus a decrease in temperature will favour the production of a higher yield of ammonia

- Considering the rate of this reaction, the following conclusions can be made:
 - Increasing the pressure of the reacting gases increases the number of collisions, thereby increasing the reaction rate
 - Thus an increase in pressure will favour the rate of production of ammonia
 - Increasing the temperature represents an increase in the average kinetic energy of the reacting particles. The primary effect of this is an increase in the number of successful collisions (i.e. more collisions will have enough energy to overcome the activation energy barrier). The secondary effect of this is to increase the number of collisions (i.e. more collisions will occur in a given period of time when the particles travel at a higher speed)
 - Thus an increase in temperature will favour the rate of production of ammonia
 - A catalyst will increase the reaction rate by providing an alternative reaction pathway with a lower activation energy
- There is a conflict with the conditions predicted for best yield and those predicted for the best reaction rate. Thus we must reach a compromise when enforcing the system conditions
- The compromised conditions for the majority of industrial plants using the Haber process include the following:
 - Maintaining the nitrogen and hydrogen into the converter at 10-25 MPa (i.e. a high pressure)
 - An excessively high temperature is not used to reduce excessive costs and minimise safety risks
 - Operating the reaction at a temperatures ranging from 350°C to 550°C (i.e. a moderate temperature)
 - Using a porous catalyst of Fe_3O_4 . The use of a catalyst with a large surface area will maximise the reaction rate with no negative (or positive) effect on the yield