Chapter 2:
Chemical Equilibrium

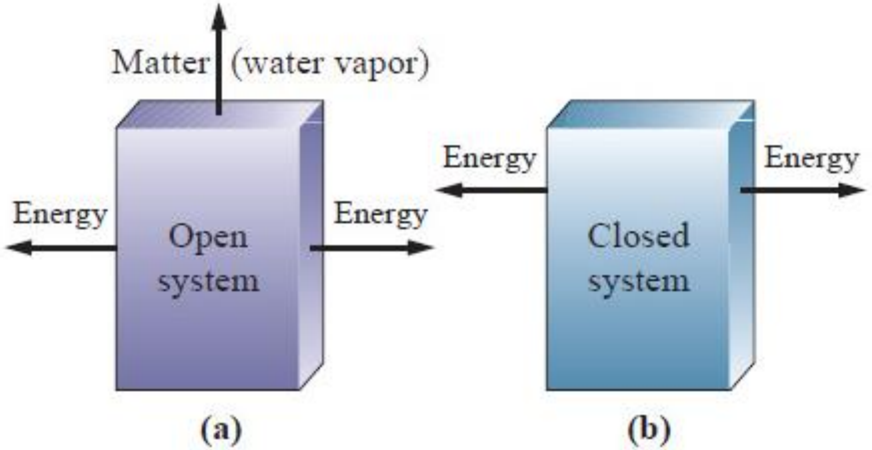
Reversible reactions and dynamic equilibrium

Chemical systems- Open and Closed System

The chemicals involved in a reaction form the chemical system. Anything around it forms the surroundings.

If the chemicals are contained within a space and cannot enter or leave, the system is a closed system.

If substances can be added or lost, the system is an open system.



▲ Figure C1.2
A closed system does not allow chemicals to enter or leave.

Physical and chemical change

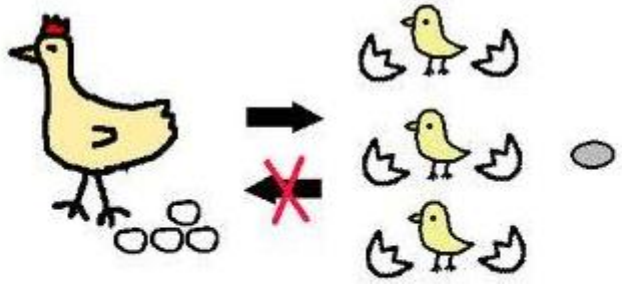
Chemical systems may be open or closed and include physical and chemical changes, which result in observable changes.

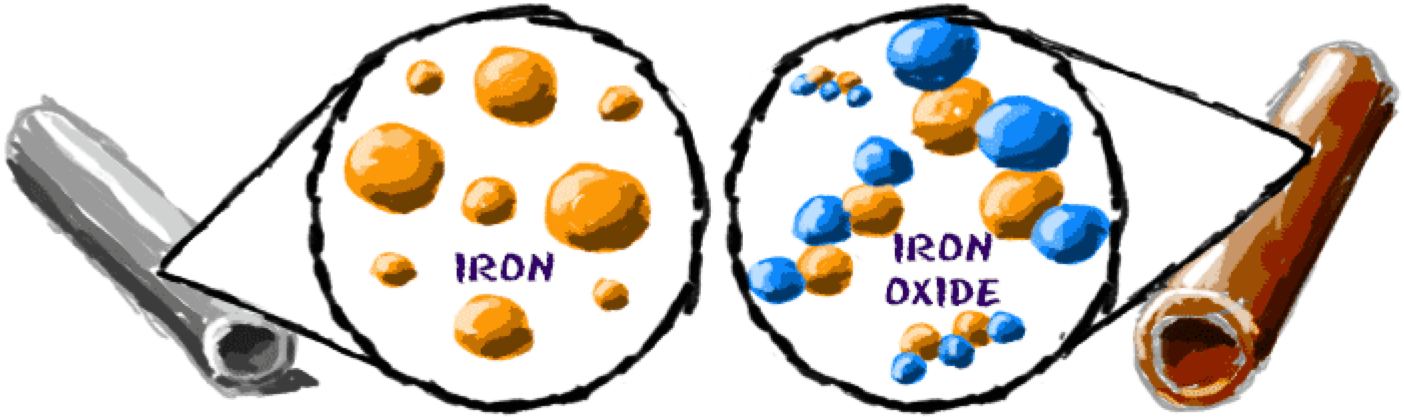
Physical change – products change state and physical properties alter. (Example: boiling water to form steam.)

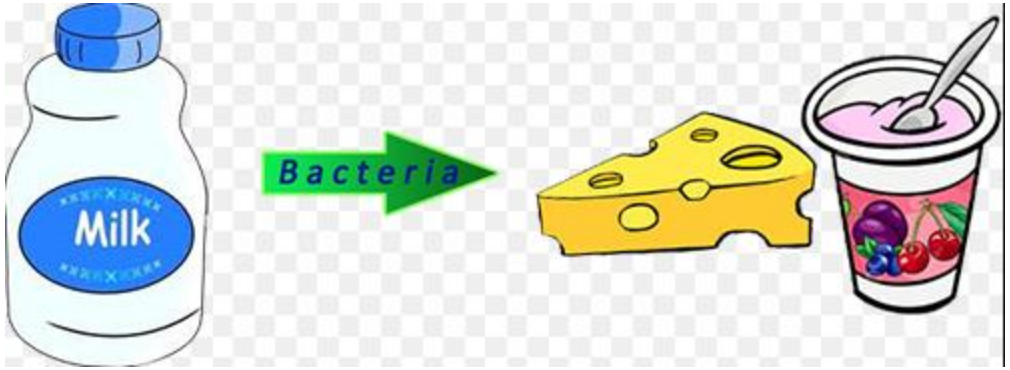
Chemical change – reactants form products with different physical and chemical properties.

Irreversible and Reversible Systems

- Products can not be converted into reactants- irreversible reactions.
- Non- reversible reactions have very high activation energy for both forward and reverse reactions.







Reversible Changes

- Products can be converted into reactants.
- Most physical changes are reversible
- Some chemical changes are reversible.
- Reversible reactions have a low Ea for both Fw and Rv reactions.
- Reversible reactions do not go completion, once the products are formed they combine to form the reactants.

$$\underbrace{A + B}_{\text{(reactants)}} \rightleftharpoons \underbrace{C + D}_{\text{(products)}}$$

Reversible reactions Examples

$$\underset{\text{Nitrogen}}{N_2} + \underset{\text{Hydrogen}}{3H_2} \rightleftharpoons \underset{\text{Ammonia}}{2NH_3}$$

$$\underset{\text{Nitrogen}}{N_2} + \underset{\text{Oxygen}}{O_2} \rightleftharpoons \underset{\text{Nitric oxide}}{2NO}$$

$$\underset{\text{Ammonium chloride}}{NH_4Cl} \rightleftharpoons \underset{\text{Ammonia}}{NH_3} + \underset{\text{Hydrochloric acid}}{HCl}$$

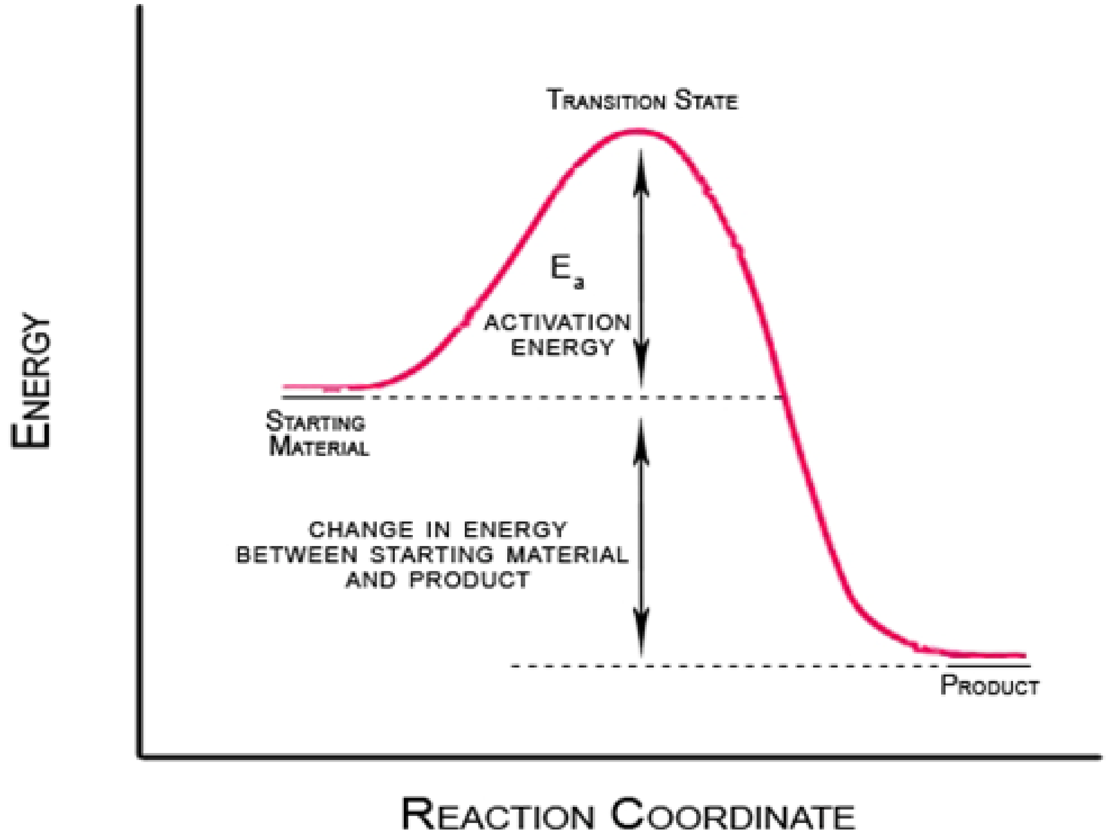
$$\underset{\text{Sulphur dioxide}}{2SO_2} + \underset{\text{Oxygen}}{O_2} \rightleftharpoons \underset{\text{Sulphur trioxide}}{2SO_3}$$

$$\underset{\text{Hydrogen}}{H_2} + \underset{\text{Iodine}}{I_2} \rightleftharpoons \underset{\text{Hydrogen iodide}}{2HI}$$

$$\underset{\text{Phosphorus pentachloride}}{PCl_5} \rightleftharpoons \underset{\text{Phosphorus trichloride}}{PCl_3} + \underset{\text{Chlorine}}{Cl_2}$$

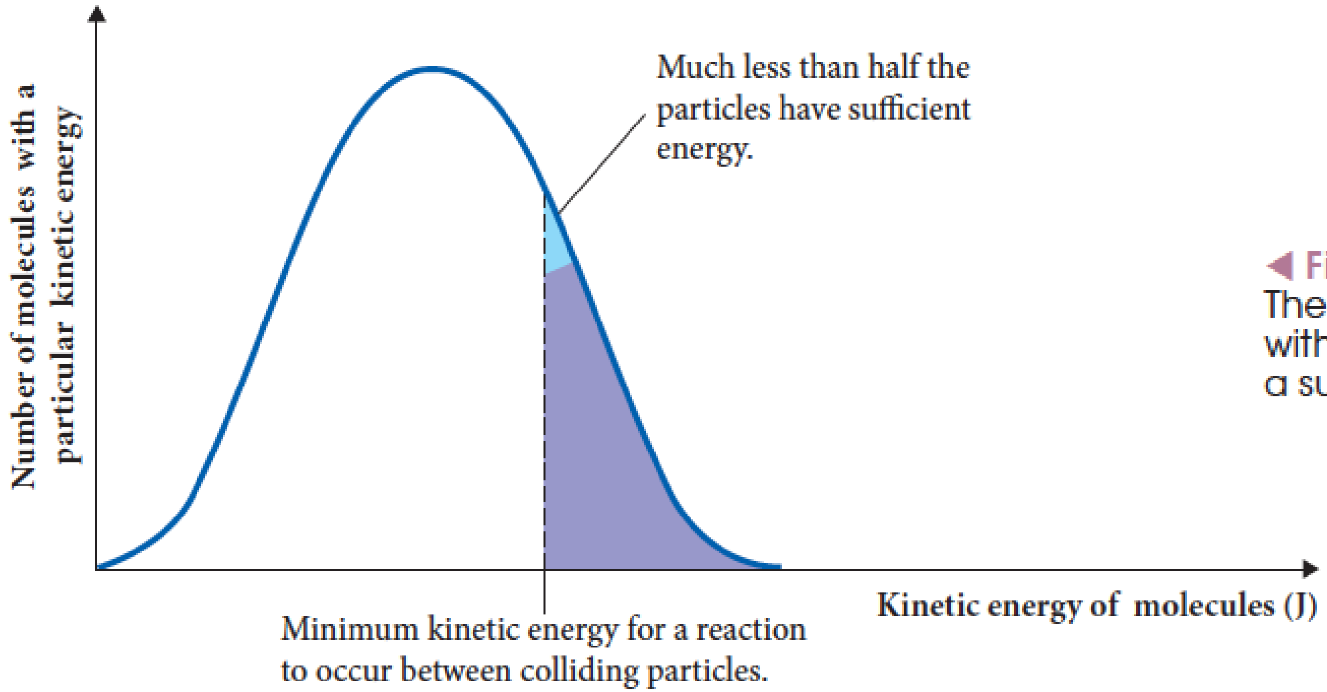
Predicting Reversibility

- Why some rxn are reversible?
- Ea- activation energy is the amount of energy to break the bond.
- Size of Ea influence the reaction proceedings.



Predicting reversibility

Reversible reactions are likely to form when the activation energies of both forward and reverse reactions are low enough that sufficient particles have energy for a successful collision.

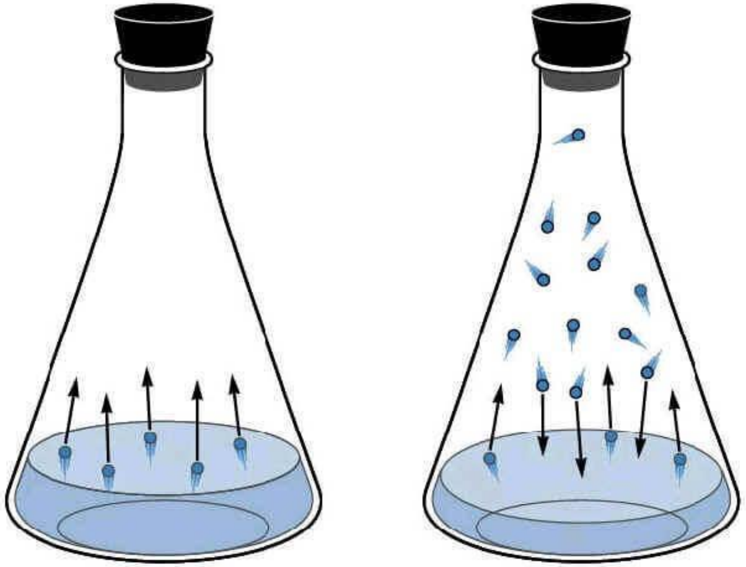


◀ Figure C1.7
The number of particles with enough energy for a successful collision.

Reversibility of Physical Changes
Evaporation and condensation of water

- $H_2O(l) \rightarrow H_2O(g)$ Evaporation
- $H_2O(g) \rightarrow H2O(l)$ Condensation

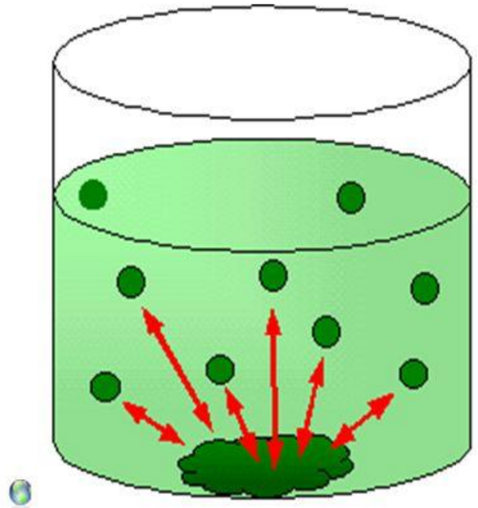
$$H_2O(l) \leftrightarrow H_2O(g)$$



- Closed system
- Rate of Fw reaction = Rate of Rv Reaction
- No further change to the observer
- State of equilibrium

Saturated salt/sugar solution

- Closed system
- Sugar molecules dissolving at the same rate as they are crystallizing.
- State of equilibrium

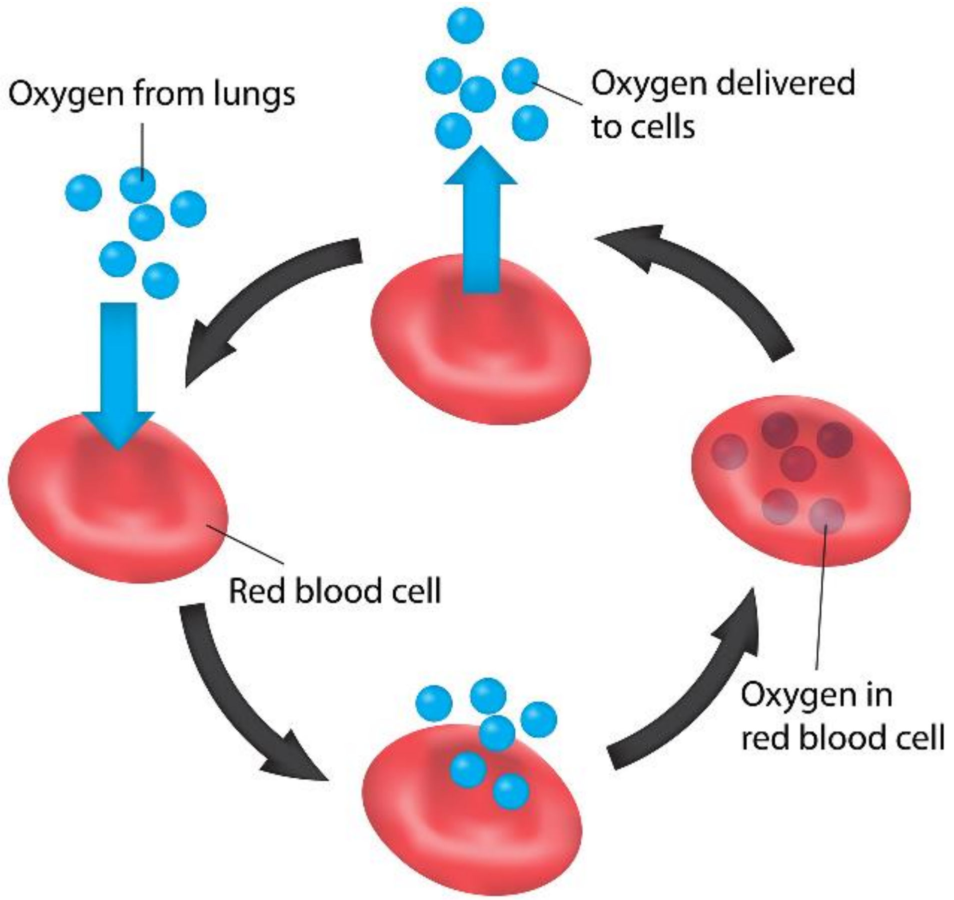


$$C_6H_{12}O_{6(s)} \rightleftharpoons C_6H_{12}O_{6(aq)}$$

Haemoglobin and Oxygen Gas

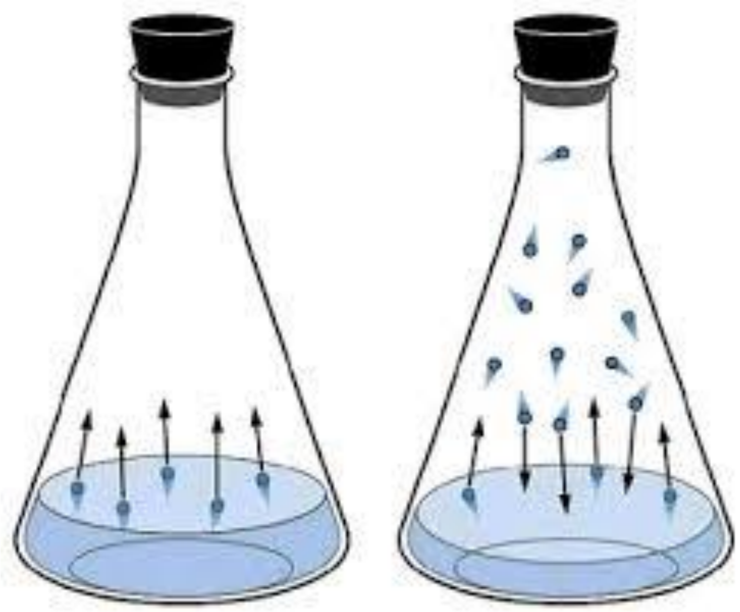
$$\underset{\text{hemoglobin}}{Hb} + \underset{\text{Oxygen}}{O_2} \rightleftharpoons \underset{\text{Oxyhemoglobin}}{HbO_2}$$

- Closed system
- Reversible reaction
- At equilibrium



Dynamic Equilibrium

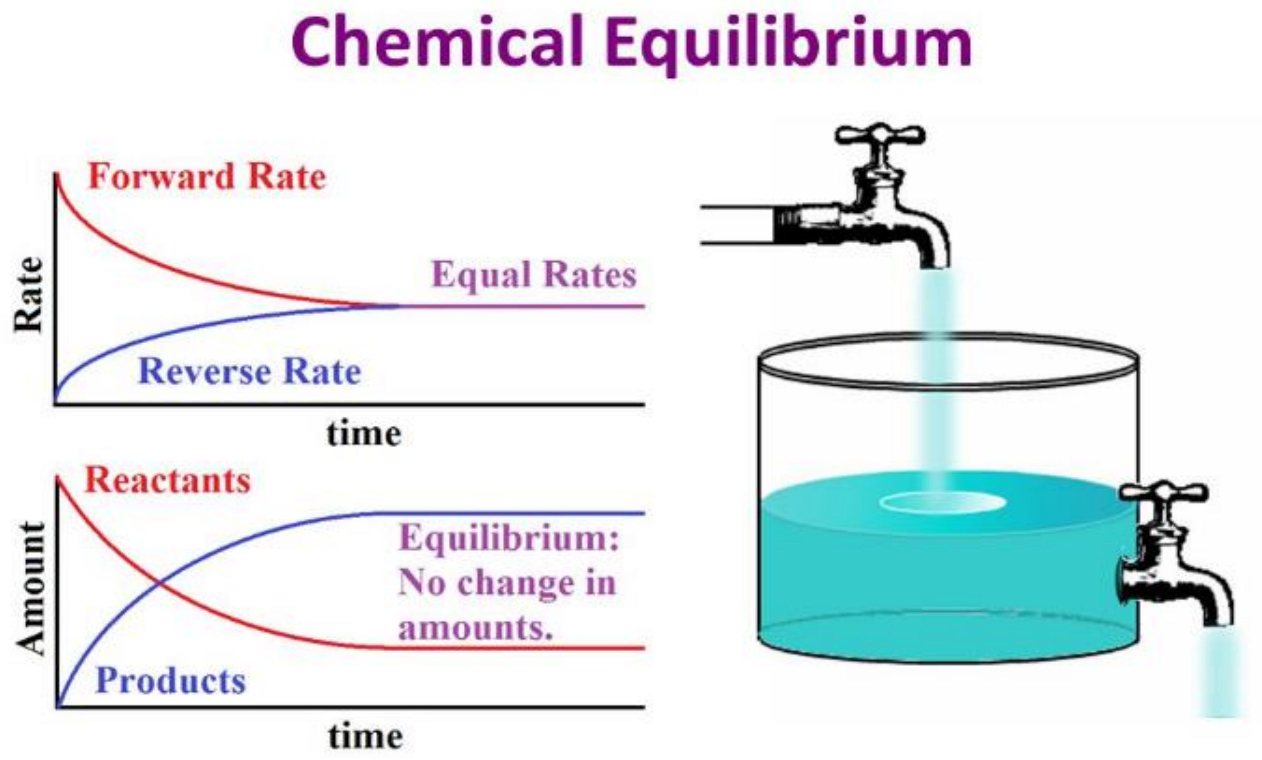
Reversible reactions in a closed system reach a state of dynamic equilibrium where the concentrations of reactants and products remain constant.



It is a state where the amount of reactants and products remains constant, however the Fw and Rv reactions still occur.
Also called a steady state system. These have constant observable properties such as pH, colour and volume.

2 types-

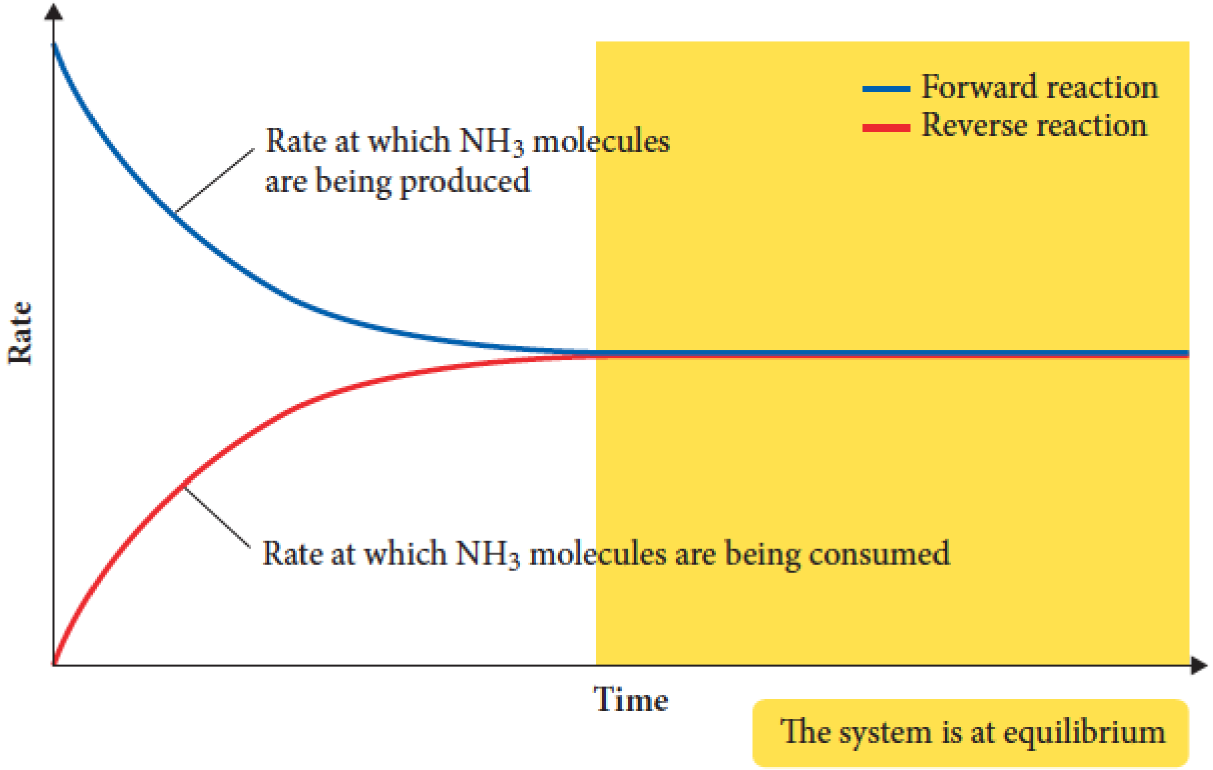
- Physical equilibrium
- Chemical equilibrium



Understanding Equilibrium

Equilibrium in chemical systems

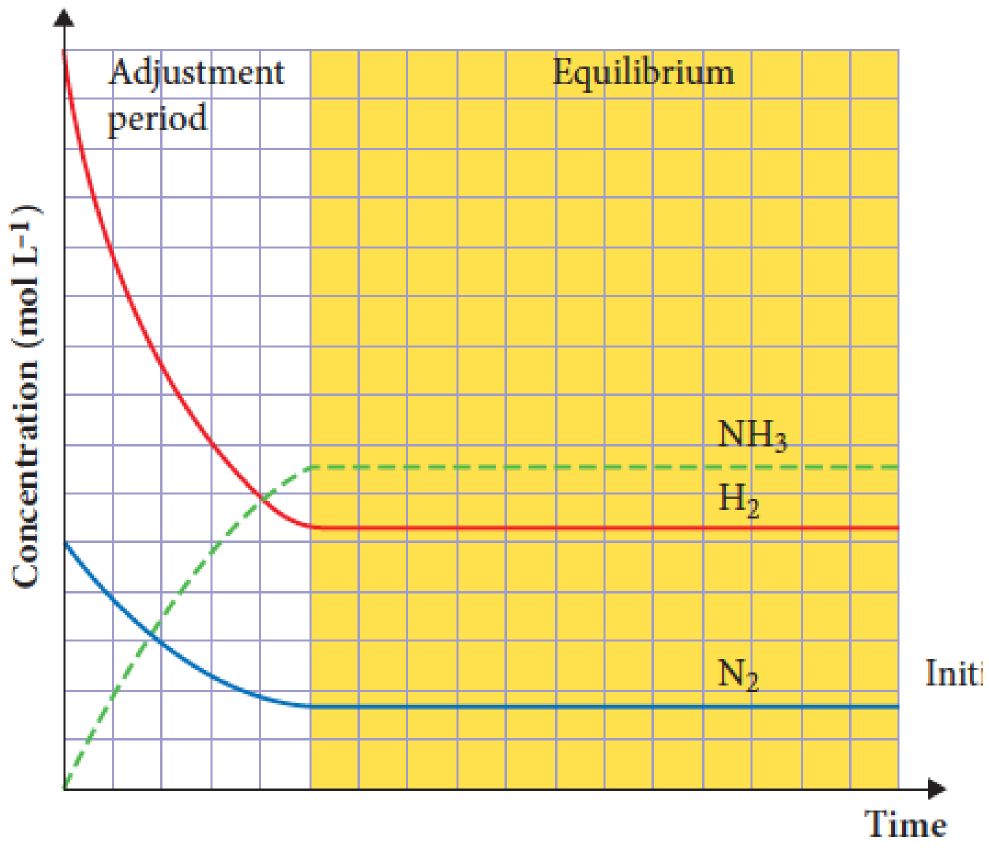
Dynamic equilibrium happens when the rates of forward and reverse reactions are equal and concentrations of products and reactants are constant.



Equilibrium in chemical systems

Adding reactants to a system results in a fast initial rate of forward reaction that gradually slows as reactants form products.

Rate of forward reaction slows and rate of reverse reaction increases as concentrations change.



Equilibrium in chemical systems

Summary

A chemical system will reach equilibrium if it:

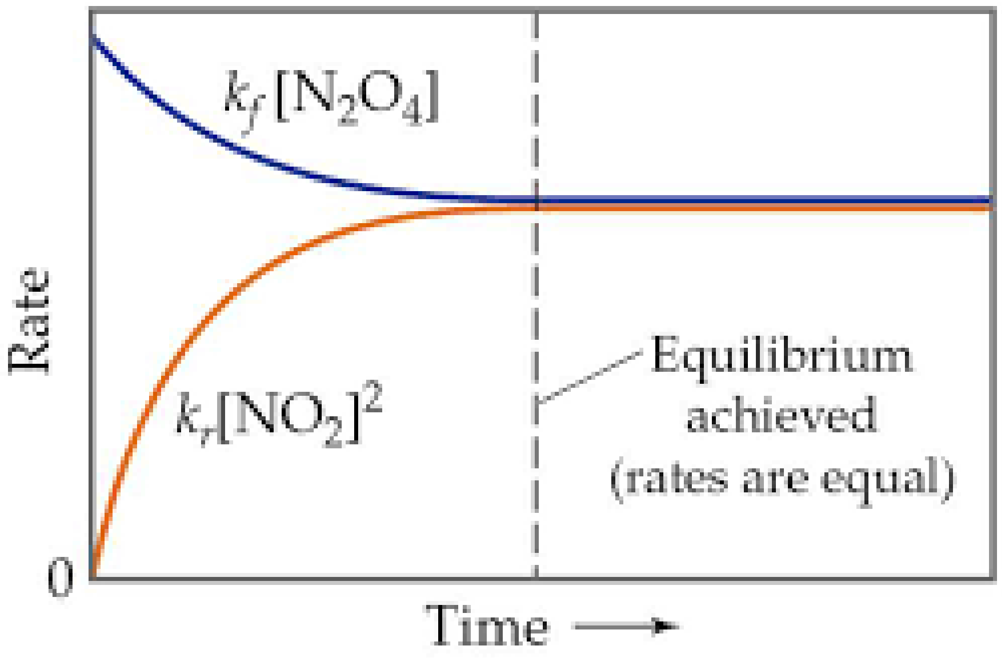
- is a closed system
- involves a reversible reaction.

At equilibrium, the:

- rate of the forward reaction is the same as the rate of the reverse reaction
- concentrations of the reactant and products remain constant
- macroscopic properties are constant.

Graphing Equilibrium Rate and Time Graph

- Time- X axis
- Rate- Y axis
- Initially Fw rate is very high, will decrease quickly then slowly.
- Initially Rv rate zero will increase quickly then slowly
- The rates will become equal when reached equilibrium

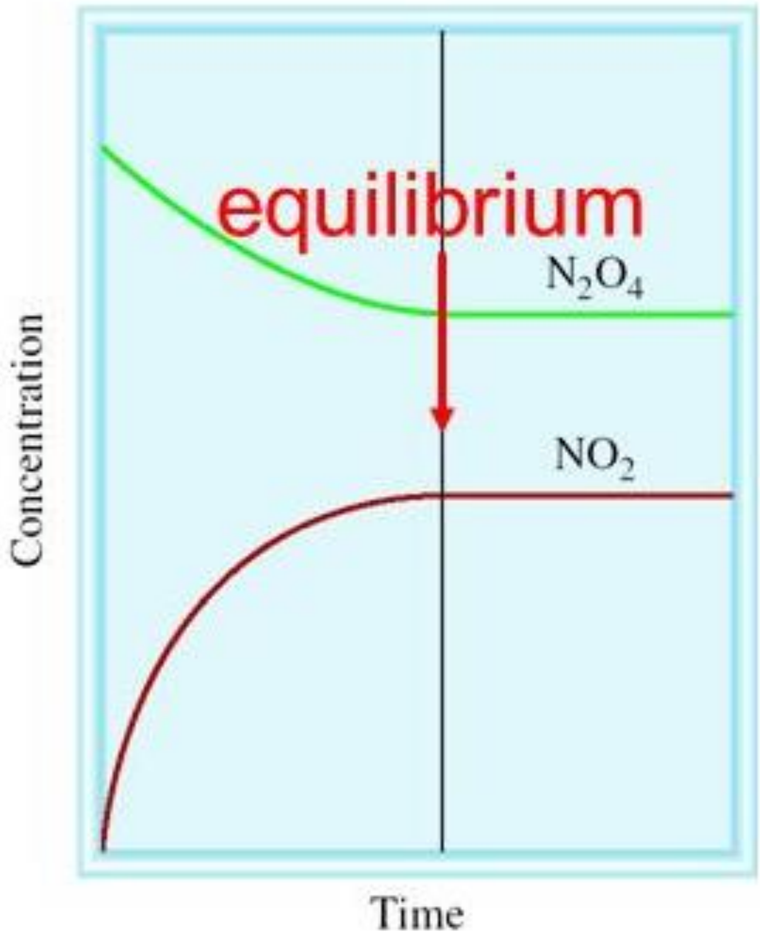


(b)

Concentration and Time Graph

- Time- X axis
- Conc- Y axis
- Initially conc of reactants very high, will decrease quickly then slowly.
- Initially conc of products zero, will increase quickly then slowly.
- Plateau same when reaches equilibrium

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$



Start with N_2O_4

Graphing reaction rate and time

1 Rate of forward reaction is initially high.

2 Rate of reverse reaction is initially zero.

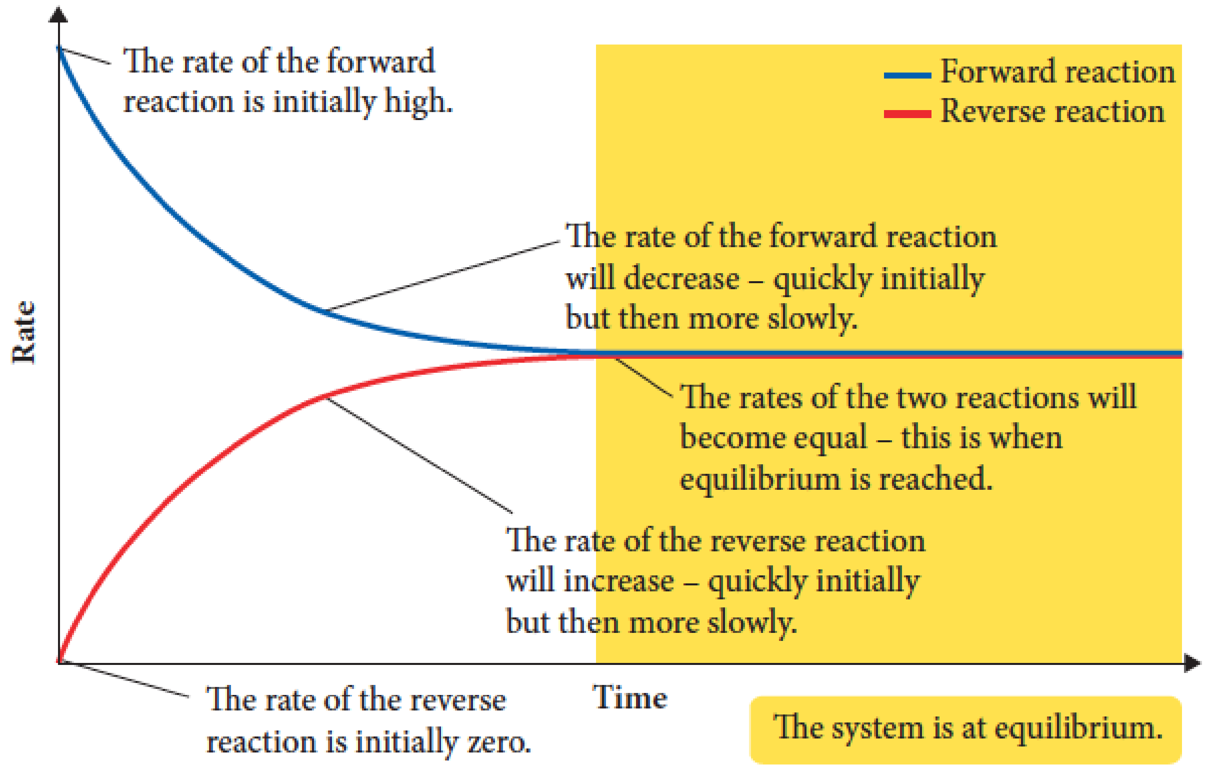


Figure C1.11 Graph of rate of reaction rate vs time for the reaction

$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$

Graphing reaction rate and time

3 Rate of the forward reaction will decrease.

4 Rate of the reverse reaction will increase.

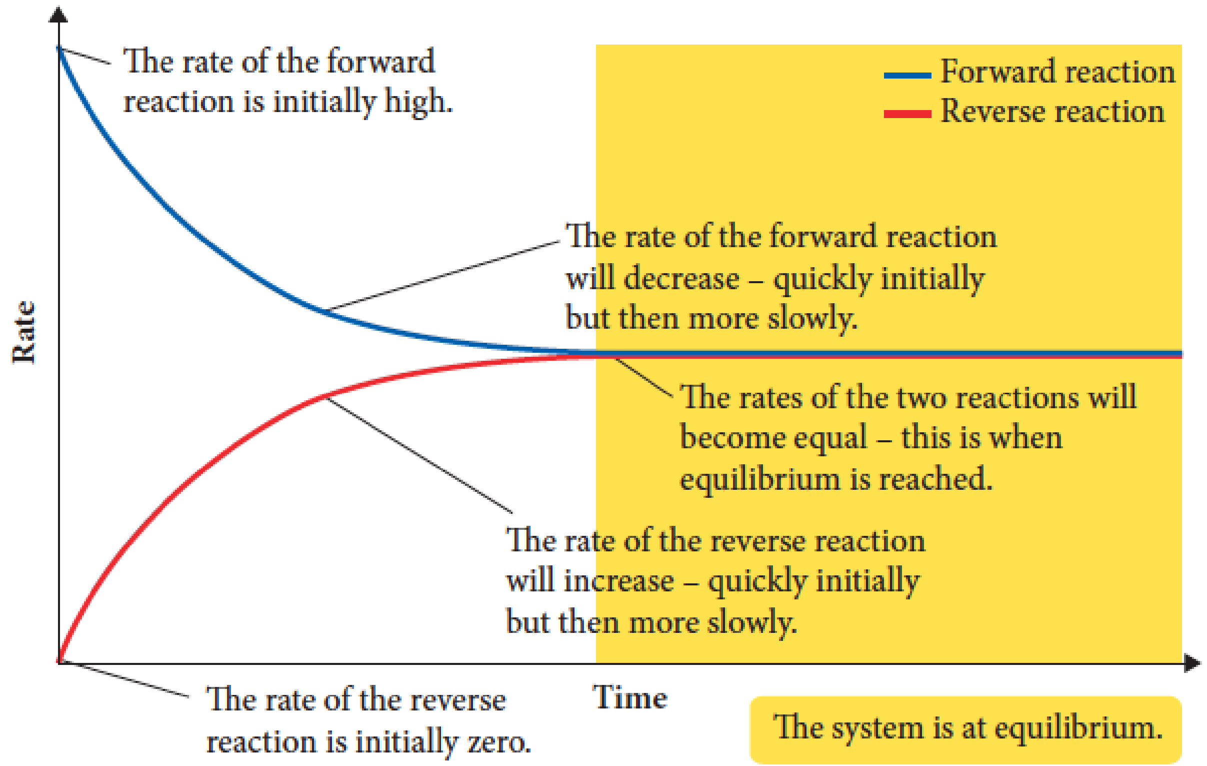


Figure C1.11 ▶ Graph of rate of reaction rate vs time for the reaction

$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$

Graphing reaction rate and time

5 Rates of the two reactions become equal and equilibrium is reached.

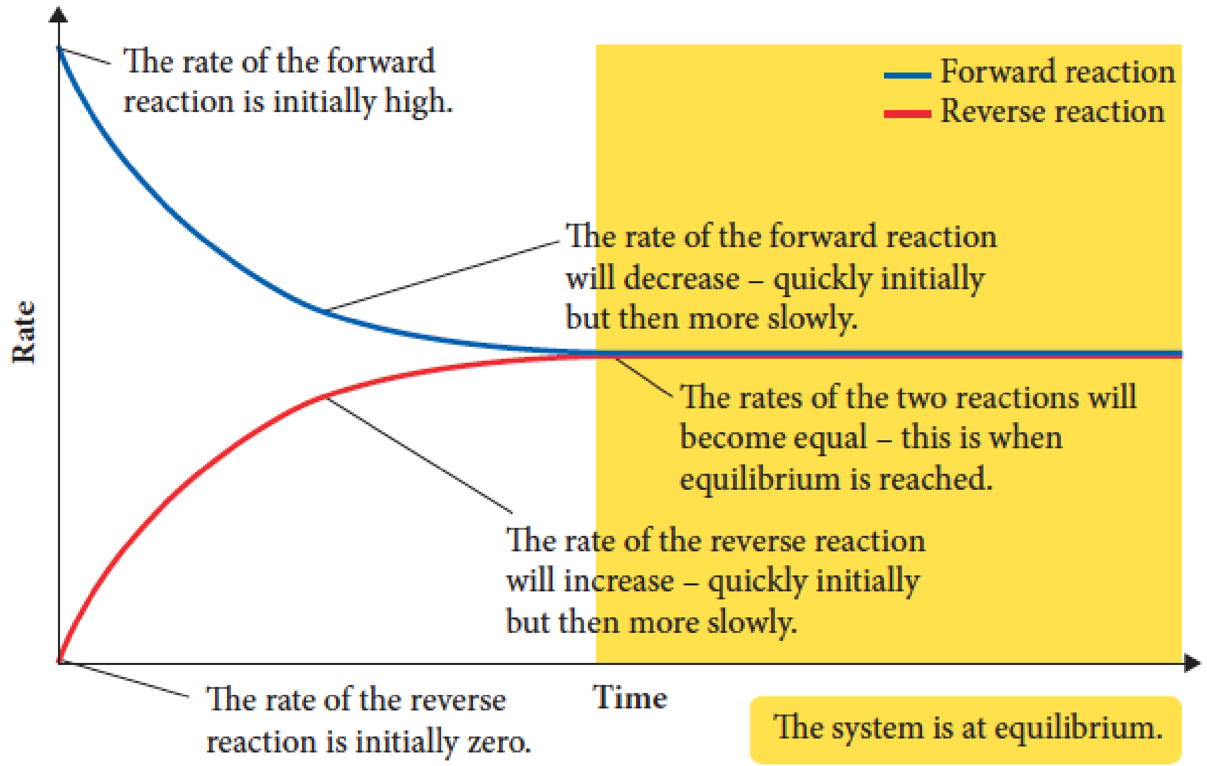


Figure C1.11 ▶
Graph of rate of reaction rate vs time for the reaction

$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$

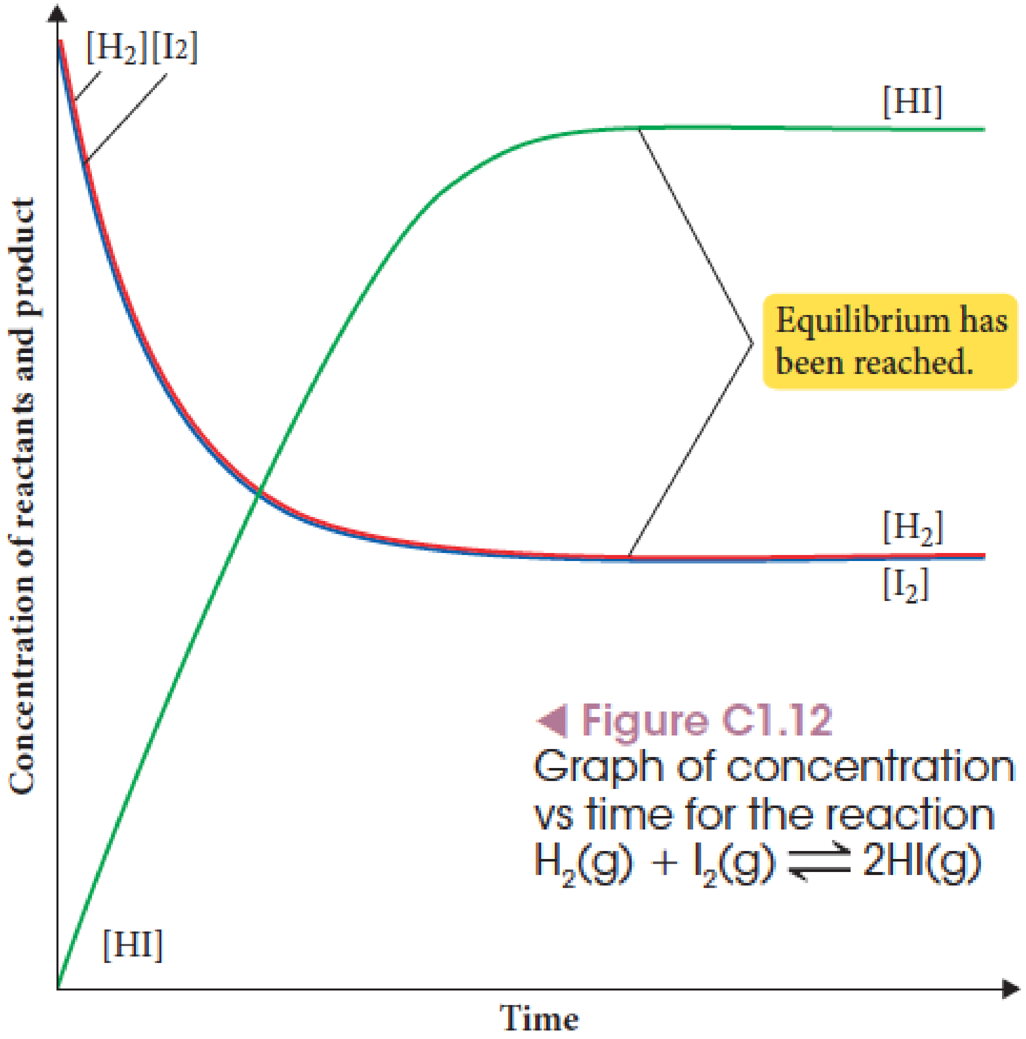
Graphing concentration and time

To discuss rate in these graphs, draw a tangent to the slope at a point.

$$\text{slope} = \frac{\text{concentration}}{\text{time}}$$

$$\text{rate} = \frac{\text{concentration}}{\text{time}}$$

So slope of line = rate reaction

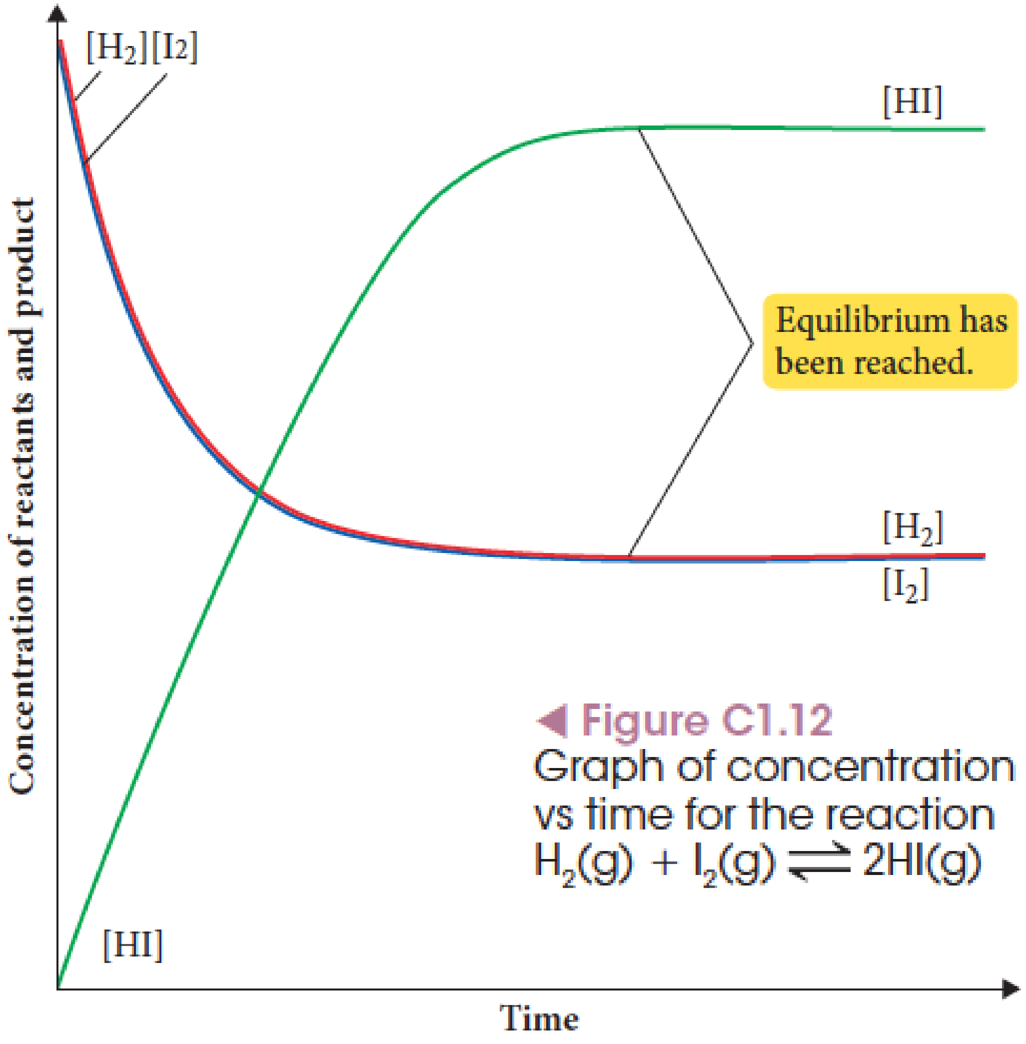


◀ Figure C1.12
Graph of concentration vs time for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Graphing concentration and time

1 Concentration of reactants is initially large.

2 Concentration of products is initially zero.

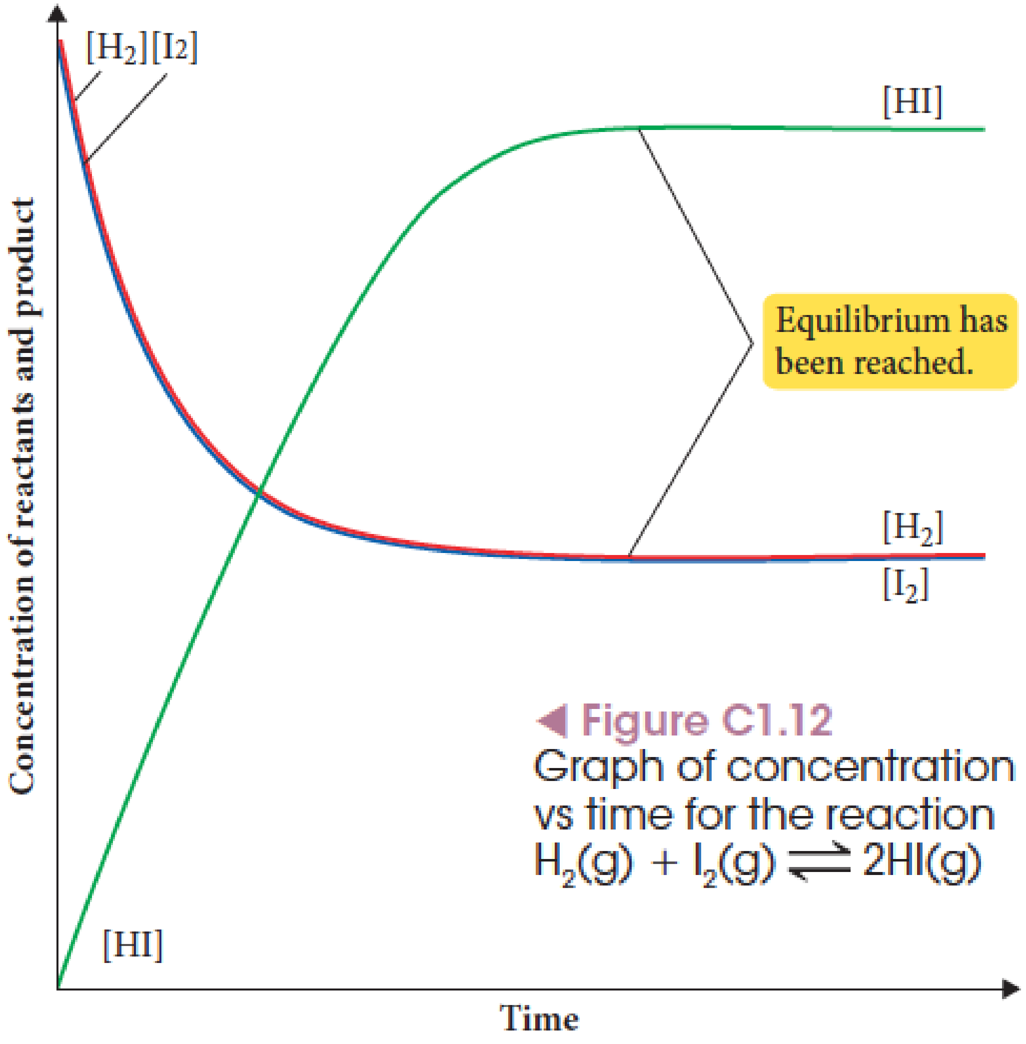


◀ Figure C1.12
Graph of concentration vs time for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Graphing concentration and time

3 Concentration of reactants decreases, initially quickly, then more slowly.

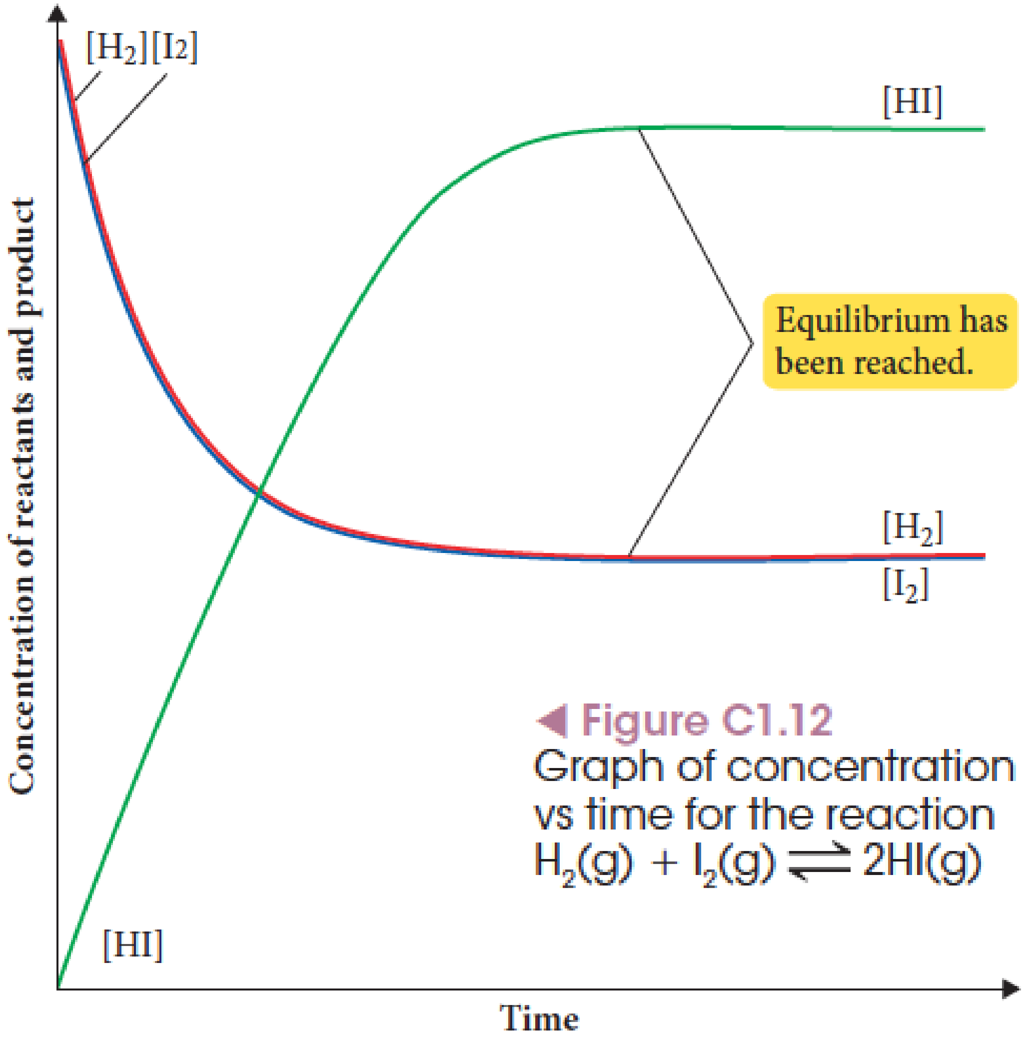
4 Concentration of products increase, initially quickly, then more slowly.



◀ Figure C1.12
Graph of concentration vs time for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Graphing Concentration and Time

5 All concentrations will plateau when the system reaches equilibrium.



◀ Figure C1.12
Graph of concentration vs time for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Graphing summary

Table C1.1 Graphing concentration and reaction rate vs time

Graph	Number of lines	Position of line at equilibrium
Concentration vs time	Any number depending on the number of reactants and products. Each may be represented on the graph by a separate line	All lines plateau as concentrations are constant. They do not need to be equal.
Reaction rates vs time	Two lines – forward reaction and reverse reaction	The two lines meet and plateau as the two rates are equal.

Chapter 2: Equilibrium

Equilibrium constants

Homogeneous and Heterogeneous Equilibria

- <u>Homogeneous reaction- </u>reactions and products are in same phase or state.
- <u>Heterogenous Reaction- </u>reactions and products are in different phase or state.

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

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Cu(s) + Zn^{2+}(aq)$$

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

Examples:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + . CO_{2(g)}$$

What is an equilibrium constant?

Equilibrium constant (also K) – the mathematical relationship between the concentrations of reactants and products. It is specific for a particular reaction at a particular temperature.

It can be calculated from the equilibrium expression.

For the reaction:

$$aA + bB \rightleftharpoons cC + dD$$

the equilibrium expression is:

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

What substances are included?

The equilibrium constant is based on the ratio of concentrations of reactants and products.

Solutions and gases vary in concentration so are included in the expression.

Solids and liquids do not vary in concentration.

- They are NOT included when the system is heterogeneous (contains more than one phase).
- They ARE included when the system is homogeneous (all solid or all liquid).

Reaction quotient

The equilibrium constant is equal to *K* when the system is at equilibrium.

If the system is not at equilibrium, the equilibrium expression $\frac{[C]^c[D]^d}{[A]^a[B]^b}$ can be used to calculate Q.

- If Q = *K* then the system is at equilibrium
- If Q > *K* then there are less products and more reactants than at equilibrium.
- If Q < *K* then there are more products and less reactants than at equilibrium.

Size of the equilibrium constant

Equilibrium constants predict the relative concentrations of products and reactants and therefore the position of equilibrium.

When calculating *K* remember that products are on top of the fraction.

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

If the *K* value is large:

- the reaction goes towards completion
- more products are present than reactants
- equilibrium lies to the right.

Size of the equilibrium constant

If the *K* value is small:

- the reaction only occurs to a small extent
- more reactants are present than products
- equilibrium lies to the left.

If the value of *K* is close to 1, then there are significant concentrations of both products and reactants present.

Yield and rate of reaction

Yield – how much product can be produced

Yield is dependent on position of equilibrium.

Reactions with low K values have low concentration of products and hence low yield.

The rate of reaction indicates how quickly this yield will be achieved.

Summary

An equilibrium constant has the following characteristics:

- It is a constant value for a particular equation representing a reaction at a given temperature.
- If the temperature of a reaction is changed, then the value of the equilibrium constant also changes.
- It indicates the relative proportions of reactants and products in an equilibrium mixture. If the equilibrium constant has a very large value, it means large concentrations of products and very small concentrations of reactants are present; in other words, the reaction is almost 100% complete. If the equilibrium constant is very small, then the concentrations of reactants must be very large and the concentrations of products very small, which means the reaction would be almost insignificant. The size of the equilibrium constant gives an indication of the extent of the reaction.
- It provides no indication of the rate of the reaction, i.e. it does not indicate how quickly a particular reaction reaches equilibrium.

Temperature affects the K value…why?

- Temperature affects the proportion of particles with enough energy to overcome the Ea.
- It also depends on weather a reaction is exothermic or Endothermic.
- <u>As the temperature of a system increases-</u>

The Effect of Temperature on K_c

- Consider the following:

Example	Endothermic reaction $2HI(g) \leftrightarrows H_{2(g)} + I_{2(g)}$	Exothermic reaction $2SO_{2(g)} + O_{2(g)} \leftrightarrows 2SO_{3(g)}$
Temp increase	Kc Increases Amont of Products increase	Kc Decreases Amount of products decrese

The Effect of Temperature on K_c

- Consider the following:

Example	Endothermic reaction $2HI(g) \leftrightarrows H_{2(g)} + I_{2(g)}$	Exothermic reaction $2SO_{2(g)} + O_{2(g)} \leftrightarrows 2SO_{3(g)}$
Temp increase	Equilibrium position shifts RIGHT – more PRODUCTS	Equilibrium position shifts LEFT- more REACTANTS
Temp decease	Equilibrium position shifts LEFT- more REACTANTS	Equilibrium position shifts RIGHT- more PRODUCTS

Chapter 2: Equilibrium

Effect of changes to temperature, pressure and concentration

Changes to equilibrium

If changes are made to:

- temperature
- concentration
- partial pressure

of an equilibrium system then the ratio of products to reactants changes.

The system will favour either the forward or reverse reaction to return the system to equilibrium.
This often results in an overall increase in a particular species in the system.

Changes to concentration and partial pressure

> The effects of changes of concentration of chemicals can be explained by applying collision theory.

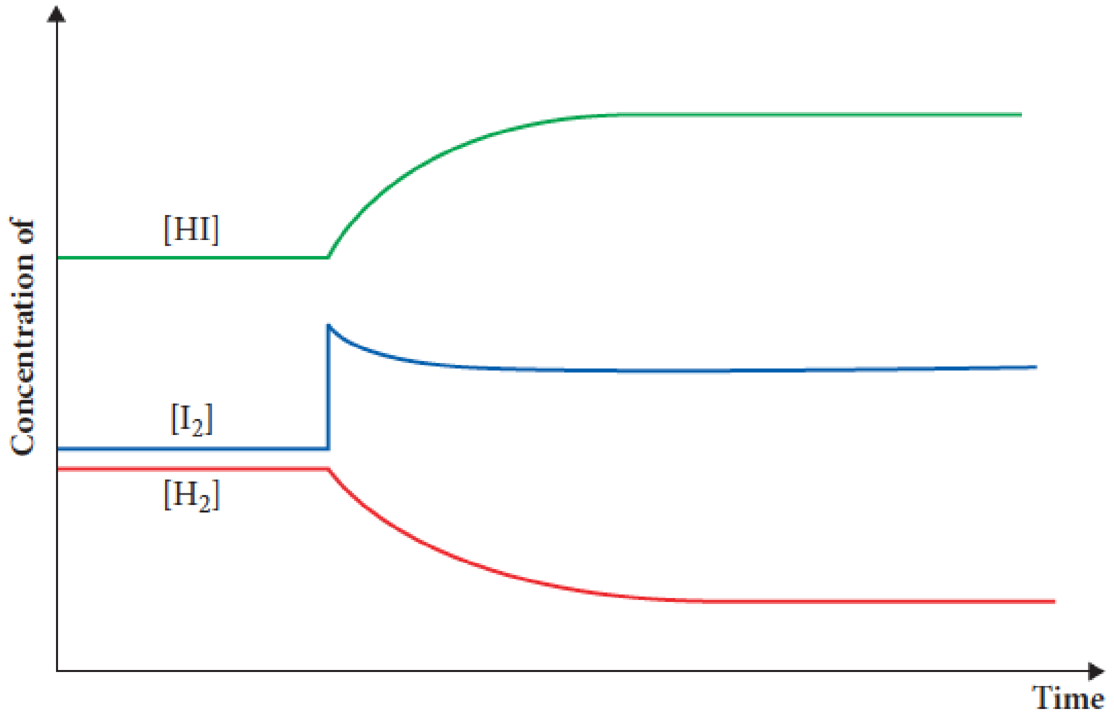
When concentration of a reactant is increased (including pressure increases), collision theory states rate of reaction will increase due to increased collisions.

- This uses additional reactant, reducing its concentration, reducing rate of forward reaction.
- Additional product will form so rate of reverse reaction increases.
- Eventually rates of the two reactions equalise.

Changes to concentration and partial pressure

Using $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ and Figure C1.13:

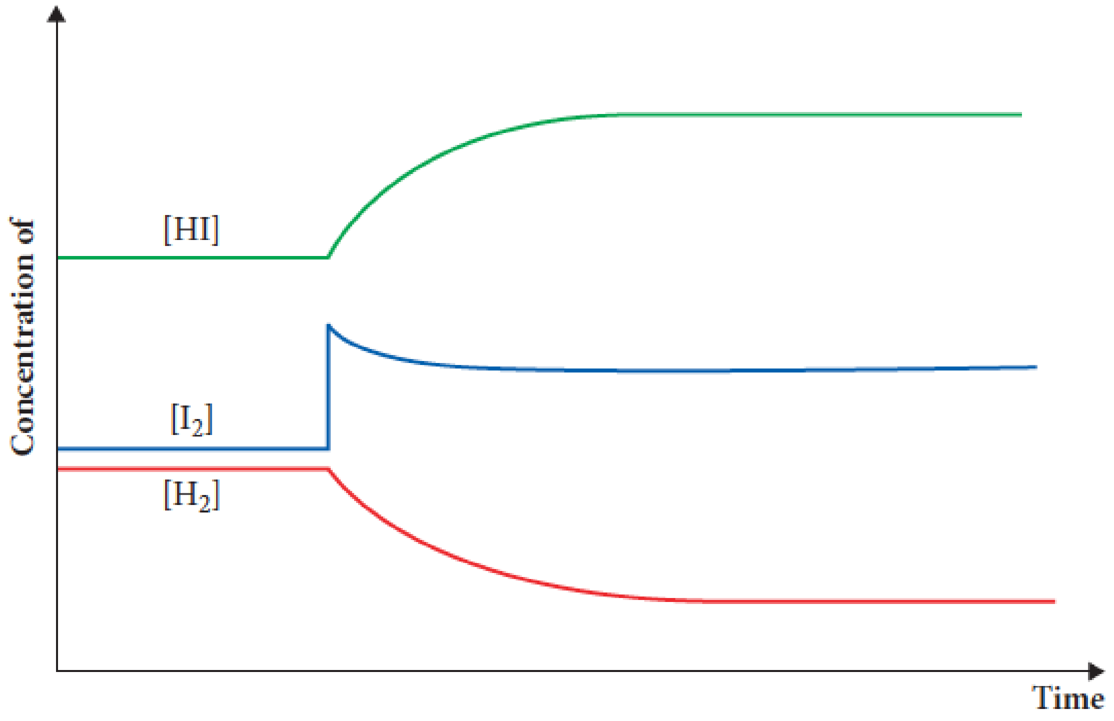
- Iodine is added to the system, increasing the rate of the forward reaction.
- Concentration of iodine and hydrogen reduce, while hydrogen iodide increases.



◀ Figure C1.13
Rate and concentrations following a change in concentration for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Changes to concentration and partial pressure

- As more hydrogen iodide is produced, the rate of the reverse reaction increases.
- This pattern continues until the forward and reverse rates are equal and equilibrium is re-established (parallel lines on graph).



◀ Figure C1.13
Rate and concentrations following a change in concentration for the reaction
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Le Chatelier’s principle

Le Chatelier's principle states that:
If a system at equilibrium is subject to a change in conditions, then the system will behave in such a way so as to partially counteract the change.

To use the principle to predict changes in a system, consider:

1. What is the change?
2. What is the opposite of the change?
3. Which reaction is favoured – forward or reverse?
4. Does equilibrium shift left or right?
5. What happens to the concentrations of each substance?

Changes to concentration/partial pressure- Le Chatelier's principle

If the concentration of a reactant is increased:

- the system responds to decrease it by favouring the forward reaction, using up the reactant
- equilibrium shifts to the right, increasing the concentration of the products and decreasing the concentration of reactants.

The system cannot fully counteract the change so the reactant concentration does not fully return to initial levels.

Changes to concentration/partial pressure- Le Chatelier's principle

Changes to partial pressure result in concentration changes and the effect is the same.

Table C1.3 The effect of a change in concentration or partial pressure on equilibrium

Imposed change		Reaction favoured (forward or reverse)	Shift in equilibrium (left or right)	Resultant change in concentration or partial pressure of reactants	Resultant change in concentration or partial pressure of products
Product or reactant altered	Increase or decrease in concentration or partial pressure				
Reactant	Increase	Forward	Right	Decrease	Increase
Reactant	Decrease	Reverse	Left	Increase	Decrease
Product	Increase	Reverse	Left	Increase	Decrease
Product	Decrease	Forward	Right	Decrease	Increase

Changes to volume and pressure

When volume or pressure of a system is changed, the concentration of all gaseous species is also changed.

The species that changes most has the greatest effect on equilibrium change.

Changes to volume and pressure

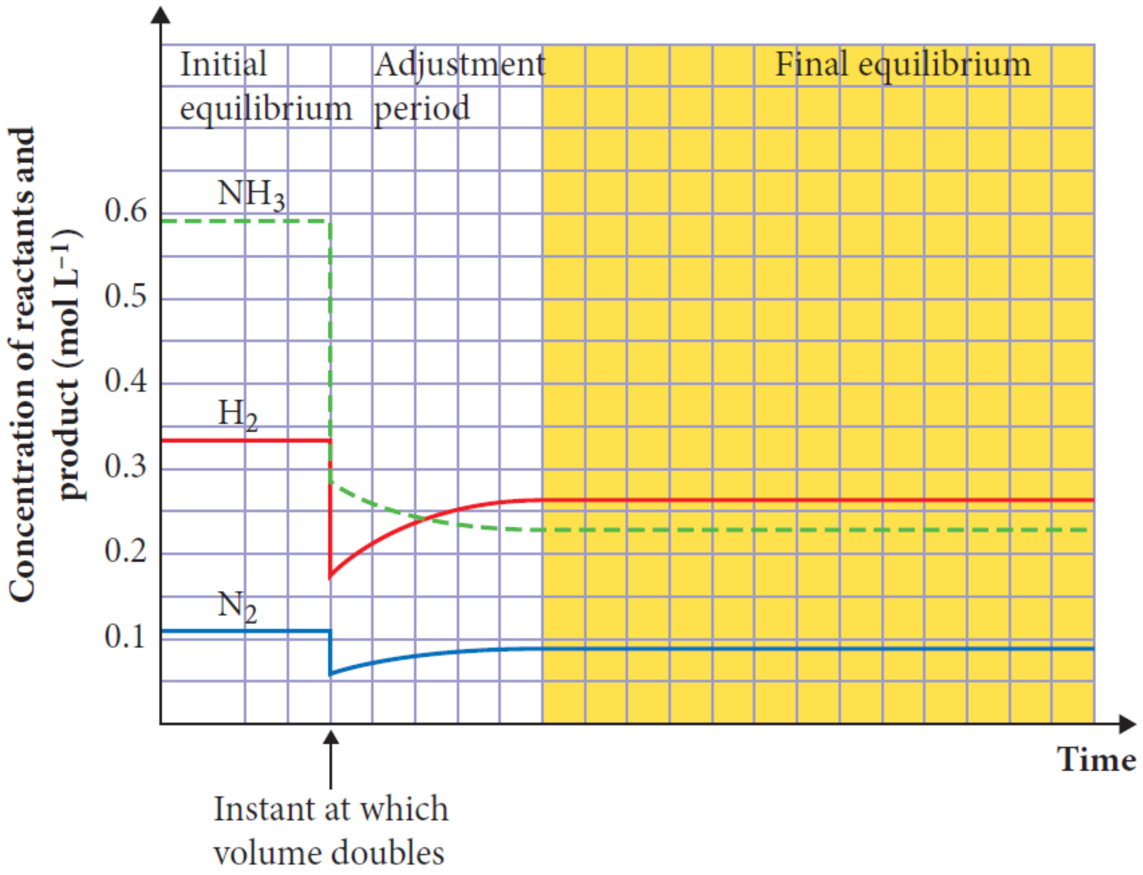
Consider $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$

- There is a ratio of 4:2 gas molecules between reactants and products.
- If pressure is increased, all gases increase in concentration but there is a greater proportion of reactant gas molecules and more collisions.
- Hence the forward reaction is favoured and more ammonia is produced.
- Again, the rates eventually equalise and equilibrium is re-established.

Changes to volume and pressure

The sharp change in all substances shows a change in pressure or volume rather than addition of one substance to the system.

Equilibrium re-established when concentrations remain constant.



◀ Figure C1.14
Changing the volume of a gaseous system

Changes to volume-Le Chatelier’s principle

If the volume of a gaseous system changes, the concentration of all aqueous or gaseous substances changes.

Le Chatelier’s principle says the system will react to reverse this change and restore the initial concentrations.

The key to predicting what happens is the number of gas molecules in reactants and products.

Changes to volume-Le Chatelier's principle

Using an example:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$1 + 3 = 4$ $\qquad$ 2

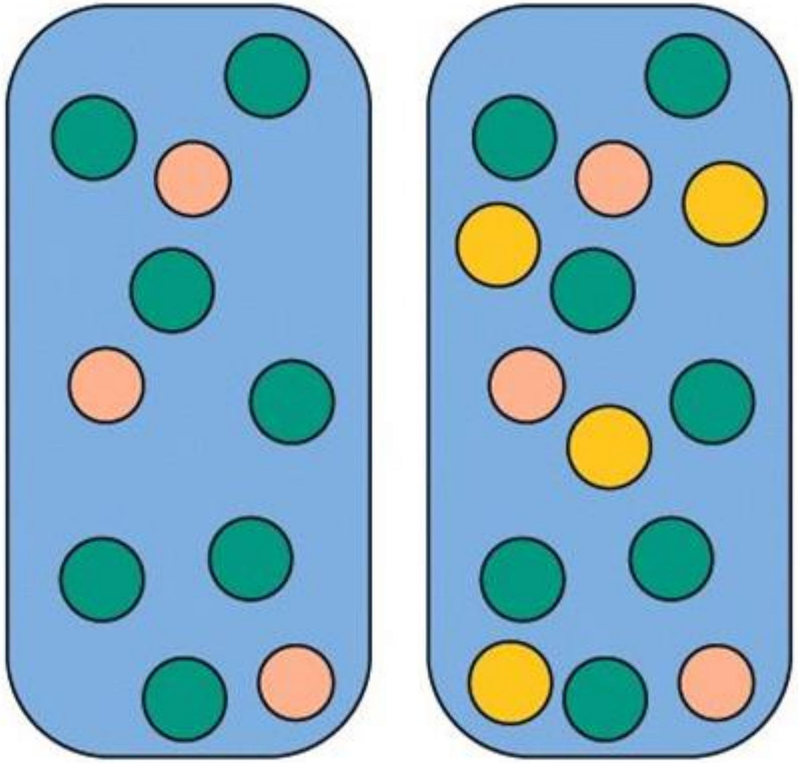
$\therefore$ 4 gas molecules used $\qquad$ 2 gas molecules produced

- If the volume of the system is decreased, then pressure of the system increases.
- Le Chatelier's principle says the system reacts to decrease the pressure by reducing the number of gas molecules.
- The forward reaction is favoured and more ammonia is produced.

Adding an Inert gas

- Equilibrium unaffected
- Total pressure of the system increases without changing the concentrations of reactants and products.

Introducing inert gas (yellow) has no effect on the equilibrium composition.

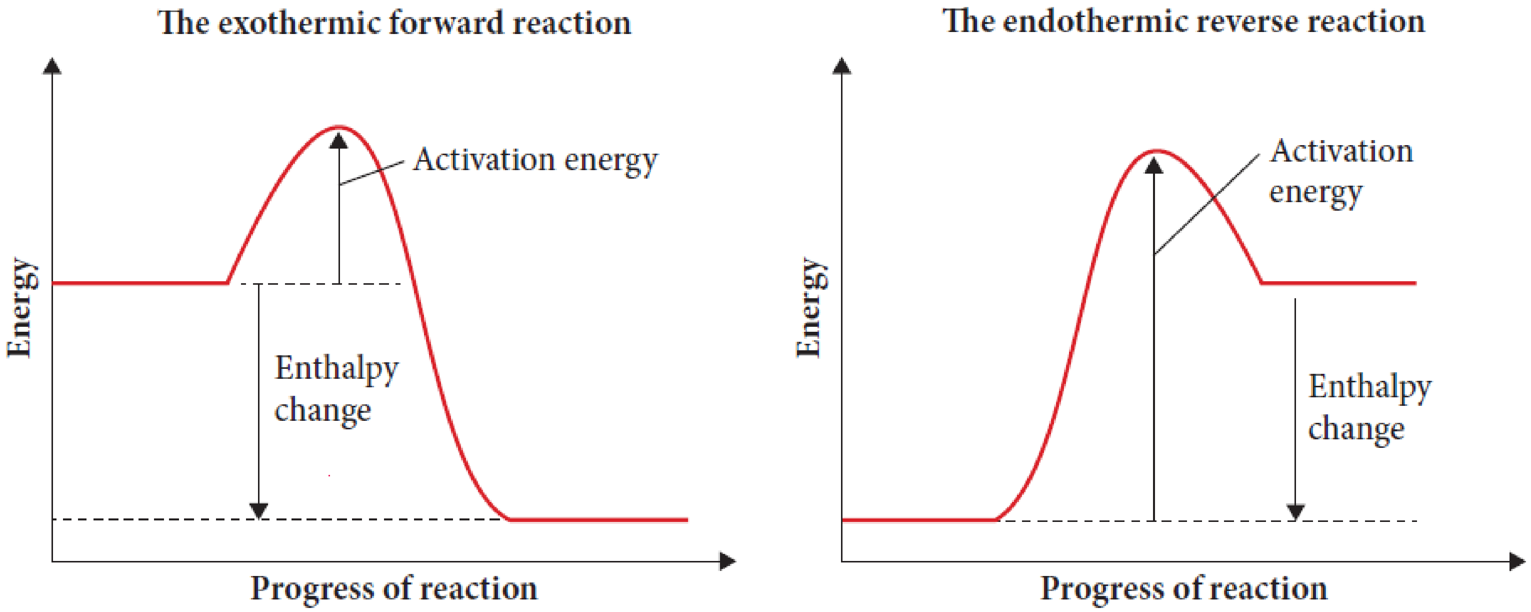


Dilution

- If we dilute a solution by adding solvent, all of the concentrations will decrease.
- When we dilute a reaction at **equilibrium** the reaction will shift in such a way to increase the total concentration.
- This means moving towards the side of the reaction with a greater number of species in solution.
- <u>Adding water does affect equilibrium</u> for a reaction with different number of moles on each side.
- ***Dilution of an aqueous ionic equilibrium favors the reaction that produces more ions.***

Changes to temperature

In an endothermic reaction, the products have more enthalpy than reactants, so energy is absorbed from the surroundings.
In an exothermic reaction, reactants have more energy so energy is lost to the surroundings.



▲ Figure C1.15 Comparing the activation energy for the forward and reverse reactions of:
reactants $\rightleftharpoons$ products + energy
Note how the activation energy for the endothermic reaction is greater than the activation energy for the exothermic reaction.

Changes to temperature

The effect of temperature changes on a chemical system can be explained by considering the enthalpy changes for the forward and the reverse reactions.

When temperature is increased, both forward and reverse reaction rates increase, but the endothermic rate will increase more.

A greater percentage of particles are able to react in the endothermic reaction due to the higher activation energy.

More endothermic products are produced, so the exothermic rate increases. Eventually equilibrium is re-established.

Changes to temperature

- The forward reaction is exothermic.
- If temperatures is increased, endothermic direction is favoured.
- Reverse reaction favours increase in SO_2/O_2.

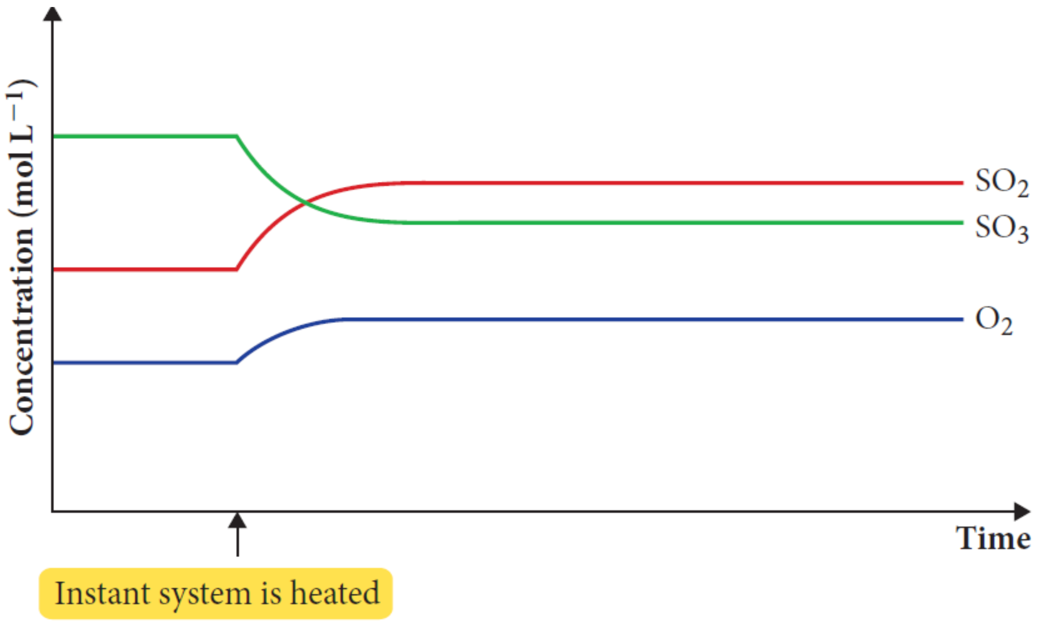


Figure C1.16 Concentrations with a change in temperature for the reaction: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

Changes to temperature - Le Chatelier’s principle

If temperature of a system is increased, then added energy is present.

Le Chatelier’s principle acts to oppose this change by driving reactions in an endothermic direction to absorb this energy.

If temperature is decreased, the exothermic direction is favoured to produce heat energy and oppose the change.

Changes to temperature - Le Chatelier's principle

Consider production of ammonia:

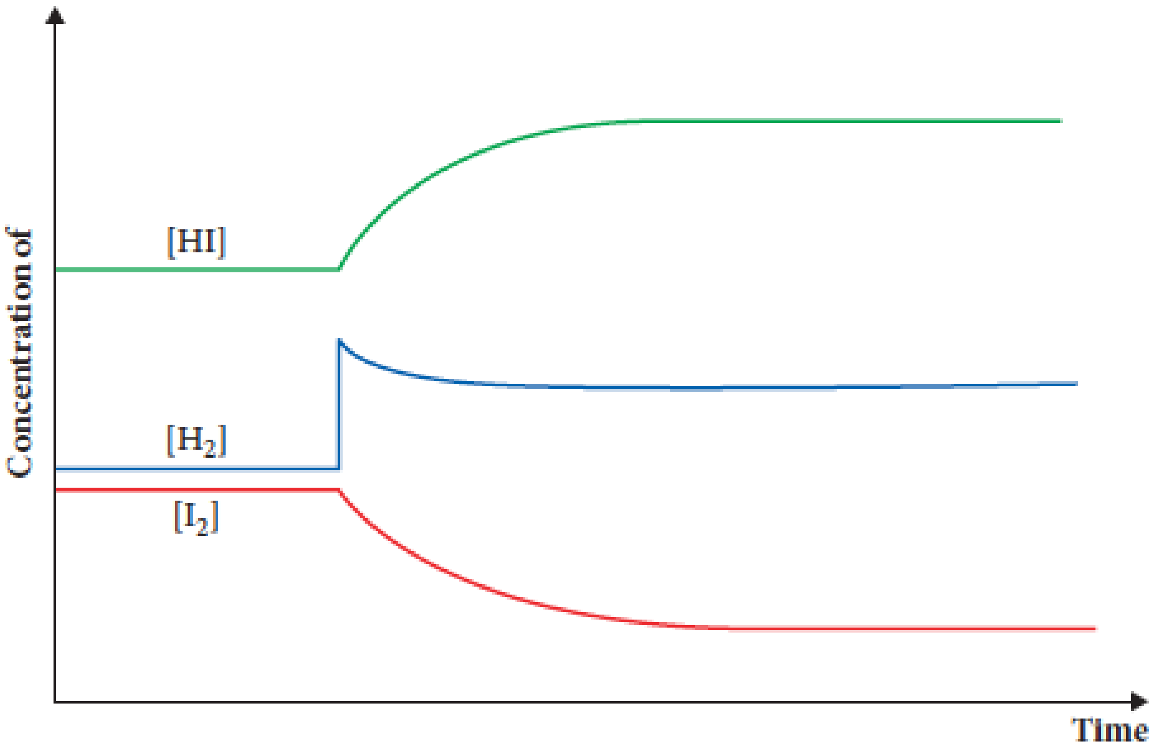
$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)\ \Delta H = -92.4\ \text{kJ mol}^{-1}$$

- The forward reaction is exothermic.
- If temperature is increased, the endothermic reaction is favoured to use up the energy.
- Reverse reaction is favoured and thus there is an increase in the production of nitrogen and hydrogen.

Graphing changes to concentration/partial pressure

Consider $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

In the graph, some hydrogen is added to the system.



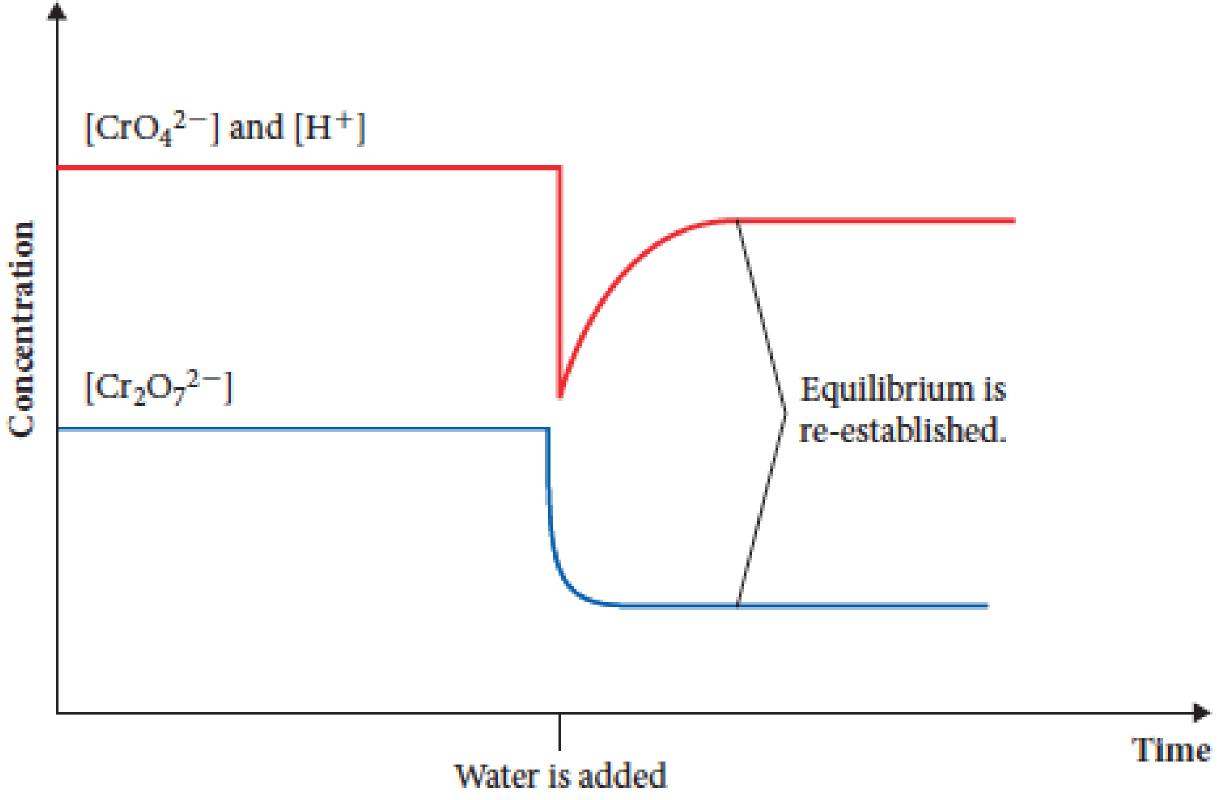
◀ Figure C1.17
Graph of the concentrations when hydrogen gas is introduced for the reaction
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Graphing changes to volume or pressure

Consider the chromate/dichromate equilbrium:

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

Water is added to decrease the concentration of all aqueous substances.

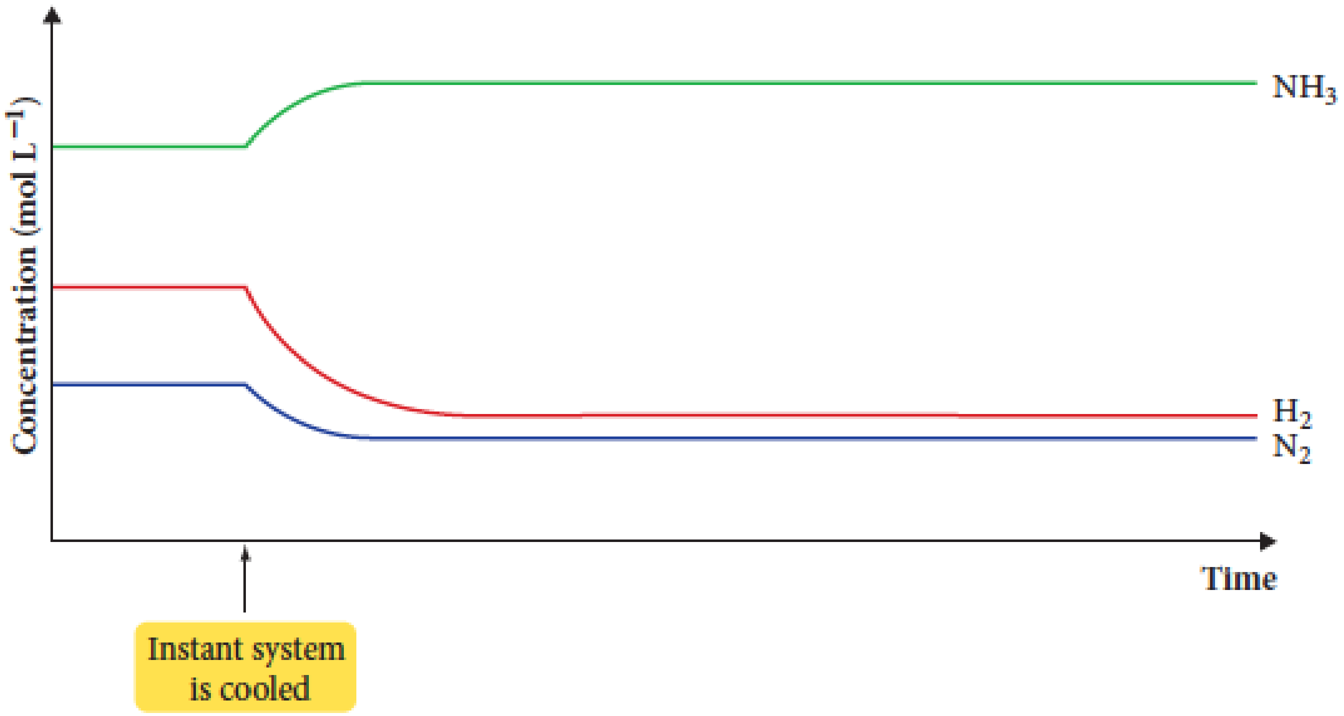


◀ Figure C1.18
Graph representing the concentration following a change in volume

Graphing changes to temperature

Consider the formation of ammonia and a decrease in temperature of the system.

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g) \; \Delta H = -92.4 \text{ kJ}$$



Presence of a Catalyst

- A Catalyst lowers the activation energy and increases the reaction rate.
- It will lower the forward and reverse reaction rates,
- Therefore, a catalyst has NO EFFECT on a system at equilibrium!
- It just gets you to equilibrium faster!