



KEEP IT SIMPLE SCIENCE

PhotoMaster Format

Chemistry Module 5

Chemical Equilibrium

Topic Outline

1. Static & Dynamic Equilibrium

Static v. dynamic

Reversible & non-reversible reactions

Open & closed systems

Examples of dynamic equilibrium

2. Factors that Affect Equilibrium

Le Chatelier's Principle

The temperature effect

The pressure effect

The concentration effect

4. Equilibrium in Solution

How ionic compounds dissolve

Equilibrium at saturation

Precipitation reactions

Solubility rules

Solubility product, K_{sp} Using K_{sp} in problems

3. The Equilibrium Constant, K_{eq}

Calculating K_{eq}

Interpretation of the value

Reciprocal values of K_{eq} How K_{eq} changes with temperatureWhat does, or does not, alter K_{eq}

Attention Teachers & Students

This module might NOT cover all the syllabus content as fully as KISS Resources usually do. This is due to time constraints, as explained by a notice at our website.

Module 5 Special Note

The Syllabus names module 5 "Equilibrium & Acid Reactions". However, there is almost no mention of acids in the Content Statement, so we have re-named it "Chemical Equilibrium". Module 6 (next) is entirely about acids & bases. Any aspects of Equilibrium which are specific to acid reactions will be covered there.

What is this topic about?

To keep it as simple as possible, (K.I.S.S. Principle) this topic covers:

1. Static & Dynamic Equilibrium

Static v. dynamic. Reversible & non-reversible reactions. Open & closed systems. Examples of dynamic equilibria.

2. Factors that Affect Equilibrium

Le Chatelier's Principle. The effects of temperature, pressure & concentration.

3. The Equilibrium Constant

Calculating the Equilibrium Constant, K_{eq} . Interpretation of the value. Reaching equilibrium from the opposite direction & reciprocal values. How K_{eq} values change with temperature. What else effects it?

4. Equilibrium in a Solution

How ionic compounds dissolve in water. Equilibrium in a saturated solution. Precipitation reactions and the "solubility rules". The Solubility Product, K_{sp} . Using K_{sp} in problems.



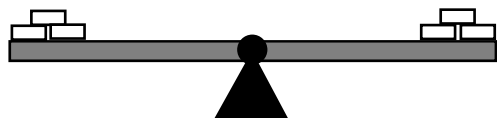
1. Static & Dynamic Equilibrium

Static Equilibrium

Imagine a see-saw. No-one is on it, there is no wind to blow on it. It is not moving and is perfectly balanced. The see-saw is in **equilibrium** because the forces acting on each side are exactly balanced.

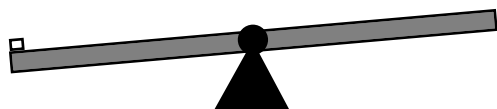


What if you load bricks on each side?



The forces on each side have changed, but they are still equal, so it remains balanced. Again, it is in "equilibrium".

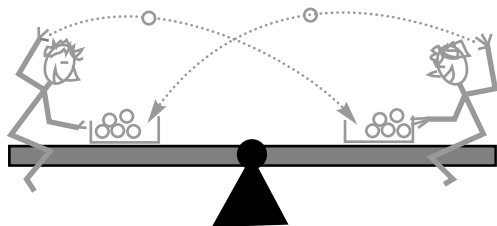
It might even be possible to add a small weight on one side only, so that the see-saw tilts slightly, but then stops moving and is again in equilibrium.



In all these cases, the equilibrium reached is "static". ("Static" means not moving) The see-saw remains still and balanced because absolutely nothing is happening to it.

Dynamic Equilibrium

Now imagine (you'd better have a good imagination) that the see-saw is actually occupied by 2 invisible demons. They are expert jugglers and each is equipped with a basket of invisible balls which they are tossing into each other's basket in a perfectly synchronised way.



The see-saw remains motionless and balanced. It is in equilibrium. But this is a **dynamic equilibrium** ("Dynamic" means moving) because, unseen by us, the forces on each side are constantly changing.

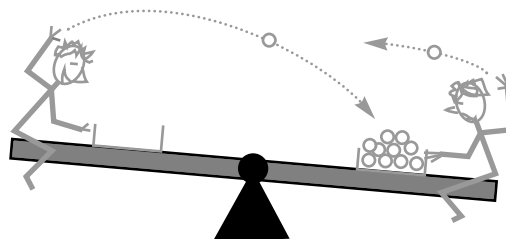
Invisible things are happening constantly, but because they occur in **both directions** at the **same rate**, we see only that the see-saw remains balanced.

Dynamic Equilibrium Can Shift

But wait!

The demon on the right is getting tired. He slows down his rate of tossing the balls. The left demon keeps up the original rate.

Extra balls begin to accumulate on the right side. The see-saw slowly tilts.



At a certain point, the left side demon is forced to slow down his tossing rate because his basket is empty and he must wait for the arrival of a ball before he can toss again.

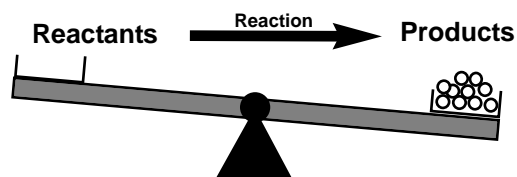
At this point, the equilibrium is re-established at a new position. Both demons are tossing balls at the same rate, so there is an equilibrium, but it is in a different position than originally.

Chemical Equilibrium

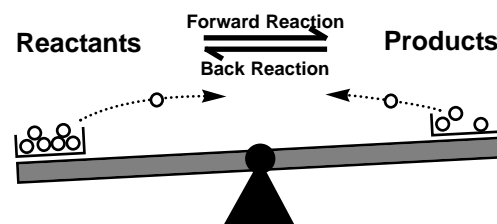
Our analogy of invisible demons tossing balls back & forth is not so different to what can happen in some chemical reactions.

Instead of baskets of balls on each side, imagine a quantity of "**reactant** chemicals" on the left and "**products**" on the right.

Some chemical reactions (such as burning a match) "go to completion". All the reactants are consumed, all the products are made and when it's all over, a **static equilibrium** is reached... it looks like nothing is happening, because nothing is happening. All reaction has ceased.



However, some chemical reactions can run forward or backwards.



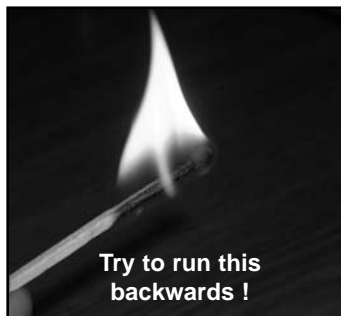
When the rate of forward reaction is equal to the rate of back reaction, a **dynamic equilibrium** is reached.



Reversible & Non-Reversible Reactions

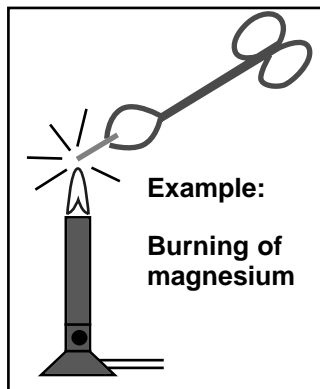
Many of the familiar chemical reactions you have seen are non-reversible. Once they begin, they run to completion and they cannot be run backwards.

There are several reasons why this reaction (photo) cannot run in reverse.



One is simply that when this is done in an open space, most of the products of the reaction disperse away into the atmosphere and are gone. It would be very difficult to round them all up again and have them re-combine to form a little stick of wood.

Even if carried out inside a sealed container, reactions like these will not run backwards because of the large enthalpy change and large increase in entropy.



There are very good thermodynamics reasons that such reactions are non-reversible.

However, there are many chemical reactions which ARE reversible.

Prac Work:

Observing Reversible Reactions

You will probably carry out some prac. work in class to observe some reversible reactions which can be followed visually because there is a colour change involved.

One of the most common examples involves the compound cobalt chloride (CoCl_2).

Cobalt and its compounds are dangerously toxic & carcinogenic, so you might experiment with "cobalt chloride paper": small pieces of filter paper impregnated with CoCl_2 .

When dry, the paper is blue. If a small drop of water is placed on it, it turns pink. This is due to a reaction between cobalt ions & water molecules which form a "complex ion" which happens to be pink.

If it is hung up & dried (eg use a hair dryer) the reaction runs backwards and it reverts to blue. This can be done back & forth, over and over.

Another common reaction involves Fe^{3+} ions and potassium thiocyanate (KSCN). Thiocyanate is a polyatomic ion (SCN^-) which forms a deep-red coloured complex with the iron ions in solution.

By manipulating the conditions, the reaction can be made to run forward and backwards repeatedly, changing colours as it goes.

Any chemical reaction can reach an equilibrium. However, a non-reversible reaction can only ever reach a static equilibrium where it has run to completion and has stopped reacting.

Only a reversible reaction can achieve a dynamic equilibrium. This can occur when the forward and reverse reactions are both occurring at the same rate.

Open & Closed Chemical Systems

Open Systems

An open system is one where substances and/or energy can be exchanged between the reaction system and the environment.

A camp fire is a classic example of open-system chemistry. As the fire burns, the smoke, the gas products of reaction and the heat energy released all freely exchanged with the environment.

A reaction taking place in a laboratory beaker might seem contained, but if gases are involved they can easily escape. Even a reaction occurring in a sealed container is an "open system" if heat energy can easily conduct through the container walls so that the inside temperature can change.

Closed Systems

A closed chemical system is one in which all substances and energy are isolated from the rest of the Universe. Technically, you could argue that there is no such thing, since there is no "perfect" heat insulator. Given time, some energy will get in or out of any sealed system.

However, a sealed container, maintained at constant temperature is an approximate "closed system".

For reactions occurring in solution (with no gases) even a simple lab. beaker or flask approximates a closed system for a short period of time.

So what? Well, the bottom line is that dynamic chemical equilibrium can only be achieved in a closed system. In an open system, a dynamic equilibrium will keep shifting because of the escape of products or evaporation, changes in temperature, etc.

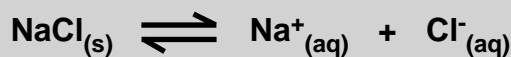
To achieve dynamic equilibrium, a reaction must be reversible AND take place in a closed system.



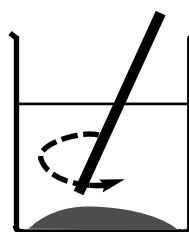
Dynamic Equilibrium in a Saturated Solution

If you keep adding and stirring salt into water until the solution is saturated, you reach a “dynamic equilibrium” between the ions still in an undissolved, solid, crystal lattice, and those in the solution as separate, hydrated ions.

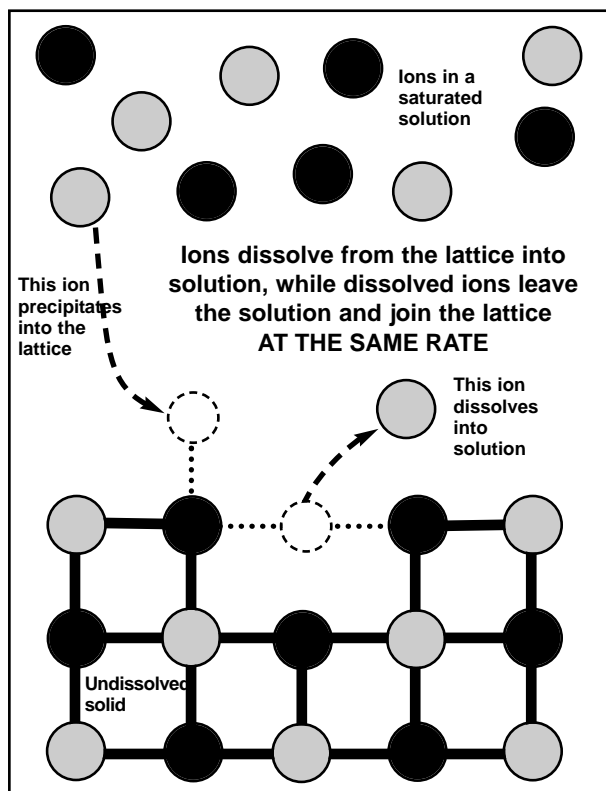
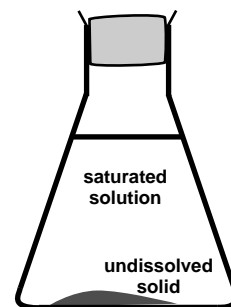
Dynamic Equilibrium in a saturated salt solution:



This double arrow means that both forward and back reactions are occurring at equal rates.



When stirred, salt dissolves until soln. is saturated



If you place the saturated solution, plus some undissolved solid into a sealed flask kept at constant temperature (ie a “closed system”) nothing seems to be happening.

The concentration of dissolved ions remains the same. The mass of undissolved solid remains the same.

However, on the atomic scale those invisible demons are at work! Constantly, some ions from the solution are precipitating as solid and some ions in the solid are dissolving into solution, as shown at left.

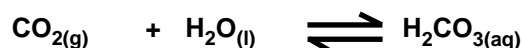
Since dissolving and precipitating occur at the same rate, the concentration of the solution does not change, and the amount of undissolved solid remains the same. At the macroscopic level, it seems that nothing is happening, but down at the atomic level things are moving... ions constantly dissolving into solution and precipitating back out of it again. This is a “Dynamic Equilibrium”

If you took a close-up photo of the solid crystals, then waited some months and took another photo, you might just be able to see that some of the crystals may have changed shape. Although forward & back reactions occur at the same rate, the positions of dissolving & precipitation don't have to be identical.

Try Worksheet 1

Equilibrium of Carbon Dioxide and Water

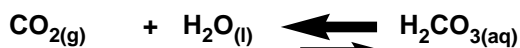
When CO_2 dissolves in water, it doesn't merely dissolve, but reacts to form the weak acid “carbonic acid”.



This is a dynamic equilibrium situation. Even when the process seems finished, there are actually two reactions (one forwards \rightarrow , one backwards \leftarrow) occurring at the same rate, so that nothing appears to be happening. This is occurring in a sealed bottle of any “fizzy” drink. What happens when you open it?

Shifting an Equilibrium

A chemical equilibrium is “dynamic”, meaning that things are moving back and forth. This also means that it is possible to “upset” an equilibrium and cause it to shift to a new balance between reactants and products.



Equilibrium shifting to the left results in less carbonic acid and the formation of more CO_2 gas. The shift in the equilibrium was caused by the pressure change which occurred when the drink was opened.



When you open and pour a fizzy drink it forms bubbles in the glass.

The sealed drink contains dissolved carbonic acid, but as soon as it is opened, CO_2 gas begins coming out of solution, because the equilibrium has shifted to the left.

Eventually a new equilibrium is established with a lot less gas dissolved... we say the drink has “gone flat”.



2. Factors That Affect Equilibrium

Understanding chemical equilibrium requires that you first understand **reaction rate**. This was covered in Module 3, including the concept of "Collision Theory". **Revise Now!**

Factors That Can Cause Equilibrium Shift

Pressure

If a reaction involves a gas, any change in the pressure of that gas will shift the equilibrium. With soft drinks, increasing the pressure of CO_2 drives the equilibrium to the right; decreasing CO_2 pressure, shifts it to the left.

From your knowledge of the gas laws, you will be aware that a change of **volume** of a container can change the pressure. Be aware that the pressure effect is really all about concentrations. (in mol L^{-1})

Temperature

If you kept the gas pressure constant, but raised the temperature, you would find the CO_2 equilibrium would shift left. (i.e. less carbonic acid) Lowering the temperature would shift it to the right (more carbonic acid).

Which way an equilibrium shifts due to temperature, depends on whether the reaction is exothermic or endothermic. This is explained below.

Concentration

The equilibrium could also be shifted by altering the concentration of (say) the carbonic acid. If you added extra $\text{H}_2\text{CO}_{3(\text{aq})}$ somehow, the equilibrium would shift left. If you reduced the concentration, (e.g. by adding an alkali which would react and destroy it) the equilibrium would shift towards the right.

Le Chatelier's Principle

In 1885, the French Chemist **Henri Le Chatelier** discovered the underlying pattern in these equilibrium shifts. The equilibrium always shifts in the direction which counteracts the change that upset it in the first place.

Le Chatelier's Principle:

If a system in equilibrium is disturbed, the system will adjust itself in the direction which counteracts the disturbance.

...in a sealed container an equilibrium is reached with both product (NH_3) and reactants (N_2 & H_2) present in a dynamic equilibrium. The concentration of all 3 gases does not change because the forward and reverse reactions are occurring at the same rate, so the concentrations remain fixed.

The ammonia reaction is exothermic, so heat energy can be thought of as a reaction product.

If the temperature was **increased**, the equilibrium will shift to the left (more reactants, less product) because this absorbs heat and counteracts the disturbance.

If the temperature was **decreased**, the equilibrium will shift to the right (more product, less reactants) because this produces heat and counteracts the disturbance.

The Temperature Effect

The dissolving of CO_2 to form carbonic acid is an exothermic reaction, so heat energy may be considered as one of the products:

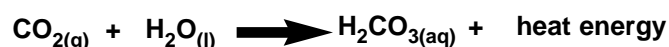


So, if the temperature is raised, the equilibrium shifts left



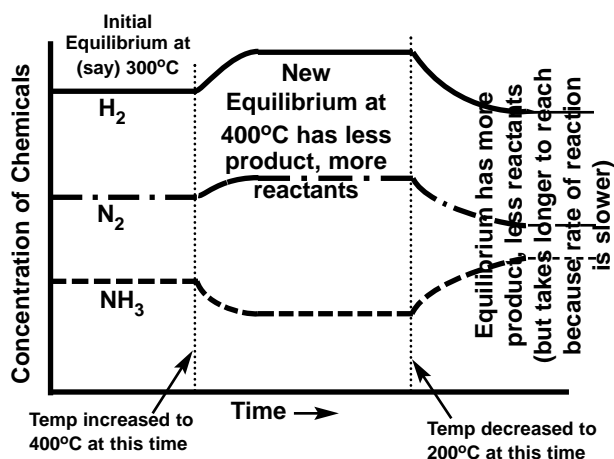
... because shifting left absorbs heat and lowers the temperature again.

If the temperature is lowered, the equilibrium shifts right. This releases heat energy and raises the temperature again.



Another Example

In the industrially important reaction to make ammonia from its elements...



An Endothermic Reaction responds the opposite way



Le Chatelier's Principle (cont.)

Effect of Concentration

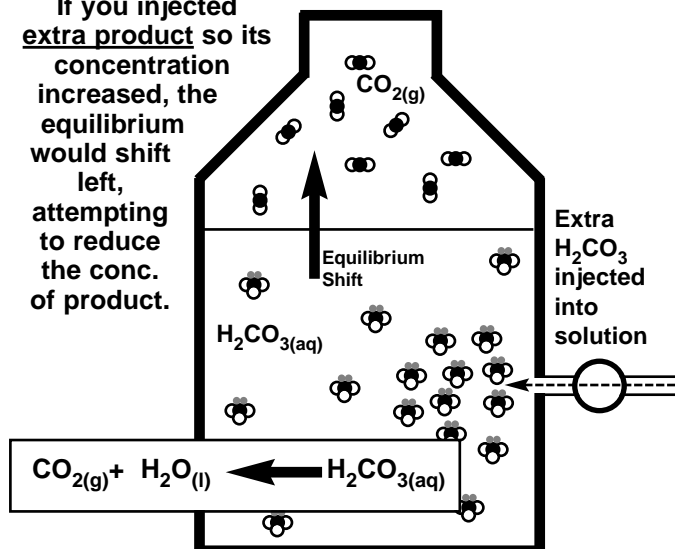
If the concentration of a reactant is increased, the equilibrium will shift right, attempting to use up the reactant and counteract the change.

If the concentration of a product is increased, the equilibrium will shift left, attempting to remove some of the product and counteract the change.

If you somehow removed product so its concentration was reduced, the equilibrium would shift right in an attempt to make more.

In every case, the equilibrium shift tries to counteract the change

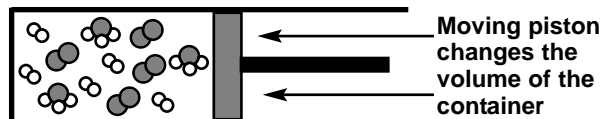
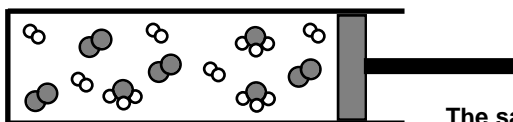
If you injected extra product so its concentration increased, the equilibrium would shift left, attempting to reduce the conc. of product.



The Pressure Effect

In reactions involving gases, changing the pressure and/or the volume of the reaction chamber may have the effect of changing the concentration, and shift the equilibrium one way or the other, according to Le Chatelier's Principle.

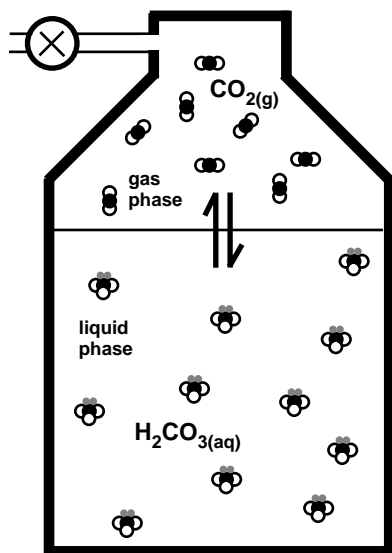
Changing the volume changes Pressure



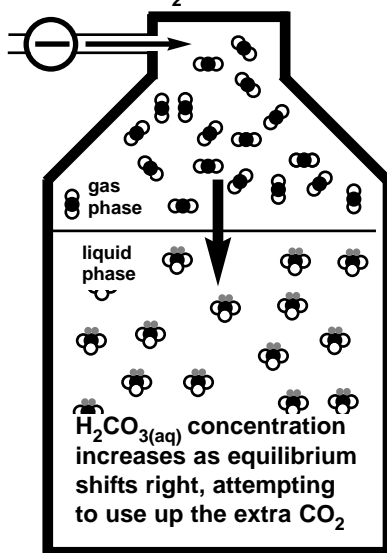
The same number of molecules are now crammed into a smaller volume, at higher pressure. This means they all have a higher concentration, in mol L^{-1}

Consider again the reaction $\text{CO}_{2(g)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_2\text{CO}_{3(aq)} + \text{heat energy}$

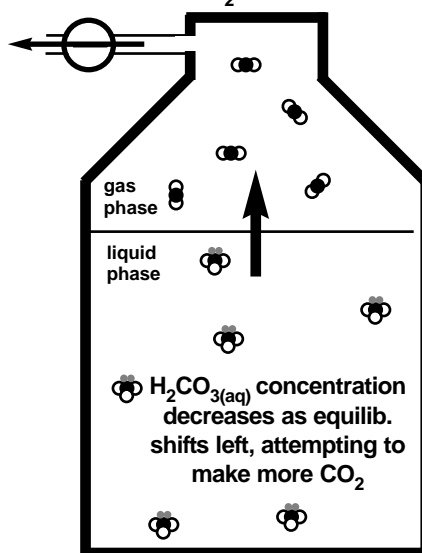
Initial Equilibrium Situation



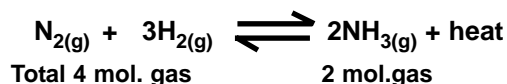
Extra CO_2 pumped in. Pressure (and concentration) of CO_2 increased.



CO_2 pumped out. Pressure (and concentration) of CO_2 decreased.



For the ammonia reaction, increasing the pressure will shift the equilibrium to the right, since there are less total gas molecules on the product side. (Look at the mole coefficients in the balanced equation)



NOTE:

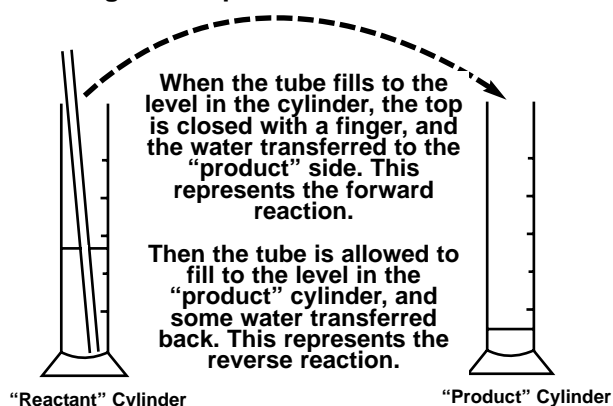
If pressure was increased by pumping another, unrelated gas (e.g. inert argon gas) into the chamber, this would increase the pressure, but would not alter the concentration of the reactant and product gases. This method of changing the pressure would NOT affect the equilibrium.



Prac Work *Modelling an Equilibrium*

Here is a simple way to simulate a dynamic equilibrium.

Use 2 measuring cylinders to represent “reactants” and “products”. The quantity of water in each represents the concentration of each. Water is transferred from one to the other (using glass tubes or pipettes) to represent the forward and reverse reactions. The glass tubes must be allowed to fill to the level in each cylinder before transfer... no sucking water up!

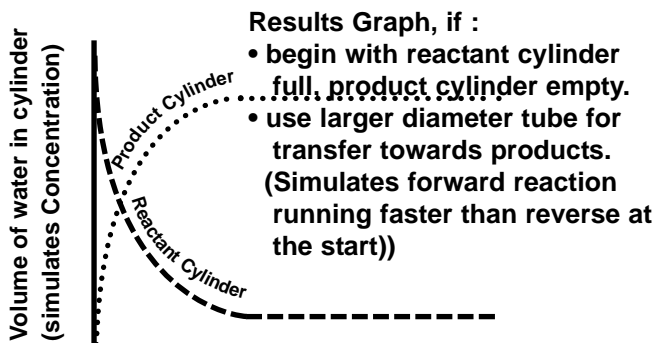
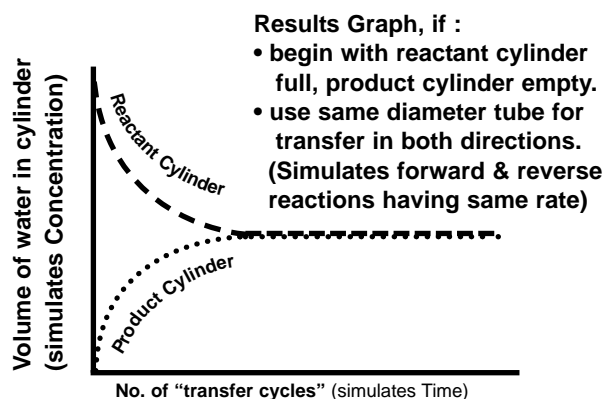


After each back-and-forth cycle, the volume of water in each cylinder can be recorded, and later graphed.

You can try using different diameter glass tubes (representing different forward and reverse reaction rates) and you can start with one cylinder full, one empty, or begin with both half-full... lots of variations possible.

Typical Results

It may take a while, but eventually the amount of water in each cylinder reaches a (more-or-less) constant amount. Despite water still being transferred back-and-forth, the amount in each cylinder stays the same... a dynamic equilibrium. The larger the diameter of the glass tube(s) used, the faster the equilibrium will be reached.

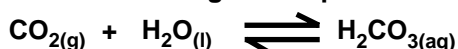


Prac Work: *Mass & Volume of CO₂ in a Fizzy Drink*

This activity gives you some timely revision of mole calculations involving mass & gas volume.

The idea is to “de-carbonate” a fizzy soft drink and measure & calculate the mass and volume of CO₂ gas released. To avoid complications with other chemicals, it is suggested you use a small bottle of “soda water”. It should be kept at room temperature throughout.

If you weigh the soft drink and container accurately, then release the pressure so that it goes flat (this may take a day or more) you will measure a small loss of mass, due to CO₂ gas escaping as the equilibrium shifts towards the left and gas escapes.



Typical Results & Analysis

For a 300mL bottle of soda water:

Start mass	= 536.9g
Final mass	= <u>535.8g</u>
mass loss	= 1.1g

moles of CO₂:

$$n = m/M$$

$$= 1.1/44.01$$

$$n(\text{CO}_2) = 0.025 \text{ mol.}$$

Volume of CO₂

(assuming standard conditions)

$$V = n \times V_M$$

$$= 0.025 \times 24.8 = 0.62 \text{ L}$$

0.62 L (620mL) of CO₂ gas released



Prac Work Observing an Equilibrium Shift Due to Temperature

Another experiment you may do, is to observe (qualitatively) an equilibrium shift occurring. This often involves observing a colour change in an equilibrium mixture, when reaction conditions are changed.

Temperature Effect on Equilibrium

Your teacher may have prepared a sample of the (toxic) gas nitrogen dioxide (NO_2) by reaction of concentrated nitric acid on copper. This gas rapidly reacts to reach the equilibrium:



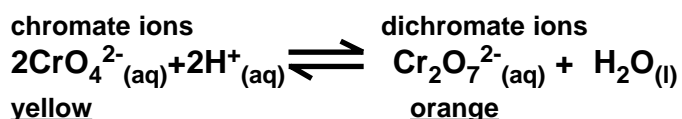
As temperature increases, the equilibrium shifts left, which forms more (brown coloured) NO_2 gas. You can observe this by comparing bottles of gas mixture which have different temperatures.



Image by Greenhorn1

Prac Work Observing an Equilibrium Shift Due to Concentration

Another commonly studied reaction is

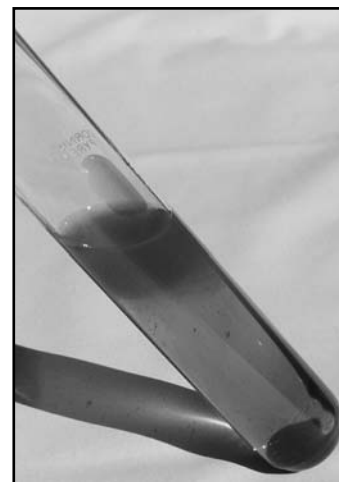


If this equilibrium shifts, the colour will become more yellow, or more orange.

You might start with a yellow solution of chromate ions in water. If a few drops of 2 mol L^{-1} sulfuric acid (H_2SO_4) are added the solution becomes more orange; the equilibrium has shifted right because the concentration of H^+ ions increased.

If a few drops of NaOH solution are added, the colour changes to yellow again.

The NaOH reacts with H^+ ions and lowers their concentration. The equilibrium shifts left, according to Le Chatelier's Principle.



Try Worksheet 2



3. The Equilibrium Constant K_{eq}

In a **closed** chemical system, at a given temperature, a chemical reaction may reach a **dynamic equilibrium** where both forward and reverse reactions are occurring at the same rate, and the concentrations of all species present become constant.

Regardless of the amounts of chemicals you begin with, the equilibrium will reach a point where the **ratio** of concentrations of reactants and products becomes a constant value.

Consider a generalised chemical equation:



W & X are the reactant chemicals.
Y & Z are the product chemicals.
a, b, c & d are the molar coefficients
("balancing numbers")

Then, at equilibrium:

The Equilibrium Constant,

$$K_{eq} = \frac{[Y]^c \times [Z]^d}{[W]^a \times [X]^b}$$

You are reminded that, in chemical shorthand, [square brackets] means "concentration in molL⁻¹"

So, $K_{eq} = \frac{(\text{Molar conc. of PRODUCTS})^{(\text{raised to powers})}}{(\text{Molar conc. of REACTANTS})^{(\text{raised to powers})}}$

Each chemical reaction has its own value for K_{eq} , which is constant at any given temperature.
The value of K changes at different temperatures.

Units of Measurement

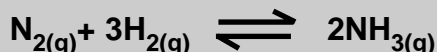
All concentrations must be in moles per litre (molL⁻¹).

The units for the constant K_{eq} vary from reaction to reaction. The syllabus does NOT require you to use any units for " K_{eq} "... values only.

Example Problem 1

Calculating the Value of K_{eq} for an Equilibrium

The reaction below has reached equilibrium at 200°C.



The molar concentrations of each species is:

0.100 molL⁻¹ 0.20 molL⁻¹ 0.22 molL⁻¹

Calculate the value of the equilibrium constant, K_{eq} .

Solution:

$$K_{eq} = \frac{[NH_3]^2}{[N_2] \times [H_2]^3} = \frac{(0.22)^2}{0.10 \times (0.20)^3}$$

$$= 61 \text{ (2 sig. figs)}$$

At 200°C, the value of K_{eq} = 61

Interpreting the Value of K_{eq}

Values for the constant K_{eq} vary enormously from one reaction to another, and also change with temperature. What do high and low values mean?

If K is very large... e.g. $K > 10^3$ (more than 1,000)

This means that the concentrations of the **PRODUCTS** are much higher than those of the reactants at equilibrium. The products must be favoured in the equilibrium, which is said to "lie to the right".

If K is very small... e.g. $K < 10^{-3}$ (less than 0.001)

This means that the concentrations of the **REACTANTS** are much higher than those of the products at equilibrium. Very little product has been made, and the equilibrium is said to "lie to the left", favouring the reactants.

If K is "middle-sized"... e.g. 0.001 to 1,000

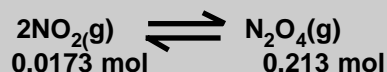
This means that the concentrations of the **PRODUCTS** and **REACTANTS** are very roughly equal at equilibrium. The reaction reaches an equilibrium "in the middle".

In example 1, the value for K was a "middle-sized" value, and if you look at the concentrations of reactants and products you will see that they were of the same "order of magnitude".

Now study example 2 for quite a different situation...

Example Problem 2 Another Equilibrium

The reaction below has reached equilibrium at 0°C in a 5.00 litre container. The **number of moles** of each species present in the container is given.



Calculate the value of the equilibrium constant, K and interpret this value.

Solution:

$$K_{eq} = \frac{[N_2O_4]}{[NO_2]^2}$$

You must NOT jump in and substitute the values given! The values are mole amounts, not concentrations. Note that it is a 5 litre container, so the concentrations are:

$$[NO_2] = 0.0173 / 5 = 0.00346 \text{ molL}^{-1}$$

$$\text{and } [N_2O_4] = 0.213 / 5 = 0.0426 \text{ molL}^{-1}$$

$$\text{Now substitute: } K = 0.0426 / (0.00346)^2 = 3.56 \times 10^3$$

At 0°C, the value of $K_{eq} = 3.56 \times 10^3$, which indicates that the equilibrium lies well to the right, favouring the production of N_2O_4 .

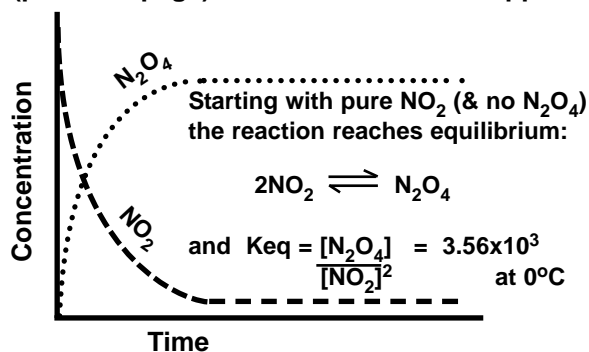


More About the Equilibrium Constant

Reciprocal Values of K_{eq}

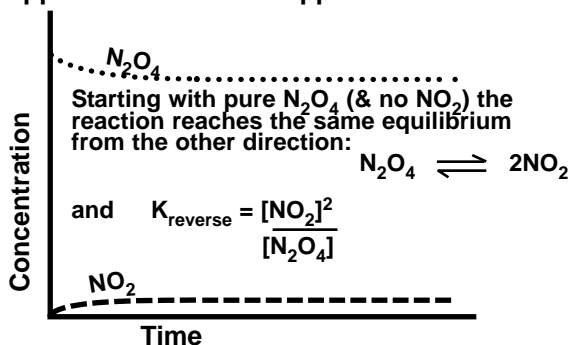
A reaction can reach equilibrium from either direction, and the equation can be written in either direction.

For example, imagine it was possible to begin with a pure sample of $\text{NO}_{2(g)}$ at 0°C . Example 2 (previous page) tells us what would happen:



Now, imagine starting with a pure sample of $\text{N}_2\text{O}_{4(g)}$ at the same temperature of 0°C .

The exact same equilibrium will be reached, but approached from the opposite direction.



Notice that the expressions for the equilibrium constants are reciprocals of each other:

$$K_{\text{rev}} = \frac{1}{K} = \frac{1}{3.56 \times 10^3} = 2.81 \times 10^{-4}$$

If an equation is written in reverse then the expression and value for K_{eq} is the reciprocal.

$$K_{\text{reverse}} = \frac{1}{K_{eq}}$$

Values of K_{eq} Change with Temperature

For any chemical reaction at equilibrium at a particular temperature, the value of K_{eq} is a constant regardless of the quantities involved.

However, the value will change at different temps.

With an understanding of Le Chatelier's Principle, and knowledge of the expression $K_{eq} = \frac{[\text{Products}]}{[\text{Reactants}]}$ you can predict the way that K_{eq} changes with temperature.

Exothermic Reactions

In an exothermic reaction, heat is a product:



As temperature increases, the equilibrium will shift left, so at the new equilibrium the [reactants] is higher and [products] is lower.

Therefore, the value of K will decrease.

Example:



Temperature ($^\circ\text{C}$)	Approx. Value of K_{eq}
0	5.0×10^8
200	60
400	0.25
600	0.005

Exothermic Reactions
 K_{eq} decreases as temperature increases

Endothermic Reactions

In an endothermic reaction, heat is a reactant:



As temperature increases, the equilibrium will shift right, so at the new equilibrium the concentration of products is higher and concentration of reactants is lower.

Therefore, the value of K will increase.

Endothermic Reactions
 K_{eq} increases as temperature increases

Now Complete Worksheets 3, 4, 5



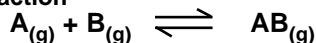
Impacts on Equilibrium & K_{eq}

Equilibrium & Collision Theory

A dynamic equilibrium is very much about the rates of reaction. Equilibrium is achieved when the rate of the forward reaction is equal to the rate of the back-reaction.

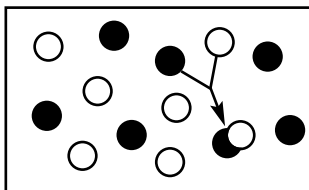
According to Collision Theory, the rate of a reaction depends on how likely it is that reactant atoms or molecules or ions collide with each other.

Imagine a generalised reaction



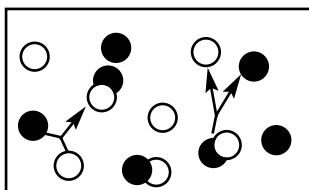
If we placed a mixture of gases A & B into a container, some would collide to form product AB.

Initially, only the forward reaction is possible because the only species present are A & B. The rate of the back reaction (at the start) is zero.



As some product AB is created, the back-reaction becomes possible. However, since the concentration of AB is low, collisions resulting in a back-reaction are very unlikely. This means the rate of back-reaction is low.

A & B continue reacting in the forward reaction. However, this reduces the concentration of A & B, so collisions become less likely and the rate of reaction begins to slow down.



Understand what happens?

The forward reaction slows down as collisions between A & B occur less often. Meanwhile, the back-reaction speeds up as the concentration of AB increases. Eventually, the forward & reverse rates must become equal and dynamic equilibrium is established.

Importance of Concentration

So, the rate of reaction in each direction depends on the rate of appropriate collisions. This in turn depends very much on the concentration of the various species.

This explains 3 aspects of equilibrium:

• The K_{eq} Formula

To calculate the Equilibrium Constant you use concentration values because these control collision rates and (therefore) reaction rates.

• Concentration & Le Chatelier's Principle

If you increase (say) the concentration of reactants, this makes collisions between reactants more likely and increases the rate of the forward reaction. This causes a "shift to the right" according to Le Chatelier's Principle.

• This Equilibrium Shift Does NOT Change K_{eq}

Although the equilibrium shifts, it later re-establishes and the ratio of concentrations *is still the same*.

***The value of K_{eq} is still the same
(at constant temperature)***

The Pressure Effect

As already noted, for reactions involving gases, pressure is really the same as concentration...

for example, higher pressure forces more gas molecules into a smaller volume.

More molecules in less volume means more moles per litre, therefore higher concentration.

All the considerations regarding concentration (at left) also apply to gas pressure, at constant temperature.

The Importance of Temperature

Temperature change can cause an equilibrium to shift by Le Chatelier's Principle. The direction of shift depends on the thermodynamics... whether the reaction is exothermic or endothermic... as previously covered.

The big difference between the "concentration effect" and the "temperature effect" is that a change in temperature also forces the reaction to equilibrate at a new, different ratio of concentrations.

This means a new value for K_{eq}

Again, whether the new value is higher or lower depends on the thermodynamics of the reaction.

What About Activation Energy E_a ?

Have you noticed that the reactions which are reversible and reach a dynamic equilibrium tend to be those taking place in liquid solution or between gases?

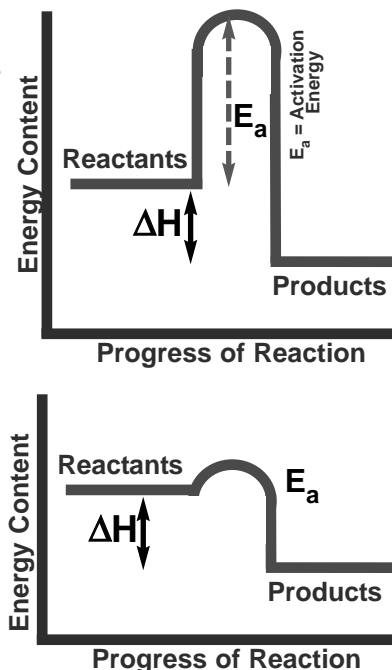
This is largely because of the increased likelihood of collisions occurring in a solution of ions or a mixture of gases. This likelihood can be linked to the concept of activation energy.

These 2 energy profiles both show an exothermic reaction. The values of ΔH are the same.

The big difference is the value of E_a . The lower diagram is more typical of reactions between gases or in solution. The "energy barrier" is much lower, so that (at any given temperature) there is more likelihood of a reactant having enough energy to start the reaction.

So, does E_a affect the position of equilibrium or the value of K_{eq} ? NO !!

You are reminded that catalysts work by lowering the E_a . This speeds up the rate of a reaction, but has NO EFFECT on the position of equilibrium or on the value of K_{eq} . So catalysts and E_a values have no effect on K_{eq} .





4. Equilibrium in Solution

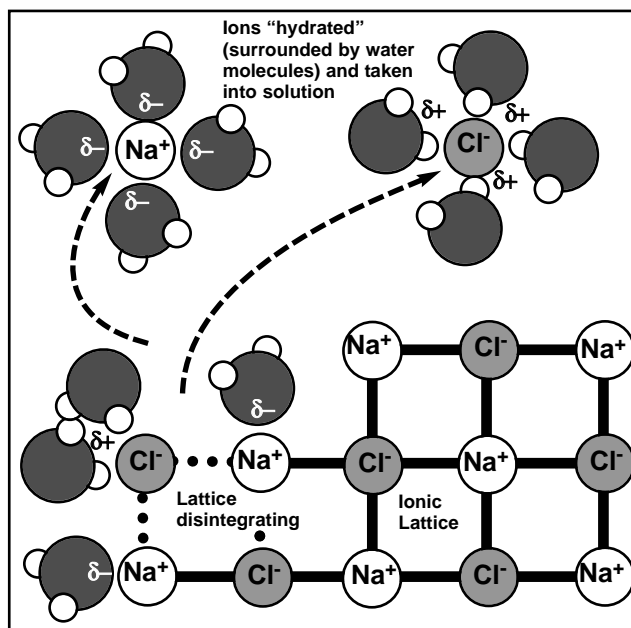
How Ionic Compounds Dissolve in Water

Ionic compounds are (generally) soluble in water, and all because water molecules are **polar**. You will recall this is because the covalent bonding between oxygen & hydrogen is uneven and results in each water molecule having small electrical charges. ($\delta+$ and $\delta-$)

Ionic compounds are composed of a strong ionic crystal lattice. It requires a high temperature to melt this lattice, but water molecules can dissolve the crystal by surrounding each ion and detaching it from the lattice.

Notice (in the diagram) how the (+ve) ions are surrounded by water molecules which are presenting the ($\delta-$) end of their dipole to the ion. The (-ve) ions are surrounded by molecules presenting the ($\delta+$) end of the dipole.

With each ion surrounded by dozens of water molecules, the attraction between the ions is “blanketed” and the individual ions can no longer get close enough to each other for their charges to bond them together.



An ionic compound in solution is made up of free moving, separate, hydrated ions.

Ionic Solutions

When an ionic compound dissolves in water, the crystal lattice disintegrates and the (+ve) and (-ve) ions become separately hydrated to form the solution.

Dissolving of sodium chloride:



The positive (+ve) ions are collectively called “cations”. Negative (-ve) ions are “anions”.

You need to be able to write an equation to describe the dissolving of any ionic compound.

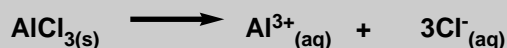
More examples:

Dissolving of magnesium nitrate:



Notice that the equation must balance in terms of the ratio of the ions. In this case there are 2 nitrate ions for each magnesium ion. Notice also that the total of (+ve) charges is the same as the total of (-ve) charges.

Dissolving of aluminium chloride:



The Limits to Solubility

Most ionic compounds are quite soluble in water, but the degree of solubility varies enormously and also varies with temperature. However, there is always a limit to that solubility and once reached, the solution becomes saturated. Once saturation is reached, adding more solid results in a dynamic equilibrium.

Equilibrium in a Saturated Solution

Earlier, we used the example of a saturated ionic solution to introduce the concept of the dynamic equilibrium.

example:



At equilibrium the “forward” dissolving reaction is occurring at the same rate as the “backwards” precipitation reaction.

Note that this equilibrium CAN be shifted according to Le Chatelier’s Principle, BUT adding extra solid will not do anything to it.

This is because any pure solid has a fixed, constant value for its concentration (in mol L^{-1}), (think about and discuss that!) so adding extra solid does NOT alter the concentration and will not shift the equilibrium. More about that later.



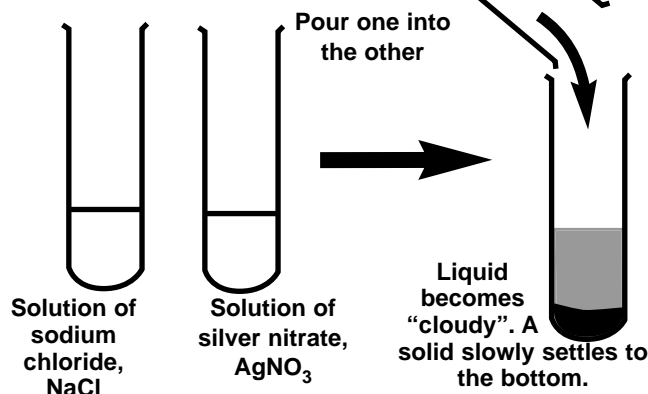
Precipitation Reactions

If you mix two different ionic solutions together, you are really mixing 4 different ions.

In many cases, nothing happens... they just mix together. However, if any combination of ions (it must be a +ve and a -ve ion combo) can form an insoluble compound, these ions will join instantly into tiny ionic lattice crystals, suspended in the liquid. The solid will slowly fall down ("precipitate") to the bottom. The other ions remain in solution.

Example:

Solutions of sodium chloride & silver nitrate mixed together.



When added together, there were 4 types of ions mixed together in solution: Na^+ , Cl^- , Ag^+ and NO_3^-

Now, the combination of Ag^+ and Cl^- ions has a very low solubility in water, so when mixed, they react.

Equations

sodium + silver
chloride nitrate → silver + sodium
chloride nitrate



However, you must also realise that when this precipitation is finished, there is still a tiny amount of Ag^+ and Cl^- ions left in solution in equilibrium with the precipitated solid:



Prac Work: The Solubility Rules

Rather than use large amounts of chemicals and lots of test tubes (as shown above) it is more efficient and manageable to use dropper bottles of ionic solutions and a "spot-test plate" as shown in the photo. This way you can quickly carry out dozens of tests to investigate which combinations of ions react to form a precipitate & which don't.

Your ultimate goal is to discover some "Solubility Rules".

DO NOT just randomly begin mixing everything with every other. It is important to be methodical and record results as you go.

Example Procedure

- Select a cation to test. (example: Cu^{2+})
- Place a drop or 2 of your solution containing Cu^{2+} in each "well" of the spot plate.
- In a result table (at right) record all the anions you have available.
- One by one, as per your table, add a drop of each anion solution to the Cu^{2+} in each well. Observe if any precipitate forms and record in the table as shown.
- Clean and dry the spot plate and repeat for another cation.

Analysis

By studying your results table, you should be able to draw conclusions such as:

"Chlorides are all soluble, except..."

"Carbonates are all insoluble, except..."



Cations	Anions					
	Cl^-	NO_3^-	SO_4^{2-}	OH^-	CO_3^{2-}	etc.
Cu^{2+}	x	x	x	ppt	ppt	
Na^+	x	x	x	x	x	
etc.						

"X" = no reaction.

"ppt" = precipitate formed. (you might also record the colour)



Predicting a Precipitate Using Your "Rules"

A simple set of "rules" discovered by experiment can be summarised as follows.

Solubility "Rules"

Mostly Soluble (and stay in solution)

Na^+ & K^+ always NO_3^- always

Cl^- Br^- & I^- (except with Ag^+ & Pb^{2+})

SO_4^{2-} (except with Ag^+ Pb^{2+} & Ba^{2+})

Mostly Insoluble (and form precipitates)

CO_3^{2-} S^{2-} (except with Na^+ & K^+)

OH^- (except with Na^+ K^+ Ba^{2+} Ca^{2+})

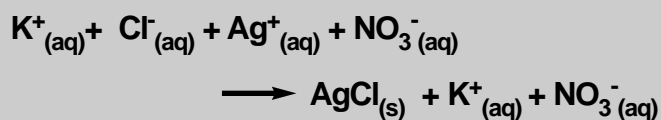
This makes it possible to predict whether or not a reaction will occur when two ionic solutions are mixed.

You must also learn to write and balance appropriate equations to describe the chemistry.

Example: Potassium chloride + silver nitrate

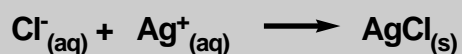
Prediction: there will be a precipitate of $\text{AgCl}_{(s)}$.

Full Ionic equation:



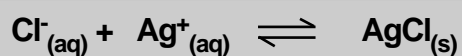
This is an ionic equation describing exactly what happened. On the left is the mixture of ions that were brought together in the 2 solutions. The Ag^+ and Cl^- ions have combined to form solid AgCl , while the other 2 ions have stayed in solution, unchanged... they are "spectators".

We can leave out the spectators to see the essential change that occurred: this is a net ionic equation.



Notice that it is simply the reverse of the equation for the dissolving of silver chloride.

But don't forget that after precipitation, there will actually be a dynamic equilibrium:



The "Solubility Rules" above are based on observations of precipitates formed by solutions with a concentration of 0.5 mol L^{-1} . If higher or lower concentration solutions are used the results may be different. This is because the final equilibrium between a precipitated solid and its dissolved ions depends on the maximum solubility of that ion pair. If the concentration of dissolved ions exceeds that maximum, then a precipitate must form. At higher concentrations, more precipitates will occur.

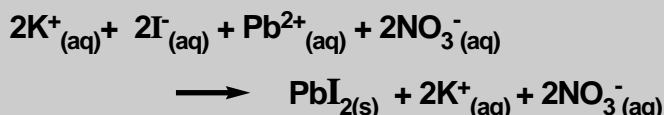
More Examples

Potassium iodide (KI) + lead(II) nitrate ($\text{Pb}(\text{NO}_3)_2$)

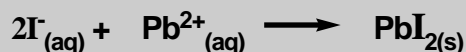
Prediction: there will be a precipitate of $\text{PbI}_{2(s)}$. Note carefully the "tricky" balancing. If you have difficulty with balancing, you should first write the equation in "molecular form" and balance, then convert to ionic form.



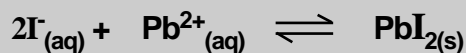
Full Ionic equation:



The net ionic equation:



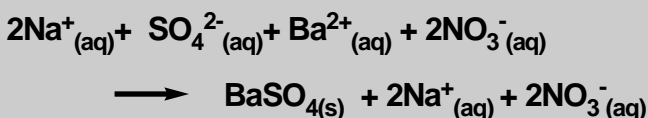
and the equilibrium reached:



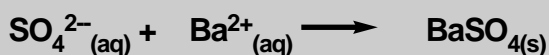
Sodium sulfate (Na_2SO_4) + barium nitrate ($\text{Ba}(\text{NO}_3)_2$)

Prediction: there will be a precipitate of $\text{BaSO}_{4(s)}$.

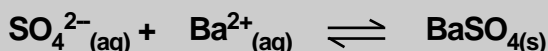
Full Ionic equation:



The net ionic equation:



and the equilibrium reached:

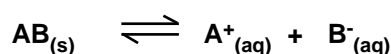


Try Worksheet 6



The "Solubility Product", K_{sp}

In order to understand solubilities and precipitations more precisely, let's look at the equilibrium constant for the dissolving of a (generalised) ionic compound.



For this reaction, $K_{eq} = \frac{[A^+_{(aq)}][B^-_{(aq)}]}{[AB_{(s)}]}$

However, (as noted before) the concentration of any pure solid is a constant value. So we can replace $[AB_{(s)}]$ with a constant value. By convention, this constant value is declared to be 1.

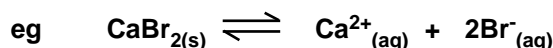
So the expression for the equilibrium becomes simply

$$K_{sp} = [A^+_{(aq)}]x[B^-_{(aq)}]$$

This equilibrium constant is commonly called the "solubility product" because it is simply the product of the concentrations of the 2 ions in a saturated solution.

The expression above is the simplest possible case, where the ionic compound forms from ions in a 1:1 ratio, such as NaCl, or KNO₃.

If the ions combine in other ratios, the K_{sp} expression becomes more complex.



and $K_{sp} = [Ca^{2+}]x[Br^-]^2$

(aq) suffixes have been omitted for simplicity)

Possibly one of the most complicated is:



$$K_{sp} = [Pb^{2+}]^3.[PO_4^{3-}]^2$$

Values of K_{sp}

The values of the solubility product can vary enormously.

For example, NaCl solution at 25°C becomes saturated when about 36g of solid salt is dissolved per 100mL of water. (= 36% w/v)

It can be calculated (Challenge... can you do it?) that this is equivalent to a concentration of about 6molL⁻¹. Since 1 mole of NaCl results in 1 mole each of the ions, then the K_{sp} for saturated NaCl is

$$K_{sp} = [Na^+]x[Cl^-] = 6x6 = 36 \text{ approx.}$$

Highly insoluble compounds have K_{sp} values which may be many orders of magnitude smaller.

eg K_{sp} for BaSO₄ = 1.08 x 10⁻¹⁰

Using K_{sp} Data

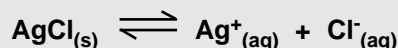
Your Chemistry Data Sheets contain a table of "Solubility Constants" at 25°C. You must learn how to use this data.

Problem 1

Use K_{sp} data to calculate the maximum solubility (in molL⁻¹) of silver chloride, AgCl, at 25°C.

Solution

(hint: it's always a good idea to write the balanced equation)



$$K_{sp} = [Ag^+]x[Cl^-] = 1.77x10^{-10} \text{ (from data table)}$$

Since $[Ag^+] = [Cl^-] = "c"$, then $c^2 = 1.77x10^{-10}$

$$\therefore c = \sqrt{1.77x10^{-10}} = 1.33x10^{-5} \text{ molL}^{-1}. (0.0000133)$$

(This equates to dissolving about 0.002g of AgCl per litre of water to reach saturation.)

Problem 2

a) A solution of sodium sulfate (Na₂SO₄) has a concentration of 0.024 molL⁻¹. What is the concentration of sulphate ions [SO₄²⁻] in the solution?

b) a) A solution of calcium chloride (CaCl₂) has a concentration of 0.016 molL⁻¹. What is the concentration of [Ca²⁺] in the solution?

c) If equal volumes of these 2 solutions were mixed, what would be the concentrations of [SO₄²⁻] and [Ca²⁺] in the final mixture? (hint: the final volume is doubled)

d) Would a precipitate of solid CaSO₄ form in this final mixture at 25°C?

The K_{sp} for calcium sulfate (CaSO₄) is 4.93x10⁻⁵.

Solution

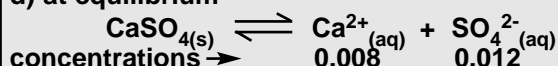
a) Each mole of Na₂SO₄ releases 1 mole of sulfate ions, so [SO₄²⁻] = 0.024 molL⁻¹.

b) Similarly, [Ca²⁺] = 0.016 molL⁻¹.

c) If the volume of solution is doubled, then final concentrations must be halved.

$$\therefore [SO_4^{2-}] = 0.012 \text{ molL}^{-1} \text{ and } [Ca^{2+}] = 0.008 \text{ molL}^{-1}.$$

d) at equilibrium



Actual "ion product" is

$$[Ca^{2+}]x[SO_4^{2-}] = 0.008 x 0.012 = 9.6 x 10^{-5}$$

$$K_{sp} (CaSO_4) = 4.93 x 10^{-5}$$

The ion product exceeds K_{sp} so a precipitate would form.

Note: the problems above involve compounds with mole ratios of 1:1. For other ratios, the problems become more complicated... over



More Problems Involving K_{sp}

Problem 3

Use K_{sp} data to calculate the maximum solubility (mol L^{-1}) of lead(II) hydroxide, Pb(OH)_2 , at 25°C .

Solution



$$K_{sp} = [\text{Pb}^{2+}]x[\text{OH}^{-}]^2 = 1.43 \times 10^{-15} \text{ (from data table)}$$

If we let $[\text{Pb}^{2+}] = "c"$, then $[\text{OH}^{-}] = 2c$ (from equation)

$$\text{Then } K_{sp} = c \times (2c)^2 = 4c^3 = 1.43 \times 10^{-15}$$

$$\therefore c = \sqrt[3]{\frac{1.43 \times 10^{-15}}{4}} = 7.62 \times 10^{-6}$$

So max. solubility of Pb(OH)_2 at 25°C
 $= 7.62 \times 10^{-6} \text{ mol L}^{-1}$.

Try Worksheet 7

Problem 4

If solutions of lead(II) nitrate and sodium chloride are mixed, a precipitate of $\text{PbCl}_{2(s)}$ will form if the actual ion product exceeds the K_{sp} value. ($= 1.70 \times 10^{-5}$)

Would a precipitate form if the solutions each had a concentration of $4.36 \times 10^{-2} \text{ mol L}^{-1}$ and equal volumes of each were mixed?

Solution

$[\text{Cl}^{-}]$ in original NaCl solution = 4.36×10^{-2} .

When mixed, $[\text{Cl}^{-}]$ is halved = $2.18 \times 10^{-2} \text{ mol L}^{-1}$.

$[\text{Pb}^{2+}]$ in original $\text{Pb(NO}_3)_2$ solution = 4.36×10^{-2} .

When mixed, $[\text{Pb}^{2+}]$ is halved = $2.18 \times 10^{-2} \text{ mol L}^{-1}$.

d) at equilibrium



$$K_{sp} = [\text{Pb}^{2+}]x[\text{Cl}^{-}]^2 = 1.70 \times 10^{-5} \text{ (from data table)}$$

Actual "ion product" is

$$[\text{Pb}^{2+}]x[\text{Cl}^{-}]^2 = 2.18 \times 10^{-2} \times (2.18 \times 10^{-2})^2 = 1.04 \times 10^{-5}$$

The ion product is less than K_{sp} so a precipitate will not form.