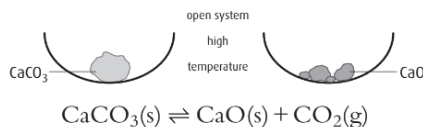# UNIT 7 - EQUILIBRIA

Reversible reactions

Reversible reactions are reactions that can go either way. For example; calcium carbonate on heating decomposes to form calcium oxide and carbon dioxide. But calcium oxide also reacts with carbon dioxide to form calcium carbonate.

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

If we carry out this experiment in a closed system, at the same temperature, we find some calcium carbonate, calcium oxide, and carbon dioxide. The reaction seems to have reached a state of equilibrium.
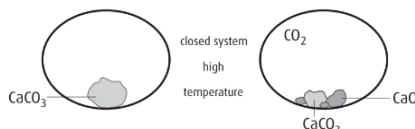

A system is said to have reached equilibrium when no further change appears to occur - macroscopic properties remain constant.

In dynamic equilibrium, macroscopic properties are constant (concentrations of all reactants and products remain constant) and the rate of forward reaction is equal to the rate of the backward reaction.
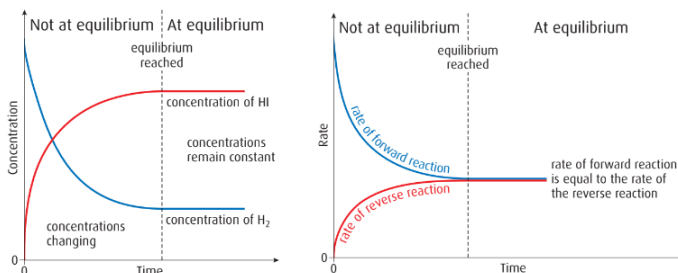
Equilibrium and Rate of Reaction

Consider the reaction

$$H_{2\,(g)} + I_{2\,(g)} \rightleftharpoons 2HI_{(g)}$$
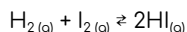
If we start with just hydrogen and iodine vapor in a closed container at a certain temperature and follow how the concentration of hydrogen and hydrogen iodide changes with time we should obtain the graph on the left.

The concentration of H_2 decreases at first until it levels off as equilibrium is achieved. The concentration of HI is initially zero and then increases until it too flattens off and does not change at equilibrium.

Characteristics of the equilibrium state

1) Macroscopic properties are constant at equilibrium.
2) At equilibrium the rate of forward reaction is equal to the rate of backward reaction
3) Equilibrium can be attained only in a closed system
   - In a closed system there is no exchange of matter with the surroundings
4) All species in the chemical equation are present in the equilibrium reaction mixture
5) Equilibrium can be attained from either direction

The Position of Equilibrium

The position of an equilibrium refers to the relative amounts of reactants and products present at equilibrium.

For example, a reaction may come to be in equilibrium when 75% of the reactants have changed into products.

At equilibrium, there is no overall change from reactants to products and it seems as if the reaction has stopped. This is not the case! The reason is the backward reaction is going at the same rate as the forward reaction maintaining the reaction in a dynamic equilibrium.

The effect of changing conditions on the position of equilibrium

Le Chatelier's Principle

If a system at equilibrium is subjected to some change, the position of equilibrium will shift to minimize the effect of the change. If we take a particular system at equilibrium under a certain set of conditions and change one of those conditions, such as temperature, pressure, or concentration the system will move to a new position to compensate for that change.
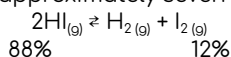
Temperature
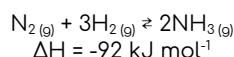
Consider the equilibrium:

$$2HI_{(g)} \rightleftharpoons H_{2\,(g)} + I_{2\,(g)}$$
$$\Delta H = +101 \text{ kJ mol}^{-1}$$
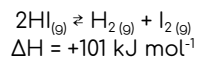
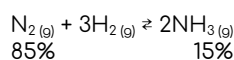At room temperature, the number of molecules of HI is roughly 28 times the total number of molecules of H_2 and I_2.

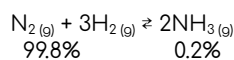However, at 700K, the number of HI molecules is only approximately seven times the total number of H_2 and I_2 molecules.

$$2HI_{(g)} \rightleftharpoons H_{2\,(g)} + I_{2\,(g)}$$
88%   12%

Consider another reaction:

$$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$$
$$\Delta H = -92 \text{ kJ mol}^{-1}$$

This time at 300K we get:

$$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$$
85%   15%

At 700K:

$$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$$
99.8%   0.2%
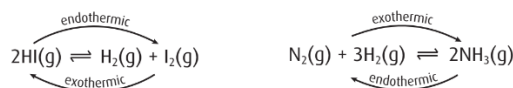
In this case, increasing the temperature causes the position of the equilibrium to shift to the left.

The difference between the two reactions is that the first reaction was endothermic and the second was exothermic.


Temperature change	Sign of ΔH for forward reaction	Direction of movement of the position of equilibrium
increase	+ve	to the right
decrease	+ve	to the left
increase	−ve	to the left
decrease	−ve	to the right

Pressure

Consider the following reaction:

$$2NO_{2\,(g)} \rightleftharpoons N_2O_{4\,(g)}$$
Brown   Colourless
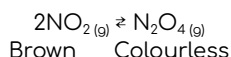
Some NO_2 is put into a sealed gas syringe, as pressure is increased, the color initially gets darker but then starts to turn colorless.
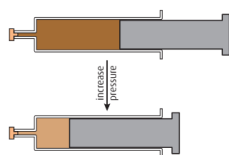
The reaction involves a decrease in the number of gaseous molecules, from two on the left-hand side to one on the right-hand side. Two moles of gas take up more space than one mole of gas, so as pressure is increased the position of equilibrium shifts to minimize the effect of pressure change.
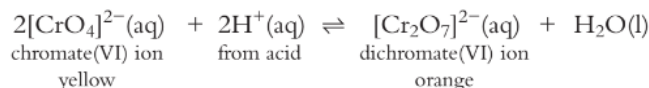
According to the Ideal Gas equation PV=nRT, the number of moles of gas is proportional to the volume and pressure of the gas.

If a reaction involves a change in the number of gas molecules, an increase in pressure results in the position of the equilibrium shifting in the direction that gives a decrease in the number of moles.

Number of gaseous reactant molecules	Number of gaseous product molecules	Direction of movement of the position of equilibrium when the pressure is increased
more	fewer	to the right
fewer	more	to the left
same	same	no change

Concentration

Consider the following system

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

chromate(VI) ion   from acid   dichromate(VI) ion

yellow   orange

The fact that the color of the solution on the left is yellow indicates that the position of the equilibria lies to the left. When acid is added, the color of the solution changes to orange.
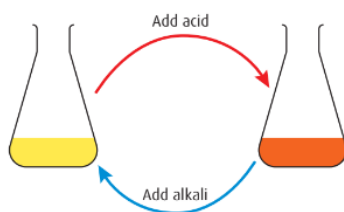

If the concentration of one of the species in an equilibrium mixture is increased, the position of equilibrium shifts to the opposite side to reduce the concentration of this species.

Concentration of reactants	Concentration of products	Direction of movement of the position of equilibrium
increased		to the right
decreased		to the left
	increased	to the left
	decreased	to the right

Equilibrium constant

For an equilibrium reaction of the form:

wA + xB ⇌ yC + zD
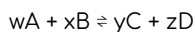
Then (at a constant temperature) = $[C]^y \cdot [D]^z / [A]^w \cdot [B]^x$ = a constant, (K_c)

Where [ ] denotes the equilibrium concentration in mol dm^{-3}. K_c is known as the Equilibrium Constant.

Note: Solids are NOT a part of equilibrium expressions because the concentration of solids is ALWAYS constant.
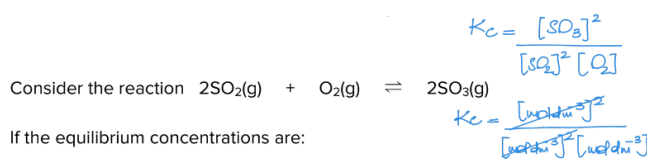
$$K_c = \frac{[SO_3]^2}{[SO_2]^2 [O_2]}$$

Consider the reaction $2SO_2(g) \ + \ O_2(g) \ \rightleftharpoons \ 2SO_3(g)$

$$K_c = \frac{[mol \, dm^{-3}]^2}{[mol \, dm^{-3}]^2 [mol \, dm^{-3}]}$$

If the equilibrium concentrations are:

SO_2: 0.016 mol dm^{-3} O_2: 0.0083 mol dm^{-3} SO_3: 0.15 mol dm^{-3}, $\boxed{mol^{-1} dm^3}$

Calculate the value of the equilibrium constant K_c , stating its units.

$$K_c = \frac{[SO_3]^2}{[SO_2]^2 \times [O_2]} = \frac{(0.15)^2}{(0.016)^2 \times 0.0083} = 1.1 \times 10^4 \ mol^{-1} \, dm^3$$

The units can be calculated by realizing:

$$\frac{conc^2}{conc^2 \times conc} = \frac{1}{conc} \qquad \text{which is} = \frac{1}{mol \, dm^{-3}} = mol^{-1} \, dm^3$$

Calculating K_c

Consider the equilibrium $P + 2Q \rightleftharpoons R + S$ (all species are aqueous)

One mole of P and one mole of Q are mixed in 1 dm³ water. Once equilibrium has been achieved 0.6 moles of P are present. How many moles of Q, R and S are present at equilibrium? What is the K_c?

$$K_c = \frac{[R][S]}{[P][Q]^2} \quad mol^{-1}dm^3$$

		Reactants		Products	
		P	**Q**	**R**	**S**
I	initial moles	1	1	0	0
R ★	moles that reacted	0.4 (1−0.4)	0.8 (1−0.8)	0.4 (0+0.4)	0.4 (0+0.4)
E	moles @ equilibrium	0.6	0.2	0.4	0.4
C	[conc] @ equilibrium	0.6/1	0.2/1	0.4/1	0.4/1

$$K_c = \frac{[0.4][0.4]}{[0.6][0.2]^2} = 6.7 \ mol^{-1}dm^3$$

Steps to calculate K_c

1) Construct the balanced equation, including state symbols (aq), (g), etc.
2) Write down the expression for K_c.
3) Calculate the moles of each substance that reacted.
4) Calculate the moles of each substance at equilibrium.
5) Divide these by the volume to get the concentration of each substance, use V if no volume is given.
6) Put the equilibrium values into the expression for Kc and calculate the answer and work out the units.

K_p

K_p is the equilibrium constant in terms of the partial pressures of the gases in the equilibrium reaction.
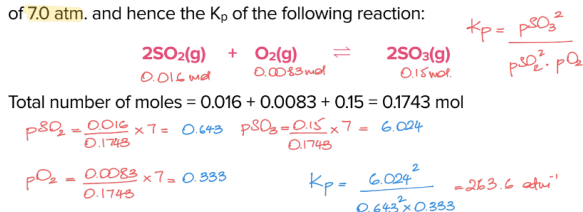
For the reaction: $nA(g) + mB(g) \rightleftharpoons xC(g) + yD(g)$

$K_p = pC^x \times pD^y / pA^n \times pB^m$

Use the value of the partial pressure of any gas in the equilibrium mixture.
    ∟ As with Kc, the units of Kp depend on the stoichiometry of the reaction.

$$\frac{atm^2}{atm^2 \times atm}$$

Calculate the partial pressure of sulfur dioxide in a mixture containing 0.016 mol SO₂, 0.0083 mol O₂ and 0.15 mol SO₃ in a vessel at a pressure of 7.0 atm. and hence the K_p of the following reaction:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
0.016 mol   0.0083 mol   0.15 mol

$$K_p = \frac{pSO_3^2}{pSO_2^2 \cdot pO_2}$$

Total number of moles = 0.016 + 0.0083 + 0.15 = 0.1743 mol

$$pSO_2 = \frac{0.016}{0.1743} \times 7 = 0.643 \quad pSO_3 = \frac{0.15}{0.1743} \times 7 = 6.024$$

$$pO_2 = \frac{0.0083}{0.1743} \times 7 = 0.333$$

$$K_p = \frac{6.024^2}{0.643^2 \times 0.333} = 263.6 \ atm^{-1}$$

Steps to calculate K_p

1) Write down the expression for K_p.
2) Calculate the moles of each substance at equilibrium – starting amount is given, assuming there was 1 mol of the reactant on the left.
3) Add up all the equilibrium moles to get the total number of moles. Work out the mole fraction of each gas (moles/total moles). Work out the partial pressure of each gas (mole fraction x total pressure).

Partial pressure of gas A:
p(A) = mole fraction of A x total pressure

Mole fraction of A = $\frac{moles \ of \ A}{total \ moles \ of \ gas}$

4) Put these partial pressures into the expression for K_p and calculate its value with units.

The Value of 'K' and the Extent of a Reaction

If the value of K_c is large it means that the position of the equilibrium is well to the right (towards products). If the value of K_c is close to 1 it means that the position of the equilibrium is close to being halfway. If the value of K_c is very small (< 1), the position of equilibrium is well to the left (towards reactants).

Reminder: the concentration of pure solids and pure liquids is constant and so is not included in the expression for K_c.

Only the partial pressures of gases are included in the expression for K_p; the other substances are ignored.

Acids and Bases

In simplest terms an acid is a substance that neutralizes a base, forming salt and water.

A base is a substance that neutralizes an acid. When an acid dissolves in water, it ionizes and forms hydrogen ions.

A better definition of an acid is a substance that releases hydrogen ions when dissolved in water.

Common Acids:

Name of acid	Formula	Ions formed in water
hydrochloric acid	HCl	$H^+ + Cl^-$
nitric acid	HNO_3	$H^+ + NO_3^-$
sulfuric acid	H_2SO_4	$2H^+ + SO_4^{2-}$
ethanoic acid	CH_3COOH	$CH_3COO^- + H^+$
benzoic acid	C_6H_5COOH	$C_6H_5COO^- + H^+$

Common Bases:

Name of base	Formula
calcium oxide	CaO
copper(II) oxide	CuO
sodium hydroxide	$NaOH$
calcium hydroxide	$Ca(OH)_2$
ammonia	NH_3

## The Brønsted-Lowry Theory of Acids and Bases

This definition is based on the idea that in an acid-base reaction, a proton is transferred from an acid to a base.

A Brønsted–Lowry acid is a proton donor.
A Brønsted–Lowry base is a proton acceptor.

$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$

the proton, H^+, is donated by the hydrogen chloride and accepted by the water…

…forming the positive hydroxonium ion…

…and leaving a negative chloride ion
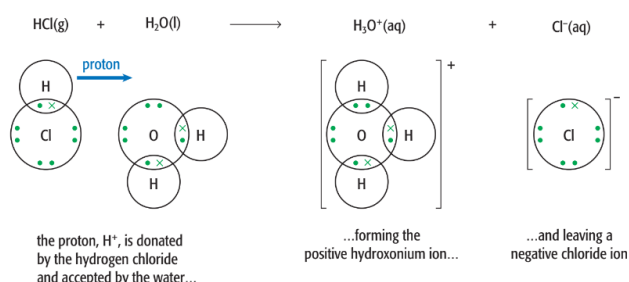
When hydrogen chloride gas dissolves in water and reacts to form hydroxonium ions, H_3O^+, and chloride ions:

Hydrochloric acid is an acid because it donates a proton to water. This means that water is acting as a Brønsted-Lowry base. The water is accepting a proton:

$$\text{H+ donated}$$
$$\underset{\text{acid}}{HCl(g)} + \underset{\text{base}}{H_2O(l)} \longrightarrow H_3O^+(aq) + Cl^-(aq)$$
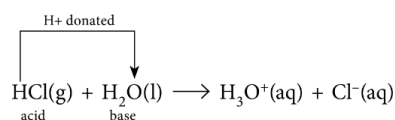
Water can also act as an acid. When ammonia reacts with water, it accepts a proton from the water and becomes an NH_4^+ ion:

$$\text{H+ donated}$$
$$\underset{\text{base}}{NH_3(g)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
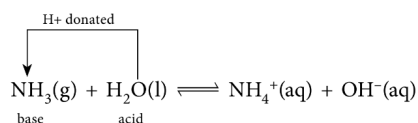
Substances like water, which can act as either acids or bases, are described as amphoteric.

Strong Acids

A strong acid is one which completely dissociates in solution.

$$HCl_{(g)} + H_2O_{(l)} \rightarrow H3O^+_{(l)\,(aq)} + Cl^-_{(aq)}$$
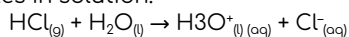
The position of the equilibrium is so far over to the right that we can show this as an irreversible reaction.

The pH of a solution depends on the concentration of hydroxonium ions, H_3O^+. The higher the concentration of hydroxonium ions, the lower the pH.

Weak Acids

A weak acid is one which only partially dissociates in solution.

$$CH_3COOH(l) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

ethanoic acid   ethanoate ion   hydroxonium ion
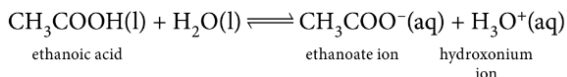
The position of the equilibrium is well over to the left. The pH is much higher compared to a solution of hydrochloric acid. This is because the concentration of hydroxonium ions in solution is far lower.

Examples; HCN, H_2S, H_2CO_3, and CH_3COOH

Strong Base

Bases that dissociate almost completely in solution are called strong bases.

$$NaOH_{(s)} + aq \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$$
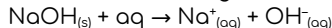
The position of the equilibrium is far over to the right. The solution formed is highly alkaline due to the high concentration of hydroxide ions present. Group 1 metal hydroxides are strong bases.

Weak Bases

Bases that dissociate to only a small extent in solution are called weak bases.

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
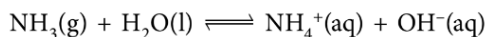
The position of equilibrium is well over to the left. The pH is much lower because the concentration of hydroxide ions in the solution is far lower.

Examples; ammonia, amines, and some hydroxides of transition metals.

Indicators

Indicators are substances, which change color according to the pH of the solution to which they are added.

pH	1	2	3	4	5	6	7	8	9	10	11	12	13	14
METHYL ORANGE				CHANGE										
LITMUS						CHANGE								
PHENOLPHTHALEIN								CHANGE						

Methyl Orange: pink $\longleftarrow$ 3 – 5 $\longrightarrow$ yellow
Litmus: red $\longleftarrow$ 6 – 8 $\longrightarrow$ blue
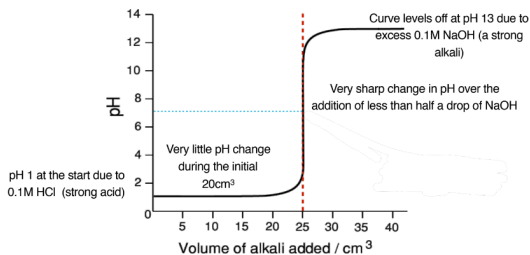Phenolphthalein: colourless $\longleftarrow$ 8 – 10 $\longrightarrow$ pink

pH Curves

While titrating acids against alkalis a drop of indicator added near the equivalence point must produce a large change in pH (at least by 2) so that the indicator can change its color.
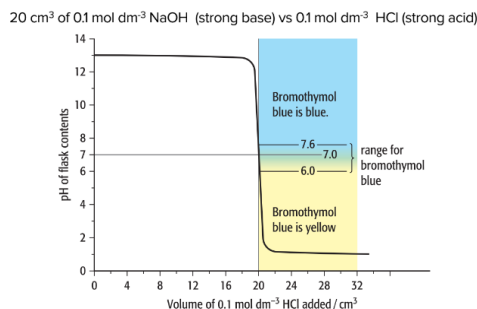
Only then there will be a sharp end point.

Endpoint: The point during a titration when a color change shows that enough of the solution in the burette has been added to react exactly with the amount of the chemical n the flask.
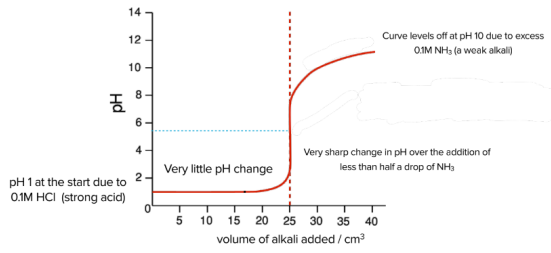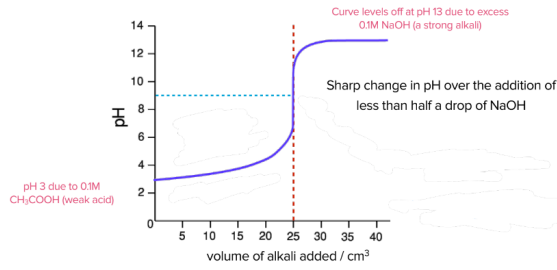
Strong Acid + Strong Base

Strong Base + Strong Acid

20 cm³ of 0.1 mol dm⁻³ NaOH (strong base) vs 0.1 mol dm⁻³ HCl (strong acid)

Strong Acid + Weak Base

Curve levels off at pH 10 due to excess 0.1M NH_3 (a weak alkali)

pH 1 at the start due to 0.1M HCl (strong acid)

Very little pH change

Very sharp change in pH over the addition of less than half a drop of NH_3

Weak Acid + Strong Base

Curve levels off at pH 13 due to excess 0.1M NaOH (a strong alkali)

Sharp change in pH over the addition of less than half a drop of NaOH

pH 3 due to 0.1M CH_3COOH (weak acid)

Weak Base + Weak Acid

There is no sharp fall in the graph line.

No acid–base indicator is suitable to determine the end-point of this reaction.

7.6

6.0

range for bromothymol blue

end-point somewhere between 19.5 and 20.5 cm^3