

CHEMICAL EQUILIBRIA

Dynamic Equilibrium

Equilibrium involves **reversible reactions** which do not go to completion.

If we consider a reaction between A and B to form C and D which is reversible.

When A and B are mixed, the molecules will form C and D.

However, as soon as molecules of C and D are formed and collide they can also react to become A and B.

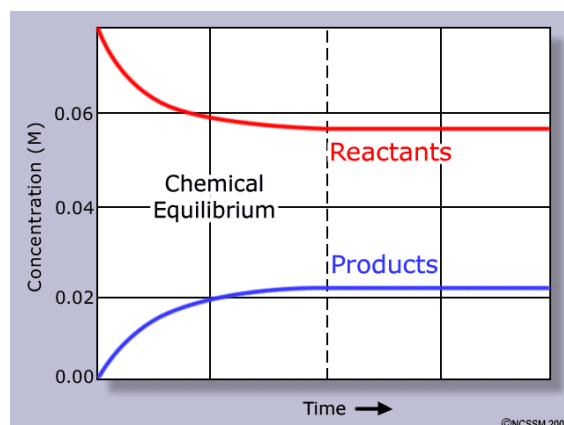
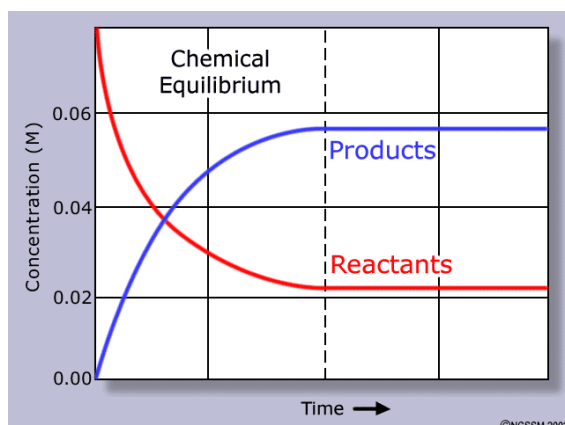
Such a reaction is written;



The reaction reaches a point at which the proportion of each chemical becomes constant. This is described as **equilibrium**.

If the reactants are mixed, their concentrations will fall, rapidly at first, but then more and more slowly, until they settle to their “equilibrium” values. Meanwhile the amounts of products will increase, until they too achieve their equilibrium amounts.

The actual values of these amounts depend on the conditions.



Equilibrium is when a reaction has a constant concentration of reactants and products.

When equilibrium is reached, the reaction has not stopped: instead, the rate at which the forward reaction is proceeding is exactly balanced by the rate of the reverse reaction. This is what is meant by “**dynamic**” equilibrium — individual molecules are reacting all the time, but the overall concentrations of the substances do not change.

Summary - at equilibrium:

- the system is closed (no substances can be added or lost).
- rate of forward reaction = rate of reverse reaction.
- all measurable variables are unchanging (concentration of each substance, pressure, temperature).

Effect of Conditions on the Equilibrium

The conditions which can be applied to a system are change in concentration, pressure, temperature and the use of a catalyst.

In an equilibrium there is a constant ratio between the concentration of reactants and products at a particular temperature.

Le Chatelier's principle states that when a reaction at equilibrium is subjected to a change in condition (temperature, pressure or concentration), the equilibrium composition / position alters to reduce the effect of the change.

Changing the Concentration

If the equilibrium is disturbed by changing the concentration of either reactants or products, the reaction will “shift” in order to re-establish the equilibrium.

Suppose that in a reaction $E \rightleftharpoons G$

- There is an equilibrium ratio of concentration of 1 : 2.
- So if the equilibrium mixture contains 1 mole of E, then there will be 2 mole of G.
- If 0.6 mole of E is added, the equilibrium is disturbed and the ratio temporarily becomes 1.6 : 2
- The increased concentration of reactant causes the rate of the forward reaction to increase.
- This means that product is formed at a faster rate and its concentration increases.
- The system shifts to the right to re-establish the equilibrium.
- This will continue until an additional 0.4 mole of E has been converted to G, and the values become 1.2 : 2.4
- The ratio of concentration is now back at 1 : 2,
- Equilibrium has been re-established.

In general, if the concentration of reactants is increased, the system can counteract this change by shifting to the right, so reducing the concentration of the reactants again. This process increases the concentration of the products and continues until the ratio returns to its original value again.

During this process the reaction has shifted to the right.

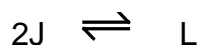
Increasing the concentration of the products correspondingly moves the position to the left.

**Increasing the concentration of a reactant causes a shift to the right.
Increasing the concentration of a product causes a shift to the left.**

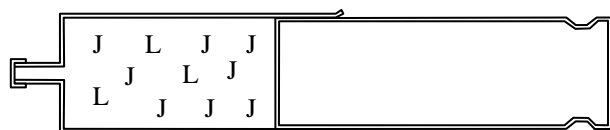
Changing the Pressure

Altering the pressure will effect a gas reaction if there are different numbers of moles of reactant and product in the equation.

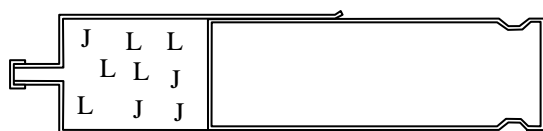
For example in a reaction.



- If the pressure of the system is increased, the system reacts to counteract the increase. In the reaction above this means that the reaction will **shift to the right**, reducing the number of gas molecules present and so reducing the pressure.



The pressure of a given volume of gas will depend upon how many gas molecules there are in it.



As the pressure is increased, two J molecules form 1 L molecules, reducing the pressure of the gas.

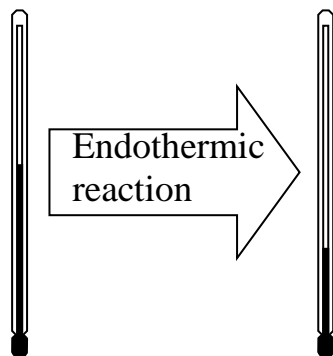
In general:

Increasing the pressure of a gaseous reaction causes a shift towards the side with fewer gas molecules.

Decreasing the pressure of a gaseous reaction causes a shift towards the side with the larger number of gas molecules.

Changing the Temperature

An endothermic reaction is one that takes in heat energy and so causes a temperature decrease.



If the temperature of an equilibrium reaction is increased, the system tries to counteract this change by reducing the temperature again by carrying out the endothermic reaction.

In general:

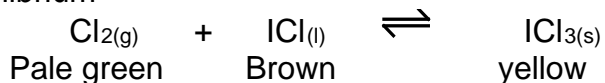
Increasing the temperature of a reaction causes a shift towards the endothermic reaction. Decreasing the temperature of a reaction causes a shift towards the exothermic reaction.

Adding a Catalyst

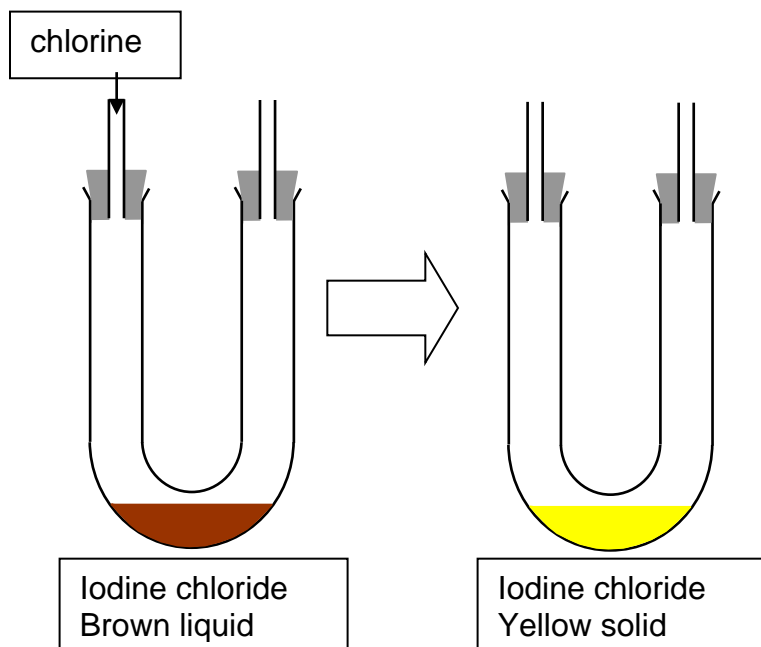
Catalysts do not alter the equilibrium constant or the position of equilibrium.
They do affect the time needed for the system to reach equilibrium.

Laboratory examples of equilibrium

The equilibrium

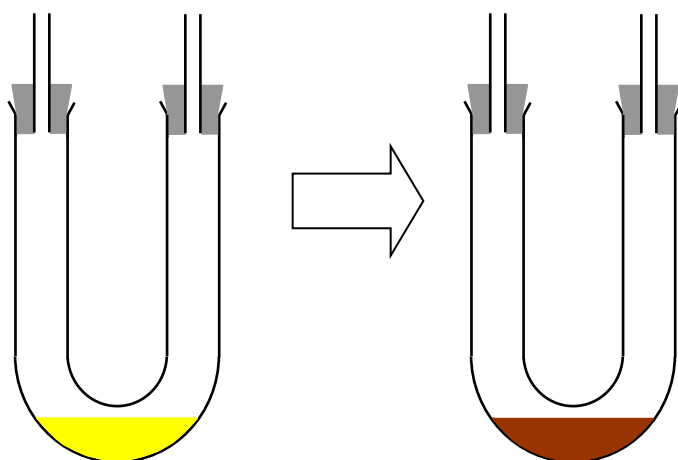


Iodine chloride is placed in a U tube and chlorine passed over it .



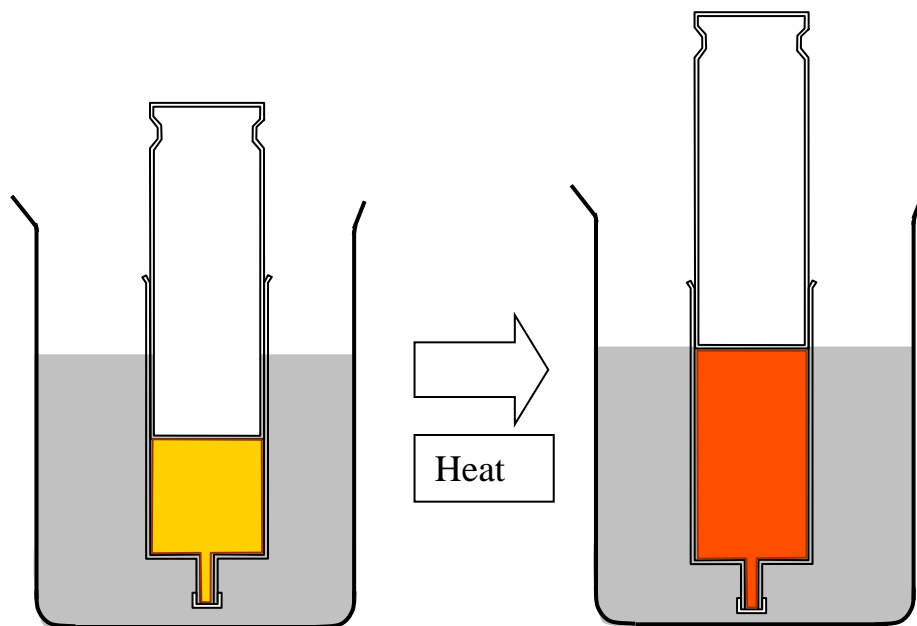
As chlorine is passed into the system its concentration is increased.
The system acts to reduce the chlorine level again by shifting to the right.

The chlorine supply is then stopped



As the chlorine concentration is decreased.
The system acts to increase it again by shifting to the left.

The equilibrium



As the temperature is increased, the system acts to oppose this change. The cooling endothermic reaction is favoured and it shifts to the right.

The Haber Process



Removing the ammonia as soon as it forms will cause the position of equilibrium to move to the right and give a bigger yield of ammonia. (This is achieved by cooling the mixture as the ammonia turns into a liquid first).

When the pressure is increased the equilibrium shifts to the side with least gas molecules. The reaction shifts from left to right, giving a bigger yield of ammonia. A Haber process plants operate between 200-400 atmospheres pressure.

Decreasing the temperature leads to a higher yield of ammonia because the reaction from left to right is exothermic and causes the temperature to rise again if ammonia is formed.

In the Haber process a moderately high temperature of around 500°C is used to speed the rate at which equilibrium is reached. This temperature is chosen in spite of the fact that a lower temperature gives a higher yield.

The optimum (best) conditions for this process which give the greatest yield are:

- 350 atmospheres; high pressure increases yield.
- about 450°C ; high temperature cuts yield but increases rate.
- and the use of a catalyst, iron, to increase the rate.

The Equilibrium Law

Le Chatelier's principle gives us an idea of the direction of change, but, where concentrations are involved, we can calculate precisely what happens using the equilibrium law.

The Equilibrium Law states - At equilibrium the concentrations of the species in the reaction system are constant.

For the general reaction $m\text{A} + n\text{B} \rightleftharpoons p\text{C} + q\text{D}$

Therefore
$$\frac{[\text{C}]^p_{\text{eq}}[\text{D}]^q_{\text{eq}}}{[\text{A}]^m_{\text{eq}}[\text{B}]^n_{\text{eq}}} = \text{a constant } K_c$$

K_c is the **Equilibrium constant**.

$$K_c = \frac{[\text{Right hand side}]_{\text{eq}}}{[\text{Left hand side}]_{\text{eq}}}$$

[] refers to the concentration of the species.

e.g. For the equilibrium $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$

when the system has come to equilibrium, the ratio given by K_c will be constant:

$$K_c = \frac{[\text{C}]^c \times [\text{D}]^d}{[\text{A}]^a \times [\text{B}]^b} \quad \text{where } [\text{C}] \text{ means concentration at equilibrium, normally in mol dm}^{-3}$$

(The main mistakes students make over this are to forget that the *right hand side of the equation goes on top*, and to forget that *concentrations are multiplied together*, not added).

Equilibria involving gases

For gases, it is often more convenient to express the equilibrium constant in terms of partial pressures:

$$K_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b} \quad \text{where } P_C \text{ is the partial pressure of C at equilibrium}$$

K_p is called the **pressure equilibrium constant**.

Note that the both types of equilibrium constant will have units, unless $(c + d) = (a + b)$. They therefore normally have different numerical values, for the same position of equilibrium.

Partial pressure and concentration.

Concentration refers to number of moles of a substance dissolved in one dm^3 of solution. For example aqueous sodium hydroxide solution having a concentration of 2 mol dm^{-3} . This is represented as $[\text{NaOH}(\text{aq})] = 2 \text{ mol dm}^{-3}$. Note [] indicates a concentration.

The same idea can be applied to a gas, if one knows the number of moles of gas and the volume of the container:

$$\text{concentration of gas} = \frac{\text{amount in moles}}{\text{volume of vessel}}$$

Units can be mol dm^{-3} or mol m^{-3} depending on how the volume of the vessel is specified.

Mole fractions

The **mole fraction** of a gas in a mixture is the fraction of the total number of moles of gas present:

$$\text{mole fraction of A} = \frac{\text{no. of moles of A}}{\text{total no. of moles}}$$

The sum of all the mole fractions must always be 1.0.

In a gas the *proportion by volume* is always the same as the *proportion by moles*, or mole fraction.

Example: a 4.00 dm^3 vessel contains 0.20 mol H_2 , 0.40 mol N_2 and 0.30 mol Ar . Calculate (i) the concentration of hydrogen; (ii) the mole fraction of hydrogen.

Answer: (i) concentration of hydrogen = $0.20 \div 4.00 = 0.050 \text{ mol dm}^{-3}$
(ii) total number of moles of gas = $0.20 + 0.40 + 0.30 = 0.90$
mole fraction of H_2 = $0.20 \div 0.90 = 0.22$

In a vessel containing a mixture of gases, the **partial pressure** of one gas is the pressure it would exert if it occupied the vessel alone.

The total pressure in a mixture of gases is the sum of all the partial pressures. It follows that:

$$\text{partial pressure of A} = \text{mole fraction of A} \times \text{total pressure}$$

For example, if one gas makes up 15% by volume of the mixture (or 15% of the molecules) its partial pressure will be $0.15 \times P$, where P is the total pressure.

If nitrogen and hydrogen are mixed in a 1:3 molar ratio, and together they have a partial pressure of 800 MPa , then:

$$\begin{aligned} \text{partial pressure of nitrogen} &= \frac{1}{4} \times 800 = 200 \text{ MPa} \\ \text{partial pressure of hydrogen} &= \frac{3}{4} \times 800 = 600 \text{ MPa}. \end{aligned}$$

Values of K_c and K_p

If K_c is large the equilibrium mixture contains mostly products and the reaction has nearly gone to completion. (A large value is any value >100).

If K_c is small the equilibrium mixture contains mostly reactants and the reaction has not proceeded very far. (A small value is any value <0.01).

The value of K_c is not altered by the addition of more reactants or products to an equilibrium mixture, it is a constant.

If more reactants are added the system will move in the forward direction to keep K_c constant.

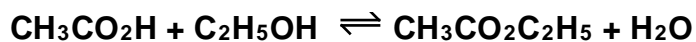
If more products are added the system will move in the reverse direction to keep K_c constant.

When K_c for a reaction is known, the relative portions of reactants and products at equilibrium can be calculated for any mixture of reactants used initially.

Calculating K_c and K_p

We normally find values for K_c and K_p from experimental data.

Example 1: Calculate K_c for the esterification of ethanoic acid by ethanol given that for a 1dm^3 of this homogeneous liquid equilibrium the amounts present are as shown below.

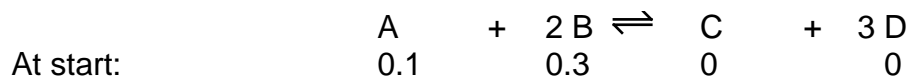


Equilibrium amount/mol 0.0255 0.0245 0.0584 0.0457

$$K_c = \frac{[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{CO}_2\text{H}][\text{C}_2\text{H}_5\text{OH}]}$$

$$K_c = \frac{0.0584 \times 0.0437}{0.0255 \times 0.0245} = 4.1 \text{ (no units for esterification reaction)}$$

Example 2; In the reaction given below, 0.1 mol of A is mixed with 0.3 mol of B, dissolved in 0.5 dm³ of water, and allowed to come to equilibrium, when the amount of D is found to be 0.06 mol. Find the equilibrium constant, K_c.



At equilibrium, we know: 0.06

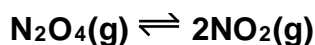
therefore: 0.1-0.02 0.3-0.04 0.02

(since 1 A → 3 D, 0.02 A → 0.06 D; 0.04 B → 0.06 D, and 0.02C is formed).

$$\begin{aligned} K_c &= \frac{[\text{C}] \times [\text{D}]^3}{[\text{A}] \times [\text{B}]^2} = \frac{(0.02/0.5) \times (0.06/0.5)^3}{(0.08/0.5) \times (0.26/0.5)^2} \\ &= \frac{0.04 \times 0.001728}{0.16 \times 0.2704} = 1.60 \times 10^{-3} \text{ mol dm}^{-3} \end{aligned}$$

Note that the number of moles is divided by the total volume (0.5) to obtain the concentration.

Example 3: If at 55°C the partial pressure of nitrogen dioxide in an equilibrium mixture is 0.67atm and the partial pressure of dinitrogen tetraoxide in the mixture is 0.33atm what is the value of K_p for the reaction at this temperature?



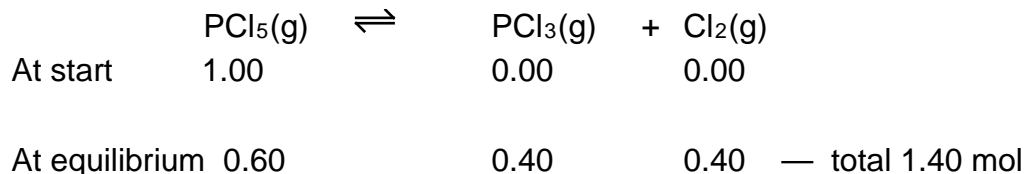
$$K_p = \frac{p_{\text{NO}_2(\text{g})}^2}{p_{\text{N}_2\text{O}_4(\text{g})}}$$

$$K_p = \frac{0.67\text{atm}^2}{0.33\text{atm}}$$

$$K_p = 1.36\text{atm}$$

Example 4: In the dissociation of phosphorus pentachloride, at 180°C and 2.00 atm pressure, the phosphorus pentachloride is found to be 40% dissociated. Find K_p .

Consider 1 mole of reactant.



mole fractions

$\frac{0.6}{1.40}$	$\frac{0.4}{1.40}$	$\frac{0.4}{1.40}$
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partial pressures

$\frac{0.6}{1.40} \times 2$	$\frac{0.4}{1.40} \times 2$	$\frac{0.4}{1.40} \times 2$
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0.857atm	0.571atm	0.571atm
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$$K_p = \frac{P_{\text{PCl}_3} \times P_{\text{Cl}_2}}{P_{\text{PCl}_5}} = \frac{0.571 \times 0.571}{0.857} = \underline{\underline{0.380 \text{ atm}}}$$

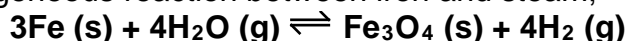
Values for solid and liquid phase in K_c and K_p .

Some equilibrium reactions involve only substances in the same phase e.g. all aqueous solutions or all gases. These are **homogeneous** reactions.

Some equilibrium reactions involve substances in different phases e.g. a pure liquid and a gas or a solid and a gas. These are **heterogeneous** reactions.

Expressions for K_c and K_p do not include values for solid and pure liquid phases in heterogeneous reactions.

For example, the heterogeneous reaction between iron and steam;

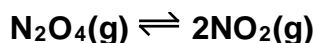


$$K_p = \frac{p^4\text{H}_2}{p^4\text{H}_2\text{O}}$$

Solids do not appear in the expression because their vapour pressures remain constant (at a constant temperature) as long as there is some of each solid present (same applies for liquids). These constant vapour pressures are incorporated into the value of K_p .

Finding equilibrium partial pressures given K_p values.

Example: What is the partial pressure of nitrogen dioxide in an equilibrium mixture if the partial pressure of dinitrogen tetraoxide in the mixture is 0.33atm and K_p at 55°C is 1.36atm for the reaction.



$$K_p = p^2\text{NO}_2(\text{g}) / p\text{N}_2\text{O}_4(\text{g})$$

$$p^2\text{NO}_2(\text{g}) = K_p * p\text{N}_2\text{O}_4(\text{g}) = 1.36\text{atm} * 0.33\text{atm} = 0.45\text{atm}$$

$$p\text{NO}_2(\text{g}) = 0.67\text{atm}.$$

The effect of temperature on K_c and K_p.

The equilibrium constant is only affected by temperature.

it does not change if concentrations or pressures are varied, nor in the presence of catalysts.

Catalysts do not alter the equilibrium constant (K_p or K_c) or the position of equilibrium. They only affect the time needed for the system to reach equilibrium.

K_c, K_p and the position of equilibrium are affected by temperature in endothermic and exothermic equilibria.

The effects are the same as predicted by Le Chateliers principle.

Exothermic reactions:

Temperature rise: - position of equilibrium moves to left, K_p and K_c become smaller.

Temperature fall: - position of equilibrium moves to right, K_p and K_c become bigger

Endothermic reactions:

Temperature rise: - position of equilibrium moves to right, K_p and K_c become bigger.

Temperature fall: - position of equilibrium moves to left, K_p and K_c become smaller.