Topic 7 → Equilibrium

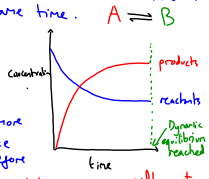
For equilibrium constants (K_c)
You need to know:

- How to deduce K_c for a homogeneous reaction (all reactants + products in same state).
- The extent of the reaction (how far the equilibrium is to the products or reactants). (Reaction Quotient → Q)
- The effect of a catalyst on K_c.

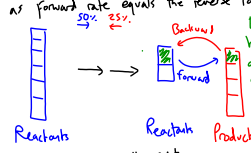
What is a dynamic equilibrium?

Many chemical reactions which go to completion (all reactants turn into products) because the products are far more energetically stable. Some reactions will not start at all because the reactants may be far more stable, or the E_a is too high.
In some reactions, where the products + reactants are of similar energetic stability we can actually have the forward reaction and the reverse reaction occuring at the same time. $A \rightleftharpoons B$

If I draw a graph of the [reactants] and [products] over time →



[reactants] drops quickly at first because there are more molecules so more chance of collisions and therefore reactions.
[products] begins at 0 but increases rapidly at first when the rate of reaction is at its fastest.
Both concentrations will eventually become constant as forward rate equals the reverse rate.



Eventhough we have a different amounts of products and reactants, the rate at which we are producing both has become constant. The equilibrium lies towards the products as there are more.

see next page for features

7.2 K_c = Equilibrium constant

The equilibrium constant shows us the 'position of equilibrium' in a chemical reaction. So it shows whether I will have more/less/same concentration of products/reactants when a dynamic equilibrium is reached.

To work out K_c for: $aA + bB \rightleftharpoons C + D$

We write: $K_c = \frac{[\text{products}]}{[\text{reactants}]} = \frac{[C][D]}{[A]^a[B]^b}$

If there are coefficients in the reaction then:
eg. $3A \rightleftharpoons 2B$ $K_c = \frac{[B]^2}{[A]^3}$ (They become power)

Q1. Express K_c for $A + 2B + 8C \rightleftharpoons 3D + 7E$

$$K_c = \frac{[D]^3[E]^7}{[A][B]^2[C]^8}$$

Q2. $H_2O_{(l)} \underset{EXO}{\overset{ENDO}{\rightleftharpoons}} H_2O_{(g)}$ $K_c = \frac{[H_2O_{(g)}]}{[H_2O_{(l)}]}$

What would happen to the value of K_c if temperature was decreased?

As less $H_2O_{(l)}$ convert to $H_2O_{(g)}$ then $[H_2O_{(l)}]$ will increase and vice versa. So K_c will decrease.

If equilibrium lies towards reactants → $K_c \ll 1$

If equilibrium lies towards products → $K_c \gg 1$

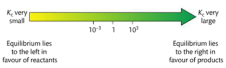
Consider the following three reactions and their K_c values measured at 550 K.

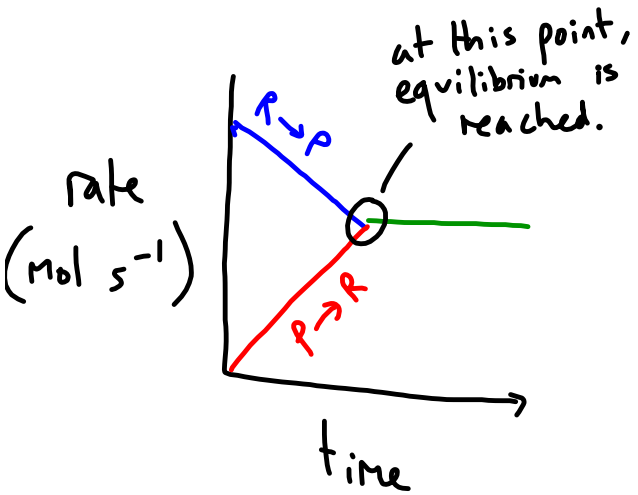
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	$K_c = 2$
$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$	$K_c = 10^{10}$
$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$	$K_c = 10^{18}$

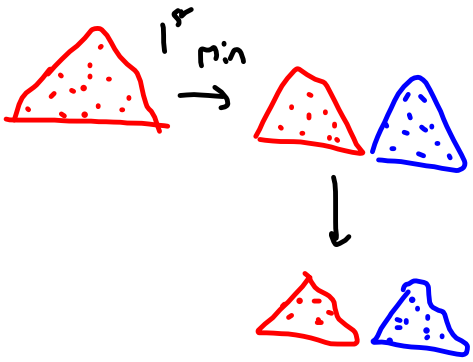
$K_c = \frac{[\text{Products}]}{[\text{Reactants}]}$

The large range in their K_c values tells us about the differing extents of these reactions. We can deduce that the reaction between H_2 and Cl_2 has taken place the most fully at this temperature, while H_2 and I_2 have reacted the least.

A good rule of thumb to apply to these situations is that if $K_c \gg 1$, the reaction is considered to go almost to completion (very high conversion of reactants into products), and if $K_c \ll 1$, the reaction hardly proceeds.

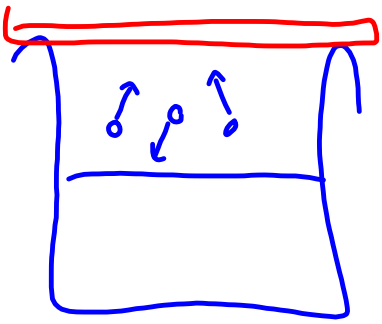






Features of a dynamic equilibrium

	Feature of equilibrium state	Explanation
1	Equilibrium is dynamic	The reaction has not stopped but both forward and backward reactions are still occurring at the same rate.
2	Equilibrium is achieved in a closed system	A closed system has no exchange of matter with the surroundings, so equilibrium is achieved where both reactants and products can react and recombine with each other.
3	The concentrations of reactants and products remain constant at equilibrium	They are being produced and destroyed at an equal rate.
4	At equilibrium there is no change in macroscopic properties	Macroscopic properties are observable properties such as colour and density. These do not change as they depend on the concentrations of the components of the mixture.
5	Equilibrium can be reached from either direction	The same equilibrium mixture will result under the same conditions, no matter whether the reaction is started with all reactants, all products, or a mixture of both.



Exercises

4 Write the equilibrium constant expression for the following reactions:

(a) $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$
(b) $4NH_3(g) + 7O_2(g) \rightleftharpoons 4NO_2(g) + 6H_2O(g)$
(c) $CH_3Cl(aq) + OH^-(aq) \rightleftharpoons CH_3OH(aq) + Cl^-(aq)$

5 Write the equations for the reactions represented by the following equilibrium constant expressions

(a) $K_c = \frac{[NO_2]^2}{[N_2O_4]}$

(b) $K_c = \frac{[CO][H_2]^3}{[CH_4][H_2O]}$

6 Write the equilibrium constant expressions for the following chemical reactions:

(a) fluorine gas and chlorine gas combine to form $ClF_3(g)$
(b) NO dissociates into its elements
(c) methane, CH_4, and steam react to form carbon monoxide and hydrogen

The reaction quotient, Q, enables us to predict the direction of reaction

Remember that the value of K_c is calculated from substituting the *equilibrium* concentrations of all reactants and products into the equilibrium constant expression. Any other values used will not give the equilibrium value K_c for that reaction at that temperature.

This in itself can be useful. If we take the concentrations of the reactants and products at one moment in time when the reaction is not at equilibrium, and substitute these into the equilibrium constant expression, we obtain a value known as the **reaction quotient, Q**. As time passes and the reaction continues, the concentrations of all reaction components change and eventually reach the equilibrium concentrations. In other words, the value of Q changes in the direction of K_c. This enables us to predict the direction in which the reaction will proceed.

For example, if we again consider the reaction:

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

for which $K_c = 49.5$ at 440 °C, as we saw on page 316.

The table below shows experimental data for the concentrations of the reaction components from experiments I and II at a time when the reaction mixture was not at equilibrium.

	Experiment I: concentration at time t / mol dm^{-3}	Experiment II: concentration at time t / mol dm^{-3}
H_2	0.0500	0.0250
I_2	0.0500	0.0350
HI	0.100	0.300

The equilibrium constant expression = $\frac{[HI]^2}{[H_2][I_2]}$

$Q \cancel{K_c} = \frac{[HI]^2}{[H_2][I_2]}$

$K_c = 49.5$

Experiment I, time t $\quad Q = \frac{(0.100)^2}{(0.0500)(0.0500)} = 4.00$

Experiment II, time t $\quad Q = \frac{(0.300)^2}{(0.0250)(0.0350)} = 103$

In experiment I, $Q < K_c$ and so Q must increase as the reaction moves towards equilibrium. This means that the net reaction must be to the right, in favour of products.

In experiment II, $Q > K_c$ and so Q must decrease as the reaction moves towards equilibrium. This means that the net reaction must be to the left, in favour of reactants.

We can summarize the use of the reaction quotient, Q, in determining the direction of reaction as follows:

- if $Q = K_c$, reaction is at equilibrium, no net reaction occurs;
- if $Q < K_c$, reaction proceeds to the right in favour of products;
- if $Q > K_c$, reaction proceeds to the left in favour of reactants.

(Cociente de reacción)

Summary - The value for K_c must be calculated when equilibrium is reached in the reaction. If we use the same expression but before we have reached equilibrium we call the value Q (reaction quotient). This value allow use to work out the direction of the reaction. If we take a reaction with a K_c of 40 and calculate Q after 5 mins of reaction time → e.g. Q = 5. This tell us the position of equilibrium must be moving towards the products as eventually Q must equal K_c (when eq. is reached).

Worked example

The equilibrium constant K_c for the reaction

$K_c = 170$

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

$K_c = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3}$

is 1.7×10^2 at 500 K.

Determine whether the reaction mixture is at equilibrium when the concentrations of the components at this temperature are as follows:

$[N_2] = 1.50$
$[H_2] = 1.00$
$[NH_3] = 8.00.$

If it is not at equilibrium, state and explain in which direction the reaction will proceed.

Solution

First write the equilibrium constant expression.

$$\frac{[NH_3]^2}{[N_2][H_2]^3}$$

Calculate the value of Q at these conditions by substituting the given concentration values into the equilibrium expression.

$$Q = \frac{(8.00)^2}{(1.50)(1.00)^3} = 42.7$$

Compare the value of Q at the given conditions with K_c.

$$42.7 < 1.7 \times 10^2$$

Therefore the reaction is not at equilibrium. It will proceed to the right in favour of products, as the value of Q must increase to be equal to K_c at equilibrium.

8. **Considérese el siguiente sistema en equilibrio:**

$$MX_5\ (g) \leftrightarrows MX_3\ (g) + X_2\ (g)$$

A 200 °C K_c vale 0,022. En un momento dado las concentraciones de las sustancias presentes son: $[MX_5] = 0{,}04$ M, $[MX_3] = 0{,}40$ M y $[X_2] = 0{,}20$ M.

Razone si, en esas condiciones, el sistema está en equilibrio. En el caso en que no estuviera en equilibrio, ¿cómo evolucionaría para alcanzarlo?

(Andalucía, 2006)

Calculamos el cociente de reacción en las condiciones del enunciado:

$$Q_c = \frac{[MX_3] \cdot [X_2]}{[MX_5]} = \frac{0{,}4 \cdot 0{,}2}{0{,}04} = 2$$

$Q_c > K_c$: el sistema no está en equilibrio. Al haber mayor concentración de productos que en el equilibrio, la reacción evolucionará hacia la izquierda para alcanzarlo.

7.2. Le Chatelier´s principle

When a system at equilibrium is subjected to a change, it will respond in such a way as to minimize the effect of the change.

This principle allows us to predict the effects of making changes on a system at equilibrium.

Changing concentration

Suppose an equilibrium is disrupted by an increase in the concentration of one of the reactants. This will cause the rate of the forward reaction to increase while the backward reaction will not be affected, so the reaction rates will no longer be equal. When equilibrium re-establishes itself, the mixture will have new concentrations of all reactants and products, and the equilibrium will have shifted in favour of products. The value of K_c will be unchanged. This is in keeping with the prediction from Le Chatelier's principle: addition of reactant causes the system to respond by removing reactant – this favours the forward reaction and so shifts the equilibrium to the right.

$K_c = \frac{[C][D]}{[A][B]}$

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

Increasing [A] ⇒ Equilibrium move towards products

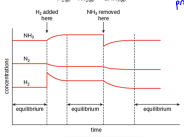
Reducing [D]

Remember ⇒ K_c remains the same

Similarly, the equilibrium could be disrupted by a decrease in the concentration of product by removing it from the equilibrium mixture. As the rate of the backward reaction is now decreased, there will be a shift in the equilibrium in favour of the products. A different equilibrium position will be achieved, but the value of K_c will be unchanged. Again this confirms the prediction from Le Chatelier's principle: removal of product causes the system to respond by making more product – this favours the forward reaction and so shifts the equilibrium to the right.

Haber process

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



Changes in the concentration of reactants or products alter the equilibrium position and so change the composition of the equilibrium mixture. But the value of K_c stays the same.

(Pressure has an effect if there are more moles on one side of the equation)

Changing pressure

For example, consider the reaction used in the production of methanol:

$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

In total there are three molecules of gas on the left side and one molecule of gas on the right side. So here high pressure will shift the equilibrium to the right, in favour of the smaller number of gas molecules, which increases the yield of CH_3OH.

Note that many common equilibrium reactions do not involve a change in the number of gas molecules and so are not affected by changes in pressure. For example, the reaction

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

has two molecules of gas on both sides of the equation. Changing pressure for this reaction will affect the rate of the reaction but not the position of equilibrium or the value of K_c.

Changes in pressure or volume will affect the position of equilibrium of a reaction if it involves a change in the number of gas molecules. The value of K_c remains unchanged.

Changing temperature

We have noted that K_c is temperature dependent, so changing the temperature will change K_c. However, in order to predict how it will change we must examine the enthalpy changes (see Chapter 5) of the forward and backward reactions. Remember that an exothermic reaction releases energy (ΔH negative), whereas an endothermic reaction absorbs energy (ΔH positive). The enthalpy changes of the forward and backward reactions are equal and opposite to each other.

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

So if we apply Le Chatelier's principle, including the enthalpy change in the chemical reaction, we can predict how a system will respond to a change in temperature.

Consider the reaction:

$2NO_2(g) \rightleftharpoons N_2O_4(g)$ $\Delta H = -57\ kJ\ mol^{-1}$

brown colourless

The negative sign of ΔH tells us that the forward reaction is exothermic and so releases heat. If this reaction at equilibrium is subjected to a decrease in temperature, the system will respond by producing heat and it does this by favouring the forward exothermic reaction. This means that the equilibrium will shift to the right, in favour of the product N_2O_4. A new equilibrium mixture will be achieved and the value of K_c will increase. So here we can see that the reaction will give a higher yield of products at a lower temperature.

Conversely, increasing the temperature favours the backward endothermic reaction, and so shifts the equilibrium to the left, decreasing the value of K_c. The reaction mixture becomes a darker colour as the concentration of NO_2 increases.

The table below illustrates the effect of temperature on the value of K_c for this reaction.

Temperature / K	K_c for $2NO_2(g) \rightleftharpoons N_2O_4(g)$
273	1300
298	170

E.g. changing the temp. not at equilibrium

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\Delta H = +181\ kJ\ mol^{-1}$

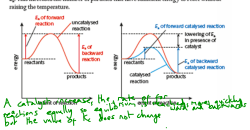
Temperature / K	K_c for $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
298	4.5×10^{-31}
900	6.7×10^{-10}
2300	1.7×10^{-3}

Increasing the temperature causes an increase in the value of K_c for an endothermic reaction and a decrease in the value of K_c for an exothermic reaction.

K_c

Addition of a catalyst

As we learned in Chapter 6, a catalyst speeds up the rate of a reaction by providing an alternate reaction pathway that has a transition state with a lower activation energy, E_a. This increases the number of particles that have sufficient energy to react without raising the temperature.



A catalyst increases the rate of both forward and backward reactions equally to equilibrium, but does not change the value of K_c

Summary

We can now summarize the effects of concentration, pressure, temperature, and catalyst on the position of equilibrium and on the value of K_c.

Effect of ...	Change in position of equilibrium	Change in value of K_c
1 concentration	changes	no change
2 pressure	changes if reaction involves a change in the number of gas molecules (when $\Delta n \neq 0$)	no change
3 temperature	changes	changes
4 catalyst	no change	no change

11 What will happen to the position of equilibrium and the value of the equilibrium constant when the temperature is increased in the following reaction?

$B_2(g) + Cl_2(g) \rightleftharpoons 2BrCl(g)$ $\Delta H^{\ominus} = +14\ kJ$

	Position of equilibrium	Value of equilibrium constant
A	shifts towards the reactants	decreases
B	shifts towards the reactants	increases
C	shifts towards the products	decreases
D	shifts towards the products	increases

12 Which changes will shift the position of equilibrium to the right in the following reaction?

$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$

I adding a catalyst
II decreasing the oxygen concentration
III increasing the volume of the container

A I and II only **B** I and III only **C** II and III only **D** I, II, and III

13 For each of the following reactions, predict in which direction the equilibrium will shift in response to an increase in pressure.

(a) $2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$
(b) $CO(g) + 2H_2 \rightleftharpoons CH_3OH(g)$
(c) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

14 How will the equilibrium

$CH_4(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g)$ $\Delta H = +ve$

respond to the following changes?

(a) addition of $H_2(g)$
(b) addition of $CH_4(g)$
(c) a decrease in the volume of the container
(d) removal of $CS_2(g)$
(e) increase in temperature

The Haber Process

Catalyst → Iron

The Haber process is based on the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -93\ \text{kJ mol}^{-1}$$

- Concentration: the reactants nitrogen and hydrogen are supplied in the molar ratio 1 : 3 in accordance with their stoichiometry in the equation. The product ammonia is removed as it forms, thus helping to pull the equilibrium to the right and increasing the yield.
- Pressure: as the forward reaction involves a decrease in the number of gas molecules, it will be favoured by a *high pressure*. The usual pressure used in the Haber process is about 2×10^7 Pa.
- Temperature: as the forward reaction is exothermic, it will be favoured by a lower temperature. However, too low a temperature would cause the reaction to be uneconomically slow, and so a *moderate temperature* of about 450 °C is used.
- Catalyst: a catalyst will speed up the rate of production and so help to compensate for the moderate temperature used. A catalyst of finely divided iron is used, with small amounts of aluminium and magnesium oxides added to improve its activity. More recently, ruthenium has become the catalyst of choice, and this has helped reduce the energy requirement.

The Contact Process

The Contact process involves a series of three simple reactions:

(i) the combustion of sulfur to form sulfur dioxide;

(ii) the oxidation of sulfur dioxide to sulfur trioxide:

Catalyst - V_2O_5

EXO

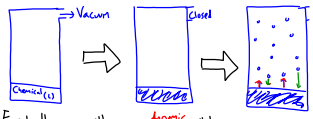
$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -196\ \text{kJ mol}^{-1}$$

(iii) The combination of sulfur trioxide with water to produce sulfuric acid.

It has been shown that the overall rate of the process depends on step (ii), the oxidation of sulfur dioxide. So applying Le Chatelier's principle to this step, we can predict the conditions that will most favour the formation of product. These are summarized in the table below.

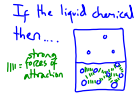
	Influence on reaction	Condition used
pressure	forward reaction involves reduction in the number of molecules of gas from three molecules reactant to two molecules product: high pressure will favour product	2×10^5 Pa (this gives a very high equilibrium yield, so still higher pressure is not needed)
temperature	forward reaction is exothermic: low temperature will increase the equilibrium yield, but decrease the rate	450 °C
catalyst	increases the rate of reaction	vanadium(V) oxide

Topic 17.1 Liquid-vapor equilibrium



Eventually we will reach a dynamic equilibrium when the rate of molecules evaporating equals the rate at which they are condensing.
The pressure caused by the molecules at dynamic equilibrium is called the vapour pressure.

If the liquid chemical has strong intermolecular forces then...



it will have a low vapour pressure (and higher BP)

If it has weak intermolecular forces then...

it will have a high vapour pressure (and low BP)

Definition: Enthalpy of vaporisation ΔH_{vap}
→ "the energy required to turn 1 mole of a liquid chemical into a gas."

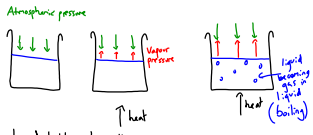
Q1. If I increased the surface area of my liquid, how would it affect the position of equilibrium?

$H_2O\ (l) \rightleftharpoons H_2O\ (g)$

It would not change the position because although there is a larger surface area for vaporisation to occur, there is also a larger surface area for condensation to occur (when a molecule hits the surface and does not have enough energy to overcome the intermolecular forces of the liquid).
Equilibrium would however, be reached more quickly as both rates are faster.

Q2. If I take a beaker of water (an open system), why will I not reach a dynamic equilibrium between evaporation/condensation?

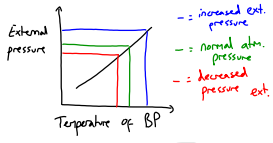
Why does a liquid boil and how is it influenced by vapour pressure / pressure of the surroundings?

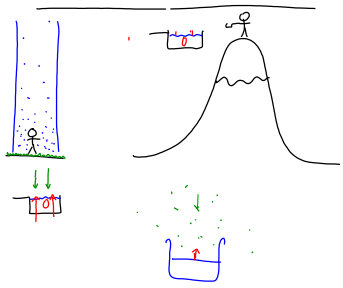


A liquid boils when the vapour pressure on the surface of the liquid becomes equal to the pressure of the surroundings (normally atmospheric pressure).

So if I increased the external pressure (like with a pressure cooker)

If I decrease external pressure (by climbing Mount Everest)





17.2 - Calculating K_c in a homogeneous equilibrium

1. For this reaction: $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

at a certain temperature, the equilibrium concentrations (in mol/dm³) are:

$[H_{2(g)}] = 0.30$ $[I_{2(g)}] = 0.30$ $[HI_{(g)}] = 3.0$

What is the value of K_c? $K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{3.0^2}{0.3 \times 0.3}$

2. When a mixture of 0.100 mol NO, 0.051 mol H_2 and 0.100 mol H_2O were placed in a 1 dm³ flask at 300 K, the following equilibrium was established:

$$2NO_{(g)} + 2H_{2(g)} \rightleftharpoons N_{2(g)} + 2H_2O_{(g)}$$

At equil. the concentration of NO was found to be 0.062 mol dm⁻³.

Determine K_c (at this temperature)

	$2NO$	$+ 2H_2$	$\rightleftharpoons N_2$	$+2H_2O$
Initial amount	0.100	0.051	0	0.100
	↓ −0.038	↓ −0.038	↑ +0.019	↑ +0.038
Final amount	0.062	0.013	0.019	0.138

$$K_c = \frac{[\text{Products}]^x}{[\text{Reactants}]^y} = \frac{[N_2][H_2O]^2}{[NO]^2[H_2]^2} = 557$$

Consider this reaction: $\Delta H = -86.5$ kJ mol⁻¹

$$Cl_{2(g)} + SO_{2(g)} \rightleftharpoons SO_2Cl_{2(g)}$$

In a 1 dm³ closed container, at 375 °C, 8.60×10^{-3} mol of SO_2 and 8.60×10^{-3} mol of Cl_2 were introduced. At equilibrium, 7.65×10^{-4} mol of SO_2Cl_2 was formed.

i) Deduce an expression for K_c.

ii) Determine value of K_c.

	Cl_2	$+ SO_2$	$\rightleftharpoons SO_2Cl_2$
Initial			
Final			

12

iii) Would K_c increase or decrease at 300 °C?

iv) If the volume of the container was increased to 1.5 dm³, what would happen to $[SO_2Cl_2]$ and K_c?

v) How would a catalyst affect $[SO_2Cl_2]$? K_c?

Worked example

A student placed 0.20 mol of $PCl_3(g)$ and 0.10 mol of $Cl_2(g)$ into a 1.0 dm³ flask at 350 °C. The reaction, which produced PCl_5, was allowed to come to equilibrium, at which time it was found that the flask contained 0.12 mol of PCl_5. What is the value of K_c for this reaction?

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Worked example

The oxidation of NO to form NO_2 occurs during the formation of smog. When 0.60 mol of NO was reacted with 0.60 mol of O_2 in a 2.0 dm³ container at 500 °C, the equilibrium mixture was found to contain 0.20 mol of NO_2. Calculate the equilibrium constant for the reaction at this temperature.

1.0

Worked example

The reaction:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

has $K_c = 0.500$ at 350 K. If the concentrations at equilibrium are:

CO 0.200 mol dm⁻³

H_2 0.155 mol dm⁻³

what is the equilibrium concentration of CH_3OH?

Solution

Write the equilibrium expression:

$$K_c = \frac{[CH_3OH]}{[CO][H_2]^2}$$

Substitute the data from the question and solve the equation to give the unknown concentration.

$$0.500 = \frac{[CH_3OH]}{(0.200)(0.155)^2}$$

Therefore $[CH_3OH] = 0.00240$ mol dm⁻³ or 2.40×10^{-3} mol dm⁻³

Worked example

The equilibrium constant K_c for the reaction

$$SO_2(g) + NO(g) \rightleftharpoons NO_2(g) + SO_2(g)$$

was found to be 6.78 at a specified temperature. If the initial concentrations of NO and SO_2 were both 0.0300 mol dm⁻³, what would be the equilibrium concentration of each component?

En un recipiente de 10 litros de capacidad se introducen 2 moles del compuesto A y 1 mol del compuesto B. Se calienta a 300 °C y se establece el siguiente equilibrio:

$$A\,(g) + 3\,B\,(g) \leftrightarrows 2\,C\,(g)$$

Cuando se alcanza el equilibrio, el número de moles de B es igual al de C. Calcule:

a) El número de moles de cada componente de la mezcla.

b) El valor de la constante K_c a esa temperatura.

Dato: $R = 0{,}082\ \text{atm} \cdot \text{L} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

(Andalucía, 2006)

En

M

Se

a)

b)

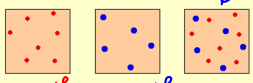
Selectivity

Equilibrium constants in gaseous equilibria > K_p

When looking at equilibrium reactions in the gaseous state, it is easier to talk in terms of 'partial pressures' instead of concentrations.

Total pressure P = $P_A + P_B + P_C + \ldots$

It is easy to see this visually:



gas A → P_A gas B → P_B mixture

Gas A is creating a pressure (its partial pressure) when its molecules hit the walls of its container. Gas B does the same. When you mix them up, they just go on doing what they were doing before. The total pressure is due to both molecules hitting the walls - in other words, the sum of the partial pressures.

The more important relationship is the second one:

P_A = mole fraction of A x total pressure

$P_A = x_A \times P$

Learn it!

That means that if you had a mixture made up of 20 moles of nitrogen, 60 moles of hydrogen and 20 moles of ammonia (a total of 100 moles of gases) at 200 atmospheres pressure, the partial pressures would be calculated like this:

gas	mole fraction	partial pressure
nitrogen	20/100 = 0.2	0.2 x 200 = 40 atm
hydrogen	60/100 = 0.6	0.6 x 200 = 120 atm
ammonia	20/100 = 0.2	0.2 x 200 = 40 atm

Partial pressures can be quoted in any normal pressure units. The common ones are atmospheres or pascals (Pa). Pascals are exactly the same as N m^{-2} (newtons per square metre).

Molar fraction (X_i) = $\frac{\text{moles of 1 substance}}{\text{total number of moles}}$

E.g.

2 moles O_2

8 moles N_2

$X_{O_2} = \frac{2}{10} = \frac{1}{5}$

$X_{N_2} = \frac{8}{10} = \frac{4}{5}$

$K_c = \frac{[\text{products}]}{[\text{reactants}]}$

$K_p = \frac{P_{\text{products}}}{P_{\text{reactants}}}$

Writing an expression for K_p

We are going to start by looking at a general case with the equation:

$$aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$$

If you allow this reaction to reach equilibrium and then measure (or work out) the equilibrium partial pressures of everything, you can combine these into the equilibrium constant, K_p.

Just like K_c, K_p always has the same value (provided you don't change the temperature), irrespective of the amounts of A, B, C and D you started with.

$$K_p = \frac{P_C^{\,c} \times P_D^{\,d}}{P_A^{\,a} \times P_B^{\,b}}$$

K_p has exactly the same format as K_c, except that partial pressures are used instead of concentrations. The gases on the right-hand side of the chemical equation are at the top of the expression, and those on the left at the bottom.

K_p in homogeneous gaseous equilibria

A homogeneous equilibrium is one in which everything in the equilibrium mixture is present in the same phase. In this case, to use K_p, everything must be a gas.

A good example of a gaseous homogeneous equilibrium is the conversion of sulphur dioxide to sulphur trioxide at the heart of the Contact Process:

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

The Contact Process equilibrium

You will remember that the equation for this is:

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

K_p is given by:

$$K_p = \frac{P_{SO_3}^{\,2}}{P_{SO_2}^{\,2} \times P_{O_2}}$$

The Haber Process equilibrium

The equation for this is:

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

. . . and the K_p expression is:

$$K_p = \frac{P_{NH_3}^{\,2}}{P_{N_2} \times P_{H_2}^{\,3}}$$

K_p in heterogeneous equilibria

A typical example of a heterogeneous equilibrium will involve gases in contact with solids.

Writing an expression for K_p for a heterogeneous equilibrium

Exactly as happens with K_c, you *don't include any term for a solid in the equilibrium expression.*

The next two examples have already appeared on the K_c page.

The equilibrium produced on heating carbon with steam

$$H_2O_{(g)} + \cancel{C_{(s)}} \rightleftharpoons H_{2(g)} + CO_{(g)}$$

Everything is exactly the same as before in the expression for K_p, except that you leave out the solid carbon.

$$K_p = \frac{P_{H_2} \times P_{CO}}{P_{H_2O}}$$

Solubility product > K_{sp} K_{sp}

This is the equilibrium constant for the equilibrium of an ionic solid and its aqueous ions. As with partial pressures, we ignore the concentration of any solids in the expression as we assume they are constant.

$$BaSO_{4\,(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

$$K_{sp} = \frac{[Ba^{2+}_{(aq)}][SO_{4\,(aq)}^{2-}]}{\cancel{[BaSO_4]}} = [Ba^{2+}_{(aq)}][SO_{4\,(aq)}^{2-}]$$

ignore

$$PbCl_{2\,(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

$$K_{sp} = [Pb^{2+}_{(aq)}]\cdot[Cl^-_{(aq)}]^2$$

Example

The solubility of lead(II) chloride at 298 K is 3.90×10^{-4} mol dm^{-3}, what is the solubility product for lead(II) chloride at this temperature?

$PbCl_2\,(s) \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$

3.90×10^{-4} mol/dm^3 | 3.90×10^{-4} mol/dm^3 | 3.90×10^{-4} $\times 2$ mol/dm^3

Solution

From the equation above, each formula unit of lead(II) chloride forms one lead ion and two chloride ions, therefore:

$[Pb^{2+}] = 3.90 \times 10^{-4}$ mol dm^{-3} and
$[Cl^-] = 2 \times 3.90 \times 10^{-4}$
$= 7.80 \times 10^{-4}$ mol dm^{-3};
substituting:

$K_{sp} = [Pb^{2+}] \times [Cl^-]^2$
$= 3.90 \times 10^{-4} \times (7.80 \times 10^{-4})^2$
$= 2.37 \times 10^{-10}$ [redacted]

$K_{sp} = [Pb^{2+}][Cl^-]^2$

$K_{sp} = 2.37\times10^{-10}$

Ions behave independently in solution and hence, in the above example, the chloride ions need not necessarily come from the lead(II) chloride, they could also come from some other solute, for example hydrochloric acid. This means that an ionic solid is significantly less soluble in a solution that already contains one of its component ions, than it is in pure water. This is known as the common ion effect.

$HCl \rightarrow H^+ + Cl^-$

$HCl \rightarrow H^+ + Cl^-$
0.1 mol dm^{-3} | 0.1 mol dm^{-3} | 0.1 mol dm^{-3}

Calculate the solubility of lead(II) chloride, in g dm^{-3}, in 0.100 mol dm^{-3} hydrochloric acid at 298 K, given its solubility product determined above.

$K_{sp} = [Pb^{2+}][Cl^-]^2$
2.37×10^{-10} | 0.1

Solution

$[Cl^-] = 0.100$ mol dm^{-3}, (assuming any ions from the lead(II) chloride are negligible), therefore

$K_{sp} = [Pb^{2+}] \times [Cl^-]^2$
$= [Pb^{2+}] \times (0.1)^2$
$(= 2.37 \times 10^{-10}$ mol^3 dm$^{-9})$

$[Pb^{2+}] = \frac{2.37 \times 10^{-10}}{0.0100}$

$= 2.37 \times 10^{-8}$ mol dm^{-3}

$= [PbCl_2]$ (note this is much less than in water)

$[Pb^{2+}] = \frac{2.37\times10^{-10}}{0.1^2}$

$[Pb^{2+}] = 2.37\times10^{-8}$ mol dm^{-3}

$PbCl_2 \rightarrow Pb^{2+} + 2Cl^-$

2.37×10^{-8} mol dm^{-3} | 2.37×10^{-8} mol dm^{-3}

$M_r(PbCl_2) = 278$

$m = n \times M_r$
$= 2.37 \times 10^{-8} \times 278$
$= 6.60 \times 10^{-6}$ g dm^{-3}

Selectividad questions

$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$

0.02 0.02 0.04

1 Una disolución saturada de hidróxido de calcio a 25ºC contiene 0,296 gramos de $Ca(OH)_2$ por cada 200 mL de disolución. Determine:

a) El producto de solubilidad del $Ca(OH)_2$ a 25ºC.

$K_{sp} = [Ca^{2+}][OH^-]^2$

$K_{sp} = 0.02 \quad 0.04$

Datos: Masas atómicas Ca = 40; O = 16; H = 1.

$Mol_{Ca(OH)_2} = \frac{0.296}{74} = 0.004$ mol

$Conc = \frac{0.004 \text{ mol}}{0.2 \text{ dm}^3} = 0.02 \text{ mol dm}^{-3}$

Kp = $3{,}2 \cdot 10^{-5}$

2 A 25ºC el producto de solubilidad del MgF_2 es $8 \cdot 10^{-8}$.

a) ¿Cuántos gramos de MgF_2 pueden disolverse en 250 mL de agua?

$MgF_2 \rightarrow Mg^{2+} + 2F^-$ $[Mg^{2+}] = x$ $K_{sp} = x \cdot (2x)^2$

$K_{sp} = [Mg^{2+}][F^-]^2$ $[F^-] = 2x$ $x = 2.7 \times 10^{-3}$ mol dm^{-3}

$0.1674 \frac{g}{dm^3} \times 0.250 \, dm^3$ $2.7 \times 10^{-3} \frac{mol}{dm^3} \times 62 \frac{g}{mol} = 0.1674 \frac{g}{dm^3}$

Mass = 0.042 g

b) ¿Cuántos gramos de MgF_2 se disuelven en 250 mL de disolución 0,1 M de $Mg(NO_3)_2$?

Datos: Masas atómicas Mg = 24; F = 19.

$K_{sp} = 8 \cdot 10^{-8}$ $MgF_2 \rightarrow Mg^{2+} + 2F^-$

$K_{sp} = [Mg^{2+}][F^-]^2$ // $[F^-] = 8.9 \times 10^{-4}$ mol dm^{-3}

0.1

$[MgF_2] = 4.45 \times 10^{-4}$ mol dm^{-3}

$4.45 \times 10^{-4} \frac{mol}{dm^3} \times 62 \frac{g}{mol} = 0.0276 \frac{g}{dm^3} \times 0.250 \, dm^3$

Mass = 0.0069 g

En diversos países la fluoración del agua de consumo humano es utilizada para prevenir caries.

a) Si el producto de solubilidad K_s del CaF_2 es $1'0 \cdot 10^{-10}$ ¿cuál es la solubilidad de una disolución saturada de CaF_2?

b) ¿Qué cantidad en gramos de NaF hay que añadir a un litro de una disolución acuosa que contiene 20 mg de Ca^{2+} para que empiece a precipitar CaF_2? Masas atómicas: F=19; Na= 23; Ca=40.

Total P → 100 atm

3 moles H_2 7 moles NH_3

K_p

$P_{H_2} = \frac{3}{10} \times 100 = 30$ atm

$P_{NH_3} = \frac{7}{10} \times 100 = 70$ atm