Equilibrium

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Class Goals

- Review of a chemical reaction
- Principles of chemical Equilibrium
- Equilibrium constant
- Principles of Le Chatelier

Chemical Equilibrium

Some reaction develop until completion, i.e. combustion

Other reactions just develop to some extension → part of the reagent does not react

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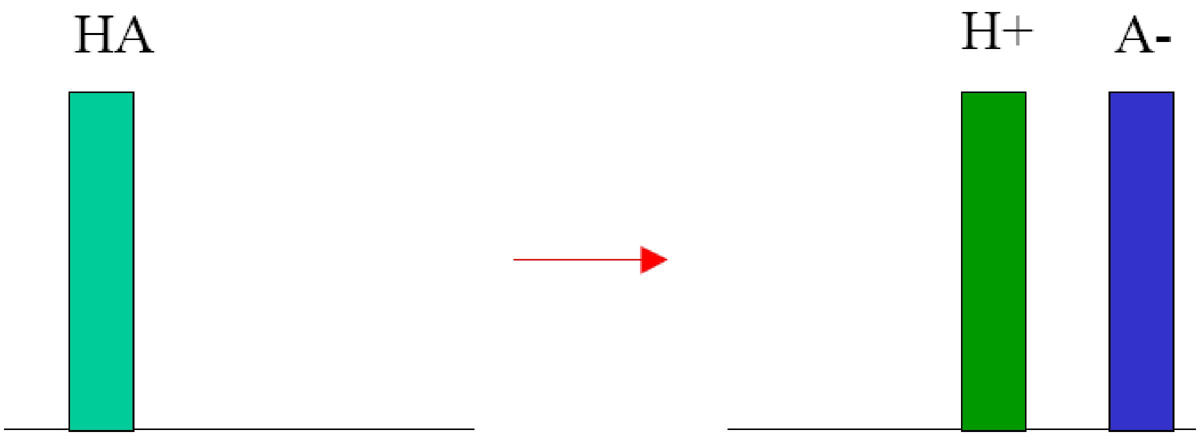
These reaction is said that reached the
CHEMICAL EQUILIBRIUM

Example: weak acid or base

Chemical Equilibrium

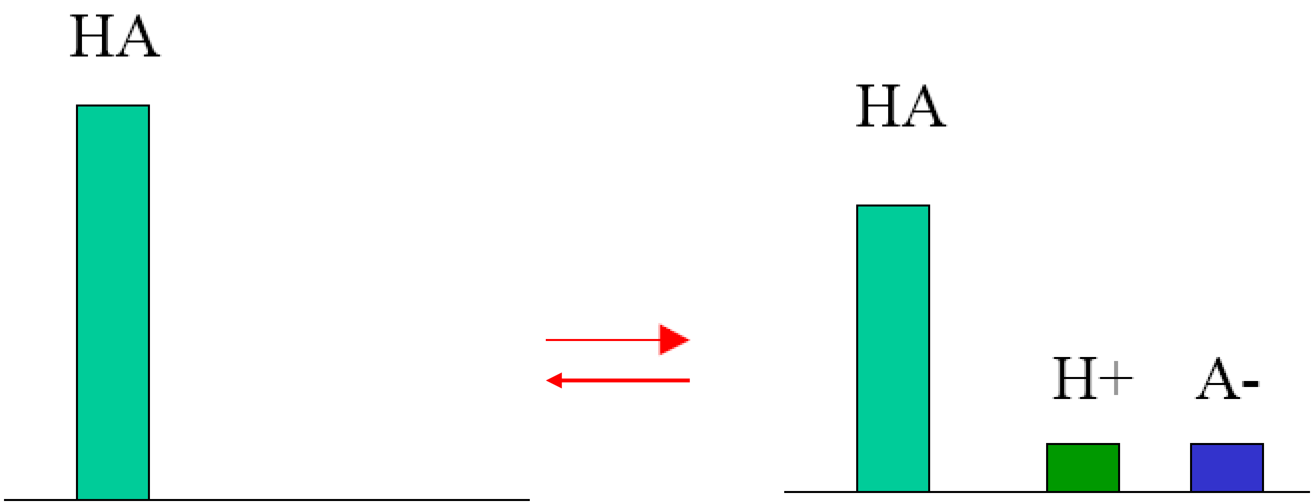


Strong acid/base:

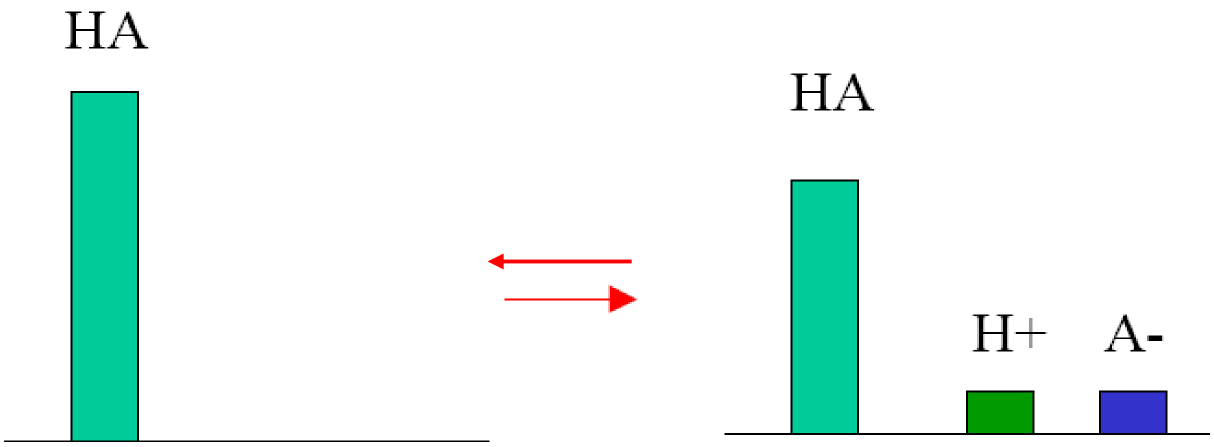
Complete reaction, only product at the end

Weak acid/base:

Partial reaction, leftover of reagent at the end



Chemical Equilibrium



Important concepts:

The amounts of reagents and product at the equilibrium is **NOT** the same

TWO reactions are occurring at the same time:
- reagents to product: direct reaction
- products back to reagents: inverse reaction

Reversible reaction

Chemical Equilibrium

Reversible reaction: when the reaction occurs both ways

Chemical Equilibrium: the situation when the **PROPORTION** between reagents and product is kept constant (not equal) in time.

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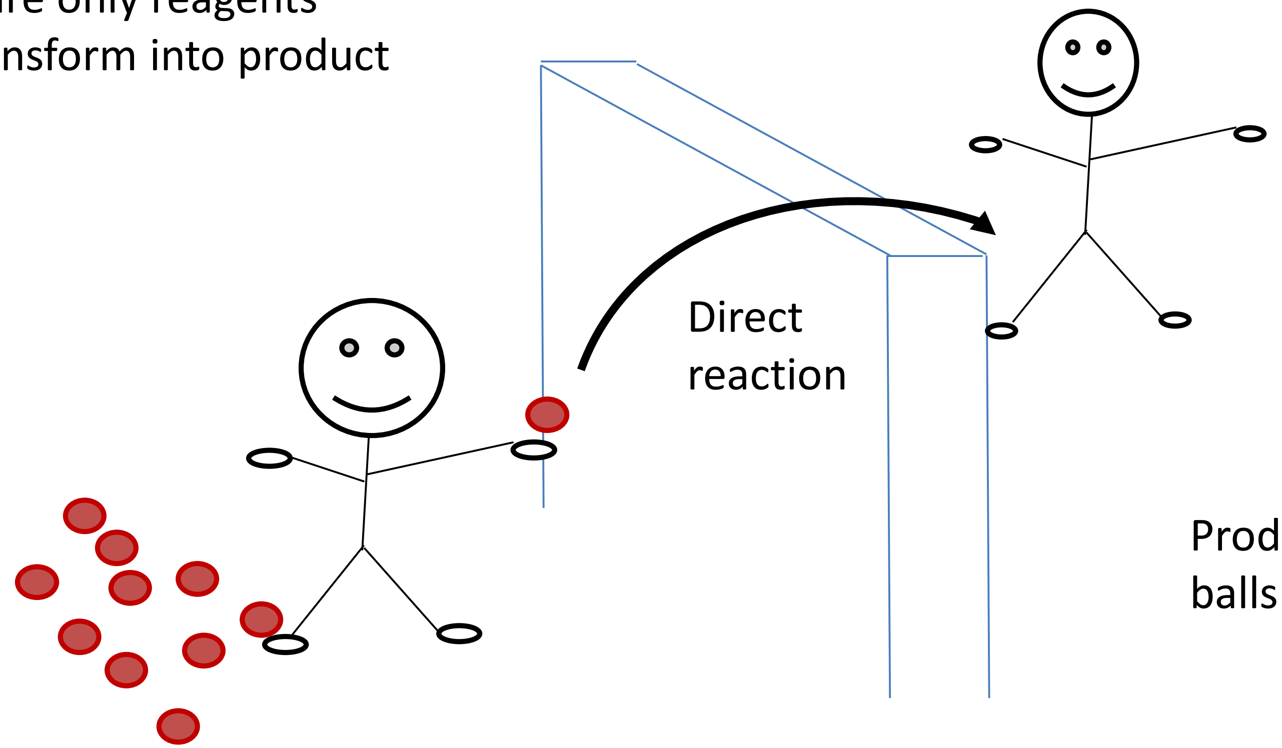
The speed of the direct reaction is equal to the speed of the inverse reaction !

How equilibrium happens

When the reaction **starts**:

there are only reagents
that transform into product



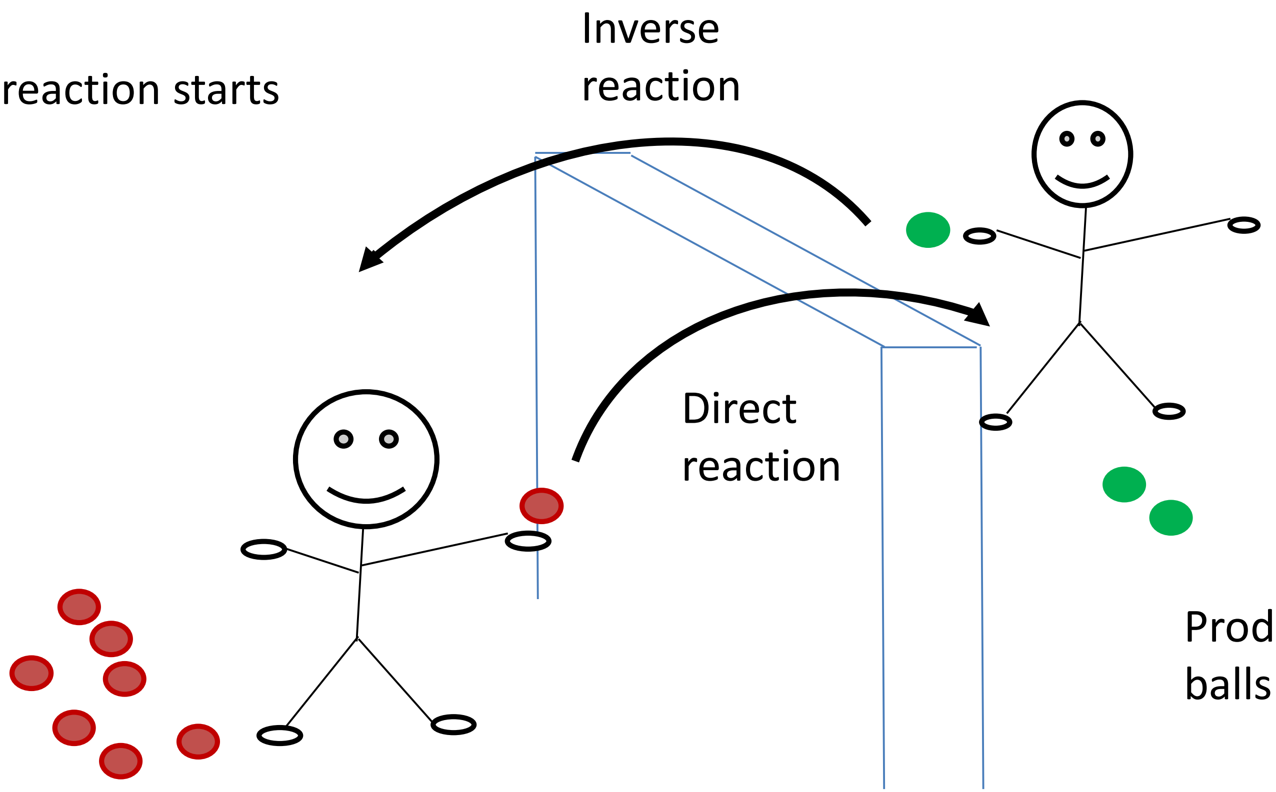
Products: 0 green balls

Reagents: 11 red balls

How equilibrium happens

The reaction develops:

Inverse reaction starts



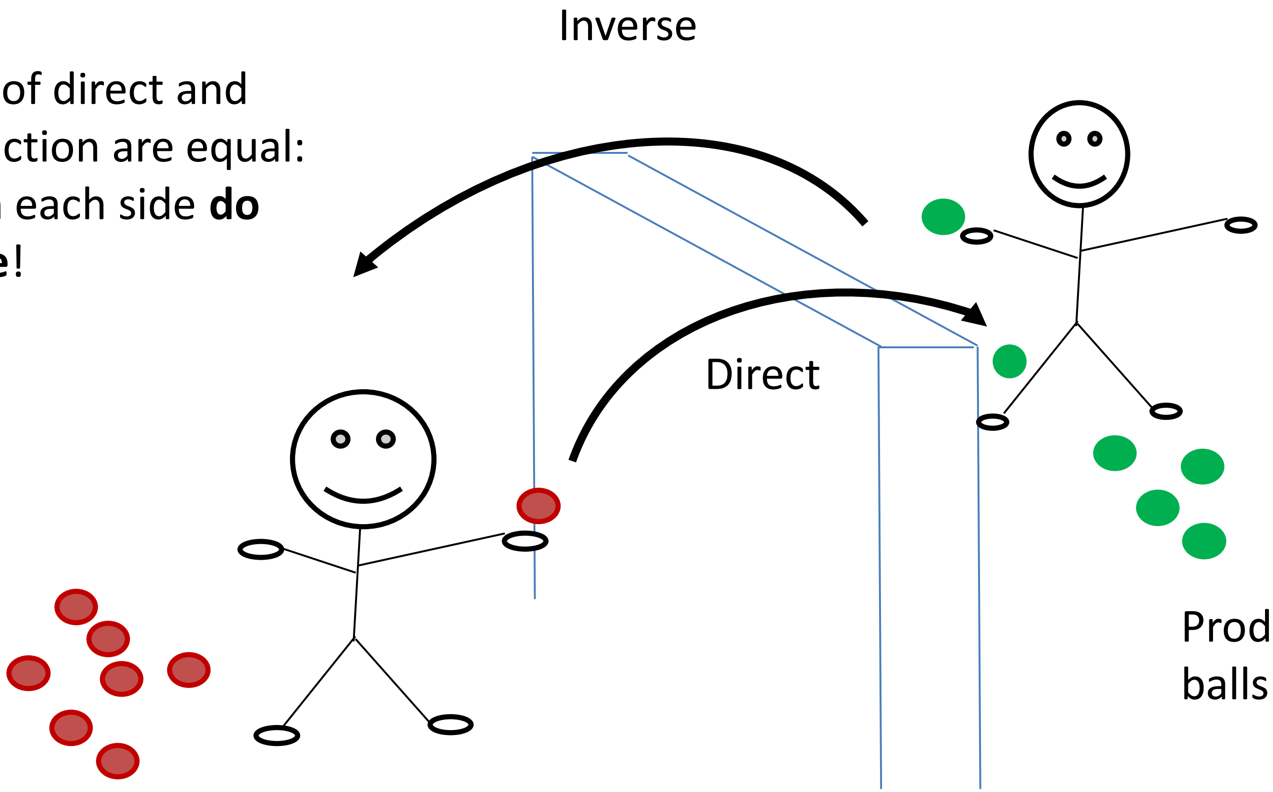
Products: 3 green balls

Reagents: 8 red balls

How equilibrium happens

At equilibrium:

The speed of direct and inverse reaction are equal: amount on each side **do not change**!



Products: 4 green balls

Reagents: 8 red balls

How to describe equilibrium

At equilibrium, the PROPORTION between reagentes and product is the same with time

This is indipendent of the initial concentration of the reagents

We can write a constant that describes the proportion:

$$\frac{[\text{ Product at equilibrium }]}{[\text{Reagents at equilibrium}]} = \text{Constant, K}$$

The equilibrium constant

Considering a generic reversible reaction:

$$aA + bB \rightleftarrows cC + dD$$

a, b, c, d are the stoichiometry coefficients

A, B, C, D define the amounts of reagents and products

The equilibrium constant will be:

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

The equilibrium constant

Considering this system at equilibrium:

$$N_2O_4\,(g) \rightleftarrows 2\,NO_2\,(g)$$

The equilibrium constant will be:

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

The equilibrium constant

Considering this system at equilibrium:

$$N_2O_4\,(g) \rightleftarrows 2\,NO_2\,(g)$$

The equilibrium constant will be:

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

K_c – always the amounts are expressed in **M = mol /L** **!**

Kc examples

$$2\,NOCl\,(g) \leftrightarrows 2\,NO(g) + Cl_2(g)$$

Kc examples

Pure solids and liquids **NEVER** appears in the expression of Kc

$S(s) + O_2(g) \leftrightarrows SO_2(g)$

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

$NH_3(aq) + H_2O\ (l) \leftrightarrows NH_4^+(aq) + OH^-(aq)$

Kc examples

<u>Exercise:</u> write the equilibrium constant of the following reactions

Chemical Reactions	K_c
$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$	
$2HI(g) \rightleftarrows H_2(g) + I_2(g)$	
$2SO_2(g) + O_2(g) \rightleftarrows 2SO_3(g)$	

Kc examples

Solution:

Chemical Reactions	K_c
$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$	$K_c = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$
$2HI(g) \rightleftarrows H_2(g) + I_2(g)$	$K_c = \dfrac{[H_2][I_2]}{[HI]^2}$
$2SO_2(g) + O_2(g) \rightleftarrows 2SO_3(g)$	$K_c = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$

More exercises...

$$S_{(s)} + O_{2(g)} \rightleftarrows SO_{2(g)}$$

$$MgO_{(s)} + CO_{2(g)} \rightleftarrows MgCO_{3(s)}$$

$$Fe_{(s)} + Cu^{+2}_{(aq)} \rightleftarrows Fe^{+2}_{(aq)} + Cu_{(s)}$$

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

At home !

More exercises...

$$S_{(s)} + O_{2(g)} \rightleftarrows SO_{2(g)} \Rightarrow K_c = \frac{[SO_2]}{[O_2]}$$

$$MgO_{(s)} + CO_{2(g)} \rightleftarrows MgCO_{3(s)} \Rightarrow K_c = \frac{1}{[CO_2]}$$

$$Fe_{(s)} + Cu^{+2}_{(aq)} \rightleftarrows Fe^{+2}_{(aq)} + Cu_{(s)} \Rightarrow K_c = \frac{[Fe^{+2}]}{[Cu^{+2}]}$$

$$CaCO_{3(s)} \rightleftarrows CaO_{(s)} + CO_{2(g)} \Rightarrow K_c = [CO_2]$$

The meaning of Kc

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

1. Knowing the value of **Kc** is possible to extimate the amount of reagents and products at equilibrium.

2. The value of Kc allows us to extimate if the reaction is **efficient** (lots of porducts)

The meaning of Kc

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

→ Numerator = products

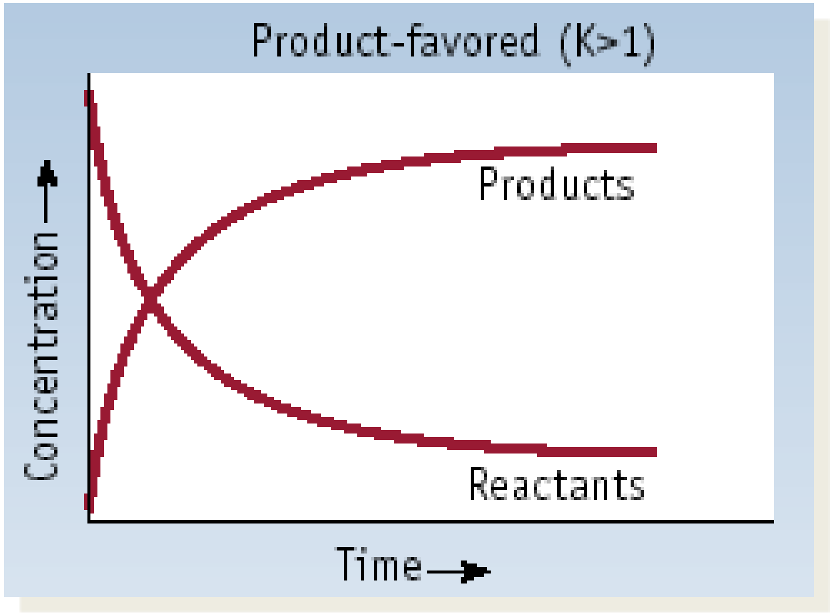
→ Denominator = reagents

Kc is a <u>fraction</u>:

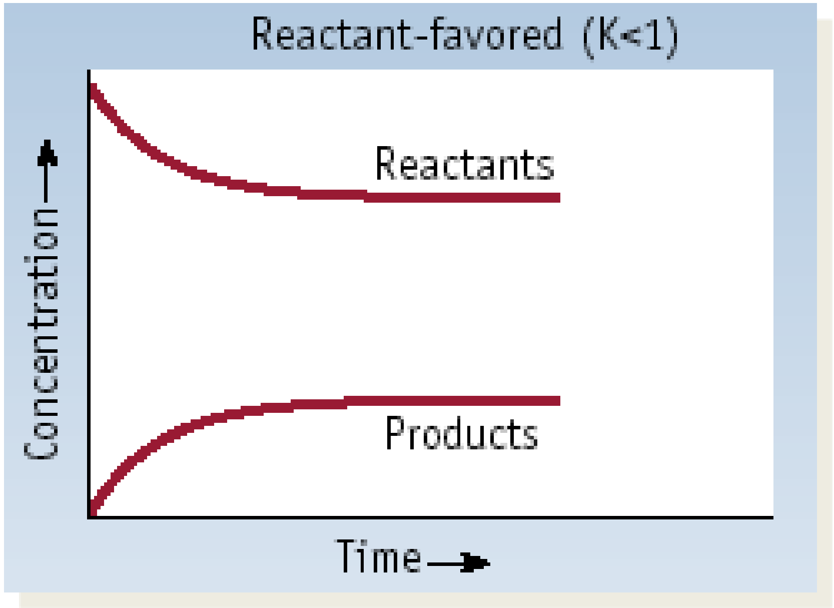
If the value of Kc is HIGHER than 1 → we have more products than reagents at the equilibrium: the reaction is product oriented

If the value of Kc is LOWER than 1 → we have a lot of leftover reagents: the reaction is not efficient

The meaning of Kc



Efficient



Not efficient

The meaning of Kc

The reaction to obtain ammonia:

$$N_2(g) + 3\,H_2(g) \rightleftarrows 2\,NH_3(g)$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = 3.5 \times 10^8$$

The meaning of Kc

The reaction to obtain ammonia:

$$N_2(g) + 3\,H_2(g) \rightleftarrows 2\,NH_3(g)$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = 3.5 \times 10^8$$

The **Kc** value is much larger than 1 → the concentration of reagents left at equilibrium is very small, lots of product!

This reaction is very efficient and product-oriented: the **Borh-Haber** cycle.

The meaning of Kc

Salt dissociation reaction:

$$AgCl(s) \leftrightarrows Ag^{+}(aq) \ + \ Cl^{-}(aq)$$

$$K_c = [Ag^{+}]\,[Cl^{-}] \ = \ 1{,}8 \times 10^{-5}$$

The Kc value is much lower than 1 → just a few amount of products are obtained at equilibrium

Is this a good reaction if I want to obtain Cl^{-} ?

Kp : constant for gases

When the reaction occurs fully in the gas phase, it is possible to express the equilibrium constant through **partial pressure**

For the following system:

$$N_2O_4\,(g) \leftrightarrows 2\,NO_2\,(g)$$

$$\boxed{K_P = \frac{P^2_{NO_2}}{P_{N_2O_4}}}$$

$\boldsymbol{K_P}$ means that the concentrations at equilibrium are expressed in terms of partial pressure.

Kp and Kc relationship

$$\boxed{K_P = K_c(RT)^{\Delta n}}$$

R = 0.0821 L·atm/K·mol

Δn = variation of the number of mols of product minus the number of mols of reagentes, in the gas state.

Kp and Kc relationship

$$\boxed{K_P = K_c(RT)^{\Delta n}}$$

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

For the Haber process, the Kc = 9.6 at 300 °C. What it the Kp ?

Kp and Kc relationship

$$\boxed{K_P = K_c(RT)^{\Delta n}}$$

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

For the Haber process, the Kc = 9.6 at 300 °C. What it the Kp ?

T = Kelvin !

R = constant 0.0826 L·atm/K·mol

Δn = mols products – mols reagents =

$$\boxed{= 4.34 \times 10^{-3}}$$

Kp and Kc relationship

$$\boxed{K_P = K_c (RT)^{\Delta n}}$$

For the following reaction:

$$2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g)$$

Kc is 4.08×10^{-3}

Calculate the value of Kp at 1000 K.

R = 0.0821 L·atm/K·mol

Answer: 0.335

Kp and Kc relationship

$$\boxed{K_P = K_c (RT)^{\Delta n}}$$

at home!

For the following reaction, Kp is 0.212 at 500 K

$$2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g)$$

Calculate the value of Kc ?

Answer: 361.77

Exercises with Kc

Type 1.

Find **Kc** knowing the concentrations of products/reagents at equilibrium [2,78 10^{-5}]

Example: $N_2 + 3H_2 \rightleftarrows 2NH_3$

Concentrations at **equilibrium**:

$[N_2]$ = 2,46 M
$[H_2]$ = 7,38 M
$[NH_3]$ = 0,166 M

Exercises with Kc

Type 2.

Find the concentration of a substance at the equilibrium, knowing the value of the constant.
What is the concentration of SO_3 at equilibrium? [0.084 M]

Example: $2\ SO_2 + O_2 \rightleftarrows 2SO_3$

Concentrations at **equilibrium**:

$[SO_2] = 0.165\ M$

$[O_2] = 0.755\ M$

Kc = 0.345

Exercises with Kc

Type 3.
Calculate the **Kc** by knowing the initial concentration of substances and at least the equilibrium concentration of one reagent/product

Example: $NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$

$[NH_3] = 0.0124$ M **initial!**

Think outside the box !

Exercises with Kc

Type 3.
Calculate the Kc by knowing the initial concentration of substances and at least the equilibrium concentration of one reagent/product

Example: $NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$

Can measure the pH and calculate!

$[NH_3] = 0.0124$ M initial

Exercises with Kc

Type 3.
Calculate the Kc by knowing the initial concentration of substances and at least the equilibrium concentration of one reagent/product

Example: $NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$

Can measure the pH and calculate!

$[NH_3]$ = 0.0124 M initial

[OH-] = 0.000464 M equilibrium

Exercises with Kc

Type 3.
Calculate the Kc by knowing the initial concentration of substances and at least the equilibrium concentration of one reagent/product

Example: $NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$

Can measure the pH and calculate!

$[NH_3] = 0.0124$ M initial → equilibrium ?

$[OH-] = 0.000464$ M equilibrium

$[NH_4^+] = ?$

Exercises with Kc

Type 3.

Calculate the Kc by knowing the initial concentration of substances and at least the equilibrium concentration of one reagent/product

Example: $NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$

Can measure the pH and calculate!

$[NH_3] = 0.0124$ M initial → equilibrium ?

$[OH^-] = 0.000464$ M equilibrium

$[NH_4^+] = ?$

DON`T FORGET ABOUT STOCHIOMETRY !!

Exercises with Kc

Type 3.
Calculate the Kc by knowing the initial concentration of substances and at least the equilibrium concentration of one reagent/product

Can measure the pH and calculate!

Example: $NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$

$[NH_3] = 0.0124$ M initial

$[OH^-] = 0.000464$ M equilibrium

$[NH_4^+] =$

Exercises with Kc

Type 4.
Calculate the concentration at equilibrium of all the substances by only knowing the starting concentrations of the reagents and Kc.

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$$

Initially, I have 0.4 M of NH_3 .

Kc = 1.8 10^{-5} .

Calculate the concentrations at equilibrium

→ **I.C.E Table**

[X = 0.0268 M]

ICE table

1. Amounts of substances either in molarity (Kc) of partial pressure (Kp)
2. Check if the reaction is balanced
3. Write the equilibrium constant correctly (indexes)
4. Remember that pure solid and liquids are not considered
5. Do not use a possible negative solution from the second degree equation !!!

Exercises with Kc

Type 4.

Calculate the concentration at equilibrium of all the substances by only knowing the starting concentrations of the reagents and Kc.

$$2SO_3 \rightleftarrows 2SO_2 + O_2$$

Initially, I have 0.5 M of SO_3 .

Kc = 1.5 10^{-3} .

Calculate the concentrations at equilibrium

[X = 0.0387 M]

Exercises with ICE table

Ex 1. $CO + H_2O \rightleftarrows CO_2 + H_2$

Reagents concentration = 1M.

Kc = 5.1

Calculate the concentrations at equilibrium. [X = 0.693 M]

Ex 2. $N_2O_4 \rightleftarrows 2NO_2$

Reagents concentration = 0. 0367M.

Kc = 4.63 10^{-3}

Calculate the concentrations at equilibrium. [X = 5.968 10^{-3} M]

Resume on equilibrium

Considerations

1. The majority of reactions do not reach full conversion of reagents into products

2.The sate of chemical equilibrium can be described by a specific fraction between product and reagent's concentrations.

3. The equilibrium constant ***Kc*** allows to estimate if the reaction is efficient to obtain the expected products

Can we perturbe the equilibrium ?

YES!

Chemical equilibrium is a dynamic process, which can be perturbed

How?

- **Addition of reagents/ products**
- **Removal of reagents/products**
- **Temperature variation**
- **Pressure variation (reaction with gases)**

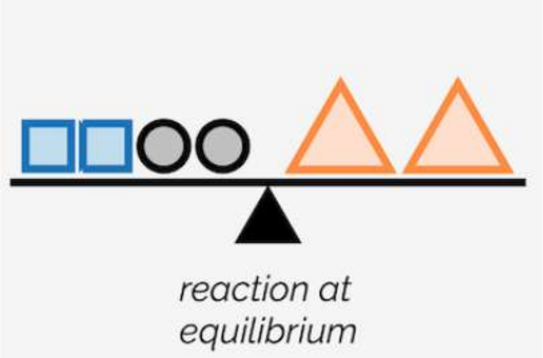
Le Chatelier's principle

A change in one of the variables that describe a system at equilibrium produces a shift in the position of the equilibrium that counteracts the effect of this change.

The system adjust to maintain the Kc value

More reagents or product can appear, but the proportion remains the same

Changing the amounts



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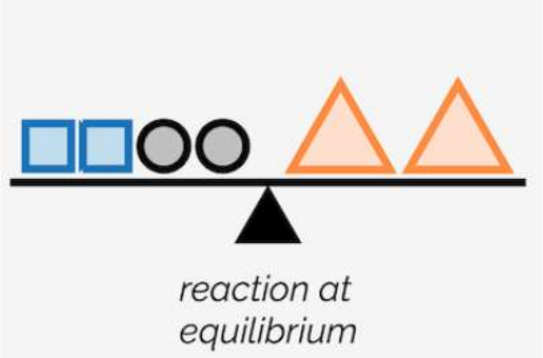

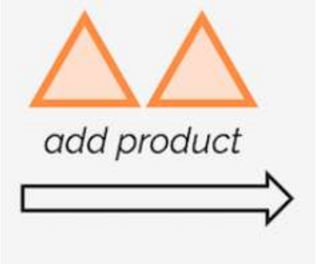

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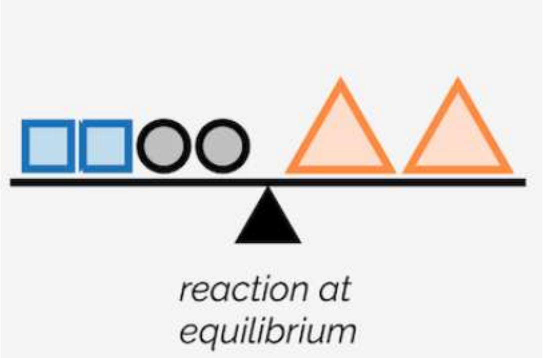
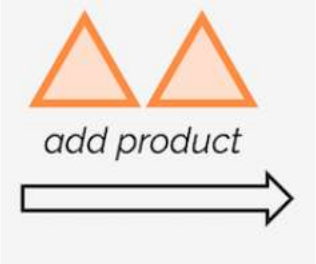
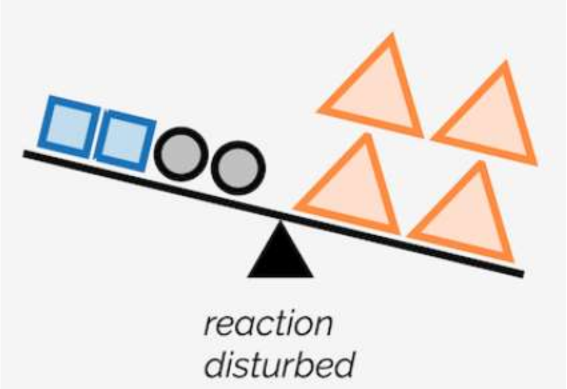
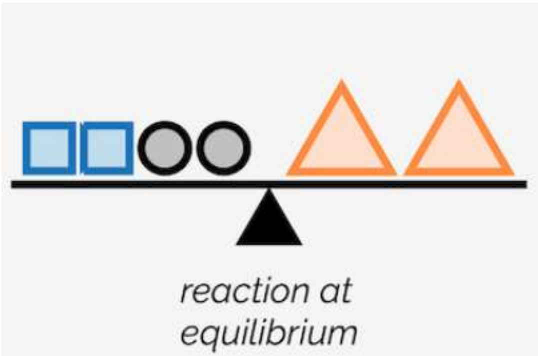


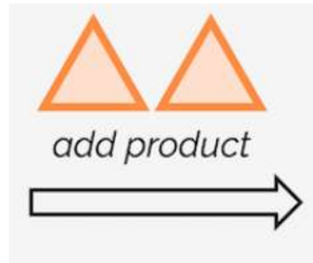


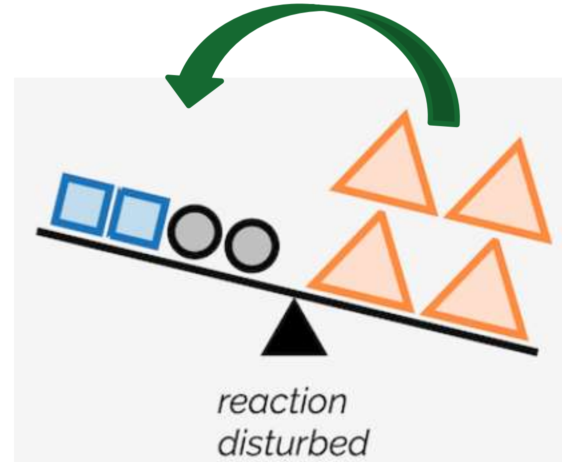


We are NOT at equilibrium anymore

Changing the amounts

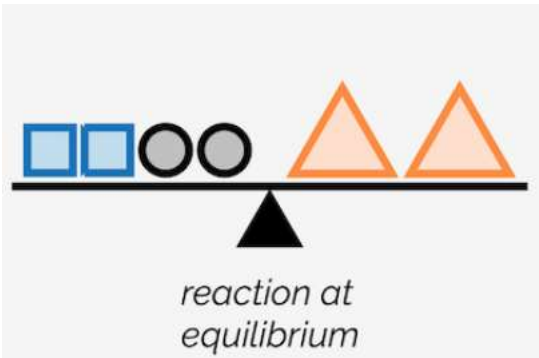


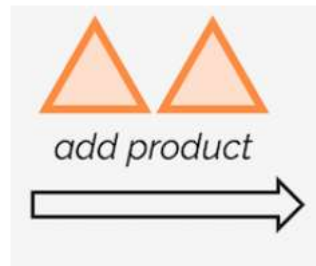


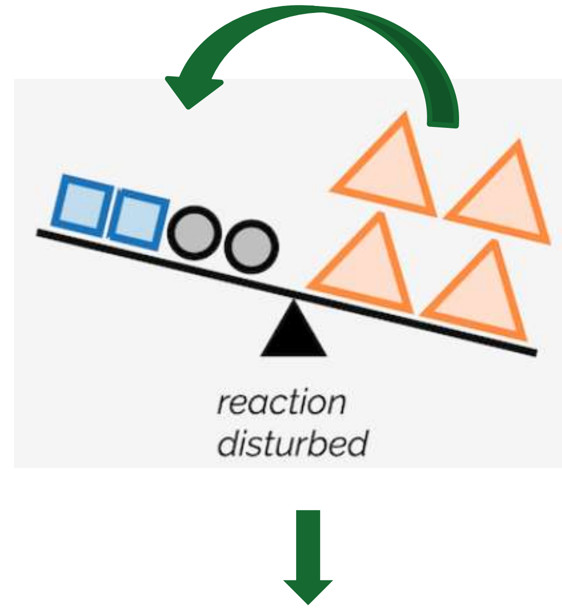


INVERSE REACTION

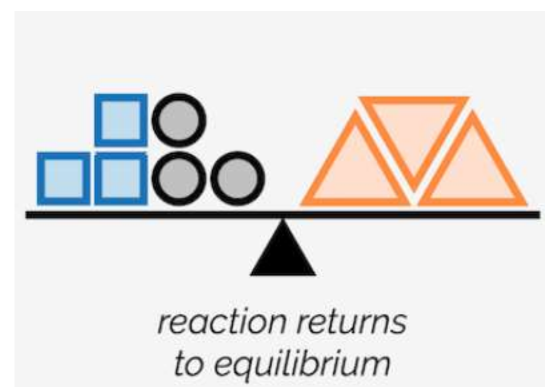
Changing the amounts







The reverse reaction will increase, so the new products are consumed and we can go back to equilibrium.



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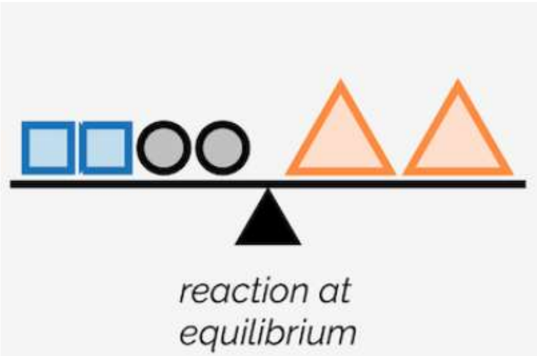
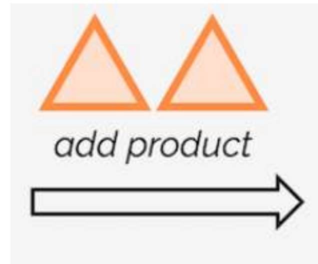
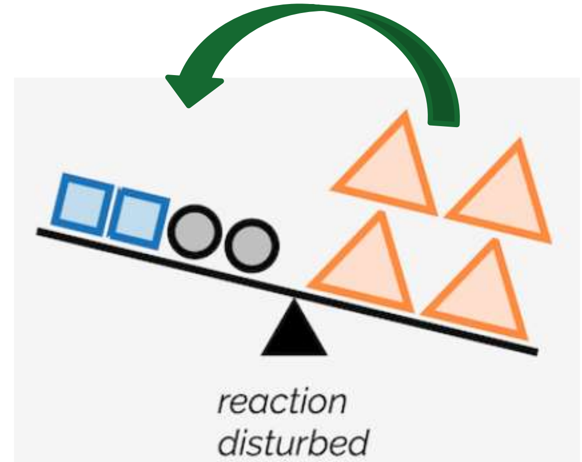
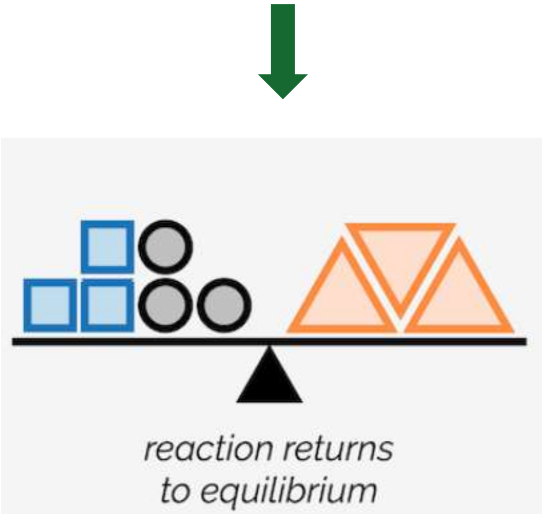




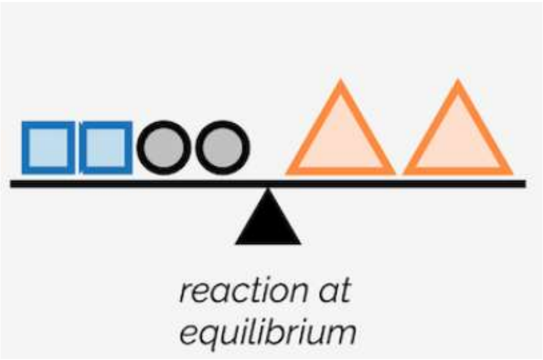




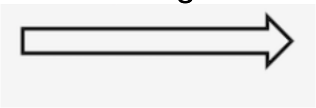
After the perturbation, the amounts of products/reagent will be different, but the proportion will be the same

Kc never changes its value !!!!!

Changing the amounts



Add reagent



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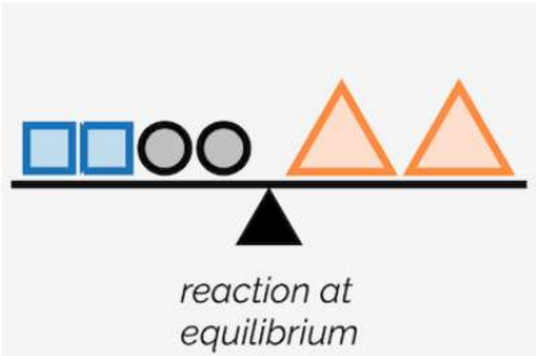

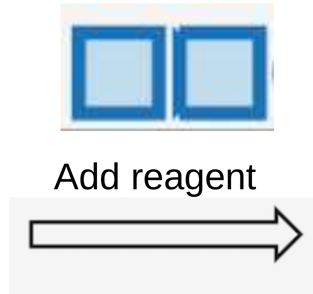

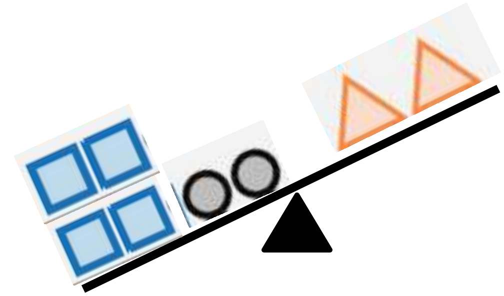

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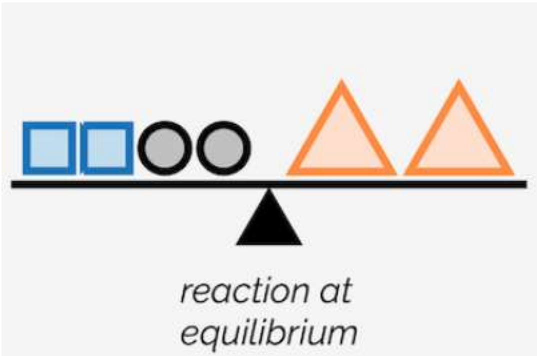

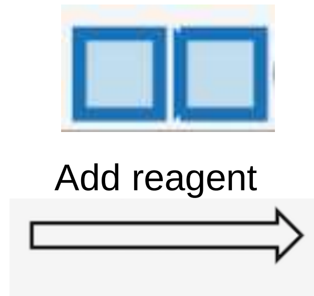

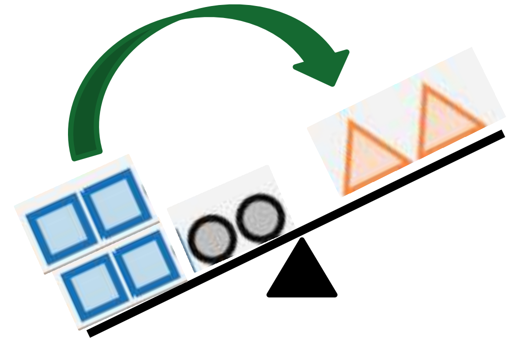

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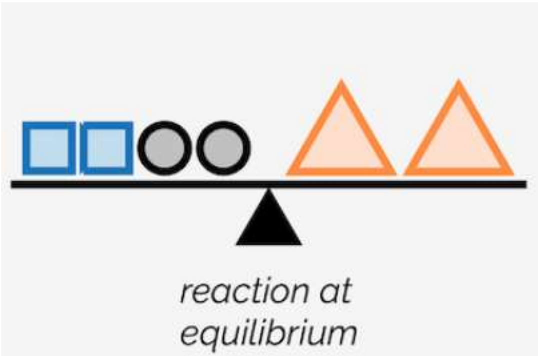
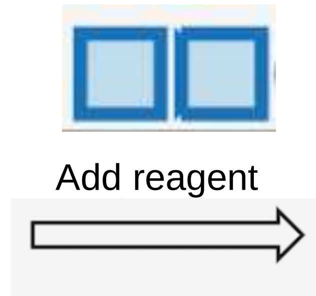
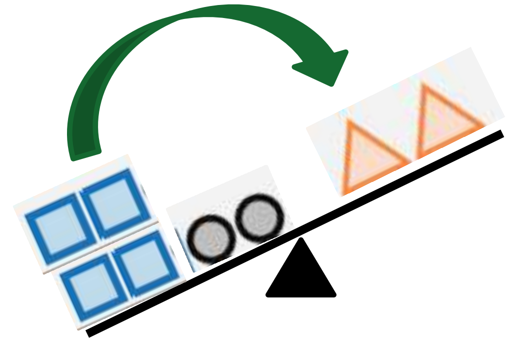
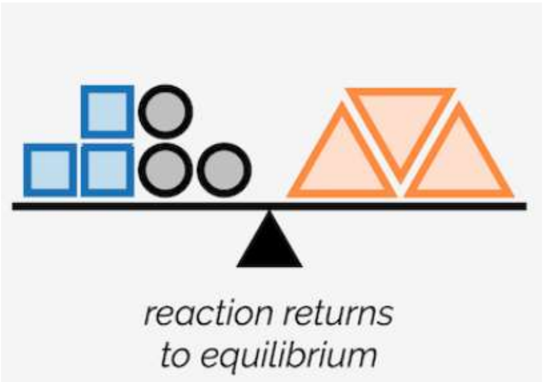


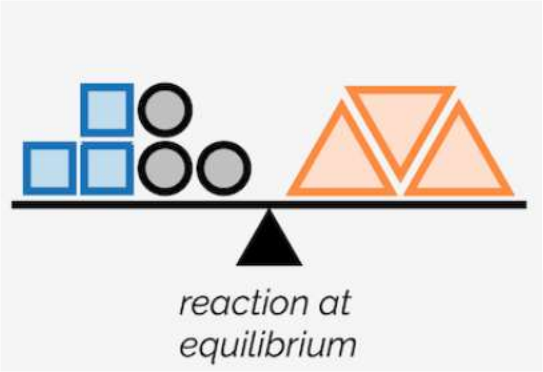




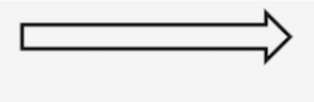


The DIRECT reaction will increase, so the new reagents are consumed and we can go back to equilibrium.

Changing the amounts



Remove reagent



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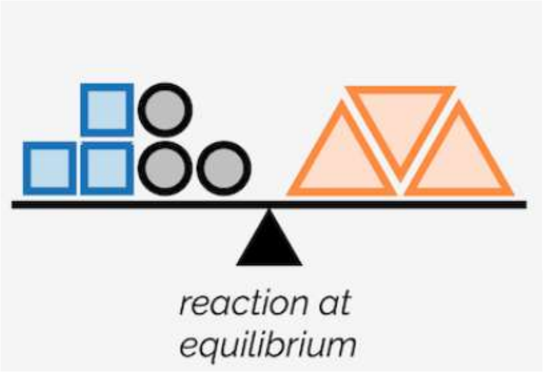

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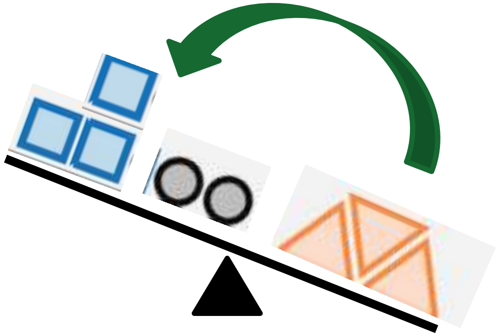

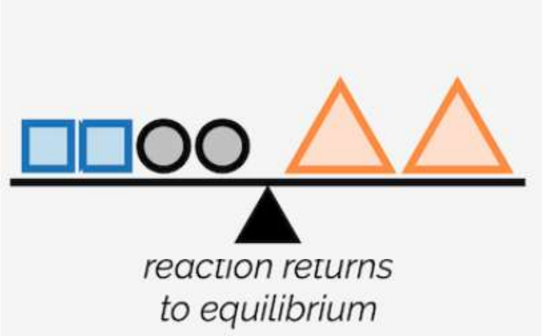

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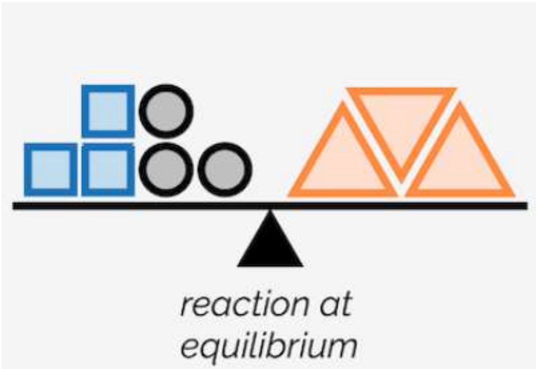

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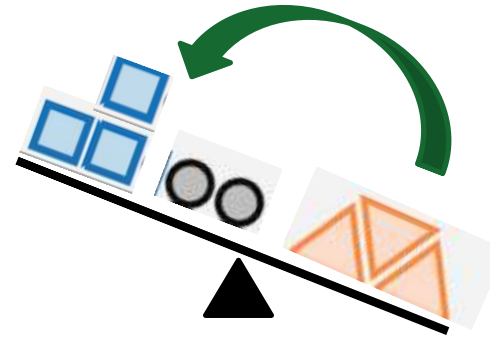

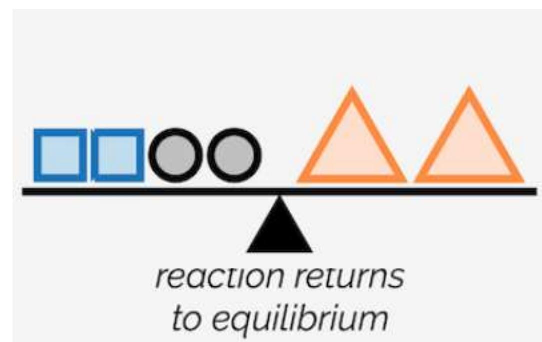

The reaction will always try to compensate the change into the opposite direction

Changing the amounts

Perturbation	**Effect**
Reagent addition	$A + B \xRightarrow[\text{direct}]{} C+D$
Reagent removal	$A + B \xLeftarrow[\text{inverse}]{} C+D$
Product Addition	$A + B \xLeftarrow[\text{inverse}]{} C+D$
Product removal	$A + B \xRightarrow[\text{direct}]{} C+D$

Changing the temperature

We need to know that exists reaction that:

- Release heat: they are called **Exothermic**
- Require heat: they are called **Endothermic**

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If I increase Heat →

If I decrease Heat →

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If I increase Heat →

If I decrease Heat →

Changing the pressure

Changing the pressure affects only reagent and products that are in a GAS state.

The total pressure within the reaction vessel depends on the **number of molecules of gas** in the container.

If the **pressure is increased**, Le Chatelier's Principle states that the reaction will counter this by shifting the equilibrium to favor the side with **fewer molecules**.

If the **pressure is decreased**, the reaction will try to favor the side with **more molecules**.

Changing the pressure

Look at the reaction below:

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

If I increase the pressure, which reaction will be favoured?

And what about this one?

$$N_2O_4\,(g) \rightleftarrows 2\,NO_2(g)$$

Manipulating Equilibrium

The Born-Haber process:

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

The pressure is kept high, so also the product will be favored

This reaction is exothermic: if we lower the temperature of the system, the product will be favored.

By lowering the temperature, NH_3 liquifies → can be removed → also favors the product.

Extreme industrial efficiency !!!