Chemical equilibrium

A dynamic equilibrium: the speed in one direction is balanced by the speed in the other.
Although no macroscopic change is visible, action is taking place.

Alcune immagini sono state prese e modificate da “Chimica” di Kotz, Treichel & Weaver, Edises 2007, III edizione

Difference between subscript in a chemical formula and a stoichiometric coefficient.

H_2O one molecule of water
2 atoms of H and 1 atom of O

$2H_2O$ two molecules of water
4 atoms of H and 2 atoms of O

H_2O_2 hydrogen peroxide
2 atoms of H and 2 atoms of O

STOICHIOMETRY OF CHEMICAL REACTIONS

Study of quantitative relationships among compounds that undergo a chemical transformation

Law of mass conservation (Lavoisier)

In a chemical reaction atoms are neither created nor destroyed.

Balancing of chemical reactions

$C + O_2 \rightarrow C\,O_2$ balanced raction

reagents products

a) $CH_4 + O_2 \rightarrow C\,O_2 + H_2O$ not balanced reaction

b) $CH_4 + O_2 \rightarrow C\,O_2 + 2H_2O$ not balanced reaction

c) $CH_4 + 2O_2 \rightarrow C\,O_2 + 2\,H_2O$ balanced reaction

Combustion of octane produces carbon dioxide and water

$C_8H_{18} + O_2 \rightarrow CO_2 + H_2O$ not balanced raction

$C_8H_{18} + O_2 \rightarrow 8CO_2 + 9H_2O$ balanced for C and H
O atoms are not balanced

$C_8H_{18} + 12.5O_2 \rightarrow 8CO_2 + 9\ H_2O$ all atoms are balanced, but coefficients are not integers

$$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$$

NB: atom numbers are balanced, mass is conserved.

Chemical equations can indicate the physical state of reagents and products.

Gas	(*g*)
Liquid	(*l*)
Solid	(*s*)
aqueous solution	(*aq*)

$$2C_8H_{18}\,(l) + 25O_2\,(g) \rightarrow 16CO_2\,(g) + 18H_2O\,(l)$$

$$Na(s) + H_2O(l) \rightarrow NaOH(aq) + H_2(g)$$

$$Na(s) + 2H_2O(l) \rightarrow NaOH(aq) + H_2(g)$$

$$Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$

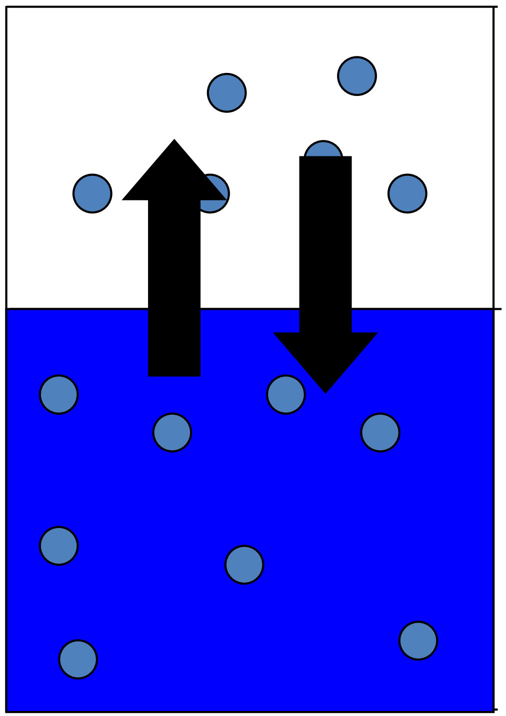
$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$

Difference between EQUILIBRIUM and STEADY STATE

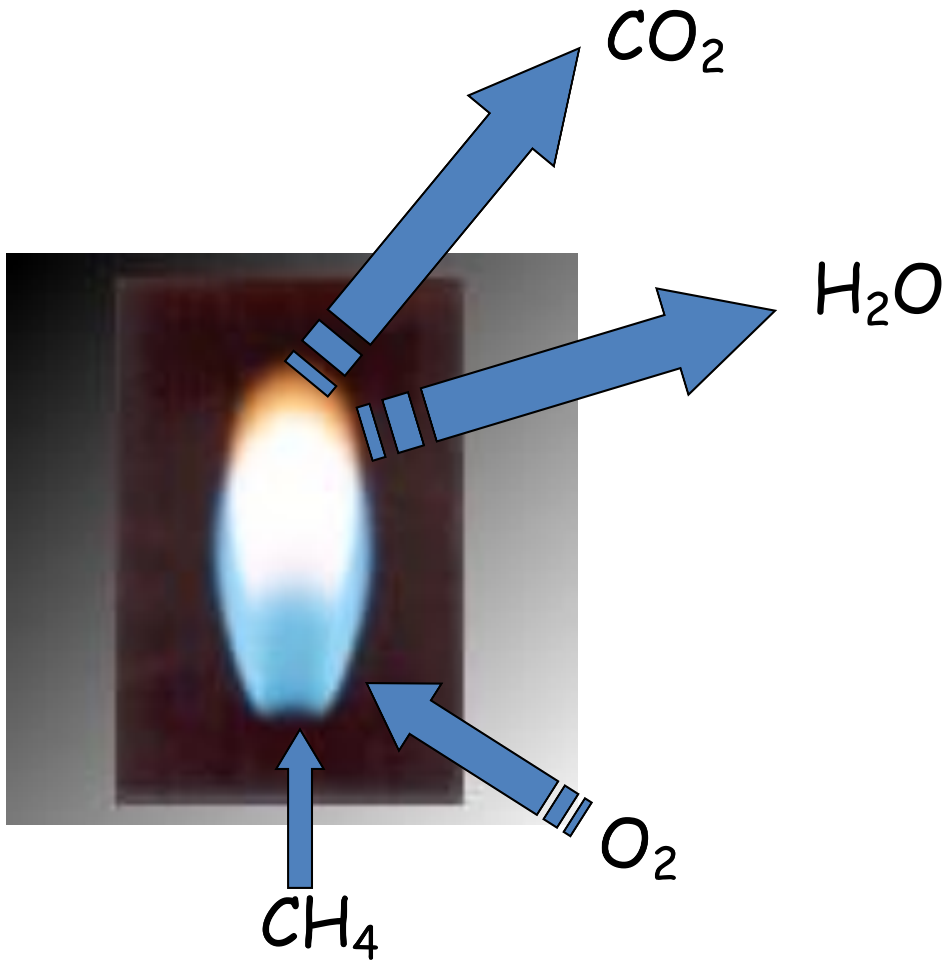
Gas burner

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

VAPOUR PRESSURE



Isolated system

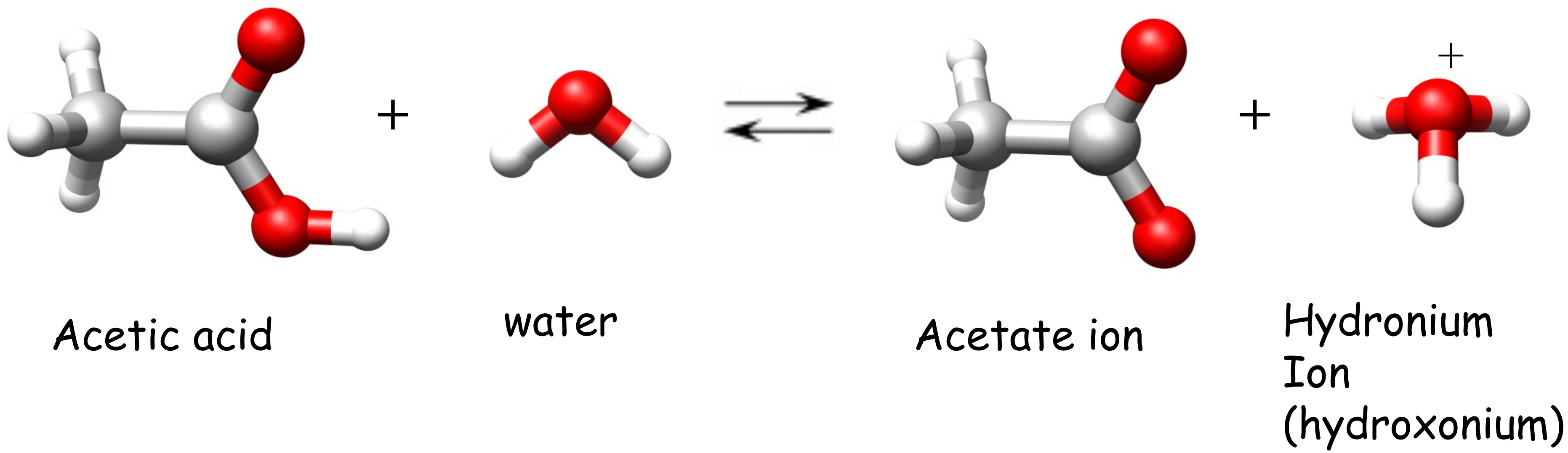


Open system

CHEMICAL EQUILIBRIUM

Chemical equilibrium is the dynamic state of a system, characterized by the formation of products and reagents at the same velocity.

$$CH_3COOH + H_2O \rightleftarrows CH_3COO^- + H_3O^+$$



REVERSIBILITY

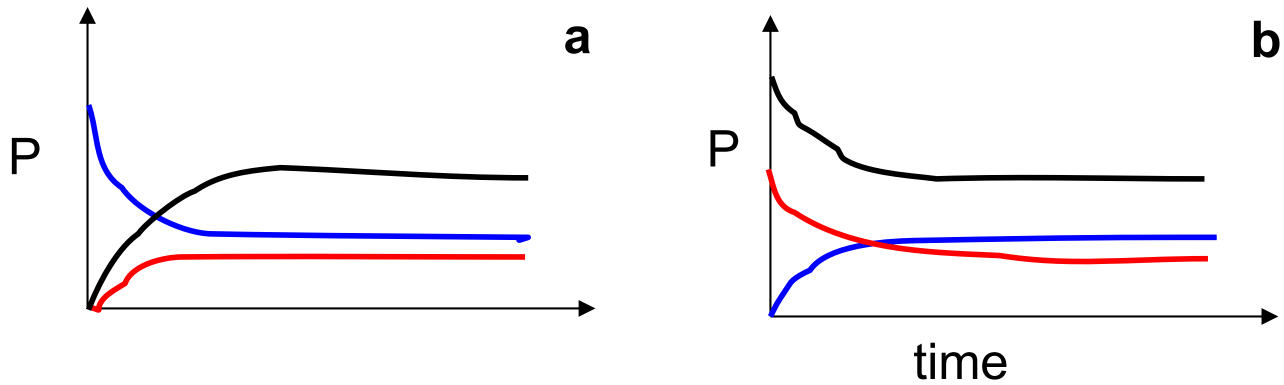
Chemical reactions are reversible processes. There are conditions of concentration, temperature and pressure in which reactants and products coexist at equilibrium.

a) $2NH_3 \rightarrow N_2 + 3H_2$

b) $N_2 + 3H_2 \rightarrow 2NH_3$

$2NH_3 \rightleftarrows N_2 + 3H_2$

2 : 1 : 3



✓Dynamic equilibrium ($\rightarrow$ = $\leftarrow$)
✓Same equlibrium, starting from reactants or products
✓It corresponds to an energy minimum

The equilibrium constant

At equilibrium there is a correlation between the concentrations of reactants and products.

In the reaction between iodine and hydrogen:

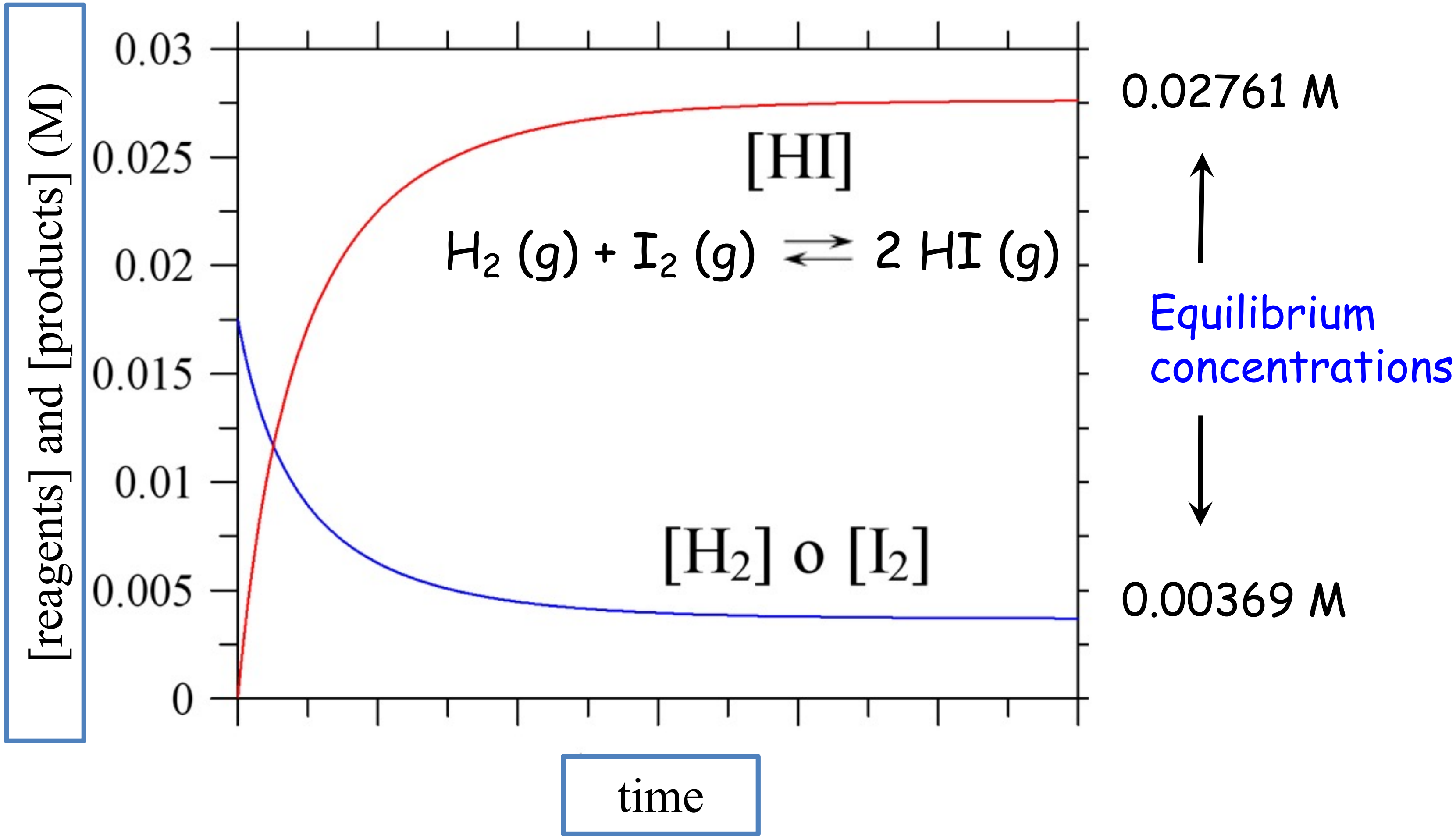
$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)$$

Experiments have shown that the ratio between the concentration of HI and the product of H_2 ed I_2, is constant if temperature is constant.

$$\frac{[HI]^2}{[H_2]\cdot[I_2]} = \text{costant (K) at equilibrium}$$

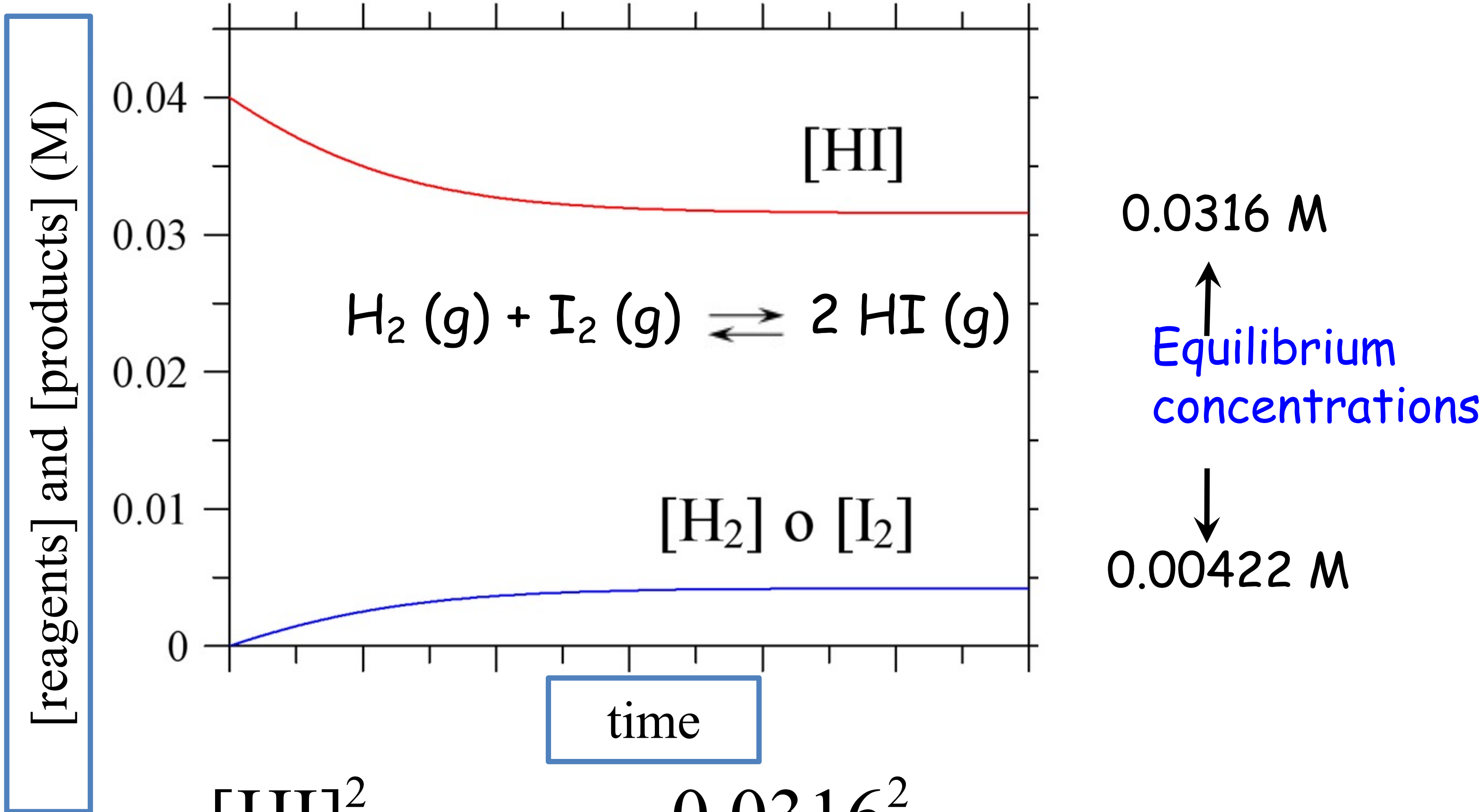
NB: molar concentrations are indicated by [ ], therefore:
[HI] = molar concentration of hdrogen iodide
$[H_2]$ = molar concentration of molecular hydrogen, etc.

If the concentrations of H_2 and I_2 in a container are initially 0.0175 mol/L at 425 ° C and HI is absent.



$$\frac{[HI]^2}{[H_2]\cdot[I_2]} = \frac{0.02761^2}{0.00369 \cdot 0.00369} = 56$$

If H_2 ed I_2 are not present and [HI] is 0.04 mol/L a 425 ° C.



$$\frac{[HI]^2}{[H_2]\cdot[I_2]} = \frac{0.0316^2}{0.00422 \cdot 0.00422} = 56$$

The initial amounts of reagents and products is irrelevant, at equilibrium their ratio will be the same.

EQUILIBRIUM CONSTANT AND THE LAW OF MASS ACTION

Since at equilibrium the concentrations of the components are constant, their ratio will be a constant, this is the law of mass action.

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

Law of mass action

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

The constant is called the equilibrium constant K_c. It is a thermodynamic constant that depends only on concentrations and on temperature, the "c" indicates that it is expressed in concentrations.

$$aA + bB \rightleftarrows cC + dD \Rightarrow \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} = K_c$$

Law of mass action

K_c will be expressed in units that depend on the algebraic sum of the exponents or that can be dimensionless if (a + b) = (c + d).

(The latter condition means that there is no change in the number of moles during the reaction)

Equilibium constant

For a generic chemical raction at a certain temperature

$$a\,A + b\,B \rightleftarrows c\,C + d\,D$$

We can define an equilibrium constant

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

In the equilibrium constant:

- All concentrations are the ones at equilibrium.
- Concentrations of the products appear in the numerator of K and those of reactants in the denominator.
- Each concentration is raised to a power equal to the stoichiometric coefficient of the corresponding species in the balanced reaction.
- Only species in the same physical phase appear in the expression of K.
- The dimension of K depends on the reaction

$$2NH_3 \rightleftharpoons N_2 + 3H_2$$

$$K_c = [N_2][H_2]^3 / [NH_3]^2$$

The magnitude of K_c indicates whether the reaction is shifted toward the formation of products or reagents.

Knowing K_c one can determine the relative amounts of reactants and products present at equilibrium.

The K_c, while representing the same reaction, can have different values depending on how the reaction is written.
It is therefore very important to know "how" the reaction is written.

$H_2 + I_2 \rightarrow 2HI$ $\quad$ $K_c = [HI]^2 / [H_2]\ [I_2]$

$2HI \rightarrow H_2 + I_2$ $\quad$ $K'_c = [H_2]\ [I_2] / [HI]^2$

The equilibrium constant of a reaction written in one direction and that of the same reaction written in the opposite direction have reciprocal values.

$$\boxed{K_c = 1/\ K'_c}$$

HETEROGENEOUS EQUILIBRIUM

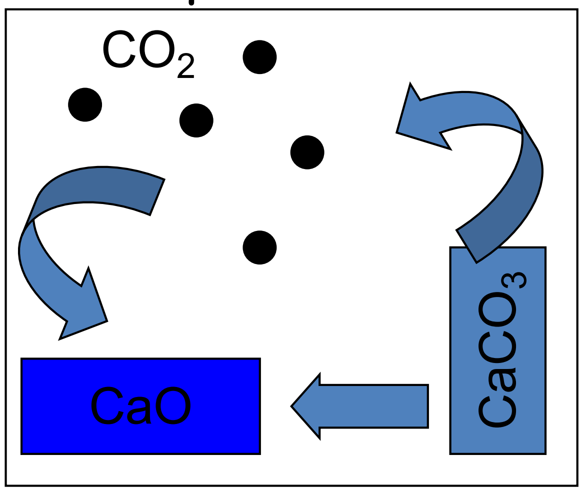
In equilibria in homogeneous systems all the components must be taken into account, while in heterogeneous systems we consider that the components in the condensed phase (solid or liquid) have a constant "concentration" (not "null" or equal to 1!), therefore their concentration can be incorporated into the equlibrium K.

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

Constant K_p is $K_p = P_{CO2}$

Constant K_c is $K_c = [CO_2]$

Equilibrium



T = 800 ° C, P = 190 mmHg

Reactions involving solids (heterogeneous)

$$S\ (s) + O_2\ (g) \rightleftarrows SO_2\ (g) \qquad K = \frac{[SO_2]}{[O_2]}$$

→

The concentration of a solid is determined by its density, and density is constant.

In general, the concentration of a solid (reactant or product) in a reaction does not appear in the expression of the equilibrium constant.

Reactions in aqueous solution

$$NH_3\ (aq) + H_2O\ (l) \rightleftarrows NH_4^+\ (aq) + OH^-\ (aq) \qquad K = \frac{[NH_4^+]\cdot[OH^-]}{[NH_3]}$$

The concentration of water (~ 55.5) is practically constant, especially if the solution is diluted.

Reactions in gaseous phase.

The concentrations appearing in the expression of the equilibrium constant are usually given in mol/L (M), and the equilibrium constant is indicated by K_C. However, the equilibrium constants for reactions that occur in the gas phase can be expressed in terms of partial pressures of reactants and products and the constant is then indicated as K_P:

$$H_2\,(g) + I_2\,(g) \rightleftarrows 2\,HI\,(g) \qquad K_C = \frac{[HI]^2}{[H_2]\cdot[I_2]}$$

From the gas state law (PV = nRT) we determine [c] = n/V = P /RT

$$K_C = \frac{[HI]^2}{[H_2]\cdot[I_2]} = \frac{\left(\frac{P_{HI}}{RT}\right)^2}{\frac{P_{H_2}}{RT}\cdot\frac{P_{I_2}}{RT}} = \frac{P_{HI}^2}{P_{H_2}\cdot P_{I_2}} = K_P$$

$K_P = K_C$ only if the constant is dimensionless.
In the reaction of synthesis of ammonia:

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

$$K_C = \frac{[NH_3]^2}{[N_2]\cdot[H_2]^3} = \frac{\left(\frac{P_{NH_3}}{RT}\right)^2}{\frac{P_{N_2}}{RT}\cdot\left(\frac{P_{H_2}}{RT}\right)^3} = \frac{P^2_{NH_3}}{P_{N_2}\cdot P^3_{H_2}}\cdot\frac{1}{(RT)^2} \longrightarrow K_P = K_C\,(RT)^2$$

In the general case: $a\,A + b\,B = c\,C + d\,D$

$$K_C = \frac{[C]^c\cdot[D]^d}{[A]^a\cdot[B]^b} = \frac{P^c_C\cdot P^d_D}{P^a_A\cdot P^b_B}\cdot(RT)^{\boxed{c+b-a-b}} = K_P\cdot(RT)^{\boxed{c+b-a-b}}$$

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

where $\Delta n = c + d - a - b$

Example 1: Write the expression for the equilibrium constant for each of the following reactions indicating their units:

a) $PCl_5\ (g) \rightleftarrows PCl_3\ (g) + Cl_2\ (g)$

$$K_C = \frac{[PCl_3]\cdot[Cl_2]}{[PCl_5]} \quad \{M\}$$

b) $2\ H_2\ (g) + O_2\ (g) \rightleftarrows 2\ H_2O\ (g)$

$$K_C = \frac{[H_2O]^2}{[H_2]^2\cdot[O_2]} \quad \{M^{-1}\}$$

c) $CO_2\ (g) + C\ (s) \rightleftarrows 2\ CO\ (g)$

$$K_C = \frac{[CO]^2}{[CO_2]} \quad \{M\}$$

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

$$K_C = \frac{[CH_3COO^-]\cdot[H_3O^+]}{[CH_3COOH]} \quad \{M\}$$

Example 2: Write the expression for the equilibrium constant KC for each of the following reactions. What is the relationship is between K_P and K_C?

a) $3\ O_2\ (g) \rightleftarrows 2\ O_3\ (g)$ $\quad K_C = \dfrac{[O_3]^2}{[O_2]^3}$ $\quad$ ozone O_3

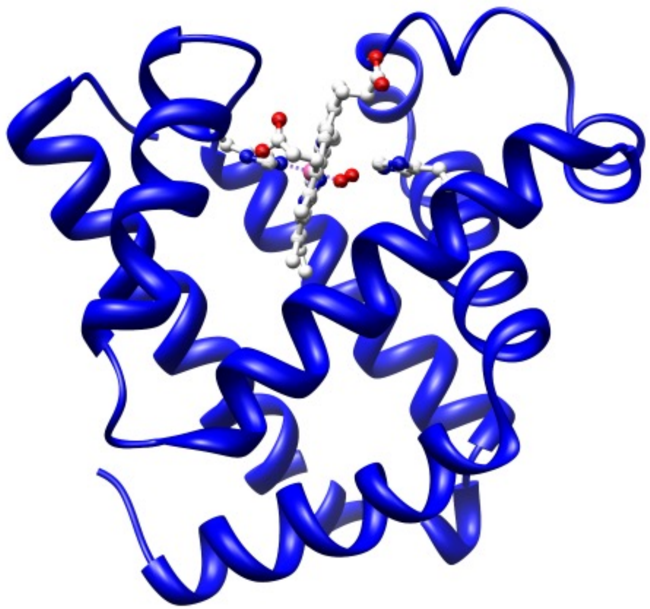
since $\quad K_P = K_C \cdot (RT)^{\Delta n}$ è $\Delta n = 2-3 = -1$ $\quad K_P = \dfrac{K_C}{RT}$

b) $2\ SO_3\ (g) = 2\ SO_2 + O_2\ (g)$ $\quad K_C = \dfrac{[SO_2]^2 \cdot [O_2]}{[SO_3]^2}$

since $\quad K_P = K_C \cdot (RT)^{\Delta n}$ è $\Delta n = 3-2 = 1$ $\quad K_P = K_C RT$

Example 3: Myoglobin is a protein that binds O_2 according to the reaction:

$$Mb\,(aq) + O_2\,(aq) \rightleftarrows MbO_2\,(aq)$$



At equilibrium: [Mb] = 3.2 mM, [O_2] = 1.4 mM e [MbO_2] = 0.896 mM. Calculate K_C.

$$K_C = \frac{[MbO_2]}{[Mb]\cdot[O_2]} = \frac{0.896}{3.2\cdot 1.4} = \boxed{0.2\ mM^{-1}}$$

Esemple 4: The reaction PCl_5 (*g*) $\rightleftarrows$ PCl_3 (*g*) + Cl_2 (*g*) has been studied at 250 ° C. At equilibrium: $[PCl_5] = 4.2\times10^{-5}$ M, $[PCl_3] = 1.3\times10^{-2}$ M e $[Cl_2] = 3.9\times10^{-3}$ M. Calculate K_C and K_P for the reaction.

$$K_C = \frac{[PCl_3]\cdot[Cl_2]}{[PCl_5]} = \frac{1.3\cdot10^{-2}\cdot3.9\cdot10^{-3}}{4.2\cdot10^{-5}} = 1.21 \text{ M}$$

Since $K_P = K_C\cdot(RT)^{\Delta n}$ and Δn = 2-1 = 1

$$K_P = K_C RT = 1.21\cdot0.082\cdot(273.15+250) = 51.8 \text{ atm}$$

The equilibrium constant of a chemical reaction is a very useful parameter:

* if the ratio of the concentrations of reactants and products corresponds to the value of the equilibrium constant, the system is at equilibrium. If it has a different value, the system is not at equilibrium and it is possible to predict in which direction the reaction will proceed.

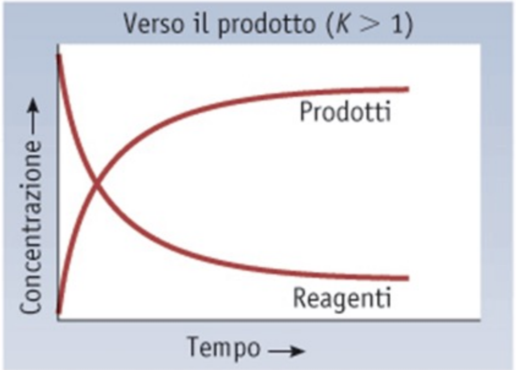
* The value of an equilibrium constant indicates whether a reaction is shifted towards the reactants or products.

* If the equilibrium concentrations of species involved in the reaction are known, the equilibrium concentration of other species can be calculated from the expression of K.

* If the initial concentrations of some species are known, the equilibrium concentration of products and reactants can be calculated from the expression of K.

K >> 1: the reaction is shifted toward the products. Equilibrium concentrations of the products are larger than concentrations of the reactants.

$$NO\ (g) + O_3\ (g) \rightleftarrows NO_2\ (g) + O_2\ (g)$$

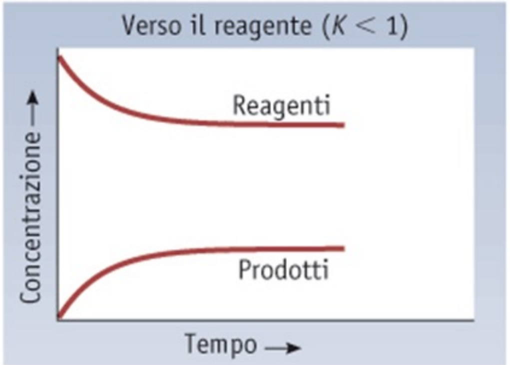


$$K_C = \frac{[NO_2]\cdot[O_2]}{[NO]\cdot[O_3]} = 6\cdot10^{34}\ \text{a}\ 25\,°C$$

The large value of K indicates that $[NO_2]\,[O_3] \gg [NO][O_2]$

K << 1: the reaction is shifted toward the reagents. Equilibrium concentrations of reactants are larger than concentrations of the products.

$$3\ O_2\ (g) \rightleftarrows 2\ O_3\ (g)$$



$$K_C = \frac{[O_3]^2}{[O_2]^3} = 6.2\cdot10^{-58}\ \text{a}\ 25\,°C$$

The small value of K indicates that $[O_3]^2 \ll [O_2]^3$

Equilibrium constants for some reactions

reaction	K_C a 25 ° C	Reaction is shifted toward
Reaction of combination with non metals		
$S\ (s) + O_2\ (g) = SO_2\ (g)$	$4.2 \cdot 10^{52}\ M^{-1}$	K > 1, products
$2\ H_2\ (g) + O_2\ (g) = 2\ H_2O\ (g)$	$3.1 \cdot 10^{81}\ M^{-1}$	K > 1, products
$N_2\ (g) + 3\ H_2\ (g) = 2\ NH_3\ (g)$	$3.5 \cdot 10^{8}\ M^{-2}$	K > 1, products
$N_2\ (g) + O_2\ (g) = 2\ NO\ (g)$	$4.2 \cdot 10^{-3}$ *	K < 1, reagents
Ionization reactions of acids and bases		
$HCO_2H\ (aq) + H_2O\ (l) = HCO_2^-\ (aq) + H_3O^+\ (aq)$	$1.8 \cdot 10^{-4}\ M$	K < 1, reagents
$CH_3CO_2H\ (aq) + H_2O\ (l) = CH_3CO_2^-\ (aq) + H_3O^+\ (aq)$	$1.8 \cdot 10^{-5}\ M$	K < 1, reagents
$H_2CO_3\ (aq) + H_2O\ (l) = HCO_3^-\ (aq) + H_3O^+\ (aq)$	$4.2 \cdot 10^{-7}\ M$	K < 1, reagents
$NH_3\ (aq) + H_2O\ (l) = NH_4^+\ (aq) + OH^-\ (aq)$	$1.8 \cdot 10^{-5}\ M$	K < 1, reagents

* at 2300 K

The reation quotient Q

The equilibrium constant K has a numerical value defined when reactants and products are at equilibrium. When reactants and products are not at equilibrium it is useful to calculate the reaction quotient Q:

$$a\,A + b\,B \rightleftarrows c\,C + d\,D$$

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

The concentrations of reagents in the expression of Q are those present in the system at any time since the beginning of the reaction until equilibrium is reached, when Q = K. The knowledge of Q is useful for 2 reasons:

1) allows to determine if the system is a t equilibrium ($Q = K$) or not ($Q \neq K$)

2) confronting Q with K we know in which direction the reaction will proceed.

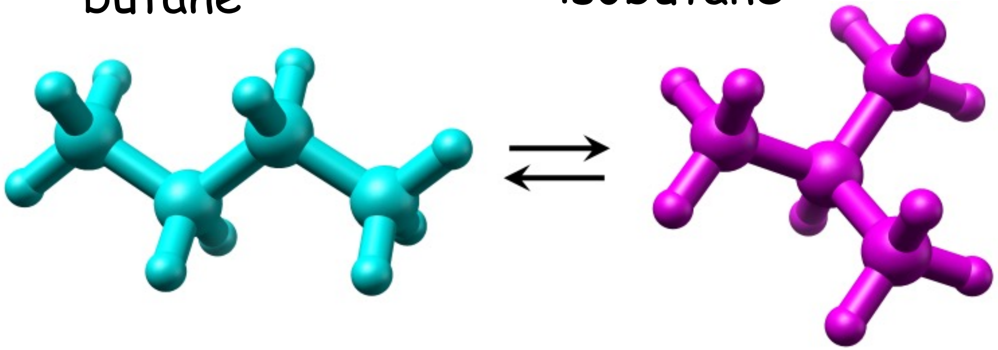
If $Q < K$, equilibrium will be reached by transforming reagents into products

If $Q > K$, equilibrium will be reached by transforming products into reagents

In the isomerization of butane (C_4H_{10}) to isobutane(C_4H_{10}) a 298 K:

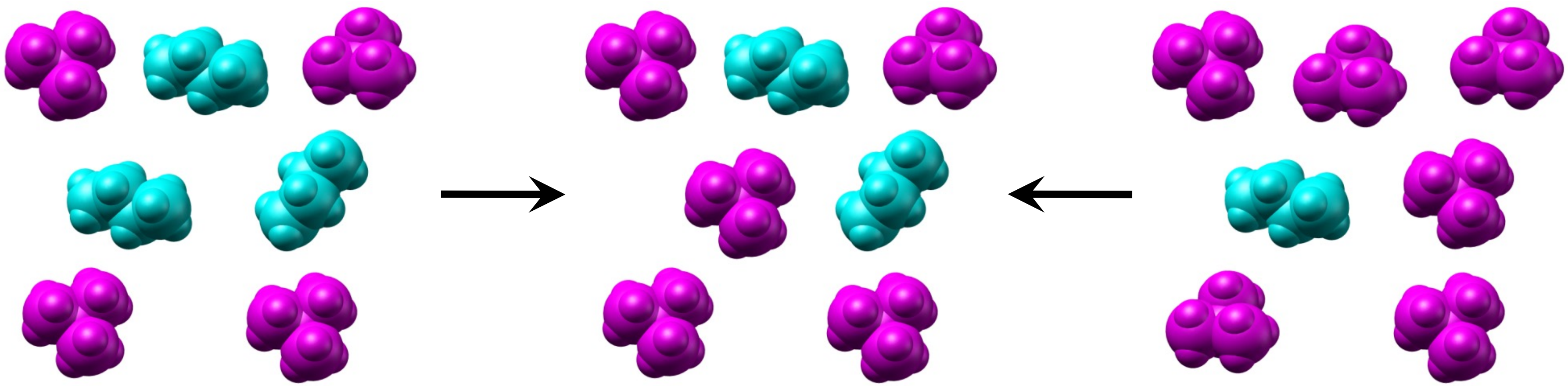
$$\text{butano }(g) \rightleftharpoons \text{isobutano }(g)$$

butane isobutane



$$K = \frac{[\text{isobutane}]}{[\text{butane}]} = 2.5$$

$$Q = \frac{4}{3} = 1.3 < K \qquad Q = \frac{5}{2} = 2.5 = K \qquad Q = \frac{6}{1} = 6 > K$$



Not at equilibrium At equilbrium Not at equilibrium

Example 5: At 2000 K, the equilibrium constant for the reaction

$$N_2\,(g) + O_2\,(g) \rightleftarrows 2\,NO\,(g)$$

$K = 4.0 \times 10^{-4}$. If $[N_2] = 0.5$ M, $[O_2] = 0.25$ M e $[NO] = 0.042$ M, determine if the reaction is at equilibrium, if it is not the case determine in which direction it will proceed.

$$Q = \frac{[NO]^2}{[N_2][O_2]} = \frac{0.042^2}{0.5 \cdot 0.25} = 1.41 \cdot 10^{-3} > K$$

The reaction is not at equilibrium Q > K.

Equilibrium can be reached transforming NO into N_2 and O_2.

$$N_2\,(g) + O_2\,(g) \rightleftarrows 2\,NO\,(g)$$

Example 6: At 298 K, the equilibrium constant for the reaction

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

is K = 170. If $[NO_2] = 0.015$ M e $[N_2O_4] = 0.025$ M, is the reaction at equilibrium? If it is not so, in which direction will it proceed?

$$Q = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0.025}{0.015^2} = 111.1 < K$$

The reaction is not at equilibrium sinc Q < K.

Equlibrium can be achieved by production of N_2O_4.

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

How to calculate the equilibrium constant

If the concentrations at equilibrium of some of the compounds involved in the reaction are known, the equilibrium concentration of other species can be calculated from the balanced chemical equation.

E.g. T=1000 K $2\ SO_2\ (g) + O_2\ (g) \rightleftharpoons 2\ SO_3\ (g)$

Before equilibrium we have 1 mol/L of SO_2 and 1 mol/L of O_2. At equilibrium we have 0.925 mol/L of SO_3 .
Calculate the equilibrium concentration of all compounds and K_C.

equation	$2\ SO_2\ (g)$ +	$O_2\ (g)$ =	$2\ SO_3\ (g)$
Initial concentrations (M)	1.0	1.0	0
variation (M)	–0.925	–0.925 / 2	+0.925
Concentrations at equilibrium (M)	0.075	0.5375	0.925

$$K_C = \frac{[SO_3]^2}{[SO_2]^2 \cdot [O_2]} = \frac{0.925^2}{0.075^2 \cdot 0.5375} = 283\ M^{-1}$$

Equilibrium constant:

In many cases K and the initial concentrations of reagents are known and we need to calculate the concentrations of species at equilibrium.

E.g. In the reaction:

$$H_2\,(g) + I_2\,(g) \rightleftarrows 2\,HI\,(g)$$

At 425 ° C, K = 55.64.

If we mix in a 0.5 L container 1.0 mole of H_2 and 1.0 mole of I_2 at 425 ° C, what are the equilibrium concentrations of H_2, I_2 e HI?

$$K_C = \frac{[HI]^2}{[H_2]\cdot[I_2]} = 56.64$$

H_2 (g) +	I_2 (g)	= 2 HI (g)
1.0 / 0.5 = 2	1.0 / 0.5 = 2	0
?	?	?
?	?	?

If x moles of H_2 and I_2 react, we will have 2 x moles of HI:

equation	H_2 (g) +	I_2 (g)	= 2 HI (g)
Initial concentrations (M)	1.0 / 0.5 = 2	1.0 / 0.5 = 2	0
variation (M)	−x	−x	+2x
Concentrations at equilibrium (M)	2−x	2−x	2x

$$K = \frac{[HI]^2}{[H_2]\cdot[I_2]} = \frac{(2x)^2}{(2-x)\cdot(2-x)} \rightarrow (K-4)x^2 - 4Kx + 4K = 0$$

$$x = \frac{2K - 4\sqrt{K}}{K-4} = \frac{2\cdot 55.64 - 4\sqrt{55.64}}{55.64-4} = 1.577\ M$$

Concentrations at equilibrium are: $[H_2] = [I_2] = 2-1.577 = 0.423$ M e $[HI] = 3.154$ M.

Perturbations of a chemical equilibrium: Le Chatelier's principle

H. L. Le Chatelier
1850-1936)

The equilibrium between reagents and products can be perturbed in three ways:

- Changing temperature
- Changing the concentration of a reactant or product
- Changing volume (for reactions in the gaseous phase)

Le Chatelier' principle: *If a chemical system at equilibrium experiences a change in concentration, temperature, volume, or partial pressure, then the equilibrium shifts to counteract the imposed change and a new equilibrium is established.*

Initial equilibrium | perturbation ($Q \neq K$) | Final equilibrium

Exothermic and endothermic reactions the solubilization of strong electrolytes in H_2O

An exothermic reaction

$NaOH\ (s) \longrightarrow Na^{+}\ (aq) + OH^{-}\ (aq) + \text{heat}$

$\Delta H_{sol} = H_{products} - H_{reagents} < 0 = -44.4\ kJ/mol$

An endothermic reaction

$NH_4NO_3\ (s) + \text{heat} \longrightarrow NH_4^{+}\ (aq) + NO_3^{-}\ (aq)$

$\Delta H_{sol} = H_{products} - H_{reagents} > 0 = +25.7\ kJ/mol$

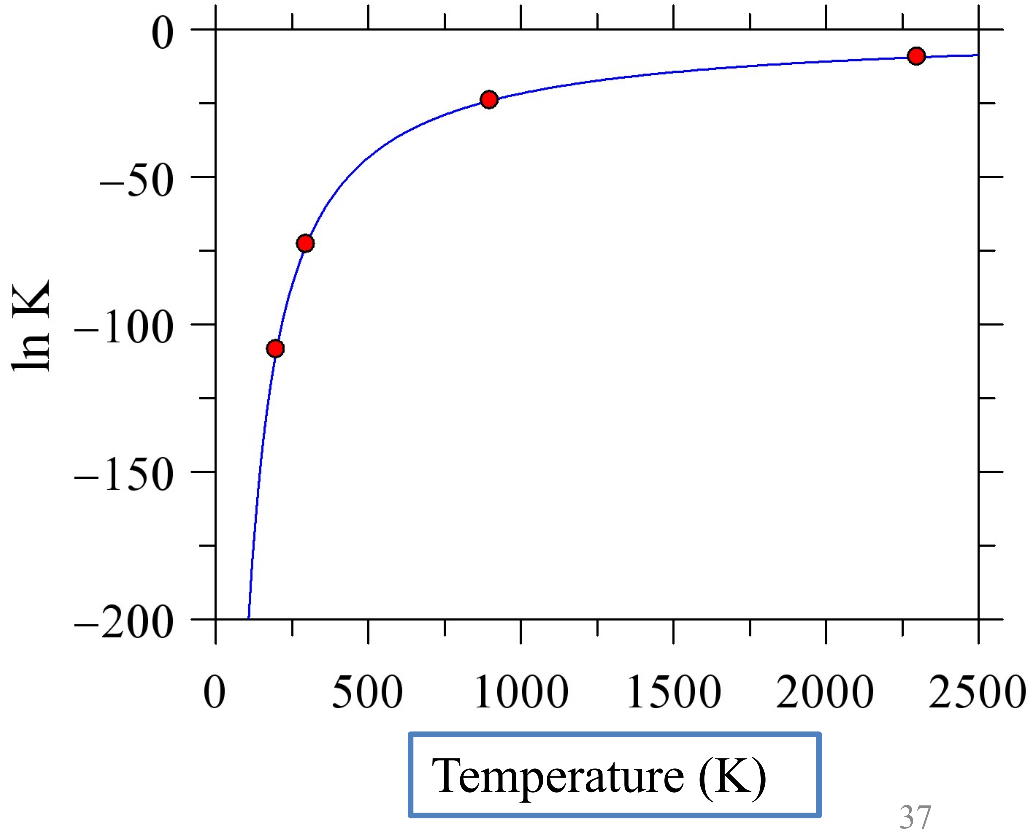
Effect of temperature on equlibrium

It is possible to make a qualitative prediction of the effect of a change in temperature depending on whether the reaction is exothermic or endothermic. The numerical value of the equilibrium constant changes.

$$N_2\,(g) + O_2\,(g) + \text{heat} \rightleftarrows NO\,(g) \qquad \Delta H_{reaction} = +180.6\ \text{kJ/mol} \qquad K = \frac{[NO]^2}{[N_2]\cdot[O_2]}$$

The reaction is endothermic: it is necessary to provide heat.

T (K)	K	ln(K)
200	6.77×10^{-48}	–108.61
298	2.20×10^{-32}	–72.89
900	3.30×10^{-11}	–24.13
2300	7.91×10^{-5}	–9.44



van't Hoff equation

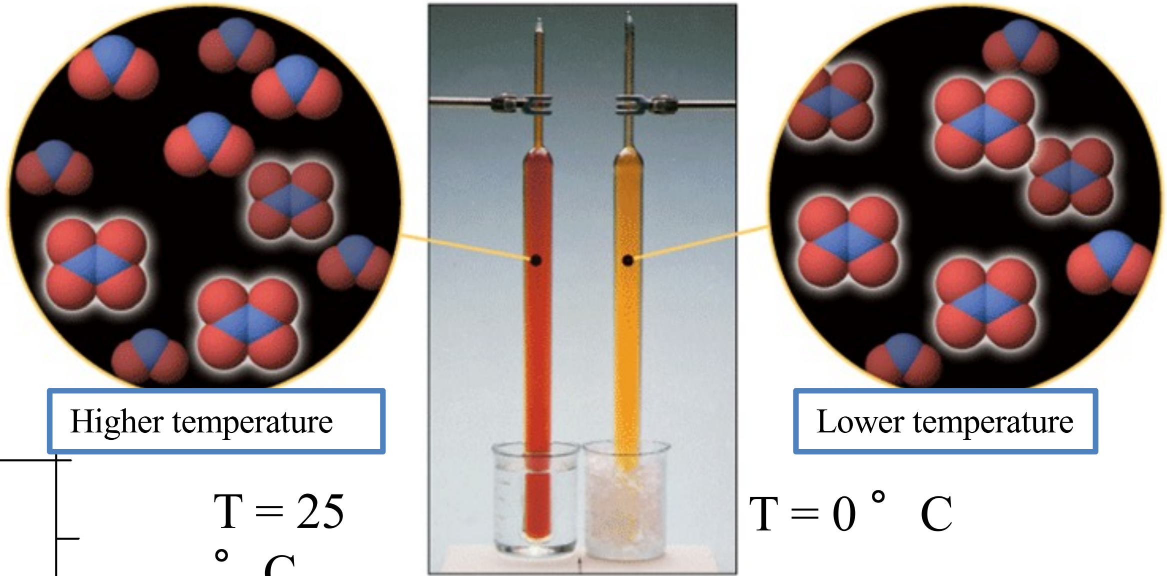
$$\ln K = -\frac{\Delta H_{reaction}}{RT}$$

$$2\,NO_2\,(g) = N_2O_4\,(g) + \text{heat} \qquad \Delta H_{reazione} = -17.08\ \text{kJ/mol}$$

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

The reaction is exothermic: it involves the release of heat.

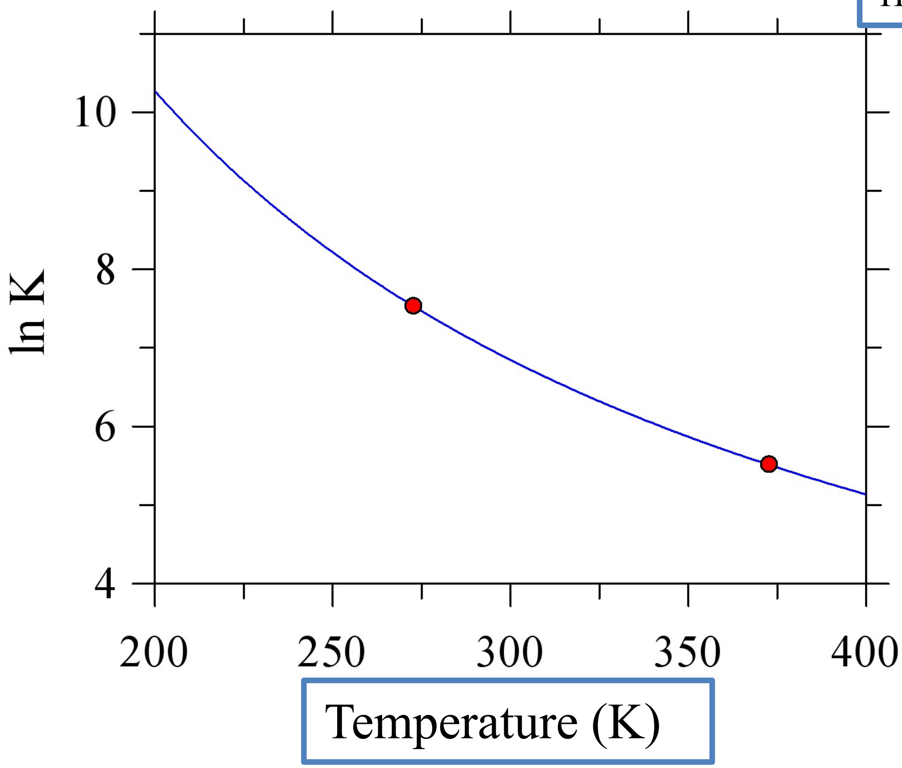
T (K)	K	ln(K)
273	1853.3	7.52
298	246.5	5.51



T = 25 ° C

T = 0 ° C

NO_2 coloured
N_2O_4 colourless



when the temperature of a system at equilibrium increases, the equilibrium will move in the direction that absorbs heat, i.e. in the endothermic reaction when the temperature of a system at equilibrium increases, it will shift in the direction that absorbs heat: the endothermic direction

when the temperature of a system at equilibrium decreases, it will shift in the direction that releases heat: the exothermic direction

if the temperature is changed, the equilbribium concentration is changed thefore the equilibrium constant changes.

The absorbed or released heat "q" can be considered as a reagent/product.

$$\text{endothermic:} \quad A + q \underset{\Delta T < 0}{\overset{\Delta T > 0}{\rightleftharpoons}} B$$

$$\text{hexothermic:} \quad A \underset{\Delta T < 0}{\overset{\Delta T > 0}{\leftrightharpoons}} B + q$$

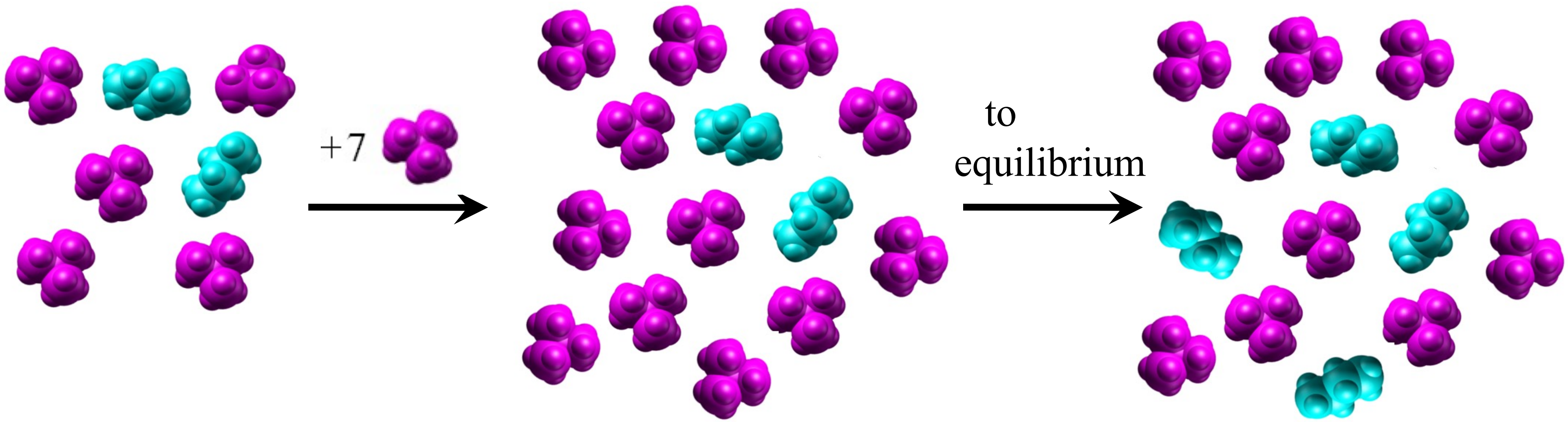
Effect of the addition or removal of a reactant or product

If the concentration of a reactant or a product is changed (at T= constant), the reaction moves toward a new equilibrium in which the reaction quotient is still equal to K.

In the isomerization reaction of butane (C_4H_{10}) to isobutane (C_4H_{10}) at 298 K:

butane (*g*) $\rightleftharpoons$ isobutane (*g*)

$$K = \frac{[\text{isobutane}]}{[\text{butane}]} = 2.5$$



$Q = 5 / 2 = K$ $\qquad$ $Q = 12 / 2 > K$ $\qquad$ $Q = 10 / 4 = K$

Effect of volume changes on equilibrium in gaseous phase

In an equilibrium that involves gases, what happens to the concentrations or partial pressures if the size of the container is changed?

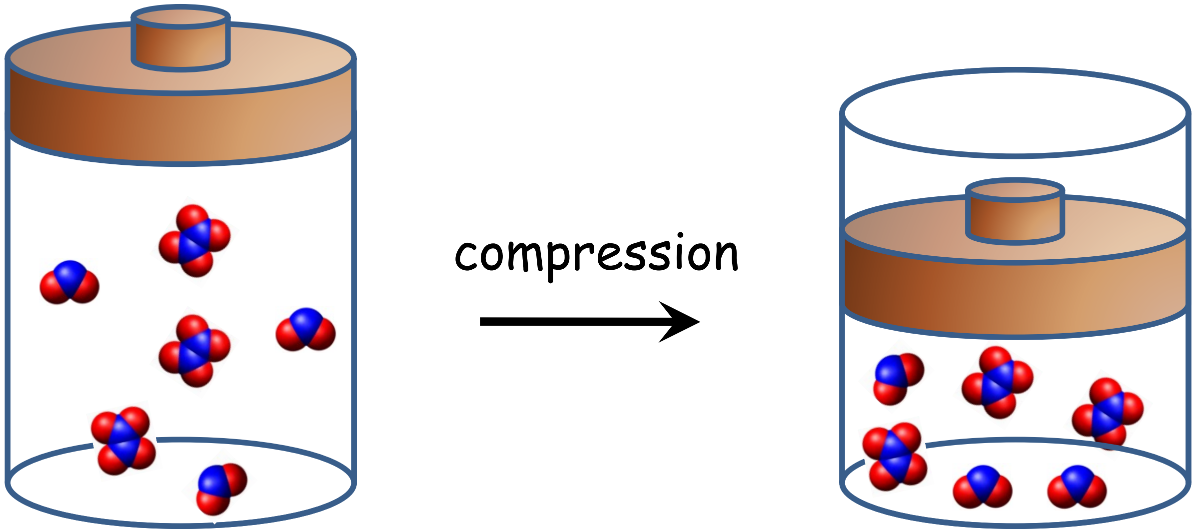
$2\ NO_2\ (g) \rightleftarrows N_2O_4\ (g)$

$$K_C = \frac{[N_2O_4]}{[NO_2]^2} = 246.5\ M^{-1}\ \text{a}\ 298\ K$$

What happens to this equilibrium if the volume of the container is suddenly halved at constant temperature?

According to Boyle's law, pressure doubles ($P_1 x V_1 = P_2 x V_2$, con $V_2 = V_1 / 2$) and also concentrations ($c = n / V = P / (RT)$)

P_1 , c_1



$P_2 = 2\ P_1$
and
$c_2 = 2\ c_1$

IN CONCLUSION

- for a reaction involving gases, the perturbation produced by a volume decrease (or increase in pressure) is balanced by a shift in the direction that results in fewer molecules of gas.

- an increase in volume (or pressure drop) produces the opposite effect: the equilibrium shifts in the direction that results in a larger number of molecules.

- For a reaction in which the number of molecules does not change (ex. A + B = 2 C), a change in volume (or pressure) can not perturb the equilibrium.

$$\Delta V < 0 \quad (\Delta P > 0)$$

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

$$\Delta V > 0 \quad (\Delta P < 0)$$

• when the temperature of a system at equilibrium increases, it will shift towards the direction that absorbes heat, i.e. the endothermic direction.

• when the temperature of a system at equilibrium decreases, it will shift towards the direction that releases heat, i.e. the hexothermic direction.

• changing the temperature will change concentrations at equilibrium and it will change K

We can consider the heat "q" as a "reagent" or a " product".

endothermic: $\mathrm{A} + q \underset{\Delta T < 0}{\overset{\Delta T > 0}{\rightleftarrows}} \mathrm{B}$

hexothermic: $\mathrm{A} \underset{\Delta T < 0}{\overset{\Delta T > 0}{\rightleftarrows}} \mathrm{B} + q$

VARIATIONS IN CONCENTRATION

Increasing the concentration of a compound in a reaction at equilibrium determines a shift in the direction that consumes part of the added material (Le Chatelier).

$$N_2 + 3H_2 \leftrightarrows 2NH_3$$

VARIATIONS IN PRESSURE

If an increase in pressure is applied, the balance shifts to achieve its decrease: for this reaction ammonia is formed since products lead to an increase in particles.

The equilibrium will shift to the right.

Effects of perturbations to the equilibrium

perturbation	Change to achieve equilibrium	Effect on the reaction	Effect on K
Reactions in solid, liquid and gaseous phase			
Increase in T ($\Delta T > 0$)	Heat is absorbed by the system	Shift towards endothermic direction	change
Decrease in T ($\Delta T < 0$)	Heat is released by the system	Shift towards exothermic direction	change
Reagents added	The reagent is partially consumed	[products] increase	No change
Products added	The product is partially consumed	[reagents] increase	No change
Reaction in gaseous phase			
V decreases P increases	Pressure increases	The reaction shifts to decrease the number of molecules	No change
P decreases V increases	Pressure decreases	The reaction shifts to increase the number of molecules	No change

equation	$2\,NO_2\,(g)$ =	$N_2O_4\,(g)$
Initial concentrations(M)	0.2 / 1	9.86 /1
Concentrations after pressure increase(M)	0.2 / 0.5 = 0.4	9.86 / 0.5 = 19.72
variation (M)	–x	+x / 2
New equilibrium concentration (M)	0.4–x	19.72+x/2

$$\xrightarrow{\hspace{2em}}$$

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

$$K_C = \frac{[N_2O_4]}{[NO_2]^2} = \frac{19.72 + \frac{x}{2}}{(0.4 - x)^2} = 246.5\ M^{-1} \rightarrow x = 0.1167\ M$$

The new equilibrium concentrations are:

$[NO_2]$ = 0.4–0.1167 = 0.2833 M e $[N_2O_4]$ = 19.72+0.1167/2 = 19.78 M

Number of moles before perturbation= (0.2 + 9.86)x1 = 10.06

Number of moles afre perturbation= (0.2833 + 19.78)x0.5 = 10.03

EQUILIBRIUM AND DISSOCIATION DEGREE

$$PCl_{5(g)} \rightleftarrows PCl_{3(g)} + Cl_{2(g)} \qquad K_p = \frac{p_{PCl_3}\, p_{Cl_2}}{p_{PCl_5}} = \frac{x^2}{1-x}$$

If 1 mole of PCl_5 is present and, at a given T, it has a dissociation degree x = 30% (= 0,3), at equilibrium we will have:

0,3 (x) n di PCl_3; 0,3 (x) n di Cl_2; 0,7 (1-x) n di PCl_5

$K = (0{,}3)^2 / 0{,}7$

Ostwald's Law (law of dilution)

In a dissociation equilibrium where c is the initial concentration:

$$\underset{c(1-\alpha)}{AB} \rightleftharpoons \underset{c\alpha}{A} + \underset{c\alpha}{B}$$

$$\text{Therefore } K_c = \frac{c^2\alpha^2}{c(1-\alpha)} = \frac{c\alpha^2}{(1-\alpha)}$$

If $\alpha \ll 1$ then $1-\alpha$ can be approximated as $=1$

$$K_c = c\alpha^2$$

Depending of the dissociation equilibrium, Ostwald's law can change formulation:

$$A_2 \rightleftharpoons 2A$$

$$c\,(1-\alpha) \qquad 2c\,\alpha$$

In this case $$K_c = \frac{4c^2\alpha^2}{c\,(1-\alpha)} = \frac{4c\alpha^2}{(1-\alpha)}$$

Why Ostwald's law or law of dilution?

The law explains why increasing dilution (=concentration decreases) the dissociation degree increases.

$$K_c = \frac{c\alpha^2}{(1-\alpha)}$$

By increasing α K_c stays constant as c decreases.

Example : The K for molecular iodine dissociation is 1000 ° C

$$I_2\,(g) \rightleftarrows 2\,I\,(g)$$

is K = 0.00376 M. What are the equilibrium concentrations if initially we have 0.105 moles of I_2 in 12.3 L at 1000 ° C?

equation	I_2 (g) =	2 I (g)
Initial concentration (M)	0.105 /12.3 = 0.0085	0
variation (M)	−x	+2x
Equilibrium concentration(M)	0.0085−x	2x

If c is the initial concentration of I_2, c = 0.105 / 12.3 = 0.0085 M

$$K = \frac{[I]^2}{[I_2]} = \frac{(2x)^2}{(c-x)}$$

$$4x^2 + Kx - Kc = 0$$

$$x = \frac{-K+\sqrt{K^2+16Kc}}{8} = \frac{-0.00376+\sqrt{0.00376^2+16\cdot 0.00376\cdot 0.0085}}{8} = 0.0024\ \text{M}$$

At equilibrium: $[I_2]$ = 0.0085–0.0024 = 0.0061 M e $[I]$ = 2x0.0024 = 0.0048 M