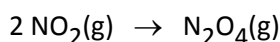


1. Chemical Equilibrium

1 Chemical Equilibrium

When gaseous $\text{NO}_2(\text{g})$ (brown) is placed in a closed vessel at room temperature, it is converted into the colourless gas N_2O_4 according to:



This reaction can be monitored by observing the colour of the gas mixture: as more and more N_2O_4 is formed, the brown colour becomes more and more pale. Eventually, the colour no longer changes as a function of time but remains light yellow.

Apparently not all NO_2 -molecules react with formation of N_2O_4 : the system reaches an equilibrium state where both compounds are present in constant concentration.

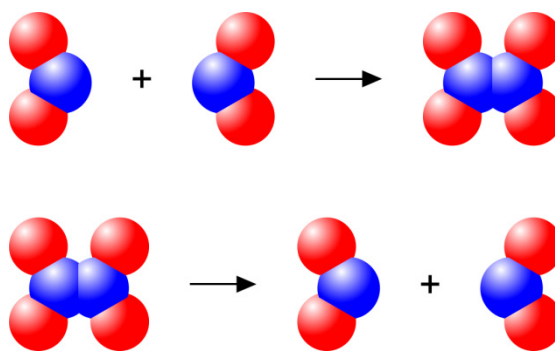
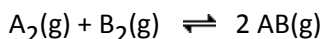


Figure 1: reaction $2 \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$, depicted by space-filling models

The occurrence of this equilibrium state can be explained as follows. For two particles to react, they have to collide with each other. During this collision, two NO_2 -molecules can react with the formation of a N_2O_4 -molecule. However, as a result of strong vibrations in a N_2O_4 -molecule, the latter may again decompose into 2 NO_2 -molecules (Figure 1). When chemical equilibrium is reached, the situation is such that the concentrations of the compounds in the mixture no longer change with time. At that moment, the rate at which N_2O_4 is formed in the forward reaction (v_f) equals the rate at which it decomposes again (v_r).

Let us now consider the hypothetical reaction



that can proceed in two directions. Figure 2.a shows how the concentrations of A_2 , B_2 and AB change as a function of time as more and more A_2 and B_2 are converted into AB . In Figure 2.b the rates of the forward and the backward reaction during the process are represented.

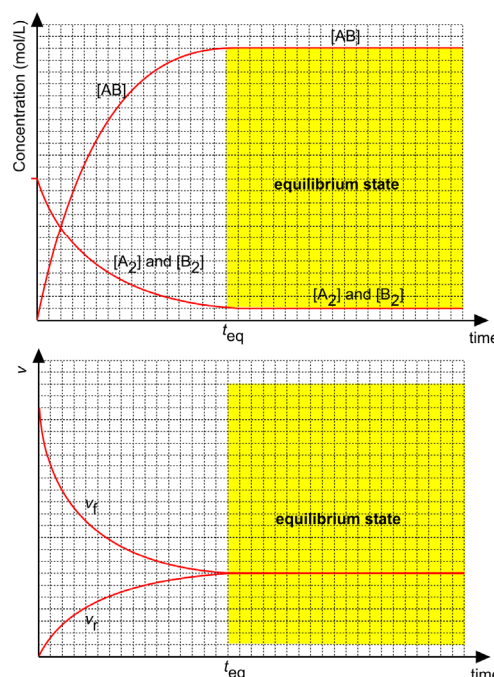
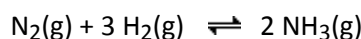


Figure 2: Concentrations of A_2 , B_2 and AB as a function of time for the reversible reaction $\text{A}_2(\text{g}) + \text{B}_2(\text{g}) \rightleftharpoons 2 \text{AB}(\text{g})$ (fig.2a); rates of the forward and the backward reaction as a function of time (fig.2b): at a time t_{eq} an equilibrium state is reached

From the figure it follows that a dynamic equilibrium state is reached when, at a time t_{eq} , the rates of the forward and the backward reactions are equal and the concentrations of all compounds hence remain constant in time.

Note

For some reactions, the rate at which equilibrium is reached is so small that it appears as if the concentrations of the reactants are unchanged. This is a.o. the case for the reaction between $\text{N}_2(\text{g})$, $\text{H}_2(\text{g})$ with formation of $\text{NH}_3(\text{g})$:



At room temperature, a mixture of these three gases remains unchanged because the rate of both the forward and the backward reaction is very small. Only at high temperatures and in the presence of a suitable catalyst an equilibrium state is reached.

2 The Equilibrium Constant

For the equilibrium $2 \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$, table 1 shows the concentrations at equilibrium of the two compounds, starting with different initial compositions of the reaction mixture.

Initial concentration		Equilibrium concentration		$Q_{\text{eq}} = \frac{[\text{N}_2\text{O}_4]_{\text{eq}}}{[\text{NO}_2]_{\text{eq}}^2}$
$[\text{N}_2\text{O}_4]_0$ ($\frac{\text{mol}}{\text{L}}$)	$[\text{NO}_2]_0$ ($\frac{\text{mol}}{\text{L}}$)	$[\text{N}_2\text{O}_4]_{\text{eq}}$ ($\frac{\text{mol}}{\text{L}}$)	$[\text{NO}_2]_{\text{eq}}$ ($\frac{\text{mol}}{\text{L}}$)	
0.1000	0.0000	0.0491	0.1018	4.74
0.0000	0.1000	0.0185	0.0627	4.72
0.0500	0.0500	0.0332	0.0837	4.74
0.0750	0.0250	0.0411	0.0930	4.76

Table 1: Equilibrium concentrations of $\text{NO}_2(\text{g})$ and $\text{N}_2\text{O}_4(\text{g})$ and concentration quotient at equilibrium (Q_{eq}) for the reaction $2 \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$ in reaction mixtures with different initial concentrations

It can be seen that, at equilibrium, the quotient $Q_{\text{eq}} = \frac{[\text{N}_2\text{O}_4]_{\text{eq}}}{[\text{NO}_2]_{\text{eq}}^2}$ has a constant value of 4.74,

independent of the initial situation. In this expression for the quotient, the equilibrium concentration of the reaction product appears as the numerator, and the reactant as the denominator. Each reactant and product is raised to the power of the appropriate stoichiometric coefficient from the balanced chemical equation (i.e. the coefficients become the exponents).

The **equilibrium condition** for this reaction at 373 K is hence expressed as:

$$\frac{[\text{N}_2\text{O}_4]_{\text{eq}}}{[\text{NO}_2]_{\text{eq}}^2} = 4.74 = K$$

K is called the **equilibrium constant**, and the above expression is called the equilibrium constant expression. The value of K for a particular reaction depends on temperature, so temperature should always be specified when K is reported.

For reactions reaching chemical equilibrium, this relationship can be generalized as follows (Guldberg and Waage, 1864):

In a closed system at constant temperature, a chemical process always proceeds towards a situation where a given ratio of the concentrations of reactants and products reaches a constant value.

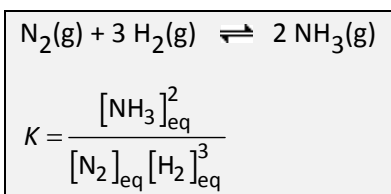
This means that, for a given system at constant temperature, the same equilibrium condition holds whether equilibrium is approached from the forward or reverse direction.

For the general equilibrium reaction: $a A + b B \rightleftharpoons c C + d D$

The condition for equilibrium is given by: $Q_{\text{eq}} = \frac{[C]_{\text{eq}}^c [D]_{\text{eq}}^d}{[A]_{\text{eq}}^a [B]_{\text{eq}}^b} = K$ ($T = \text{constant}$)

The expression for Q_{eq} is determined by the balanced chemical equation: the nominator contains the product of the concentrations of the reaction products, whereas the denominator contains the product of the equilibrium concentrations of the reactants. Each reactant and product is expressed to the power of the appropriate stoichiometric coefficient in the balanced chemical reaction.

For the production of ammonia this means:



The value of K only depends on temperature.

In general, the ratio $Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ is called the **concentration quotient** Q . The value of Q can be

calculated at every stage of the reaction, i.e. also when the systems is not yet at equilibrium. For the reaction from the left to the right with $t < t_{\text{eq}}$ the value of Q increases until Q equals K at $t = t_{\text{eq}}$ (see Figure 3).

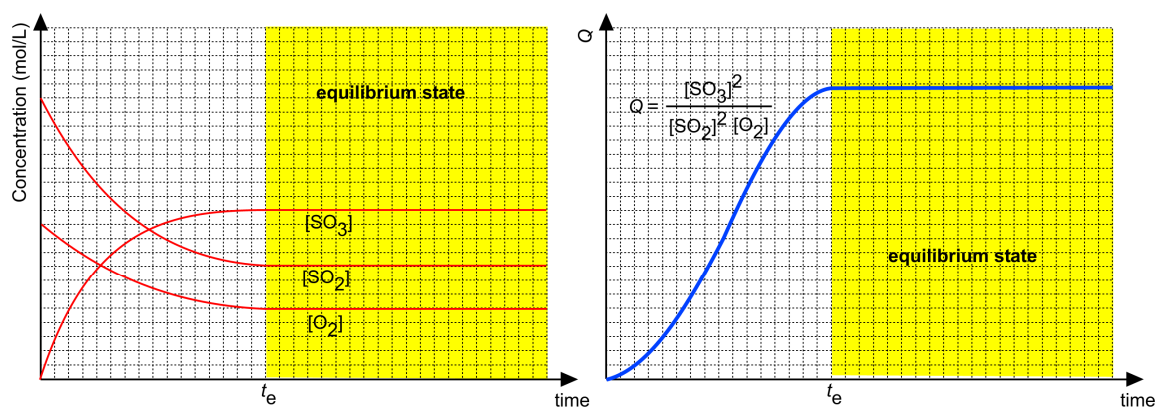
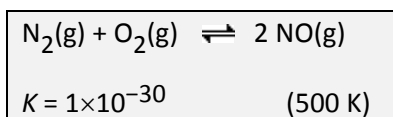


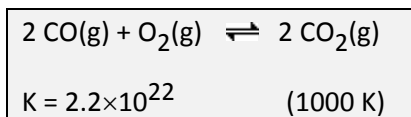
Figure 3: Concentrations of SO_2 , O_2 and SO_3 as a function of time for the reversible reaction $O_2(g) + 2 SO_2(g) \rightleftharpoons 2 SO_3(g)$ (fig.3a); evolution of the concentration quotient Q as a function of time (fig.3b): at equilibrium Q equals the equilibrium constant K

When $Q = K$, the condition for chemical equilibrium holds. For different reactions, the equilibrium constant K may vary between very small and very large values.

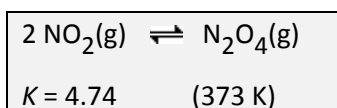
1. Small value of K : at equilibrium only a small amount of products has been formed.



2. Large value of K : at equilibrium only a small amount of reactants is present in the equilibrium mixture.



3. Intermediate values of K : at equilibrium a substantial amount of reactants and products are present in the reaction mixture.

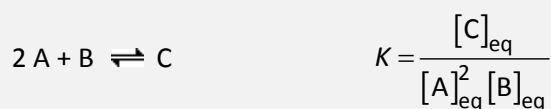


Note

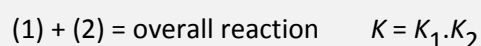
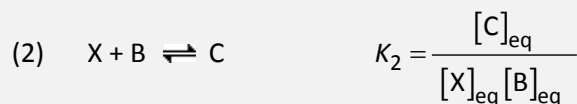
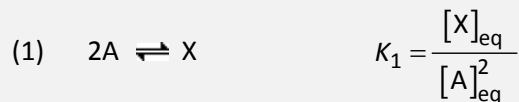
In this text (and many other chemistry books), K values are dimensionless. This is because, from a thermodynamic point of view, each concentration term in the equilibrium constant expression should be divided by its standard (reference) concentration i.e. $1 \frac{\text{mol}}{\text{L}}$ when the concentrations are given in $\frac{\text{mol}}{\text{L}}$. This means that each term in parentheses is dimensionless and K has no units.

Relationship between the Chemical Reaction and the Equilibrium Constant

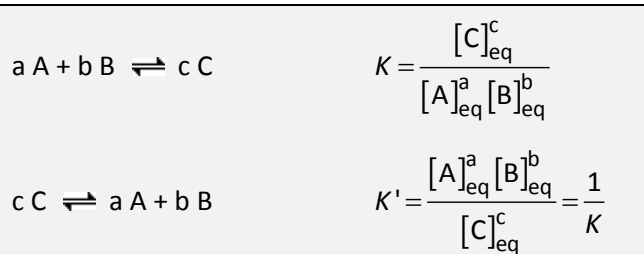
When a chemical reaction can be expressed as a combination of different chemical equilibria, the equilibrium constant for the overall reaction is equal to the product of the equilibrium constants of the individual reactions. For example, suppose we have the following equation:



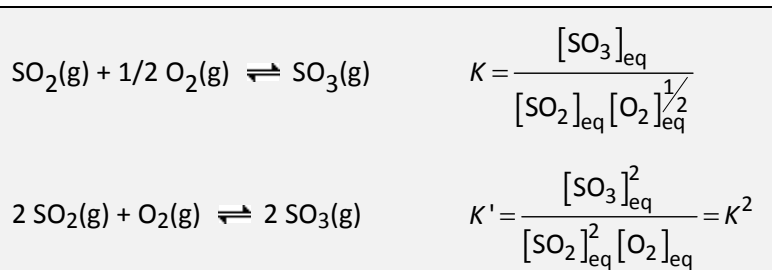
This reaction can be written as the sum of:



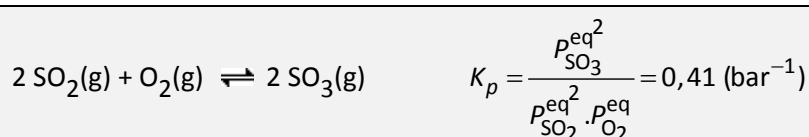
When the direction of a reaction is reversed, the new equilibrium constant is the reciprocal of the original one.



When the coefficients in an equation are multiplied by a factor, the equilibrium constant is raised to a power equal to that factor.



For chemical reactions involving gases, it is common to express the equilibrium condition in terms of the partial pressure of reactants and products, rather than concentrations. The corresponding equilibrium constant is denoted as K_p . For example:



with $p_{\text{SO}_3}^{\text{eq}}$, $p_{\text{SO}_2}^{\text{eq}}$, $p_{\text{O}_2}^{\text{eq}}$ the partial pressures at equilibrium, expressed in bar. Like K , K_p has no unit because the pressures in the equilibrium constant expression are divided by their standard state, which is a pressure of 1 bar.

The relationship between K_c and K_p can be determined as follows.

According to the ideal gas law, $P = \frac{n}{V} \cdot RT = [\dots] \cdot RT$. When we apply this for the partial pressure of each component, we have:

$$K_p = \frac{P_{\text{SO}_3}^{\text{eq}^2}}{P_{\text{SO}_2}^{\text{eq}^2} \cdot P_{\text{O}_2}^{\text{eq}}} = \frac{[\text{SO}_3]_{\text{eq}}^2}{[\text{SO}_2]_{\text{eq}}^2 [\text{O}_2]_{\text{eq}}} \cdot \frac{(RT)^2}{(RT)^2 \cdot RT} = K_c \cdot (RT)^{-1}$$

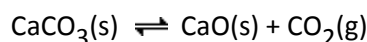
with K_c the equilibrium constant when the amount of the species is expressed in mol.L⁻¹.

In the given case we calculate the value of K_c as follows:

$$\begin{aligned} K_c = K_p \cdot RT &= 0.41 \text{ (bar}^{-1}\text{)} \times 8.314 \frac{\text{J}}{\text{mol.K}} \times 1100 \text{ K} = 0.41 \left(10^5 \frac{\text{N}}{\text{m}^2}\right)^{-1} \times 8.314 \frac{\text{N.m}}{\text{mol.K}} \times 1100 \text{ K} \\ &= 3.75 \times 10^{-2} \frac{\text{m}^3}{\text{mol}} = 37.5 \left(\frac{\text{L}}{\text{mol}}\right) \end{aligned}$$

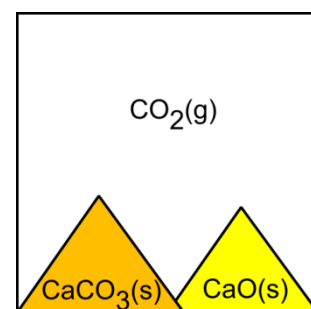
Besides reactions where all reactants and products are in the same phase, there are also chemical processes where more than one phase exists in the reaction mixture. These reactions are called **heterogeneous equilibria**. In the equilibrium constant expressions for this type of reaction, the concentrations of pure solids and liquids are not included. The reason is that the reference state for pure liquids and solids is the pure liquid or solid itself. In the expression for K , these compounds are hence included by a value 1.

In the reaction:



three phases and three components are involved: solid CaCO₃(s), solid CaO(s) and gaseous CO₂(g). Only the gas can be in a state which is different from its standard reference state, i.e. the gas at a pressure of 1 bar. The equilibrium constant expression is:

$$K_c = [\text{CO}_2]_{\text{eq}} \text{ of } K_p = P_{\text{CO}_2}^{\text{eq}}$$

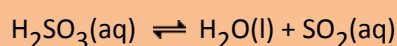


In this closed system, equilibrium is reached when the concentration or the partial pressure of CO₂(g) has a value equal to K_c or K_p , respectively.

Worked example 1



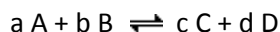
$$K_p = \frac{P_{\text{H}_2}^{\text{eq}^4}}{P_{\text{H}_2\text{O}}^{\text{eq}^4}} \quad K_c = \frac{[\text{H}_2]_{\text{eq}}^4}{[\text{H}_2\text{O}]_{\text{eq}}^4}$$



$$K_c = \frac{[\text{SO}_2]_{\text{eq}}}{[\text{H}_2\text{SO}_3]_{\text{eq}}}$$

3 The Direction of an Equilibrium Reaction

For a general reaction:



the direction can be predicted by comparison of the actual value of the reaction quotient Q with that of the equilibrium constant K ($= Q_{\text{eq}}$). At every moment in a chemical process, the actual value of Q can be calculated by means of:

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

The following situations may hold:

$$Q = K$$

The system is in equilibrium, no macroscopic changes will occur.

$$Q < K$$

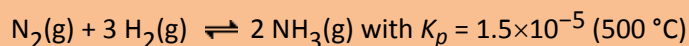
No equilibrium. From the expression for Q it follows that equilibrium can be reached when reactants are used up to form products. When this happens Q increases to the point where it equals K .

$$Q > K$$

No equilibrium. From the expression for Q it follows that equilibrium can be reached when products are used up to form reactants. When this happens Q decreases to the point where it equals K .

Worked example 2

The production of ammonia from nitrogen gas and hydrogen gas is given by:



When we start from gas mixtures with the following initial compositions (pressures in bar), in what direction will the reaction proceed?

	Mixture 1	Mixture 2
NH_3	1.0	1.0
N_2	1.0	20
H_2	3.0	60

$$Q = \frac{P_{\text{O,NH}_3}^2}{P_{\text{O,N}_2} \cdot P_{\text{O,H}_2}^3}$$

Mixture 1

$$Q = \frac{1^2}{1 \times 3^3} = 3.7 \times 10^{-2} > K_p$$

Equilibrium is reached by reaction $2 \text{NH}_3 \rightarrow \text{N}_2 + 3 \text{H}_2$ until $Q = K_p$

Mixture 2

$$Q = \frac{1^2}{20 \times 60^3} = 2.3 \times 10^{-7} < K_p$$

Equilibrium is reached by reaction $\text{N}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3$ until $Q = K_p$

Worked example 3

For the reaction

$\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$ the equilibrium constant K_c is 0.771 at 750 °C. In what direction does the reaction proceed when we start from the following initial concentrations :

$\text{H}_2(\text{g})$: 0.010 mol.L⁻¹; $\text{CO}_2(\text{g})$: 0.020 mol.L⁻¹ ; $\text{H}_2\text{O}(\text{g})$: 0.030 mol.L⁻¹; $\text{CO}(\text{g})$: 0.040 mol.L⁻¹

What are the concentrations of all compounds at equilibrium?

Answer

1. Direction of the reaction:

$$Q = \frac{0.030 \times 0.040}{0.010 \times 0.020} = 6.0 > K_c$$

Equilibrium is reached by reaction $\text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{CO}_2(\text{g})$ until $Q = K_c$

2. Calculation of the equilibrium concentrations

mol.L ⁻¹	$\text{H}_2(\text{g})$	$\text{CO}_2(\text{g})$	$\text{H}_2\text{O}(\text{g})$	$\text{CO}(\text{g})$
Initial concentration [] _o	0.010	0.020	0.030	0.040
Change in concentration Δ[]	+ x	+ x	- x	- x
Equilibrium concentration [] _{eq}	0.010 + x	0.020 + x	0.030 - x	0.040 - x

$$K_c = \frac{(0.030 - x) \times (0.040 - x)}{(0.010 + x) \times (0.020 + x)} = 0.771$$

$x_1 = 0.012$ ($x_2 = 0.40$, this solution is not valid)

$[\text{H}_2]_{\text{eq}} = 0.022 \text{ mol.L}^{-1}$

$$[\text{CO}_2]_{\text{eq}} = 0.032 \text{ mol.L}^{-1}$$

$$[\text{H}_2\text{O}]_{\text{eq}} = 0.018 \text{ mol.L}^{-1}$$

$$[\text{CO}]_{\text{eq}} = 0.028 \text{ mol.L}^{-1}$$

Worked example 4

For the reaction $2 \text{NOCl}(\text{g}) \rightleftharpoons \text{Cl}_2(\text{g}) + 2 \text{NO}(\text{g})$ the equilibrium constant K_c is 1.6×10^{-5} at 35°C . What are the concentrations at equilibrium of all compounds when the initial concentrations are: $[\text{NOCl}(\text{g})]_0 = 0.50 \text{ mol.L}^{-1}$; $[\text{Cl}_2(\text{g})]_0 = [\text{NO}(\text{g})]_0 = 0 \text{ mol.L}^{-1}$

Answer

mol.L ⁻¹	NOCl(g)	Cl ₂ (g)	NO(g)
Initial concentration [] ₀	0.50	0	0
Change in concentration Δ[]	- 2x	+ x	+ 2x
Equilibrium concentration [] _{eq}	0.50 - 2x	x	2x

At equilibrium we have:

$$K_c = \frac{(2x)^2 \times x}{(0.50 - 2x)^2} = 1.6 \times 10^{-5}$$

This cubic equation can be simplified. Indeed, because the equilibrium constant K_c is very small, the change in concentration x will be also be very small and we can write:

$$0.50 - 2x \approx 0.50$$

The expression for the equilibrium constant becomes:

$$K_c = \frac{4x^3}{(0.50)^2} = 1.6 \times 10^{-5}$$

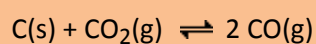
$$\Rightarrow x = 0.010 \text{ mol.L}^{-1}$$

$$[\text{NOCl}]_{\text{eq}} = 0.48 \text{ mol.L}^{-1}; [\text{NO}]_{\text{eq}} = 0.020 \text{ mol.L}^{-1}; [\text{Cl}_2]_{\text{eq}} = 0.010 \text{ mol.L}^{-1}$$

Worked example 5

In a sealed, constant volume container, containing only solid graphite C(s) at 1080 K, an amount of $\text{CO}_2(\text{g})$ is added until the pressure of the gas P_{CO_2} is 0.458 atm.

C (s) reacts with $\text{CO}_2(\text{g})$ in an equilibrium reaction given by :



At equilibrium the global pressure in the container, P_{eq} , is 0.757 atm. Calculate K_p .

Answer

For this heterogeneous reaction the expression for K_p is: $K_p = \frac{(P_{\text{CO}})^2}{P_{\text{CO}_2}}$ (note that we do not include the pure solid). We hence need to calculate the pressure of the gases at equilibrium.

First, the global pressure at equilibrium is given by : $P_{\text{eq}} = P_{\text{CO}} + P_{\text{CO}_2}$.

Further the balanced reaction equation shows that the reaction of 1 mole CO_2 leads to the formation of 2 moles of CO. Because the reaction takes place in a constant volume container, it follows from the ideal gas law that a decrease of the pressure of CO_2 with an amount x leads to increase of the CO pressure with an amount $2x$:



$$P = n \frac{RT}{V} = n \times C^{\text{te}}$$



atm	C(s)	CO ₂ (g)	CO(g)	Global (CO + CO ₂)
Initial pressure	-	0.458	0	0.458
Change in pressure	-	- x	+ $2x$	+ x
Pressure at Equilibrium	-	0.458 - x	$2x$	0.458 + x

Because the global pressure at equilibrium is 0.757 atm, $x = 0.299$ atm.

$$\Rightarrow P_{\text{CO}_2\text{eq}} = 0.458 \text{ atm} - 0.299 \text{ atm} = 0.159 \text{ atm}$$

$$\Rightarrow P_{\text{COeq}} = 2 \times 0.299 \text{ atm} = 0.598 \text{ atm}$$

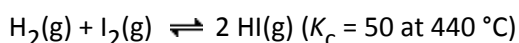
$$K_p = \frac{(P_{\text{CO}})^2}{P_{\text{CO}_2}} = \frac{(0.598)^2}{0.159} = 2.25$$

4 Le Chatelier's Principle

If an outside influence upsets an equilibrium, the system undergoes a change in a direction that counteracts the disturbing influence and returns to a new equilibrium.

4.1 Adding or Removing a Product or Reactant

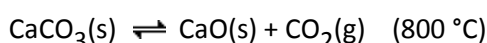
Consider a mixture of $\text{H}_2(\text{g})$, $\text{I}_2(\text{g})$ and $\text{HI}(\text{g})$, where equilibrium holds according to



When the amount of $\text{H}_2(\text{g})$ in this mixture is increased, Q becomes larger than K . As a consequence, in the system $\text{H}_2(\text{g})$ and $\text{I}_2(\text{g})$ will react to form $\text{HI}(\text{g})$ until a new equilibrium state is reached. (Figure 4). Addition of an extra amount of $\text{HI}(\text{g})$ would shift the equilibrium to the left by conversion of HI in H_2 and I_2 . An analogous shift to the left would occur when hydrogen gas or nitrogen gas is removed from the reaction vessel.

When a product in an equilibrium reaction is continuously removed from the reaction mixture, the reaction will proceed until all reactants are converted in products.

When the decomposition of CaCO_3 :



proceeds in a closed vessel, the reaction will proceed until the partial pressure of CO_2 equals K_p :
 $P_{\text{CO}_2} = K_p$.

In an open vessel, CO_2 is continuously removed, so the reaction will proceed until all CaCO_3 has decomposed: the reaction goes to completion.

4.2 Changes in Pressure and Volume

There are two ways of changing the pressure in a closed container with a constant volume:

- Changing the concentration of gaseous compounds: in this case the system will react as explained for changes in concentration.
- Adding an inert gas that does not take part in the reaction: no effect as this gas has no influence on the partial pressure of the reactants and products.

When the volume of a gas mixture is changed, this also changes the global pressure in the vessel.

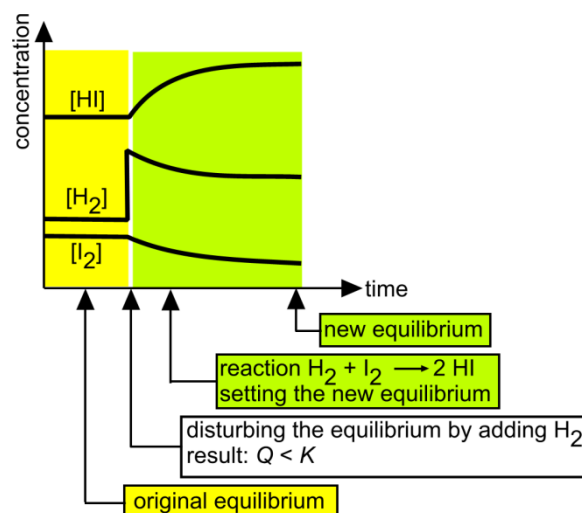
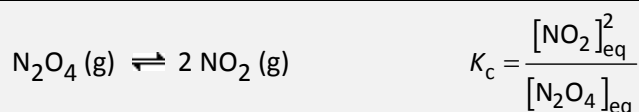


Figure 4 : evolution of the concentrations of $\text{H}_2(\text{g})$, $\text{I}_2(\text{g})$ and $\text{HI}(\text{g})$ when hydrogen gas is added to an equilibrium mixture of these compounds

When the volume is decreased, the global pressure will increase. As a result, the system will react towards a new equilibrium with a smaller number of gas molecules. This can be seen in the following example.



The molar concentration of every component is expressed by:

$$[\text{NO}_2]_{\text{eq}} = \frac{n_{\text{NO}_2}^{\text{eq}}}{V} \quad [\text{N}_2\text{O}_4]_{\text{eq}} = \frac{n_{\text{N}_2\text{O}_4}^{\text{eq}}}{V}$$

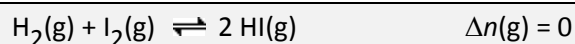
With n the number of moles and V the volume of the container. The equilibrium constant is given by:

$$K_c = \frac{n_{\text{NO}_2}^{\text{eq}^2}}{n_{\text{N}_2\text{O}_4}^{\text{eq}}} \cdot \frac{1}{V}$$

When P increases, V decreases. For the equation above to stay valid, the ratio $\frac{n_{\text{NO}_2}^{\text{eq}^2}}{n_{\text{N}_2\text{O}_4}^{\text{eq}}}$ should

decrease: $n_{\text{N}_2\text{O}_4}^{\text{eq}}$ should become larger whereas $n_{\text{NO}_2}^{\text{eq}}$ should decrease. The system will react with formation of N_2O_4 until a new equilibrium is reached.

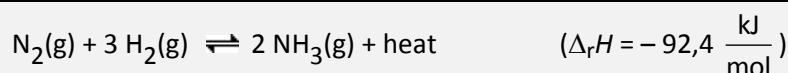
When in a reaction the amount of moles is the same on each side of the equation, i.e. $\Delta n(\text{g}) = 0$, the pressure has no influence on the position of the equilibrium:



The influence of pressure is only taken into consideration for reactions where gases take part in the process, for systems with only solids, pure liquids or solutions, the effect of changes in pressure can usually be neglected.

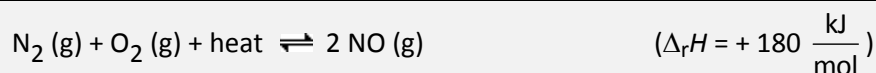
4.3 Influence of the Temperature

When the temperature of the reaction mixture is changed, the direction of the shift of the equilibrium can be determined by considering the heat, used or produced during the reaction, as a component of the process. For an exothermic reaction (reaction enthalpy $\Delta_r H < 0$).



Within this point of view, an increase of temperature means that one of the reaction products is added: the equilibrium will shift to the left. Lowering the temperature means that, the heat, produced in the reaction is removed, in this situation the equilibrium will shift in the direction of formation of ammonia.

For an endothermic reaction ($\Delta_r H > 0$) we have the opposite effect. For the production of NO according to:



An increase of temperature means that heat is added to the mixture and the equilibrium will shift to the right.

Note

The value of the equilibrium constant K is a function of temperature. The effect of temperature on K can be understood from the effect of the heat supply as explained:

Endothermic reactions: K increases with increasing T

Exothermic reactions: K decreases with increasing T

4.4 Influence of a Catalyst

A catalyst influences the rate of the forward and the backward reaction by lowering the activation energy of the process. As a consequence, both rates are increased in a similar way and a catalyst has hence no effect on the position of the equilibrium. Neither K nor $\Delta_r H$ are changed, but the equilibrium is reached more rapidly.

Worked example 6

Consider the reaction: $\text{Fe}^{3+}(\text{aq}) + \text{SCN}^{-}(\text{aq}) \rightleftharpoons \text{FeSCN}^{2+}(\text{aq})$

In what direction will the equilibrium shift after the addition of:

- water until the volume is doubled
- $\text{AgNO}_3(\text{aq})$
- $\text{Fe}(\text{NO}_3)_3(\text{aq})$
- $\text{NaOH}(\text{aq})$

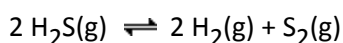
Answer

- to the left
- to the left (AgSCN is insoluble)
- to the right
- to the left

5 Problems

1

At a given temperature, $K_c = 1.6 \times 10^{-2}$ for the reaction:



What is K_c for each of the following equilibria?

- a. $\frac{1}{2} \text{S}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{H}_2\text{S}(\text{g})$
 b. $5 \text{H}_2\text{S}(\text{g}) \rightleftharpoons 5 \text{H}_2(\text{g}) + \frac{5}{2} \text{S}_2(\text{g})$

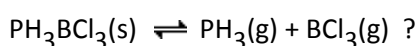
2

Calculate K_c for the following equilibria:

- a. $\text{CO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{COCl}_2(\text{g}) \quad K_p = 3.9 \times 10^{-2} \quad (1000 \text{ K})$
 b. $\text{S}_2(\text{g}) + \text{C}(\text{s}) \rightleftharpoons \text{CS}_2(\text{g}) \quad K_p = 28.5 \quad (500 \text{ K})$

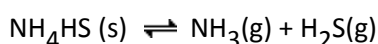
3

When 0.15 moles of $\text{PH}_3\text{BCl}_3(\text{s})$ are placed in a container with $V = 3 \text{ L}$ at constant temperature, it is found that at equilibrium, 8.4×10^{-3} moles of $\text{PH}_3(\text{g})$ are formed. What is K_c at this temperature for the reaction:



4

$\text{NH}_4\text{HS}(\text{s})$ decomposes according to



with $K_p = 0.11$ at $250 \text{ }^\circ\text{C}$. When 55.0 g $\text{NH}_4\text{HS}(\text{s})$ is brought in a closed vessel of 1 L at this temperature, what is the pressure of $\text{NH}_3(\text{g})$ at equilibrium?

5

The reaction $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ proceeds in a closed vessel with constant volume at 556 K . We define n_0 as the number of moles PCl_5 that is initially present, α is defined as the fraction of PCl_5 -molecules that has dissociated into PCl_3 and Cl_2 . Derive an expression for K_p as a function of α and the global pressure at equilibrium P . When $K_p = 4.96$ and $P = 1 \text{ bar}$, calculate α .

6

For the reaction $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g})$ is $K_c = 0.10$ at $2000 \text{ }^\circ\text{C}$. 1.62 moles of N_2 and 1.62 moles O_2 are placed in a closed vessel of 2.000 L . Calculate the equilibrium concentrations for all components. What is the global pressure in the vessel?

7

For the equilibrium $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$, the following equilibrium concentrations are found at 556 K in a closed container: $[\text{PCl}_5] = 0.72 \frac{\text{mol}}{\text{L}}$; $[\text{PCl}_3] = [\text{Cl}_2] = 0.28 \frac{\text{mol}}{\text{L}}$. What are the new equilibrium concentrations when the volume of the container is doubled?

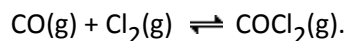
8

At 1000°C, $K_p = 167.5$ (bar) for the reaction $\text{C}(\text{grafite}) + \text{CO}_2(\text{g}) \rightleftharpoons 2 \text{CO}(\text{g})$

In a high pressure container of 1 L, 0.500 mole of $\text{CO}(\text{g})$ and an excess amount of graphite are heated to 1000°C. What is the global pressure when equilibrium is reached?

9

At 100°C, $K_p = 1.5 \times 10^8$ (bar^{-1}) for the following reaction:



Calculate the partial pressure of CO at 100 °C in a vessel that originally contained only COCl_2 at a pressure of 0.250 bar.

10

What is the effect of the following changes on the equilibrium position of the reaction $2 \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$.

- Dividing the partial pressure of NO_2 by 2
- Dividing the volume of the container by 2
- Adding Ar to a partial pressure of 1 bar.

6 Answers**1**

- 7.9
- 3.2×10^{-5}

2

- 3.2
- 28.5

3

$$7.8 \times 10^{-6}$$

4

0.33 bar

5

$$K_p = \frac{\alpha^2 P}{(1 - \alpha^2)}$$

$$\alpha = 0.91$$

6

$$[\text{N}_2] = [\text{O}_2] = 0.700 \frac{\text{mol}}{\text{L}} ; [\text{NO}] = 0.221 \frac{\text{mol}}{\text{L}} ; P = 306 \text{ bar}$$

7

$$K_c = 0.109 \text{ en } [\text{PCl}_5] = 0.315 \frac{\text{mol}}{\text{L}} , [\text{PCl}_3] = [\text{Cl}_2] = 0.185 \frac{\text{mol}}{\text{L}}$$

8

119.7 bar

9

$$4.08 \times 10^{-5} \text{ bar} ; \text{Hint: suppose } V = 1 \text{ L and consider } x \text{ to be very small.}$$

10

Shift of the equilibrium

- a) To the left
- b) To the right
- c) No effect