1

Chemical equilibrium

GOALS

1. Formulate equilibrium constants
2. Interconvert K_c and K_p
3. Apply Le Châtelier
4. Interpret the magnitude of K_c
5. Carry simple equilibrium calculations

REACTIONS rarely occur to completion. Once the products are formed they can follow a backward reaction to regenerate the reactants and at the same time, reactants regenerate produce products. Overall chemical reactions proceed until an equilibrium is reached. The equilibrium conditions determine how profitable a reaction can be as it describes how much of the products stay as products. This chapter covers the idea and basic principles of chemical equilibrium. We will describe the role of an equilibrium constant which gives insight into the mixtures of reactants and products in equilibrium. Also, we will discuss the different types of equilibrium constants in terms of molarity and pressure and the role of a reaction quotient giving insight into the direction in which a chemical reaction proceeds towards the equilibrium. Finally, we will cover Le Châtelier principle that describes once an equilibrium is altered, in which direction does a chemical reaction proceed to recover the equilibrium state.

1.1 Chemical Equilibrium

This section covers basic ideas about chemical equilibrium. First, we will introduce the concept of the forward and reverse reaction. Next, we will define the idea of equilibrium, based on the speed of the forward and reverse reactions.

`Discussion:` How can you make a reaction go faster? Give three possible answers.

`Forward and reverse reactions` In chemical reactions reactants form products. We call this the *forward reaction*:

$$\text{reactants} \longrightarrow \text{products}$$

However, once the products form they can also generate reactants through the *reverse reaction*:

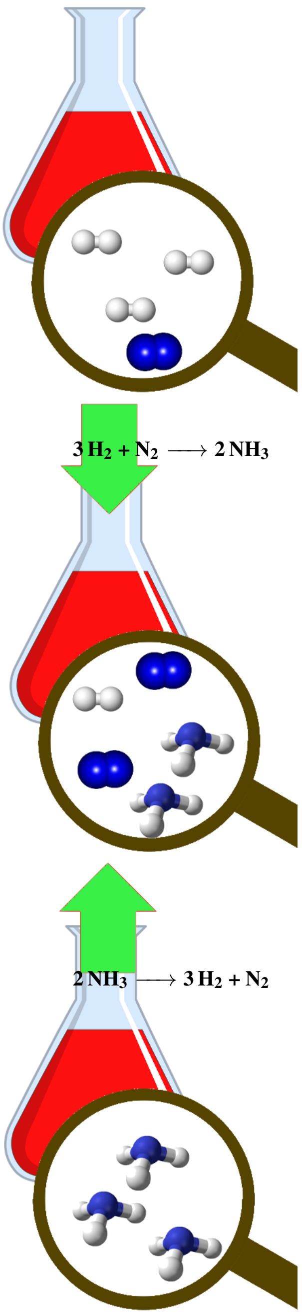
$$\text{reactants} \longleftarrow \text{products}$$

`Equilibrium` In chemical reactions, both the forward and the reverse reaction happen synchronously, so that when products form they also generate reactants. However, both the reverse and forwards reactions have different speeds. In the beginning, the forward reaction proceeds at a faster pace than the reverse so that the reaction advances. Once products form, the reverse reaction will start speeding. A reaction reaches *chemical equilibrium* when both the forward and reverse reactions proceed at the same speed. Chemical reactions normally are written down with a double arrow that indicates equilibrium:

$$\text{reactants} \rightleftharpoons \text{products}$$

For example, the chemical process that forms ammonia from nitrogen and hydrogen can proceed using the forward and reverse reaction

$$3\,H_2 + N_2 \underset{\text{Reverse Reaction}}{\overset{\text{Forward Reaction}}{\rightleftharpoons}} 2\,NH_3$$



▼The forward reaction goes from reactants to products whereas the reverse reaction goes from products to reactants.

`Equilibrium and concentration` It is just a matter of time that a reaction reaches equilibrium. Initially, the forward process normally proceeds at high speed as products start to form. This is because initially there is an abundance of reactants. Once the products start to accumulate the forward process will start happening. This is because at that point there is an increasing amount of product molecules that can go back to reactants. Eventually, the forward and reverse rates become equal as the reaction reaches equilibrium. When the equilibrium has been reached, reactants and products have very specific concentrations. At the same time, a reaction in equilibrium contains a mixture of reactants and products.

Sample Problem 1

Write down the forward and reverse reactions for:

$$CH_4(g) + 2\,O_2(g) \rightleftharpoons CO_2(g) + 2\,H_2O(g)$$

SOLUTION

(a) The forward reaction is $CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g)$ and the reverse $CH_4(g) + 2\,O_2(g) \longleftarrow CO_2(g) + 2\,H_2O(g)$

STUDY CHECK

Write down the forward and reverse reactions for the reaction:

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

1.2 The equilibrium constant

Reactions in equilibrium are characterized buy an equilibrium constant. This next section will show you how to interpret and calculate the value of the equilibrium constant of a reaction. We will show you how to interpret and calculate the numerical value of an equilibrium constant.

`Equilibrium mixtures` Imagine you start a chemical reaction. Initially, products will form and reactants will disappear. At equilibrium, you will have a mixture of reactants and products with the forward and reverse processes happening at the same rate. The question is: an equilibrium mixture would contain more reactants or perhaps more products? The equilibrium constant helps predict just that.

Table 1.1 Different K_c values at 298K

Reaction	K_c	Equilibrium mixture
$2\,NH_{3(g)} \rightleftharpoons N_{2(g)} + 3\,H_{2(g)}$	17	Products > Reactants
$H_{2(g)} + I_{2(g)} \rightleftharpoons 2\,HI_{(g)}$	50	Products > Reactants
$2\,SO_{3(g)} \rightleftharpoons 2\,SO_{2(g)} + O_{2(g)}$	0.3	Products < Reactants
$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$	0.2	Products < Reactants

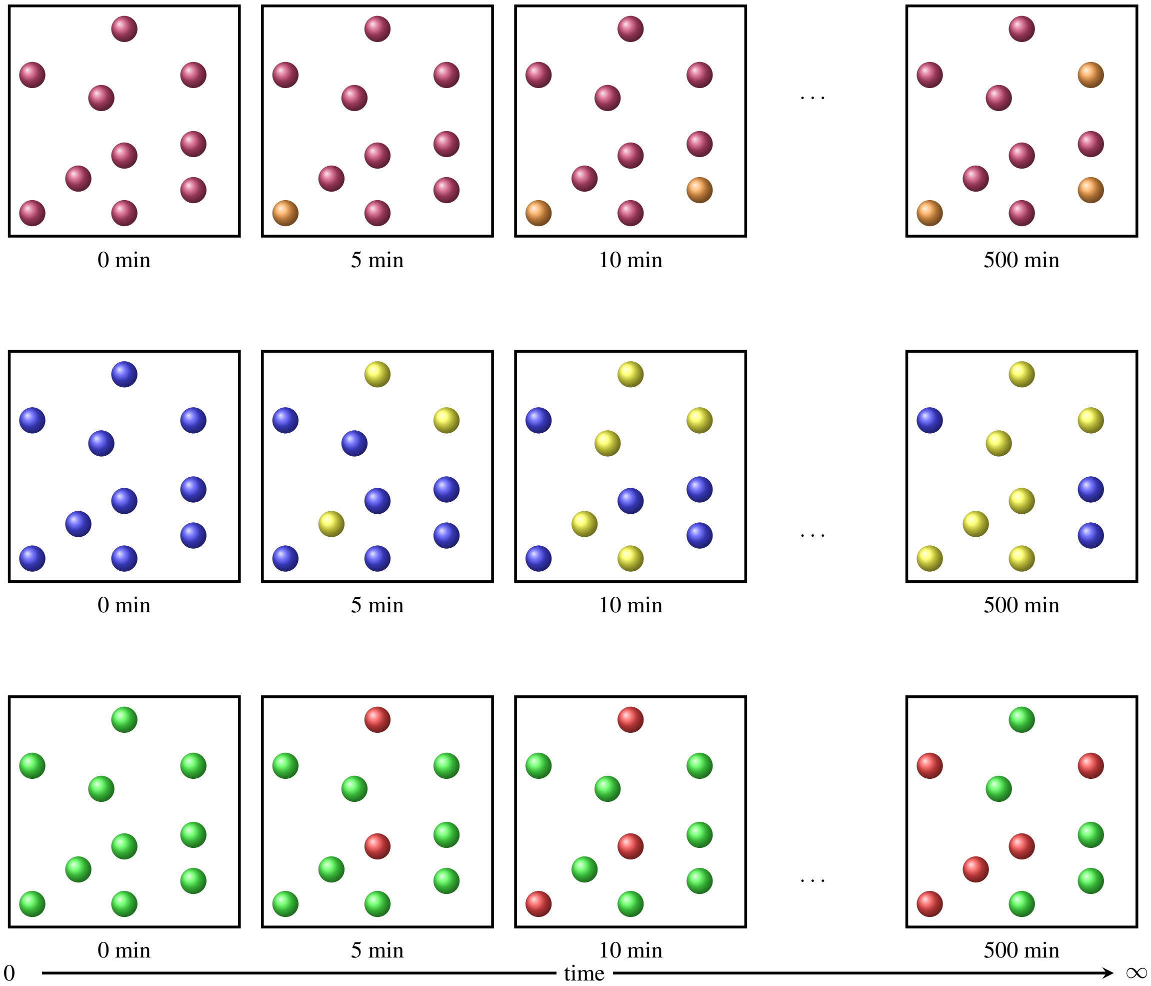
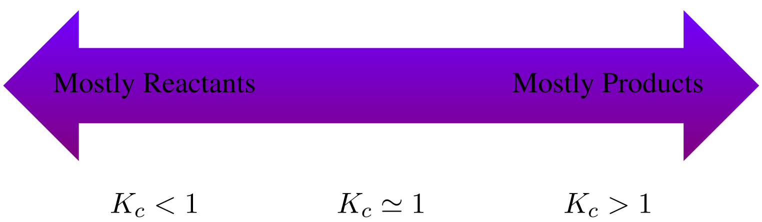
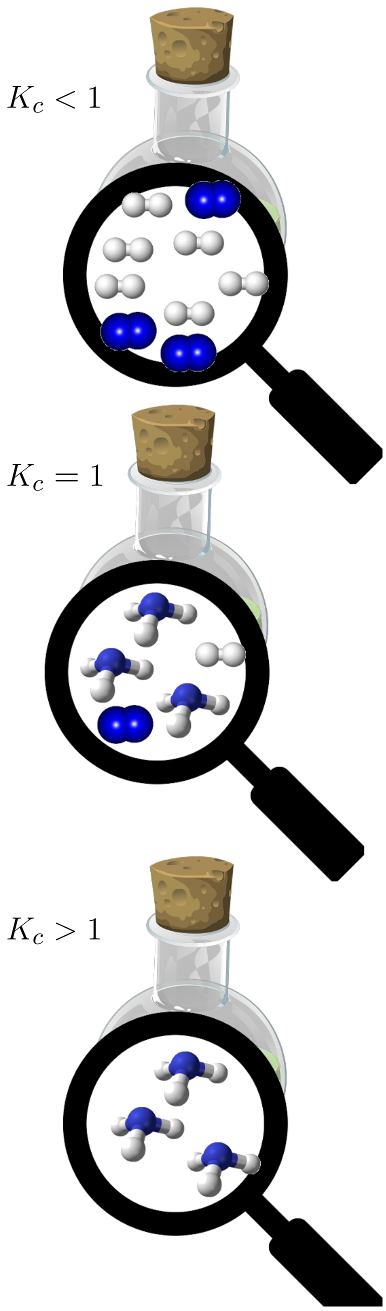


Figure 1.1 Three equilibrium situations

The equilibrium constant of a reaction The equilibrium constant associated with a reaction K_c indicates whether there is an abundance of reactants or products at equilibrium. Each reaction has one K_c value that depends only on temperature and the subscript $_c$ represents concentration. On one hand, if K_c is larger than one there will be a larger concentration of products than reactants in the equilibrium mixture. On the other hand, if K_c is smaller than one there will be a larger concentration of reactants than products in the equilibrium mixture. If K_c is close to one then both reactants and products will have the same concentration in the equilibrium mixture.



In terms of units, equilibrium constants are unit-less numbers–a number without units. In other words, they have no unit and they are simply expressed as a number.



▼The magnitude of the equilibrium constant indicates whether there is more products or reactants in an equilibrium mixture.

Sample Problem 2

The value of K_c for the following reaction at 300K is 4×10^{31}. Indicate whether the equilibrium mixture will contain mostly reactants, mostly products or both.

$$Cl_{2(g)} + H_{2(g)} \rightleftharpoons 2\,HCl_{(g)}$$

SOLUTION

As K_c is larger than one, an equilibrium mixture of Cl_2, H_2 and HCl will contain mainly products, that is will be mainly made of HCl.

STUDY CHECK

The value of K_c for $F_2(g) \rightleftharpoons 2\,F(g)$ at 500K is 7×10^{-13}. Indicate whether the equilibrium mixture will contain mostly reactants, mostly products or both.

`Equilibrium constant expression` Let's consider a general equilibrium reaction in which A and B react to form C and D

$$\underbrace{\mathrm{aA} + \mathrm{bB}}_{\text{Reactants}} \rightleftharpoons \underbrace{\mathrm{cC} + \mathrm{dD}}_{\text{Products}}$$

The stoichiometric coefficients of the reaction are: a, b, c and d. The expression for the equilibrium constant depends only on the concentration of the reactants and products. In order to refer to concentration we will user square brackets. For example $[A]$ means the concentration of A. Hence, the expression of the equilibrium constant will be:

$$\boxed{K_c = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}} \quad \text{Equilibrium constant} \tag{1.1}$$

Let us break down the expression of K_c. On top of the fraction we have the equilibrium concentration of the products to the power of its coefficients. For example $[C]^c$ means the equilibrium concentration of C to the power of the coefficient c. On the bottom of the fraction we have the concentration of the reactants to the power of its coefficients. All concentrations in K_c are timed.

product concentration

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

reactant coefficient

Let's focus on the reaction below:

$$CH_{4(g)} + 2\,O_{2(g)} \rightleftharpoons CO_{2(g)} + 2\,H_2O_{(g)}$$

The expression of the equilibrium constant would be:

$$K_c = \frac{[CO_2] \cdot [H_2O]^2}{[CH_4] \cdot [O_2]^2}$$

Equilibrium involving solids, liquids and solutions Let us analyze an example of a reaction involving solids or liquids:

$$CaCO_3 \cdot H_2O_{(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)} + H_2O_{(l)}$$

Solids and liquids have no concentration and hence they should not included in the expression of K_c. For the example above:

$$K_c = [CO_2]$$

Differently for reaction involving aqueous solutions, for example:
$HCl_{(Aq)} \rightleftharpoons H^+_{(Aq)} + Cl^-_{(Aq)}$ $\qquad K_c = \frac{[H^+]\cdot[Cl^-]}{[HCl]}$
Overall, remember that in the expression of K_c you can only include gases (g) or aqueous solutions (aq) as you can ignore solids and liquids without a well-defined concentration.

Sample Problem 3

Write down the expression of K_c for the following reactions:
(a) $2\,NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$
(b) $C_3H_{8(g)} + 5\,O_{2(g)} \rightleftharpoons 4\,H_2O_{(g)} + 3\,CO_{2(g)}$
(c) $Zn_{(s)} + 2\,HCl_{(Aq)} \rightleftharpoons ZnCl_{2(Aq)} + H_{2(g)}$

SOLUTION

Remember you can only include gas and aqueous solution in the expression of K_c. For the first example

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

For the second example,

$$K_c = \frac{[H_2O]^4 \cdot [CO_2]^3}{[C_3H_8] \cdot [O_2]^5}$$

For the last example:

$$K_c = \frac{[ZnCl_2] \cdot [H_2]}{[HCl]^2}$$

STUDY CHECK

Write down the expression of K_c for the following reaction:
$Pb^{2+}_{(Aq)} + 2\,I^-_{(Aq)} \rightleftharpoons PbI_2(s)$.

Equilibrium constant in terms of pressures The equilibrium constant K_c is the ratio of the concentration of products and reactants. As concentration is related to pressure–remember the chapter about gases–we can also express an equilibrium constant in terms of pressures, we call this K_p.

$$\boxed{K_p = \frac{P_{\text{Products}}}{P_{\text{Reactants}}} = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}} \quad \text{Equilibrium constant} \tag{1.2}$$

Let's focus on an example. Think about the reaction below that involved just gases:

$$CH_{4(g)} + 2\,O_{2(g)} \rightleftharpoons CO_{2(g)} + 2\,H_2O_{(g)}$$

The expression of the equilibrium constant would be:

$$K_p = \frac{P_{CO_2} \cdot P^2_{H_2O}}{P_{CH_4} \cdot P^2_{O_2}}$$

K_p values larger than one imply that in the mixture the pressure of products is larger than the pressure of reactants and the opposite is true for values smaller than one.

`Relating` K_c `and` K_p The values of K_c and K_p are related by the following formula:

$$\boxed{K_p = K_c(RT)^{\Delta n}} \tag{1.3}$$

where:

K_p is the equilibrium constant in terms of pressure
K_c is the equilibrium constant in terms of concentration
R is the constant of the gases in pressure units (0.082 atmL/molK)
T is the absolute temperature (in Kelvins)
Δn is the change of stoichiometry of the reaction

Let us analyze the role of Δn for the reaction:

$$C_3H_8 + 5\,O_2 \rightleftharpoons 4\,H_2O + 3\,CO_2$$

Δn represents the number of molecules of products with respect to the number of molecules of reactants: 7-6=1. For this reaction, we have that $K_p = K_c(RT)$. However, the power on the relationship will depend on the stoichiometry of the reaction. At the same time, the relationship between both constant depends on the temperature.

Sample Problem 4

For the following reaction

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

The value of K_c at 300K is 17. Calculate the value of K_p at the same temperature.

SOLUTION

First we will write down the expression of both equilibrium constants:

$$K_c = \frac{[NH_3]^2}{[N_2]\cdot[H_2]^3} \qquad K_p = \frac{P^2_{NH_3}}{P_{N_2}\cdot P^3_{H_2}}$$

We will also calculate Δn in order to establish the relationship between both constants:

$$\Delta n = 1 + 3 - 2 = 2$$

We have that:

$$K_p = K_c(RT)^{\Delta n} = K_c(RT)^2$$

Given than K_c at 300K is 17:

$$K_p = K_c(RT)^{\Delta n} = 17(0.082 \cdot 300)^2 = 10287$$

In equilibrium, the pressure of products will be larger than the pressure of reactants.

STUDY CHECK

For the following reaction

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

The value of K_p at 300K is 0.05. Calculate the value of K_c at the same temperature.

1.3 Using equilibrium constants

We saw that the equilibrium constant of a reaction tells you whether there are more reactants or products in an equilibrium mixture. At the same time, one can use K_c to quantitatively calculate the value of the equilibrium concentration of reactants and products. This section will explain how to do this.

Solving from K_c Let's analyze the reaction of hydrogen (H_2) and iodine (I_2) to produce hydrogen iodide (HI):

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

The equilibrium constant at 300K is $3 \cdot 10^{-1}$. Analyzing a reaction mixture we find that the concentration of H_2 is 1M and the concentration of I_2 is 2M. We want to calculate how much HI do we have in the mixture. As the concentrations of reactants and products are linked together through K_c we can certainly solve for $\left[\mathrm{HI}\right]$. The expression for K_c is:

$$K_c = \frac{\left[\mathrm{HI}\right]^2}{\left[\mathrm{H_2}\right] \cdot \left[\mathrm{I_2}\right]}$$

and we know that $\left[\mathrm{H_2}\right] = 1M$ and $\left[\mathrm{I_2}\right] = 2M$. Plugging the values in the expression of K_c, and given the numerical value of K_c we have:

$$3 \cdot 10^{-1} = \frac{\left[\mathrm{HI}\right]^2}{1 \cdot 2^2}$$

Solving for $\left[\mathrm{HI}\right]$ we have

$$\left[\mathrm{HI}\right]^2 = 1.2$$

To solve for $\left[\mathrm{HI}\right]$ we have to use an square root:

$$\left[\mathrm{HI}\right] = \sqrt[2]{1.2} = 1.09M$$

Sample Problem 5

The value of the equilibrium constant for the reaction

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

is $3 \cdot 10^8$ at 300K. An analysis of an equilibrium mixture gave a concentration of nitrogen and ammonia of 2M, respectively. Calculate the equilibrium concentration of hydrogen at 300K.

SOLUTION

The value of the equilibrium constant for the formation of ammonia is:

$$K_c = \frac{\left[\mathrm{NH_3}\right]^2}{\left[\mathrm{H_2}\right]^3 \cdot \left[\mathrm{N_2}\right]}$$

We know $\left[\mathrm{NH_3}\right]$ and $\left[\mathrm{N_2}\right]$ and both values are 2M, and we also know $K_c = 3 \cdot 10^8$. Plugging these values into the previous equations we obtain:

$$3 \cdot 10^8 = \frac{2^2}{\left[\mathrm{H_2}\right]^3 \cdot 2}$$

we can solve for $\left[\mathrm{H_2}\right]$:

$$\left[\mathrm{H_2}\right]^3 = 6.6 \cdot 10^{-9}$$

In order to obtain $\left[\mathrm{H_2}\right]$ we need a a cubic root:

$$\left[\mathrm{H_2}\right] = \sqrt[3]{6.6 \cdot 10^{-9}} = 1.9 \cdot 10^{-3} M$$

STUDY CHECK

The value of the equilibrium constant for the reaction

$$C_3H_{8(g)} + 5\,O_{2(g)} \rightleftharpoons 4\,H_2O_{(g)} + 3\,CO_{2(g)}$$

is 500 at a given temperature. An analysis of an equilibrium mixture gave a concentration of water, carbon dioxide and C_3H_8 of 1M. Calculate the equilibrium concentration of oxygen at that temperature.

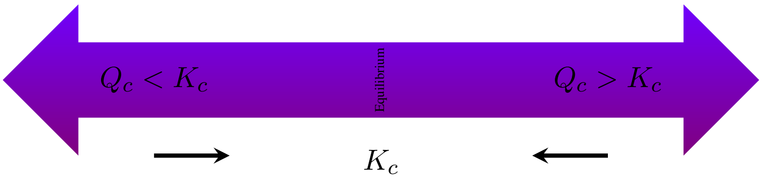
1.4 Concentration or pressure ratio

In a chemical reaction, if we prepare a mixture of reactants they will generate products. At equilibrium reactants and products exist at a very specific ratio given by the equilibrium constant. What if we would prepare a mixture containing both reactants and products? Given that both reactants and products are related by an equilibrium, how would the concentrations change? In other words, would the reaction proceed towards the right producing products or the left producing reactants? This section introduces the use of a concentration (or pressure) ratio that helps predicts the direction in which a mixture of reactants and products will proceed towards the equilibrium.

`Definition of concentration ratio` Equilibrium constant are ratios of equilibrium concentration or pressure of products over reactants measured after the system has reacted for an infinite time. Concentration ratio Q_c are ratios of concentration of products over reactants away from the equilibrium. In another words, they represent the reaction away from the equilibrium.

$$\boxed{Q_c = \frac{\left[\mathrm{Products}\right]_{noneq}}{\left[\mathrm{Reactants}\right]_{noneq}} = \frac{\left[C\right]^c_{noneq} \cdot \left[D\right]^d_{noneq}}{\left[A\right]^a_{noneq} \cdot \left[B\right]^b_{noneq}}} \quad \text{concentration ratio} \qquad (1.4)$$

Use of concentration ratios Concentration ratios helps predict whether a reaction will proceed towards the left or towards the right when we start with a mixture of reactants and products away from equilibrium.



If Q_c is larger than K_c the reaction will proceed towards the left producing reactants. On the other hand, if Q_c is smaller than K_c the reaction will proceed towards the right producing products. If Q_c equals to K_c then the reaction is in equilibrium.

Sample Problem 6

In two different experiments, we prepare mixtures of four chemicals interconnected by the following equilibrium:

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)} \qquad K_c = 0.48$$

Indicate if any of the mixtures is in equilibrium. If it is not, indicate whether the reaction will evolve towards the left or the right to reach equilibrium.

Experiment	1	2
$[CO_2]$	0.0040	0.037
$[H_2]$	0.0040	0.046
$[CO]$	0.0203	0.011
$[H_2O]$	0.0203	0.0011

SOLUTION

We will compute the concentration ratio for each experiment and compare the value with k_c. If Q_c is larger than k_c the reaction will proceed to the left whereas if Q_c is smaller than k_c the reaction will proceed to the right.

Experiment	1	2
$[CO_2]$	0.0040	0.037
$[H_2]$	0.0040	0.046
$[CO]$	0.0203	0.011
$[H_2O]$	0.0203	0.0011
Q_c	3.8×10^{-4}	140

None of the mixtures are in equilibrium as Q_c differs from k_c. In the first experiment the reaction will proceed to the right and in the second experiment the reaction will proceed to the left.

STUDY CHECK

We prepare mixtures of four chemicals in an experiment. These chemicals are interconnected by the following equilibrium:

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)} \qquad K_c = 0.48$$

Indicate if the mixture is in equilibrium. If it is not, indicate whether the reaction will evolve towards the left or the right to reach equilibrium.

Experiment	1
$[CO_2]$	0.0005
$[H_2]$	0.0076
$[CO]$	0.0094
$[H_2O]$	0.0025

▼Henry Louis Le Châtelier was a french chemist who devised a principle used by chemists to predict the effect a changing condition has on a system in chemical equilibrium.

1.5 Le Châtelier principle

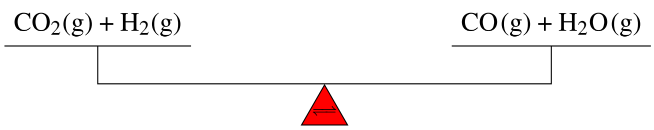
At this point, we have covered the idea of equilibrium and we have seen that the forward and reverse reactions have the same rate at equilibrium. Now, what happens if you alter this equilibrium? Le Châtelier principle claims a reaction will go back to its original equilibrium state by shifting left or right.

`Le Châtelier principle` When a reaction is in equilibrium the forward and reverse reactions proceed at the same speed. Also in an equilibrium state, the concentrations of reactants and products have very specific values. Imagine that you create stress conditions by adding reactants or products or even changing the temperature. This stress will have an impact on the equilibrium and the reaction eventually will reach a new state of equilibrium by somehow counteracting this stress. Le Châtelier principle says that when a stress is placed in a reaction (adding or removing reactant or products, increasing decreasing temperature) the equilibrium will be shifted in the direction that relieves that stress.

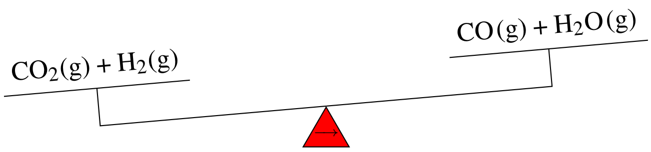
`Change in concentration` Let us consider the following equilibrium:

$$CO_2(g) + H_2(g) \rightleftharpoons CO\,(g) + H_2O\,(g)$$

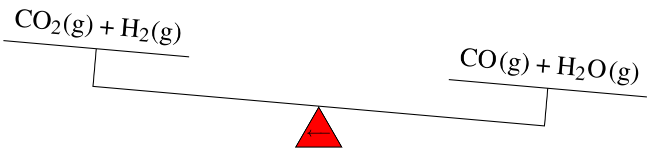
K_c for this reaction equals to one at 1200K. This means that the concentration of reactants and products are the same. We can represent this by means of this balance or seesaw



If we add some CO_2 the equilibrium will be affected. To counteract on this stress, the reaction will restore the equilibrium by decreasing the amount of CO_2. This can only be achieved by displacing the equilibrium to the right, so that CO_2 is removed. Mind that CO_2 is consumed if the reaction moves from reactants $\longrightarrow$ to products and it is produced when going from products $\longleftarrow$ to reactants. We can represent this with the following seesaw.



As we added CO_2 the reactants now weight more and hence the reaction has to proceed to the right $\longrightarrow$. Now imagine we remove some $CO_2(g)$. Again, the equilibrium will be affected and the reaction will restore its equilibrium state by by doing the opposite, that is producing $CO_2(g)$ as the reaction proceeds from reactants $\longleftarrow$ to products. Again using the seesaw:

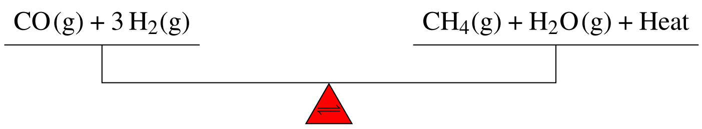


We can also add a different chemical that is not involved in the equilibrium. In this case, the equilibrium will not be affected by this change.

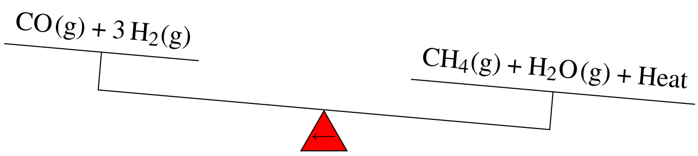
Temperature change Let us consider the following equilibrium that produces heat–remember we describe these types of reactions as exothermic:

$$CO\,(g) + 3\,H_2(g) \rightleftharpoons CH_4(g) + H_2O\,(g) + \text{Heat}$$

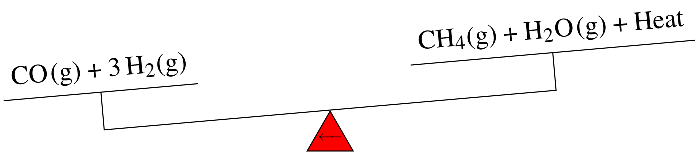
Again, this reaction is in equilibrium so we can use the same seesaw analogy.

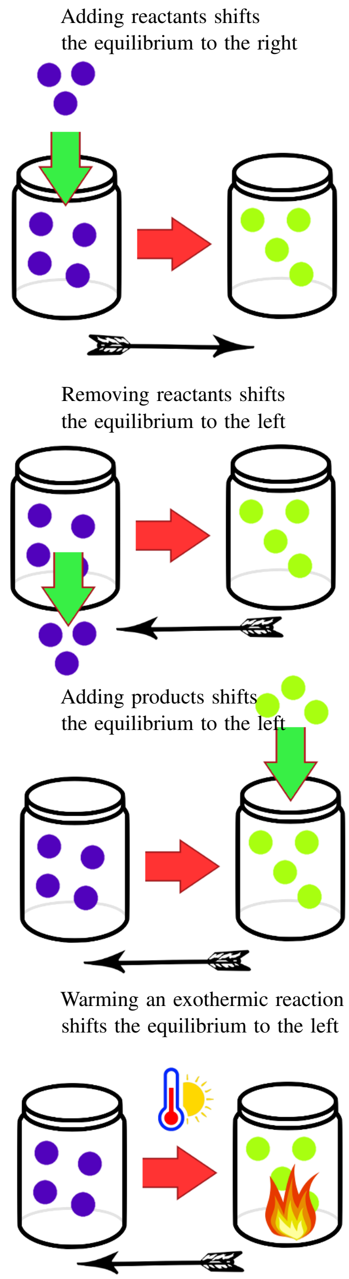


If we increase the temperature of the system, the equilibrium will be affected. To go back to an equilibrium state the reaction will decrease the temperature of the container. As the reaction produces heat, a way to decrease the system temperature is to generate reactants ($\longleftarrow$). Again, using the scale that means:



Differently now if we decrease the temperature, the reaction will increase the temperature by going back to its equilibrium state going from reactants $\longrightarrow$ to products. This is because heat is produced as a product





▼Le Châtelier principle helps predicts the outcome of altering an equilibrium mixture.

Table 1.2 Le Châtelier principle

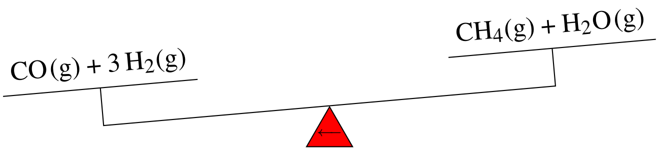
Parameter	Change	Effect
Concentration	Add reactants	$\longrightarrow$
	Remove reactants	$\longleftarrow$
	Add products	$\longleftarrow$
	Remove products	$\longrightarrow$
Volume	Increase volume	More moles
	Decrease volume	Less moles
Catalyst	Add a catalyst	No effect
Temperature	Endothermic reaction	
	Increase temperature	$\longrightarrow$
	Decrease temperature	$\longleftarrow$
Temperature	Exothermic reaction	
	Increase temperature	$\longleftarrow$
	Decrease temperature	$\longrightarrow$

`Volume change`

We can also think about increasing or decreasing the volume in which the reaction takes place. This change will have an impact on the reaction equilibrium as the concentrations of reactants and products will be altered by this change. Changes in volume will shift the reaction towards the left or right depending on the overall stoichiometric change of the reaction, that is on whether the reaction produces or consumes molecules. For reactions that generate matter, that is, in the case that $\Delta n > 0$, increasing the volume will follow the increase of the number of moles. In other words, by increasing the volume, the equilibrium will shift towards the products, that is towards the right. For reactions that consume matter ($\Delta n < 0$), increasing the volume will shift the equilibrium towards the reactants, that is towards the left. For example, the reaction below consumes molecules:

$$\mathrm{CO\,(g) + 3\,H_2\,(g) \rightleftharpoons CH_4\,(g) + H_2O\,(g)}$$

if we increase the volume of the container in which the reaction takes place, the equilibrium will shift towards the left:



The opposite shift will follow a volume decrease as the reaction shift towards the right.

Sample Problem 7

For the next endothermic reaction indicate whether the reaction will shift right ($\longrightarrow$) or left ($\longleftarrow$) after the following changes:

$$\mathrm{N_2\,(g) + O_2\,(g) + Heat \rightleftharpoons 2\,NO\,(g)}$$

(a) adding reactants (b) adding products (c) decreasing the temperature.

SOLUTION

(a) Adding reactants always displaces the equilirbium so that reactants are consumed, hence the reaction will proceed $\longrightarrow$. (b) After adding products the reaction will tend to reduce the amount of products, and hence it will go $\longleftarrow$. (c) The reaction is endothermic that means that it consumes heat. If we decrease the temperature it will tend to increase the temperature and hence heat needs to be formed. This will only happen if the reaction proceeds ($\longleftarrow$).

STUDY CHECK

For next exothermic reaction indicate whether the reaction will shift right ($\longrightarrow$) or left ($\longleftarrow$) after the following changes:

$$\mathrm{C\,(g) + O_2\,(g) \rightleftharpoons CO_2\,(g) + Heat}$$

(a) removing reactants (b) removing products (c) decreasing the temperature.

CHAPTER 1

Chemical Equilibrium

Equilibrium constants

1.1 True or false:(a) At equilibrium, the rate of the reverser reaction is twice the rate of the forward reaction (b) At equilibrium, the concentration of products do not change (c) At equilibrium, the concentration of reactants do not change (d) At equilibrium, the concentration of reactants and products do not change

1.2 True or false:(a) At equilibrium, the rate of the reverse reaction do not change (b) At equilibrium, the rate of the forward reaction do not change (c) At equilibrium, the rate of the reverse reaction equals the rate of the forward reaction (d) At equilibrium, the concentration of reactants and products are not constant

1.3 Write down the forward and reverse reactions for the following reactions in equilibrium:

(a) $CH_{4(g)} + O_{2(g)} \rightleftharpoons CO_{2(g)} + H_2O_{(g)}$

(b) $2\,Mg_{(s)} + O_{2(g)} \rightleftharpoons 2\,MgO_{(s)}$

1.4 For the reactions below and given the value of the equilibrium constant indicate whether the equilibrium mixture will have: (a) More reactants than products (b) More products than reactants (c) Same amount of products and reactants

(a) $CO_{2(g)} + H_2O_{(g)} \rightleftharpoons CH_{4(g)} + O_{2(g)}$ $\quad K_c = 0.001$

(b) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2\,NO_{(g)}$ $\quad K_c = 2 \cdot 10^{25}$

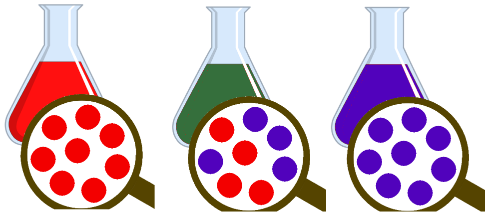
(c) $2\,NO_{(g)} + O_{2(g)} \rightleftharpoons 2\,NO_{2(g)}$ $\quad K_c = 6.4 \cdot 10^{9}$

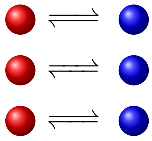
1.5 For the reactions below and given the value of the equilibrium constant indicate whether the equilibrium mixture will have: (a) More reactants than products (b) More products than reactants (c) Same amount of products and reactants

(a) $N_{2(g)} + 3\,H_{2(g)} \rightleftharpoons 2\,NH_{3(g)}$ $\quad K_c = 1$

(b) $2\,NO_{(g)} + Cl_{2(g)} \rightleftharpoons 2\,NOCl_{(g)}$ $\quad K_c = 6.5 \cdot 10^{4}$

1.6 Indicate which of the following diagrams represent better the system at equilibrium:





(a) $K_c = 10$

(b) $K_c = 0.1$

(c) $K_c = 1$

1.7 Write down the expression of K_c for the following reaction:

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

(b) $CO_{(g)} + 2\,H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$

(c) $C_2H_{6(g)} + Cl_{2(g)} \rightleftharpoons C_2H_2Cl_{(s)} + HCl_{(g)}$

1.8 Write down the expression of K_c for the following reaction:

(a) $BaCO_{3(s)} \rightleftharpoons Ba^{2+}_{(aq)} + {CO_3}^{2-}{}_{(aq)}$

(b) $2\,H_{2(g)} + O_{2(g)} \rightleftharpoons 2\,H_2O_{(l)}$

Using equilibrium constants

1.9 The reaction of carbon monoxode with hydrogen to produce methanol has a equilibrium constant in terms of concentration that at a certain temperature is larger than one

$$CO(g) + 2\,H_2(g) \rightleftharpoons CH_3OH(g) \qquad K_c = 14.5$$

Calculate: (a) the equilibrium concentration of hydrogen (H_2) given that the equilibrium concentration of methanol (CH_3OH) and carbon monoxice (CO) for the reaction is 2M, respectively. (b) the equilibrium concentration of hydrogen (H_2) given that the equilibrium concentration of methanol (CH_3OH) and carbon monoxide (CO) for the reaction are 3M and 1M, respectively.

1.10 Consider the following reaction:

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

(a) Write down the expression of K. (b) Calculate the numerical value of K for the reaction if the concentrations at equilibrium at 1000K are 2M for SO_3, 0.3M for O_2 and 1M for SO_2. (c) indicate whether an equilibrium mixture will contain mostly products, mostly reactants or maybe both.

1.11 Complete the table and calculate K_c and K_p at 300K:

Reaction	K_c	K_p
$2\,NH_{3(g)} \rightleftharpoons N_{2(g)} + 3\,H_{2(g)}$	17	
$2\,SO_{3(g)} \rightleftharpoons 2\,SO_{2(g)} + O_{2(g)}$	0.243	
$SO_2Cl_{2(g)} \rightleftharpoons SO_{2(g)} + Cl_{2(g)}$		0.05
$Cl_{2(g)} + Br_{2(g)} \rightleftharpoons 2\,BrCl_{2(g)}$		0.196

Concentration ratio

1.12 For the reactions below indicate whether they will evolve towards the right or towards the left in order to reach equilibrium.

Reaction	K_c	Q
$2\,NH_{3(g)} \rightleftharpoons N_2 + 3\,H_2$	17	20
$2\,SO_{3(g)} \rightleftharpoons 2\,SO_{2(g)} + O_{2(g)}$	0.243	10
$H_{2(g)} + I_2 \rightleftharpoons 2\,HI_{(g)}$	50	0.1
$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$	0.196	0.196

1.13 For the decomposition of calcium chloride hexahydrate

$$CaCl_2 \cdot 6\,H_2O(s) \rightleftharpoons CaCl_2(s) + 6\,H_2O(g)$$

we have that K_c=3.5 $\times$ 10^{-54} and Q=10 at 300K. Indicate towards which direction the reaction will evolve to reach equilibrium.

Le Châtelier principle

1.14 Using the Le Châtelier principle indicate whether the reaction below

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

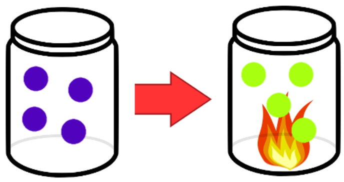
will shift in the direction of products ($\longrightarrow$) or reactants ($\longleftarrow$) after the following actions: (a) add SO_2 (b) add SO_3(c) remove O_2

1.15 According to Le Châtelier principle indicate whether the reaction will shift in the direction of products ($\longrightarrow$) or reactants ($\longleftarrow$):

(a) $CO(g) + 2\,H_2(g) \rightleftharpoons CH_3OH(g) + \text{Heat}$ increase temperature

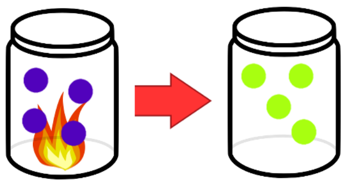
(b) $2\,B(s) + 3\,H_2(g) + \text{Heat} \rightleftharpoons B_2H_6(g)$ increase temperature

1.16 According to Le Châtelier principle indicate whether the following reaction will shift in the direction of products ($\longrightarrow$) or reactants ($\longleftarrow$) after the following changes:



(a) adding reactants (b) increasing temperature (c) decreasing temperature

1.17 According to Le Châtelier principle indicate whether the following reaction will shift in the direction of products ($\longrightarrow$) or reactants ($\longleftarrow$) after the following changes:



(a) adding products (b) removing products(c) increasing temperature

Answers **1.1** (a) At equilibrium, the rate of the reverser reaction is twice the rate of the forward reaction (False) (b) At equilibrium, the concentration of products do not change (False) (c) At equilibrium, the concentration of reactants do not change (False) (d) At equilibrium, the concentration of reactants and products do not change (True) **1.3** (a) $CH_{4(g)} + O_{2(g)} \longrightarrow CO_{2(g)} + H_2O_{(g)}$; $CH_{4(g)} + O_{2(g)} \longleftarrow CO_{2(g)} + H_2O_{(g)}$ (b) $2\,Mg_{(s)} + O_{2(g)} \longrightarrow 2\,MgO_{(s)}$;$2\,Mg_{(s)} + O_{2(g)} \longleftarrow 2\,MgO_{(s)}$ **1.5** (a) same amount (b) More products **1.7** (a) $K_c = \frac{\left[SO_3\right]^2}{\left[SO_2\right]^2 \cdot \left[O_2\right]}$; $K_p = \frac{p_{SO_3}^2}{p_{SO_2}^2 \cdot p_{O_2}}$ (b) $K_c = \frac{\left[CH_3OH\right]}{\left[H_2\right]^2 \cdot \left[CO\right]}$;$K_p = \frac{p_{CH_3OH}}{p_{H_2}^2 \cdot p_{CO}}$ (c) $K_c = \frac{\left[HCl\right]}{\left[C_2H_6\right] \cdot \left[Cl_2\right]}$; $K_p = \frac{p_{HCl}}{p_{C_2H_6} \cdot p_{Cl_2}}$ **1.9** (a) 0.034 M (b) 0.46M **1.11** (a) $2\,NH_{3(g)} \rightleftharpoons N_{2(g)} + 3\,H_{2(g)}$; 17 ;10288 (b) $2\,SO_{3(g)} \rightleftharpoons 2\,SO_{2(g)} + O_{2(g)}$; 0.243 ;5.977 (c) $SO_2Cl_{2(g)} \rightleftharpoons SO_{2(g)} + Cl_{2(g)}$; 2×10^{-3} ;0.05 (d) $Cl_{2(g)} + Br_{2(g)} \rightleftharpoons 2\,BrCl_{2(g)}$;0.196 ;0.196 **1.13** $<$ $-$ **1.15** (a) $\longleftarrow$ (b) $\longrightarrow$ **1.17** (a) $\longleftarrow$ (b) $\longrightarrow$ (c) $\longrightarrow$