

## 9

# Chemical equilibrium

**R**EACTIONS 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.

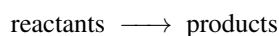


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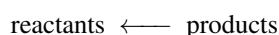
## 9.1 Chemical Equilibrium

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.

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

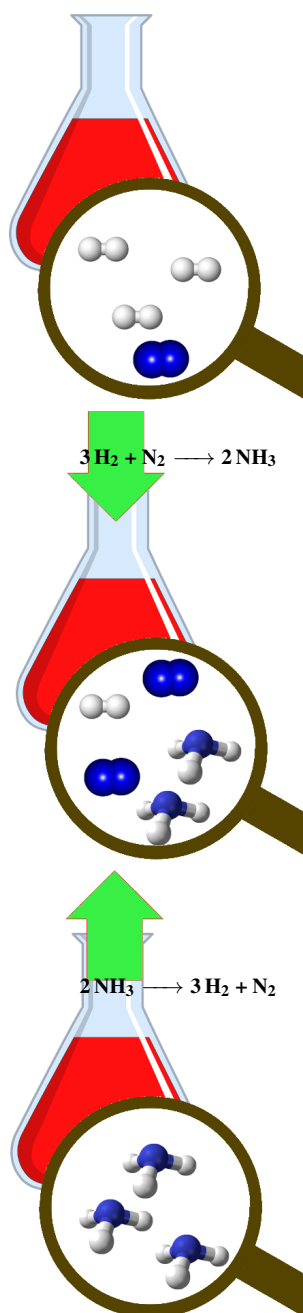


However, once the products form they can also generate reactants through the *reverse reaction*:



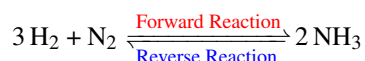
*Equilibrium* In chemical reactions, both the forward and the reverse reaction happen synchronously, so that when products form they also generate reactants. However, both the reverse and forwards reactions have different speeds. In the beginning, the forward reaction proceeds at a faster pace than the 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:





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

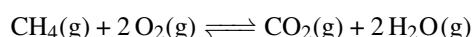
For example, the chemical process that forms ammonia from nitrogen and hydrogen can proceed using the forward and reverse reaction



*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:



#### SOLUTION

(a) The forward reaction is  $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$  and the reverse  $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \longleftarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$

#### STUDY CHECK

Write down the forward and reverse reactions for the reaction:



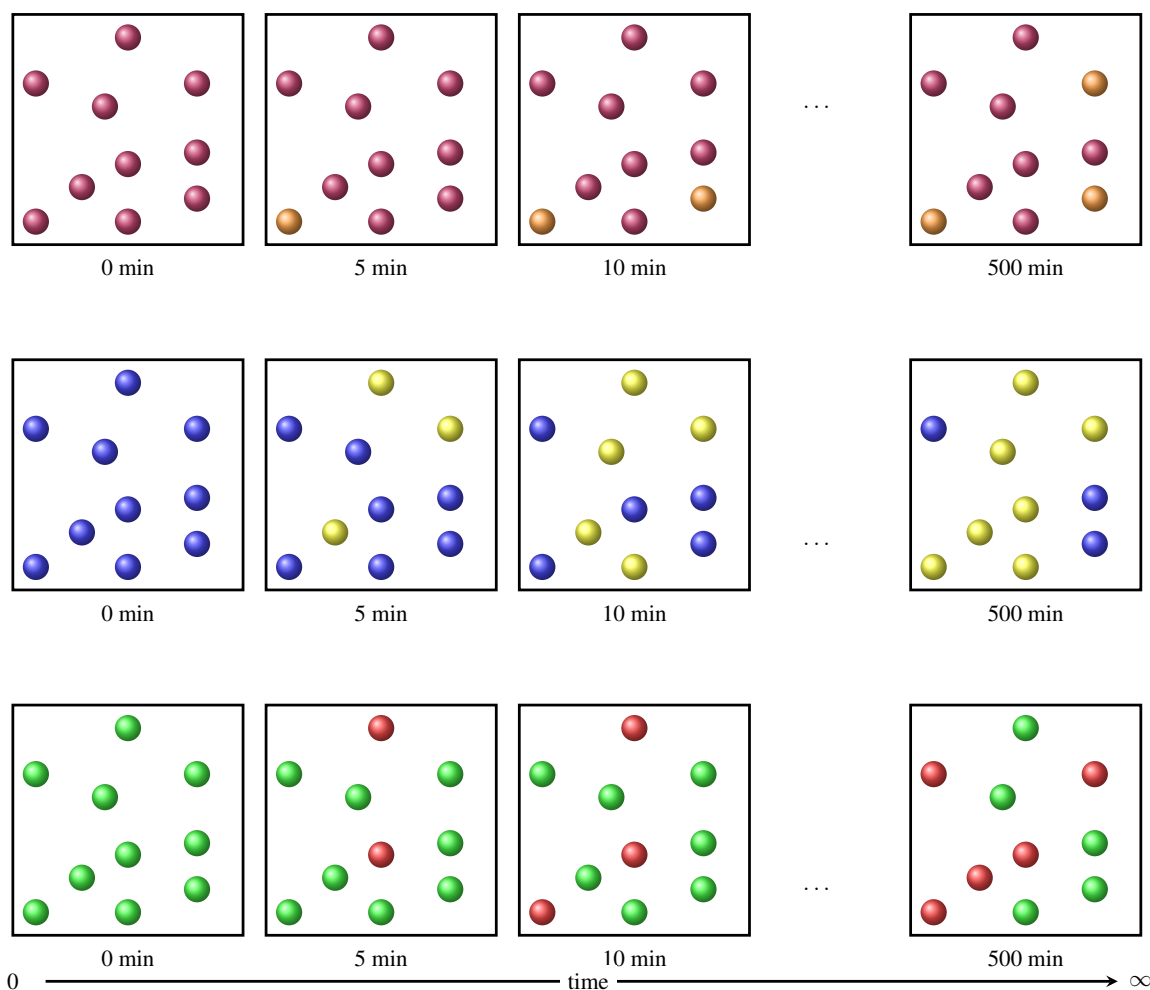
## 9.2 The equilibrium constant

Reactions in equilibrium are characterized by 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.

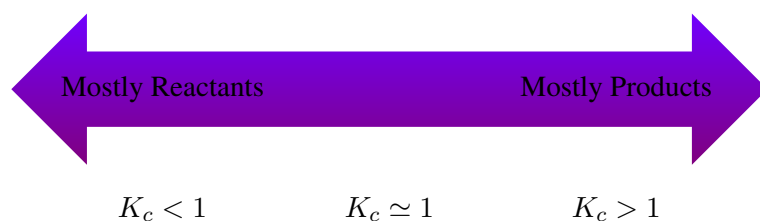
Table 9.1 Different  $K_c$  values at 298K

Reaction					$K_c$	Equilibrium mixture
$2 \text{NH}_3(\text{g})$	$\rightleftharpoons$	$\text{N}_2(\text{g})$	+	$3 \text{H}_2(\text{g})$	17	Products > Reactants
$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	$\rightleftharpoons$	$2 \text{HI}(\text{g})$	50	Products > Reactants
$2 \text{SO}_3(\text{g})$	$\rightleftharpoons$	$2 \text{SO}_2(\text{g})$	+	$\text{O}_2(\text{g})$	0.3	Products < Reactants
$\text{H}_2\text{O}(\text{l})$	$\rightleftharpoons$	$\text{H}_2\text{O}(\text{g})$			0.2	Products < Reactants



**Figure 9.1** 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.



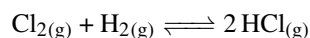
In terms of units, equilibrium constants are unit-less numbers—a number without units. In other words, they have no unit and they are simply expressed as a number.



▼ 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  $4 \times 10^{31}$ . Indicate whether the equilibrium mixture will contain mostly reactants, mostly products or both.



### SOLUTION

As  $K_c$  is larger than one, an equilibrium mixture of  $\text{Cl}_2$ ,  $\text{H}_2$  and  $\text{HCl}$  will contain mainly products, that is will be mainly made of  $\text{HCl}$ .

### STUDY CHECK

The value of  $K_c$  for  $\text{F}_2(g) \rightleftharpoons 2 \text{F}(g)$  at 500K is  $7 \times 10^{-13}$ . 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  $D$



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 use square brackets. For example  $[A]$  means the concentration of  $A$ . Hence, the expression of the equilibrium constant will be:

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b} \quad \text{Equilibrium constant} \quad (9.1)$$

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.

$$K_c = \frac{\overset{\substack{\blacktriangleleft \text{product concentration}}}{[C]^c \cdot [D]^d}}{\underset{\substack{\blacktriangleright \text{reactant coefficient}}}{[A]^a \cdot [B]^b}}$$

Let's focus on the reaction below:



The expression of the equilibrium constant would be:

$$K_c = \frac{[\text{CO}_2] \cdot [\text{H}_2\text{O}]^2}{[\text{CH}_4] \cdot [\text{O}_2]^2}$$

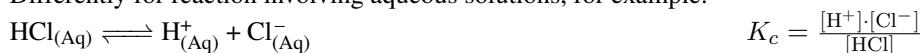
*Equilibrium involving solids, liquids and solutions* Let us analyze an example of a reaction involving solids or liquids:



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

$$K_c = [\text{CO}_2]$$

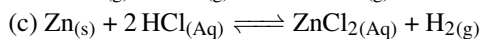
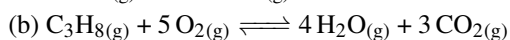
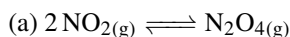
Differently for reaction involving aqueous solutions, for example:



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:



### SOLUTION

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

$$K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$$

For the second example,

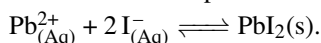
$$K_c = \frac{[\text{H}_2\text{O}]^4 \cdot [\text{CO}_2]^3}{[\text{C}_3\text{H}_8] \cdot [\text{O}_2]^5}$$

For the last example:

$$K_c = \frac{[\text{ZnCl}_2] \cdot [\text{H}_2]}{[\text{HCl}]^2}$$

### STUDY CHECK

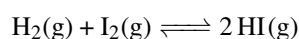
Write down the expression of  $K_c$  for the following reaction:



## 9.3 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 ( $\text{H}_2$ ) and iodine ( $\text{I}_2$ ) to produce hydrogen iodide ( $\text{HI}$ ):



The equilibrium constant at 300K is  $3 \cdot 10^{-1}$ . Analyzing a reaction mixture we find that the concentration of  $\text{H}_2$  is 1M and the concentration of  $\text{I}_2$  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  $[HI]$ . The expression for  $K_c$  is:

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

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

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

Solving for  $[HI]$  we have

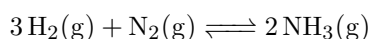
$$[HI]^2 = 1.2$$

To solve for  $[HI]$  we have to use an square root:

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

#### Sample Problem 4

The value of the equilibrium constant for the reaction



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:

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

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

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

we can solve for  $[H_2]$ :

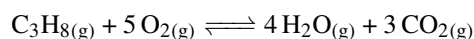
$$[H_2]^3 = 6.6 \cdot 10^{-9}$$

In order to obtain  $[H_2]$  we need a cubic root:

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

#### STUDY CHECK

The value of the equilibrium constant for the reaction



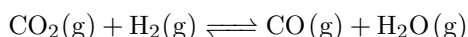
is 500 at a given temperature. An analysis of an equilibrium mixture gave a concentration of water, carbon dioxide and  $C_3H_8$  of 1M. Calculate the equilibrium concentration of oxygen at that temperature.

## 9.4 Le Châtelier principle

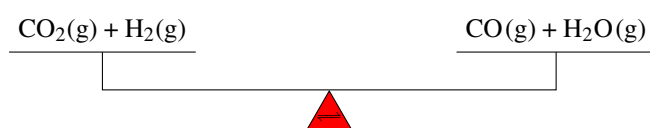
At this point, we have covered the idea of equilibrium and we have seen that the forward and reverse reactions have the same rate at equilibrium. Now, what happens if you alter this equilibrium? Le Châtelier principle claims a reaction will go back to its original equilibrium state by shifting left or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

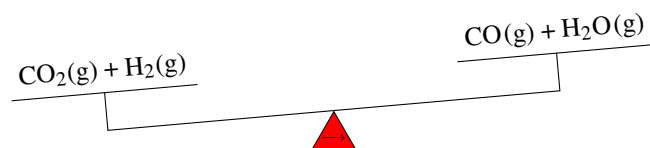
*Change in concentration* Let us consider the following equilibrium:



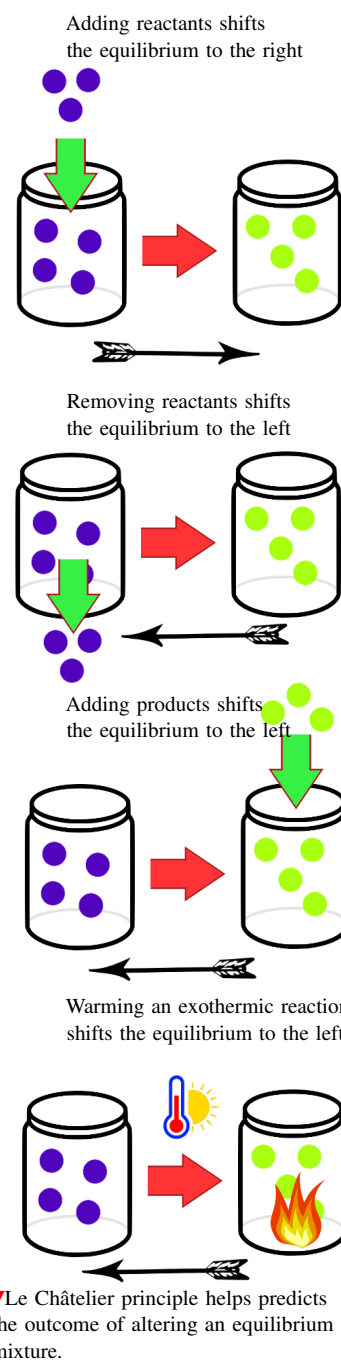
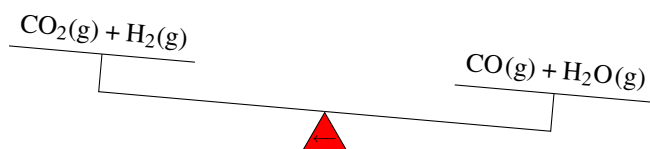
$K_c$  for this reaction equals to one at 1200K. This means that the concentration of reactants and products are the same. We can represent this by means of this balance or seesaw



If we add some  $\text{CO}_2$  the equilibrium will be affected. To counteract on this stress, the reaction will restore the equilibrium by decreasing the amount of  $\text{CO}_2$ . This can only be achieved by displacing the equilibrium to the right, so that  $\text{CO}_2$  is removed. Mind that  $\text{CO}_2$  is consumed if the reaction moves from reactants  $\rightarrow$  to products and it is produced when going from products  $\leftarrow$  to reactants. We can represent this with the following seesaw.



As we added  $\text{CO}_2$  the reactants now weight more and hence the reaction has to proceed to the right  $\rightarrow$ . Now imagine we remove some  $\text{CO}_2(\text{g})$ . Again, the equilibrium will be affected and the reaction will restore its equilibrium state by by doing the opposite, that is producing  $\text{CO}_2(\text{g})$  as the reaction proceeds from reactants  $\leftarrow$  to products. Again using the seesaw:

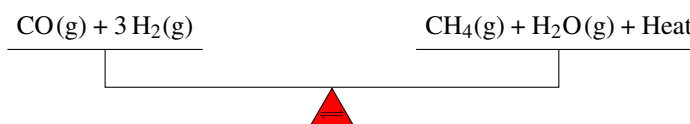


We can also add a different chemical that is not involved in the equilibrium. In this case, the equilibrium will not be affected by this change.

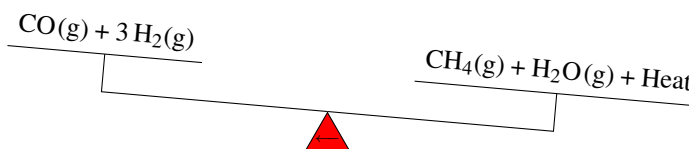
*Temperature change* Let us consider the following equilibrium that produces heat—remember we describe these types of reactions as exothermic:



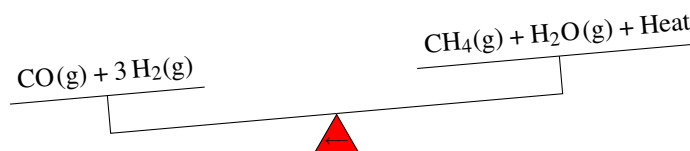
Again, this reaction is in equilibrium so we can use the same seesaw analogy.



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 (  $\leftarrow$  ). Again, using the scale that means:

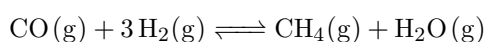


Differently now if we decrease the temperature, the reaction will increase the temperature by going back to its equilibrium state going from reactants  $\rightarrow$  to products. This is because heat is produced as a product

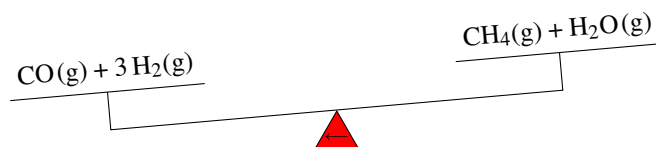




**Volume change** We can also think about increasing or decreasing the volume in which the reaction takes place. This change will have an impact on the reaction equilibrium as the concentrations of reactants and products will be altered by this change. Changes in volume will shift the reaction towards 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:



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.

**Table 9.2 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	$\longrightarrow$
Temperature	Decrease temperature	$\longleftarrow$
	Exothermic reaction	
	Increase temperature	$\longleftarrow$
	Decrease temperature	$\longrightarrow$

#### Sample Problem 5

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



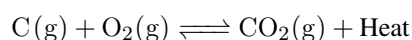
(a) adding reactants (b) adding products (c) decreasing the temperature.

#### **SOLUTION**

(a) Adding reactants always displaces the equilibrium 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:



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

## CHAPTER 9

### CHEMICAL EQUILIBRIUM

**9.1** True or false: (a) At equilibrium, the rate of the reverse 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

**9.2** 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

### EQUILIBRIUM CONSTANTS

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

- (a)  $\text{CH}_4(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$   
 (b)  $2 \text{Mg}(\text{s}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{MgO}(\text{s})$

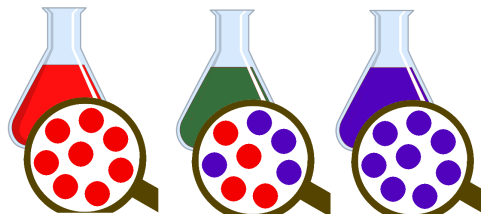
**9.4** For the reactions below and given the value of the equilibrium constant indicate whether the equilibrium mixture will have: (a) More reactants than products (b) More products than reactants (c) Same amount of products and reactants

- (a)  $\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CH}_4(\text{g}) + \text{O}_2(\text{g}) \quad K_c = 0.001$   
 (b)  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g}) \quad K_c = 2 \cdot 10^{25}$   
 (c)  $2 \text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g}) \quad K_c = 6.4 \cdot 10^9$

**9.5** 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)  $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g}) \quad K_c = 1$   
 (b)  $2 \text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2 \text{NOCl}(\text{g}) \quad K_c = 6.5 \cdot 10^4$

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



- (a)  $\text{red} \rightleftharpoons \text{blue} \quad K_c = 10$   
 (b)  $\text{red} \rightleftharpoons \text{blue} \quad K_c = 0.1$   
 (c)  $\text{red} \rightleftharpoons \text{blue} \quad K_c = 1$

**9.7** Write down the expression of  $K_c$  for the following reaction:

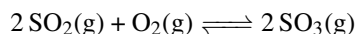
- (a)  $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$   
 (b)  $\text{CO}(\text{g}) + 2 \text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$   
 (c)  $\text{C}_2\text{H}_6(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{C}_2\text{H}_5\text{Cl}(\text{g}) + \text{HCl}(\text{g})$

**9.8** Write down the expression of  $K_c$  for the following reaction:

- (a)  $\text{BaCO}_3(\text{s}) \rightleftharpoons \text{Ba}^{2+}_{(\text{aq})} + \text{CO}_3^{2-}_{(\text{aq})}$   
 (b)  $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{H}_2\text{O}(\text{l})$

### LE CHÂTELIER PRINCIPLE

**9.9** Using the Le Châtelier principle indicate whether the reaction below

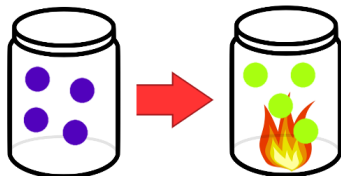


will shift in the direction of products (  $\longrightarrow$  ) or reactants (  $\longleftarrow$  ) after the following actions: (a) add  $\text{SO}_2$  (b) add  $\text{SO}_3$  (c) remove  $\text{O}_2$

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

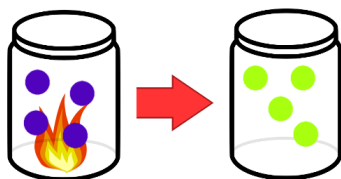
- (a)  $\text{CO}(\text{g}) + 2 \text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g}) + \text{Heat}$  increase temperature  
 (b)  $2 \text{B}(\text{s}) + 3 \text{H}_2(\text{g}) + \text{Heat} \rightleftharpoons \text{B}_2\text{H}_6(\text{g})$  increase temperature

**9.11** 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

**9.12** 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 9.1** (a) At equilibrium, the rate of the reverse 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) **9.3** (a)  $\text{CH}_4(\text{g}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$ ;  $\text{CH}_4(\text{g}) + \text{O}_2(\text{g}) \longleftarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$  (b)  $2 \text{Mg}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow 2 \text{MgO}(\text{s})$ ;  $2 \text{Mg}(\text{s}) + \text{O}_2(\text{g}) \longleftarrow 2 \text{MgO}(\text{s})$  **9.5** (a) same amount (b) More products **9.7** (a)  $K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 \cdot [\text{O}_2]}$ ;  $K_p = \frac{p_{\text{SO}_3}^2}{p_{\text{SO}_2}^2 \cdot p_{\text{O}_2}}$   
 (b)  $K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{H}_2]^2 \cdot [\text{CO}]}$ ;  $K_p = \frac{p_{\text{CH}_3\text{OH}}}{p_{\text{H}_2}^2 \cdot p_{\text{CO}}}$  (c)  $K_c = \frac{[\text{HCl}]}{[\text{C}_2\text{H}_6] \cdot [\text{Cl}_2]}$ ;  $K_p = \frac{p_{\text{HCl}}}{p_{\text{C}_2\text{H}_6} \cdot p_{\text{Cl}_2}}$  **9.9** (a)  $\longrightarrow$  (b)  $\longleftarrow$   
 (c)  $\longleftarrow$  **9.11** (a)  $\longrightarrow$  (b)  $\longleftarrow$  (c)  $\longrightarrow$