

# Ch. 4. Chemical equilibrium

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.

## 4.1 Chemical Equilibrium

This section covers basic ideas about chemical equilibrium. First, we will introduce the concept of the forward and reverse reactions. 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*:

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

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

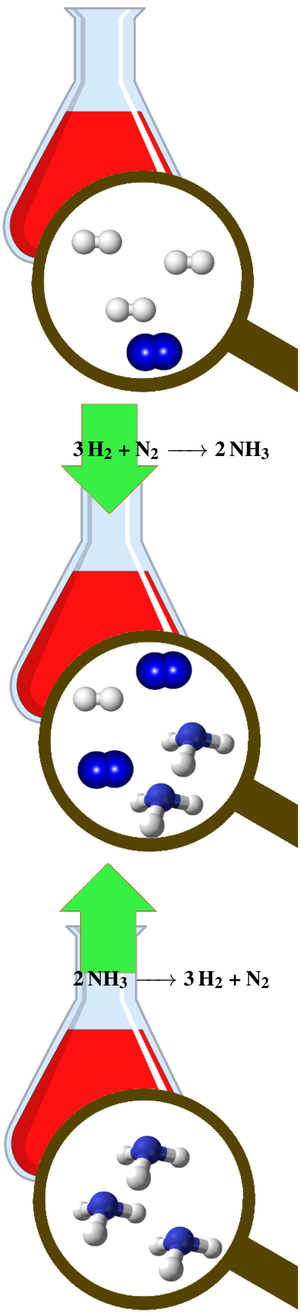
$$\text{reactants} \longleftarrow \text{products}$$

*Equilibrium* In chemical reactions, both the forward and the reverse reactions happen synchronously, so that when products form they also generate reactants. However, both the reverse and forward 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

$$3\,H_{2(g)} + N_{2(g)} \underset{\text{Reverse Reaction}}{\overset{\text{Forward Reaction}}{\rightleftharpoons}} 2\,NH_{3(g)}$$




▼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 before 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 that depend on temperature. 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:

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

## 4.2 The equilibrium constant

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

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

**Table 4.1 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 |

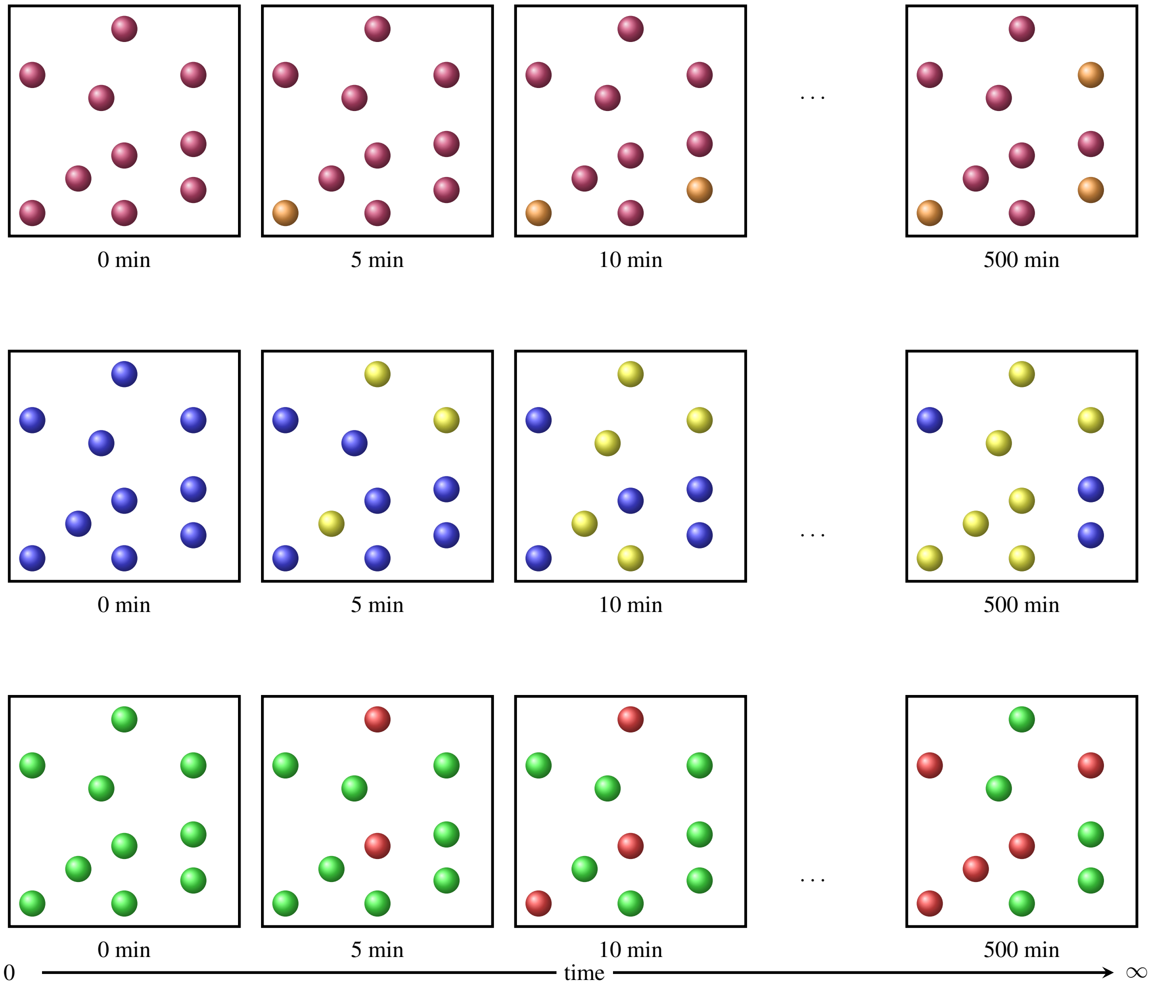
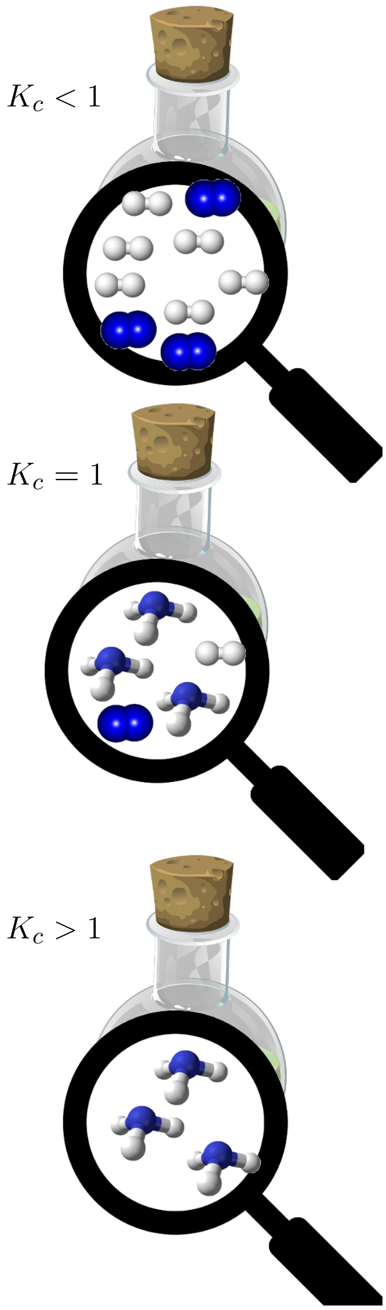



**Figure 4.1** Three equilibrium situations

`The equilibrium constant of a reaction` The equilibrium constant associated with a reaction $K_c$ indicates whether reactants or products are abundant 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 (see Figure 4.1). 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 (see Table 4.1 for examples).


$K_c < 1$ $K_c \simeq 1$ $K_c > 1$

In terms of units, equilibrium constants are unitless 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.

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

**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 $7 \times 10^{-13}$. 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 $D$

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

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. 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:

$$\boxed{K_c = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}} \quad \text{Equilibrium constant} \qquad (4.1)$$

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 be included in the expression of $K_c$. For the example above:

$$K_c = [CO_2]$$

Differently for a 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 $K_p$.

$$\boxed{K_p = \frac{P_{\text{Products}}}{P_{\text{Reactants}}} = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}} \quad \text{Equilibrium constant} \qquad (4.2)$$

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 implies 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:

$$\boxed{K_p = K_c(RT)^{\Delta n}} \tag{4.3}$$

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)
$\Delta n$ is the change of stoichiometry of the reaction

Let us analyze the role of $\Delta n$ for the reaction:

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

$\Delta n$ 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 of the relationship will depend on the stoichiometry of the reaction. At the same time, the relationship between both constants 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 $\Delta n$ 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.

## 4.3 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 we have in the mixture. As the concentrations of reactants and products are linked together through $K_c$ we can certainly solve for $[\mathrm{HI}]$. The expression for $K_c$ is:

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

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

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

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

$$[\mathrm{HI}]^2 = 0.6$$

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

$$[\mathrm{HI}] = \sqrt[2]{0.6} = 0.77M$$

**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:

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

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

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

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

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

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

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

**STUDY CHECK**

The value of the equilibrium constant for the reaction

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

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

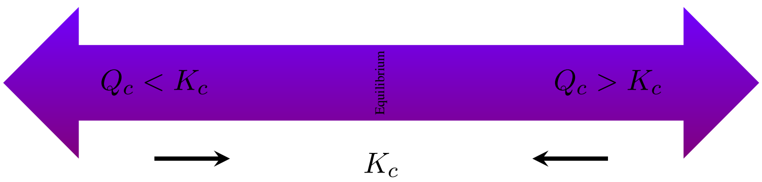
## 4.4 Concentration or pressure ratio

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 toward the right, hence producing products, or the left to produce reactants? This section introduces the use of a concentration (or pressure) ratio that helps predict the direction in which a mixture of reactants and products will proceed toward equilibrium.

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

$$\boxed{Q_c = \frac{[\text{Products}]_{noneq}}{[\text{Reactants}]_{noneq}} = \frac{[C]^c_{noneq} \cdot [D]^d_{noneq}}{[A]^a_{noneq} \cdot [B]^b_{noneq}}} \quad \text{concentration ratio} \tag{4.4}$$

`Use of concentration ratios` Concentration ratios help predict whether a reaction will proceed toward the left or toward 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 $K_c$ 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 |
| $Q_c$ | $3.8 \times 10^{-4}$ | 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:

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

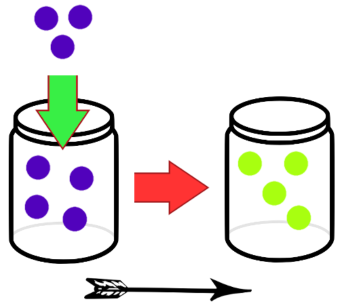
Indicate if the mixture is in equilibrium. If it is not, indicate whether the reaction will evolve towards the left or the right to reach equilibrium.

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

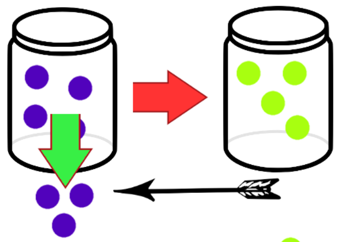
## 4.5 Le Châtelier principle

▼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.

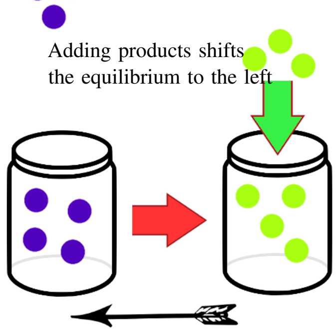
Adding reactants shifts the equilibrium to the right



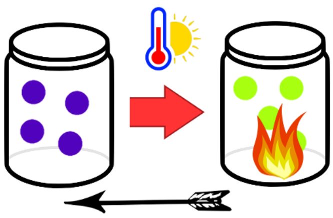
Removing reactants shifts the equilibrium to the left



Adding products shifts the equilibrium to the left



Warming an exothermic reaction shifts the equilibrium to the left



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

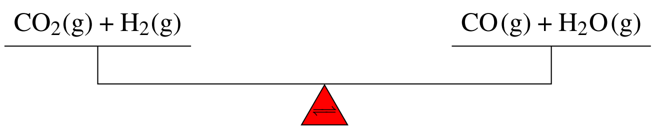
At this point, we have covered the idea of equilibrium and we have seen that the forward and reverse reactions have the same rate at equilibrium. Now, what happens if you alter this equilibrium? Le Châtelier principle claims a reaction will go back to its original equilibrium state by shifting left or 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 stress is placed in a reaction (adding or removing reactant or products, increasing or decreasing temperature) the equilibrium will be shifted in the direction that relieves that stress. Table 4.2 displays different aspects regarding Le Châtelier's principle in terms of parameter change and consequence.

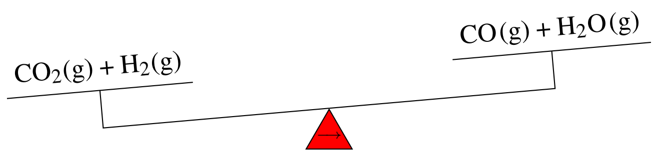
`Change in concentration` Let us consider the following equilibrium:

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

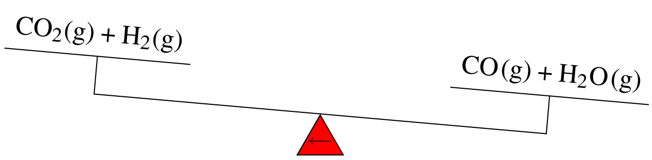
$K_c$ for this reaction equals one at 1200K. This means that the concentration of reactants and products are the same. We can represent this using this balance or seesaw




If we add some $CO_2$ the equilibrium will be affected. To counteract 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 weigh 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 doing the opposite, that is producing $CO_2(g)$ as the reaction proceeds from reactants $\longleftarrow$ to products. Again using the seesaw:

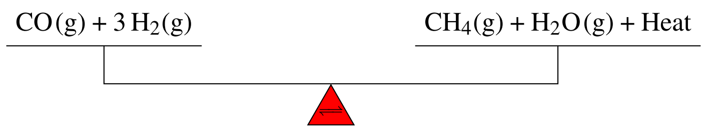



We can also add a different chemical that is not involved in the equilibrium. In this case, the equilibrium will not be affected by this change.

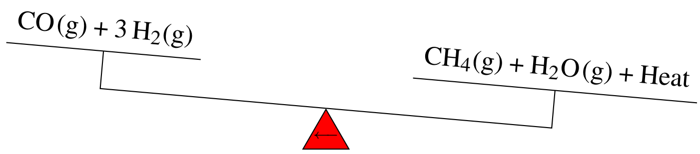
*Temperature change* Let us consider the following equilibrium that produces heat–remember we describe these types of reactions as exothermic:

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

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

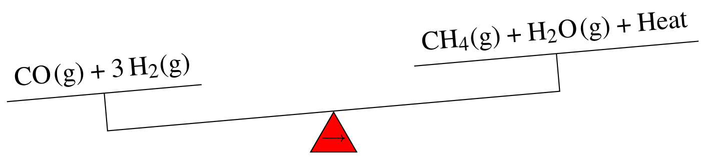


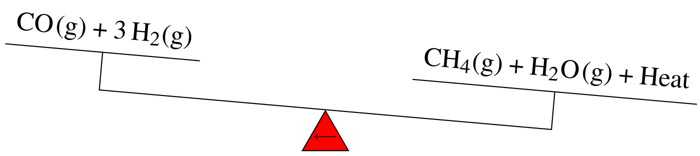
**Table 4.2 Le Châtelier principle**

| 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 | $\longleftarrow$ |
| 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:

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

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

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

(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:

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

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

# CHAPTER 4

## Chemical Equilibrium

**4.1** 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

**4.2** 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

**4.3** 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) $2\,Mg_{(s)} + O_{2(g)} \rightleftharpoons 2\,MgO_{(s)}$

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

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

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

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

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

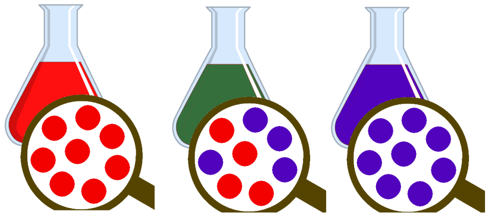
(c) $2\,NO_{(g)} + O_{2(g)} \rightleftharpoons 2\,NO_{2(g)}$ $\quad K_c = 6.4 \cdot 10^{9}$

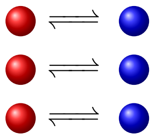
**4.6** For the reactions below and given the value of the equilibrium constant indicate whether the equilibrium mixture will have: (a) More reactants than products (b) More products than reactants (c) Same amount of products and reactants

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

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

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



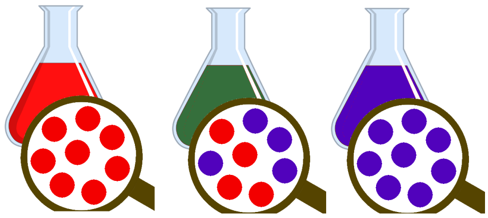


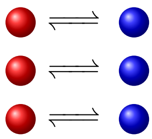
(a) $K_c = 10$

(b) $K_c = 0.1$

(c) $K_c = 1$

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





(a) $K_c = 1$

(b) $K_c = 0.04$

(c) $K_c = 200$

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

**4.10** 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

**4.11** 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.

**4.12** Consider the following reaction:

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

(a) Write down the expression of $K_c$. (b) Calculate the numerical value of $K_c$ 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 equal amounts of reactants and products.

**4.13** Complete the table and calculate $K_c$ and $K_p$ at 300K:

| | Reaction | $K_c$ | $K_p$ |
|---|---|---|---|
| (a) | $2\,NH_{3(g)} \rightleftharpoons N_{2(g)} + 3\,H_{2(g)}$ | 17 | |
| (b) | $SO_2Cl_{2(g)} \rightleftharpoons SO_{2(g)} + Cl_{2(g)}$ | | 0.05 |

**4.14** Complete the table and calculate $K_c$ and $K_p$ at 300K:

| | Reaction | $K_c$ | $K_p$ |
|---|---|---|---|
| (a) | $2\,SO_{3(g)} \rightleftharpoons 2\,SO_{2(g)} + O_{2(g)}$ | 0.243 | |
| (b) | $Cl_{2(g)} + Br_{2(g)} \rightleftharpoons 2\,BrCl_{2(g)}$ | | 0.196 |

### Concentration ratio

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

| | Reaction | $K_c$ | $Q$ |
|---|---|---|---|
| (a) | $2\,NH_{3(g)} \rightleftharpoons N_2 + 3\,H_2$ | 17 | 20 |
| (b) | $2\,SO_{3(g)} \rightleftharpoons 2\,SO_{2(g)} + O_{2(g)}$ | 0.243 | 10 |

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

| | Reaction | $K_c$ | $Q$ |
|---|---|---|---|
| (a) | $H_{2(g)} + I_2 \rightleftharpoons 2\,HI_{(g)}$ | 50 | 0.1 |
| (b) | $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$ | 0.196 | 0.196 |

**4.17** 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.

**4.18** For the decomposition of calcium chloride hexahydrate

$$2\,NH_{3(g)} \rightleftharpoons N_2 + 3\,H_2$$

we have that $K_c$=17 and $Q$=10 at 300K. Indicate towards which direction the reaction will evolve to reach equilibrium.

### Le Châtelier principle

**4.19** 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 $O_2$

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

$$2\,NH_{3(g)} \rightleftharpoons N_2 + 3\,H_2$$

will shift in the direction of products ( $\longrightarrow$ ) or reactants ( $\longleftarrow$ ) after the following actions: (a) add $NH_3$ (b) add $N_2$(c) remove $H_2$

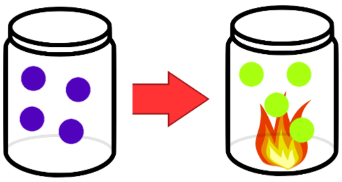
**4.21** According to Le Châtelier principle indicate whether the reaction will shift in the direction of products ( $\longrightarrow$ ) or reactants ( $\longleftarrow$ ) after we increase temperature:

$$CO(g) + 2\,H_2(g) \rightleftharpoons CH_3OH(g) + Heat$$

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

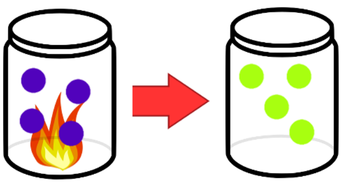
$$2\,B(s) + 3\,H_2(g) + Heat \rightleftharpoons B_2H_6(g)$$

**4.23** 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

**4.24** 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** **4.1** (a) False (b) False (c) False (d) True **4.2** (a) True (b) True (c) True (d) False **4.3** (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) $2\,Mg_{(s)} + O_{2(g)} \longrightarrow 2\,MgO_{(s)}$;$2\,Mg_{(s)} + O_{2(g)} \longleftarrow 2\,MgO_{(s)}$ **4.4** (a) $BaCO_{3(s)} \longrightarrow Ba^{2+}_{(aq)} + {CO_3}^{2-}{}_{(aq)}$; $BaCO_{3(s)} \longleftarrow Ba^{2+}_{(aq)} + {CO_3}^{2-}{}_{(aq)}$ (b) $2\,H_{2(g)} + O_{2(g)} \longrightarrow 2\,H_2O_{(l)}$ ; $2\,H_{2(g)} + O_{2(g)} \longleftarrow 2\,H_2O_{(l)}$ **4.5** (a) More reactants (b) More products (c) More products **4.6** (a) same amount (b) More products **4.7** (a) Left (b) Right (c) Center **4.8** (a) Center (b) Right (c) Left **4.9** (a) $K_c = \frac{\left[SO_3\right]^2}{\left[SO_2\right]^2 \cdot \left[O_2\right]}$ ; $K_p = \frac{p^2_{SO_3}}{p^2_{SO_2} \cdot p_{O_2}}$ (b) $K_c = \frac{\left[CH_3OH\right]}{\left[H_2\right]^2 \cdot \left[CO\right]}$;$K_p = \frac{p_{CH_3OH}}{p^2_{H_2} \cdot p_{CO}}$ (c) $K_c = \frac{\left[HCl\right]}{\left[C_2H_6\right] \cdot \left[Cl_2\right]}$ ; $K_p = \frac{p_{HCl}}{p_{C_2H_6} \cdot p_{Cl_2}}$ **4.10** (a) $\left[Ba^{2+}\right] \cdot \left[{CO_3}^{2-}\right]$ (b) $\frac{1}{\left[H_2\right]^2 \cdot \left[O_2\right]}$ **4.11** (a) 0.034 M (b) 0.46M **4.12** (a) $\frac{\left[SO_3\right]^2}{\left[SO_2\right]^2 \cdot \left[O_2\right]}$ (b) 13.3 (c) mostly products **4.13** (a) $K_c$ =17 ;$K_p$ =10288 (b) $K_c = 2 \times 10^{-3}$ ;$K_p$ =0.05 **4.14** (a) $K_c$ =0.243 ;$K_p$ =5.977 (b) $K_c$ =0.196 ;$K_p$ =0.196 **4.15** (a) $<-$ (b) $<-$ **4.16** (a) $->$ (b) $<=>$ **4.17** $<-$ **4.18** $->$ **4.19** (a) $\longrightarrow$ (b) $\longleftarrow$ (c) $\longleftarrow$ **4.20** (a) $\longrightarrow$ (b) $\longleftarrow$ (c) $\longrightarrow$ **4.21** $\longleftarrow$ **4.22** $\longrightarrow$ **4.23** (a) $\longrightarrow$ (b) $\longleftarrow$ (c) $\longrightarrow$ **4.24** (a) $\longleftarrow$ (b) $\longrightarrow$ (c) $\longrightarrow$