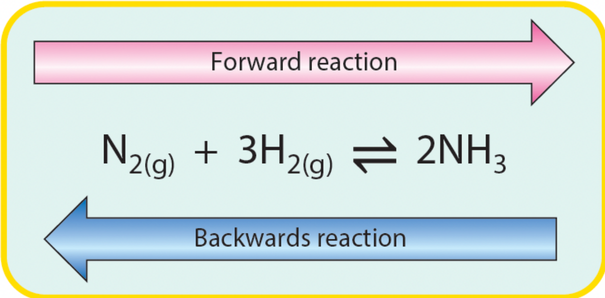
Chapter 21: Chemical Equilibrium

Many chemical reactions are **reversible reactions**. These are reactions in which reactants react to form products, but products can also react together to form reactants.



When the rates of the forward and backward reactions have become equal, and when the concentrations of reactants and products have become constant, chemical equilibrium – a state of balance - has been reached.

It is important to note that this is all assumed to occur in a **closed system**.

Chemical equilibrium is a state in which the **rate** of the forward reaction is equal to the **rate** of the backward reaction.

Chemical equilibrium is a state reached in a reversible reaction when the concentrations of reactants and products remain constant.

Chemical equilibrium is said to be dynamic because, at equilibrium, there are reactions continuously occurring.

The **state of equilibrium can be achieved from either direction of the reaction.**

Product-favoured = forward reaction favoured
Reactant-favoured = backwards reaction favoured

ΔH is always given for the forward reaction.
A **negative ΔH** indicates that the forward reaction is **exothermic**
A **positive ΔH** indicates that the forward reaction is **endothermic.**

Le Châtelier's principle

Le Châtelier's Principle states that systems at equilibrium react to oppose applied stresses.

- A 'stress' is any change in the conditions of the system.
- A change in temperature, pressure or concentration would all be considered a stress on the system.
- It is important to note that the system will absorb the stress and reach equilibrium again. When the **rates** of the forward and backward reactions **once again become equal, equilibrium is re-established.**
- **The position of equilibrium, however, will have changed, along with the concentrations of the reactants and products.**

Applying Le Châtelier's principle

Stress	System wants to	It will favour
Increase temperature	Lower temperature back down - absorb extra heat	Endothermic
Decrease temperature	Raise temperature back up - produce extra heat	Exothermic
Addition of reactant	Use up extra reactant	Favour forward reaction
Addition of product	Use up extra product	Favour backward reaction
For reactions Involving all-gases and unequal number of molecules		
Increase pressure	Lower pressure back down	Reaction producing the smaller number of molecules
Decrease pressure	Raise pressure back up	Reaction producing the larger number of molecules
Adding a catalyst has no effect on the position of equilibrium. It only causes equilibrium to be reached faster		

A change in pressure **will only have an affect on all-gaseous reactions with unequal number of molecules.**

Catalysts:

- lower the activation energy of both the forward and backwards reactions.
- speed up the rate at which equilibrium is reached
- do not change the position of equilibrium

There is no point adding a catalyst once equilibrium has already been reached – it will have no effect.

Using Le Châtelier's principle to predict optimal conditions

We can also use Le Châtelier's principle to predict conditions for optimising product yields.

Optimising product yields = favouring FORWARD reaction.

Example 1

The forward reaction of the following equation is endothermic: $\mathbf{CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}}$
How would you maximise the yield of methanol, CH_3OH?

Example 2

What conditions of temperature and pressure would maximise the yield of nitrogen?
$2NO_{(g)} \rightleftharpoons N_{2(g)} + O_{2(g)}$ $\Delta H = -183$ kJ

Experiment Investigation 21: Investigating how changes in temperature and concentration can affect the state of equilibrium.

This can be investigated by carrying out an experiment *(see page 334 of the textbook & page 49 of the lab book for more),* or by using secondary data.

You must be able to predict and explain the colours seen when a solution at equilibrium is subjected to increased/ decreased temperature, and when the concentration of reactants is increased/ decreased. You can do this by applying your knowledge of Le Châterler's principle (see notes above).

K_c – the equilibrium constant

A value greater than one = product-favoured
A value less than one = reactant-favoured

Only a change in temperature will affect the value of K_c.
A change in concentration, pressure or catalyst **will not affect** the K_c value.

Writing K_c expressions

- **Place products on the top**
- **Place reactants on the bottom**
- Place everything in **square brackets**
- When there is more than one reactant or product the concentrations are **multiplied** together.
- Any reactant or product that has a number in front of it in the chemical equation is **set to the power of that number** when written in the K_c expression.

Factors that affect K_c

Only a change in temperature will affect the value of K_c (i.e. if the temperature changes, K_c changes). A change in concentration, pressure or catalyst will not affect the K_c value.

Example 3

The value for K_c for the following equation is 2.5 at a given temperature.

$$PCl_3 + Cl_2 \rightleftharpoons PCl_5 \qquad \Delta H = -87.9 \text{ kJ mol}^{-1}$$

(a) If the temperature were increased, what would be the effect, if any, on the value of K_c? Explain your answer.
(b) Additional Cl_2 was added to the container holding the equilibrium mixture. Why is the value of K_c for the new equilibrium the same as before, i.e. 2.5?

(a) If the temperature is increased, the system will respond by favouring the endothermic reaction – here, that's the backwards reaction. Equilibrium shifts to the left, more reactants are formed, and the value of K_c decreases.

(b) A change in concentration does not affect the value of K_c. Only a change in temperature affects K_c.

K_c calculations

If finding K_c = no need to use X **If given K_c = must use 'x'**

Step One: Write an expression for K_c

Step Two: Draw and fill in a RICE @1L table.

Step 3: Sub values into K_c expression and solve!

R- Reaction			
I – Initially			
C - Change			
E – equilibrium			
@1L			

R = Ratio: Fill in the ratio of the reactants and products

I = Initially: Fill in the number of moles of reactants and products at the start of the reaction.

C = Change: How many moles were used up or formed as the reaction proceeds?

E = Equilibrium: How many moles of each substance are present at equilibrium?

@ 1L – You must divide by the size of the container (in L) to find the moles/L.
Note: The values subbed into a RICE table must be in mole

The **change for the product(s)** is **always positive** (it is being produced)
The **change for reactants** is **always negative** (they are being used up).

**** CAREFUL: The MAIN MISTAKE students make is that they do not remember to calculate the change using the RATIO. ****

Example 5

In an experiment 6.0 moles of nitrogen and 18.0 moles of hydrogen were mixed and allowed to come to equilibrium in a sealed 5L vessel at a certain temperature. It was found that there were 6 moles of ammonia in the equilibrium mixture. Write the equilibrium constant expression for the reaction (shown below) and calculate the value of the equilibrium constant (K_c) at this temperature.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta H = -92.4 \text{ kJ}$$

Step One: Write an expression for K_c

Step Two: Draw and fill in a RICE @1L table.

Step 3: Sub values into K_c expression and solve!

Example 6

In the Contact process for the manufacture of sulfuric acid, the key stage is the reaction of sulfur dioxide and oxygen, in contact with a vanadium(V) oxide (V_2O_5) catalyst, to form sulfur trioxide. Chemical equilibrium is established according to the following balanced equation:

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \qquad \Delta H = -196 \text{ kJ}$$

A mixture of 96g of sulfur dioxide and 24g of oxygen was placed in a 50 litre container and reached equilibrium with sulfur trioxide at a certain temperature. At equilibrium, 112g of sulfur trioxide were present.

(a) Write the equilibrium constant (K_c) expression for this reaction.

(b) Calculate the value of K_c under these conditions.

Step One: Write an expression for K_c

Step Two: Draw and fill in a RICE @1L table.

Step 3: Sub values into K_c expression and solve!

K_c calculations using the quadratic formula

When you are **given K_c** and asked to calculate concentrations of reactants and/or products, **you must use x to indicate unknown quantities and you will be solving the equation containing x using the quadratic formula or by taking the square root of both sides).**

Example 7

At 373K, the value of K_c for the following reaction is 4.

$$\mathbf{CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}}$$

Calculate the number of moles of ethyl ethanoate ($CH_3COOC_2H_5$) at equilibrium when 3 moles of ethanoic acid (CH_3COOH) are mixed with 2.5 moles of ethanol (C_2H_5OH).

Step One: Write an expression for K_c

Step Two: Do a RICE @1L table

Step 3: Write the K_c constant, sub in numbers, and solve!

Example 8

The value of K_c for the following equilibrium reaction is 4.0 at a temperature of 373K.

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

What mass of ethyl ethanoate ($CH_3COOC_2H_5$) would be present in the equilibrium mixture if 0.25 moles of ethanoic acid (CH_3COOH) and 0.25 moles of ethanol (C_2H_5OH) were mixed and equilibrium was established at this temperature?

Step One: Write an expression for K_c

Step Two: Do a RICE @1L table

Step 3: Write the K_c constant, sub in numbers, and solve!

Example 9

Consider the equilibrium represented by the following balanced equation: $\mathbf{2BrCl_{(g)} \rightleftharpoons Br_{2(g)} + Cl_{2(g)}}$. Calculate the percentage decomposition into bromine and chlorine of 0.200 moles of BrCl, placed initially into a 5 litre closed container, and allowed to reach equilibrium at 1200ºC according to the equation above. Take the value of K_c at this temperature as 0.220. Give your answer correct to the nearest whole number

Step One: Write an expression for K_c

Step Two: Do a RICE @1L table

Step 3: Write the K_c constant, sub in numbers, and solve using the minus b formula!