Starter

Explain what is meant by the term 'dynamic equilibrium' with reference to the following reaction:

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

Objectives

- Know the conditions needed for a change in the position of equilibrium

- Describe and explain how these changes in conditions effect the position of equilibrium

Recap

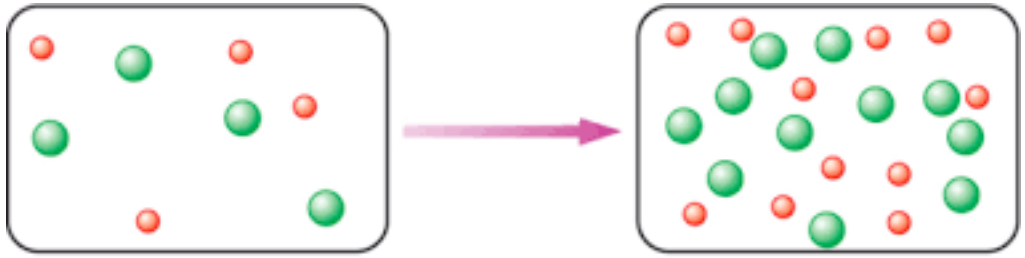
What conditions must be met for dynamic equilibrium to be established?

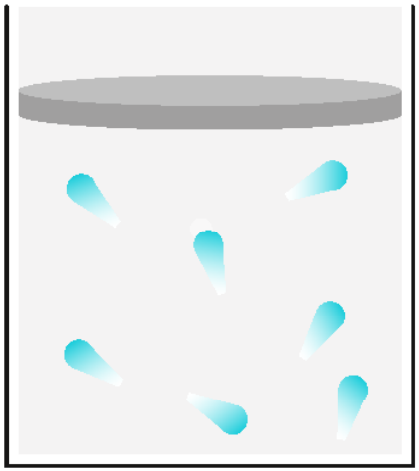
- Reaction must be reversible
- Reactions must be in a closed container

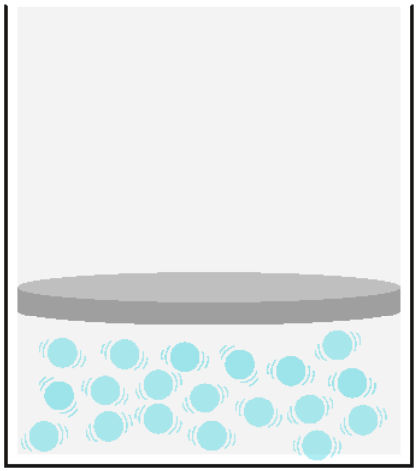
With the reaction being in a closed container, do the conditions remain the same?

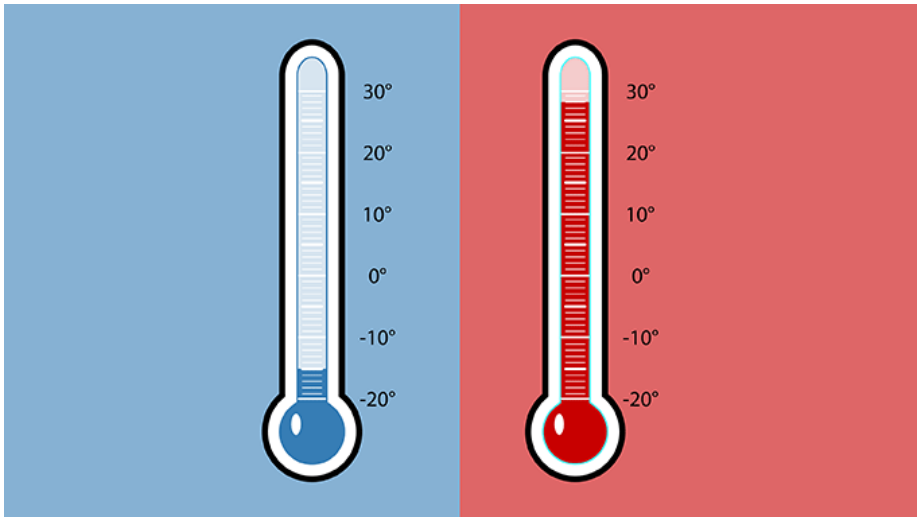
What do you think would happen to the position of equilibrium if the conditions were to change?

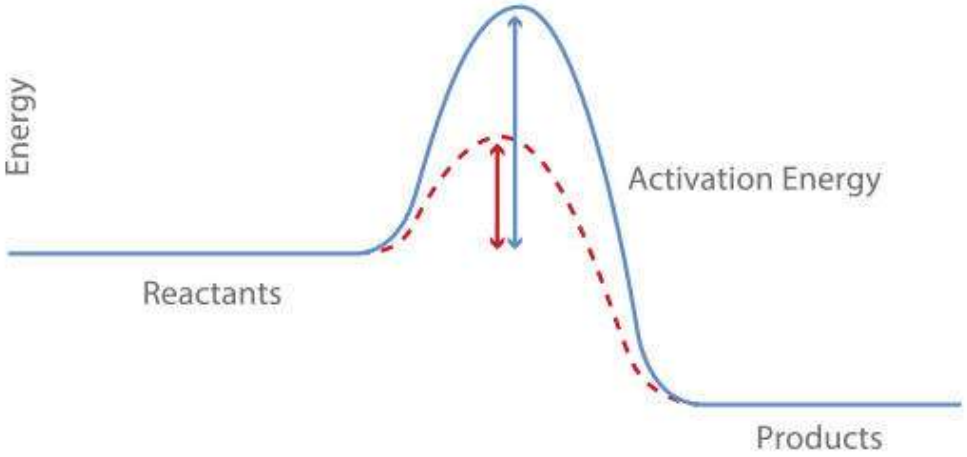
Factors that affect the position of equilibrium









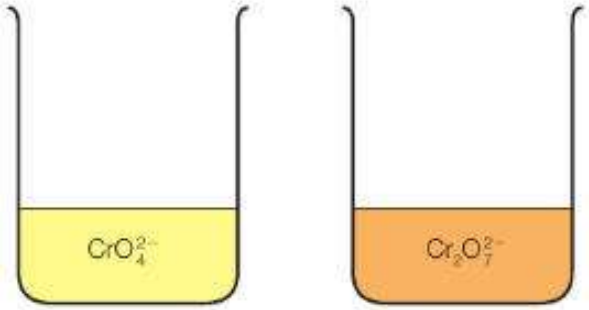


Changes in the equilibrium position

When a reaction mixture reaches a position of equilibrium, the composition of the equilibrium mixture (i.e. the concentration of each component) will not alter as long as the conditions remain the same.

However, if we change a condition (i.e. add some more of, or remove one of, the components, or change the temperature of the system) then the composition may change. This is often referred to as 'changing the position of equilibrium', and we refer to the position being moved to the right, to the left or not changed.

For example, if acid is added to a yellow solution containing chromate(VI) ions, CrO_4^{2-}, the solution turns orange. This is because of an increase in the amount of dichromate(VI) ions, $Cr_2O_7^{2-}$.



$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$

yellow orange

▲ **fig A** Beakers containing solutions of chromate(VI) ions and dichromate(VI) ions.

The equilibrium position moves to the right when the acid (H^+) is added. If sufficient alkali is added to the orange solution, it will turn yellow as the amount of CrO_4^{2-} ions increases and exceeds the amount of $Cr_2O_7^{2-}$ ions. The equilibrium position moves to the left when alkali (OH^-) is added.

An aqueous solution contains dichromate(VI) ions, $Cr_2O_7^{2-}$, and chromate(VI) ions, CrO_4^{2-}, in equilibrium. This solution is a pale orange colour.

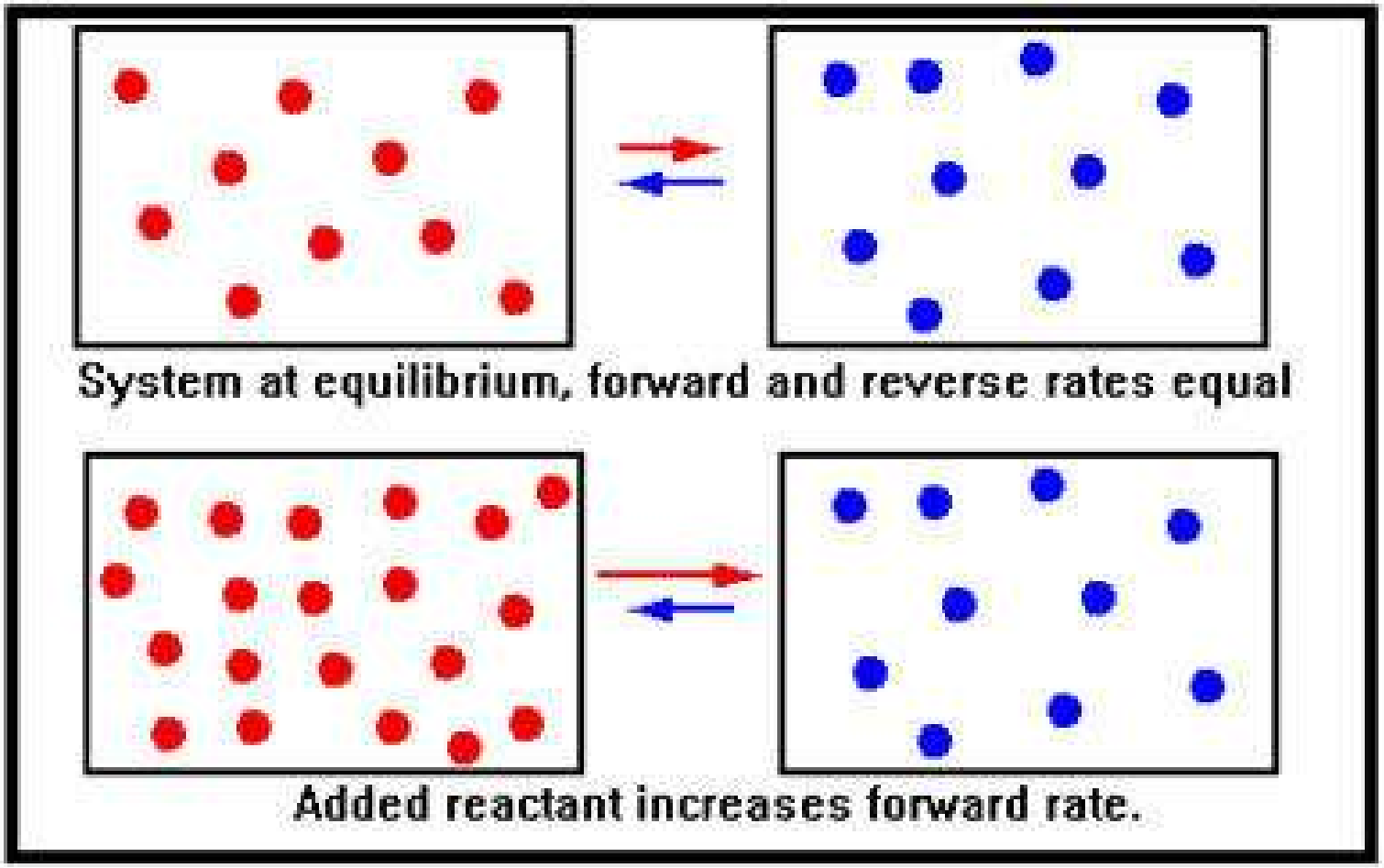
$$Cr_2O_7^{2-}(aq) + H_2O(l) \rightleftharpoons 2CrO_4^{2-}(aq) + 2H^+(aq)$$

orange yellow

What would be seen when a few drops of concentrated sodium hydroxide solution are added to the equilibrium mixture?

- ☐ **A** No visible change.
- ☐ **B** The mixture turns green.
- ☐ **C** The mixture turns a deeper orange.
- ☐ **D** The mixture turns yellow.

Change in concentration



https://www.youtube.com/watch?v=7zuUV455zFs

Change in concentration

CONCENTRATION OF REACTANTS	CONCENTRATION OF PRODUCTS	CHANGE IN POSITION OF EQUILIBRIUM
increased		
decreased		
	increased	
	decreased	

When we increase or decrease the reactants or products, in which direction will the position of equilibrium shift to?

https://www.youtube.com/watch?v=7zuUV455zFs

The rate of the reaction between sodium thiosulfate solution and dilute hydrochloric acid increases as the concentration of sodium thiosulfate increases.

Which of these occurs when the concentration of the sodium thiosulfate solution increases at constant temperature?

	Activation energy	Particles
☐ A	decreases	collide more frequently
☐ B	decreases	collide with more energy
☐ C	stays the same	collide more frequently
☐ D	stays the same	collide with more energy

Change in pressure

The effect of changing pressure only applies to reversible reactions involving gases. At a given temperature, the pressure of a gaseous mixture depends only on the number of gas molecules in a given volume. So the pressure of a gaseous mixture may be:

- increased by reducing the volume
- reduced by increasing the volume

Alternatively the pressure at which a reaction can be carried out can be:

- increased by initially using more moles of the reactants in the same volume
- decreased by using fewer moles of the reactants in the same volume

https://www.youtube.com/watch?v=7zuUV455zFs

Change in pressure

NUMBER OF MOLES OF REACTANTS	NUMBER OF MOLES OF PRODUCTS	CHANGE IN POSITION OF EQUILIBRIUM WHEN THE PRESSURE IS INCREASED
more	fewer	
fewer	more	
same	same	

table B The change in the position of equilibrium when the pressure is increased and the number of moles of reactants or products is increased, decreased or not changed.

https://www.youtube.com/watch?v=7zuUV455zFs

Change in pressure

- When a reaction involving gases is carried out at higher pressure, the position of equilibrium will shift the position in the direction that produces fewer moles of gas.
- Carrying out the reaction at a lower pressure will shift the position of equilibrium in the direction that produces more moles of gas.

In the Haber process, increasing the pressure will move the position in which direction? Will there be more products or reactants produced? When the pressure is decreased, in which direction will the position of equilibrium move to? Will there be more products or reactants produced?

Change in temperature

- If the temperature of an equilibrium mixture is raised, the rates of both the forward and the backward reactions will increase
- However, the increase in the rate of the endothermic reaction will be greater than the increase in the rate of the exothermic reaction
- Therefore an increase in temperature will shift the position of equilibrium in the direction of the endothermic reaction
- The change in the position of equilibrium depends on whether the forward reaction is exothermic or endothermic

TEMPERATURE CHANGE	THERMICITY OF FORWARD REACTION	CHANGE IN POSITION OF EQUILIBRIUM
increased	exothermic (ΔH –ve)	
decreased	exothermic (ΔH –ve)	
increased	endothermic (ΔH +ve)	
decreased	endothermic (ΔH +ve)	

The following system was allowed to reach equilibrium at 450 °C.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -197 \text{ kJ mol}^{-1}$$

How would a decrease in pressure and an increase in temperature affect the equilibrium position?

	Shift in equilibrium position with a decrease in pressure	Shift in equilibrium position with an increase in temperature
☐ A	left	left
☐ B	left	right
☐ C	right	left
☐ D	right	right

Addition of a catalyst

What effect do you think a catalyst has on the position of equilibrium?

- A catalyst has no effect on the yield of a product
- It speeds up both the forward and backward reactions, but at the same rate
- This means there is no overall change in the rate of product being produced, and therefore the yield of the desired product
- However the advantage of adding a catalyst at the beginning of the reaction is it will reduce the time required to establish equilibrium

Limitations of predictions

The first thing to recognise is that the qualitative predictions we have made about the effect of concentration, pressure and temperature on the position of equilibrium are just that – predictions.

The arguments we have used are *not* explanations of why changes sometimes occur. In fact, there are occasions when it is impossible to predict the direction of change, or indeed when the prediction turns out to be incorrect.

For example, if an equilibrium mixture of $NO_2(g)$ (brown) and $N_2O_4(g)$ (colourless) in a closed container is placed into a beaker of hot water at room temperature, both the temperature and the pressure of the gaseous mixture will rise.

The equation for the reaction is:

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \Delta H = -57.2\,kJ\,mol^{-1}$$

Because the forward reaction is exothermic, we would predict that an increase in temperature would shift the equilibrium to the left.

However, since there are fewer moles of gas on the right-hand side of the equation, we would predict that an increase in pressure would shift the equilibrium to the right.

We do not know which effect is greater, so we cannot make a prediction of which way the equilibrium will shift. In practice, the mixture becomes darker in colour, so the temperature effect must be greater than the pressure effect.This is because the equilibrium must have shifted to the left to produce more brown $NO_2(g)$.

Objectives

- Know the conditions needed for a change in the position of equilibrium

- Describe and explain how these changes in conditions effect the position of equilibrium

Plenary

What effect does a catalyst have on the position of equilibrium?