
1.6 Chemical equilibria and Le Chatelier's principle

Reversible reactions:

- Consider the reaction:



- The reaction stops when all of the limiting reagent has been used up.
- The reaction is said to go to completion and this is indicated by \rightarrow
- Some reactions are reversible though and are indicated by \rightleftharpoons



Characteristics of the dynamic equilibrium

- Equilibrium can only be established in a **closed system**. Matter cannot be exchanged with the surroundings (this will affect the position of the equilibrium), but energy can be exchanged.
- Equilibrium can be approached from **either direction**. The products can be used as the reactants to set up the equilibrium – reversible reactions.
- Equilibrium is a **dynamic state** – At equilibrium the rate in both directions **must** be the same.
- Dynamic equilibrium is **stable under fixed conditions but is sensitive to changes in concentration, pressure and temperature**.
 - The concentrations of the reactant and products no longer change and are a fixed amount
 - The extent of how far the reaction has gone towards the products is called '**the position of the equilibrium**'

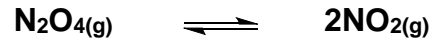
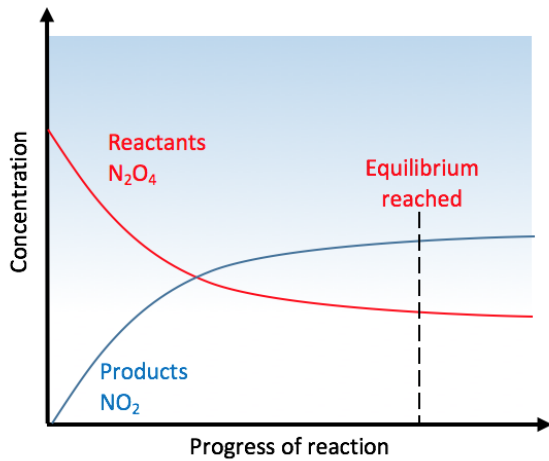
Equilibrium is stable under these conditions

Factors affecting the position of equilibrium:

- 1) Changing the concentration of reactants or products
- 2) Changing the pressure (if gases involved)
- 3) Changing temperature

- The effects of these changes can be predicted:

Approaching equilibrium



Initially:

N_2O_4 molecules decompose into 2 NO_2 molecules, the rate of the forward reaction is fast.

Because there are very few molecules of NO_2 , the reverse reaction can only happen slowly.

As the reaction proceeds:

There are now fewer N_2O_4 molecules available to decompose, the rate of the forward reaction decreases.

There are now more NO_2 molecules present so the rate of the reverse reaction increases.

At equilibrium

The rate of the forward reaction equals the rate of the reverse reaction

The concentrations of reactants and products now remain constant.

Le Chatelier's Principle

When a reaction at equilibrium is subject to a change in concentration, pressure or temperature, the position of the equilibrium will move to counteract the change.

- The position of the equilibrium shifts so as to oppose the change imposed upon it.
- It is possible to use these to make an equilibrium system shift in the direction we want.

1) Changing concentration

- This reaction shows how a reversible reaction can be manipulated by changing the concentration of the reactants then products:



Increasing concentration:

- **Adding H₂ – increases the concentration of H₂**
- **Equilibrium shifts to the products**
- **To reduce the concentration of the H₂ – counteracting the change**
- The mixture will become less purple

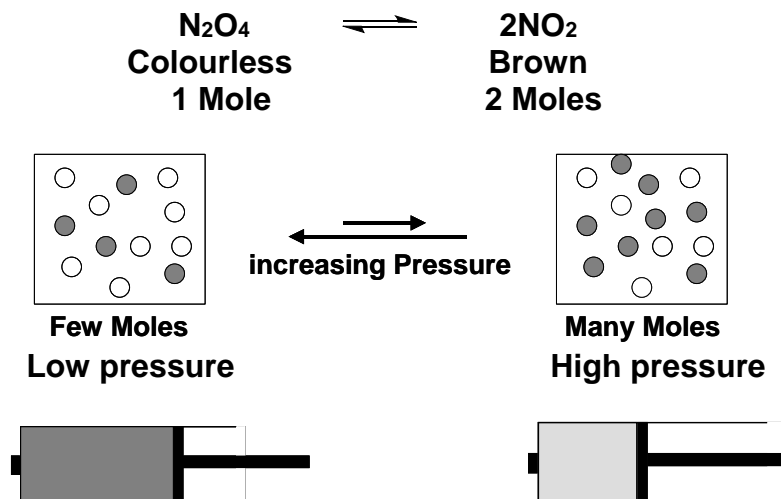
Decreasing concentration:

- **Removing I₂ – decreases the concentration of I₂**
- **Equilibrium shifts to the reactants**
- **To increase the concentration of the I₂ – counteracting the change**
- The mixture will become more purple

The equilibrium moves to oppose the change in concentration

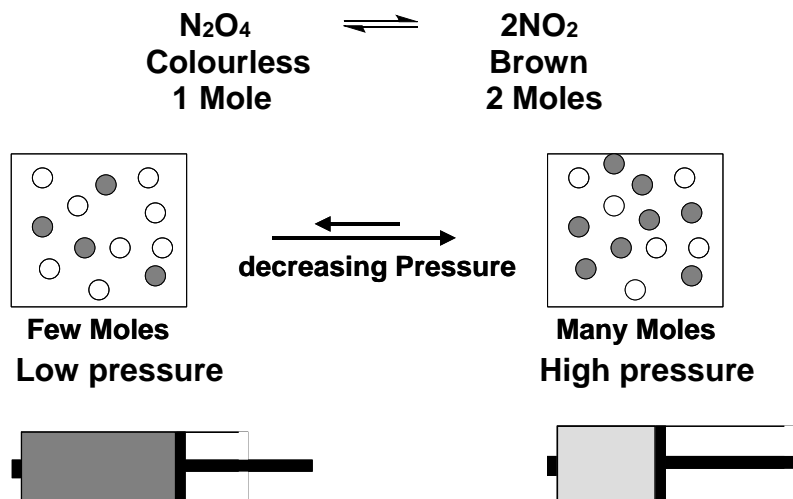
2) Changing pressure – gases only

Increasing pressure:



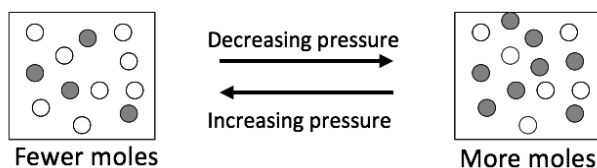
- **Equilibrium** shifts to the **reactants**
- This is the side with **fewer moles of gas**
- This will **reduce the pressure** – counteracting the change
- The mixture will become less brown

Decreasing pressure:

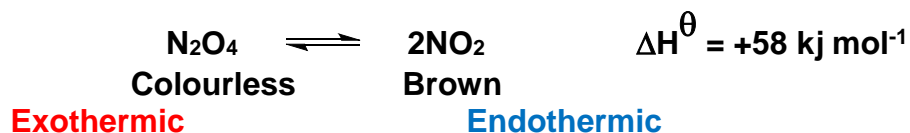


- **Equilibrium** shifts to the **products**
- This is the side with **more moles of gas**
- This will **increase the pressure** – counteracting the change
- The mixture will become more brown

The equilibrium moves to oppose the change in pressure



3) Changing temperature:



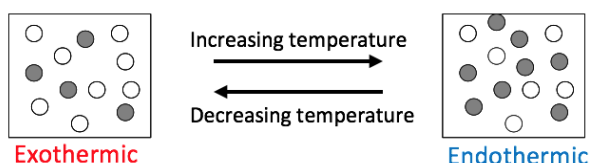
Increasing temperature:

- **Equilibrium** shifts to the **products**
- As this is the **endothermic direction**
- This will **decrease temperature** – counteracting the change
- The mixture will become more brown

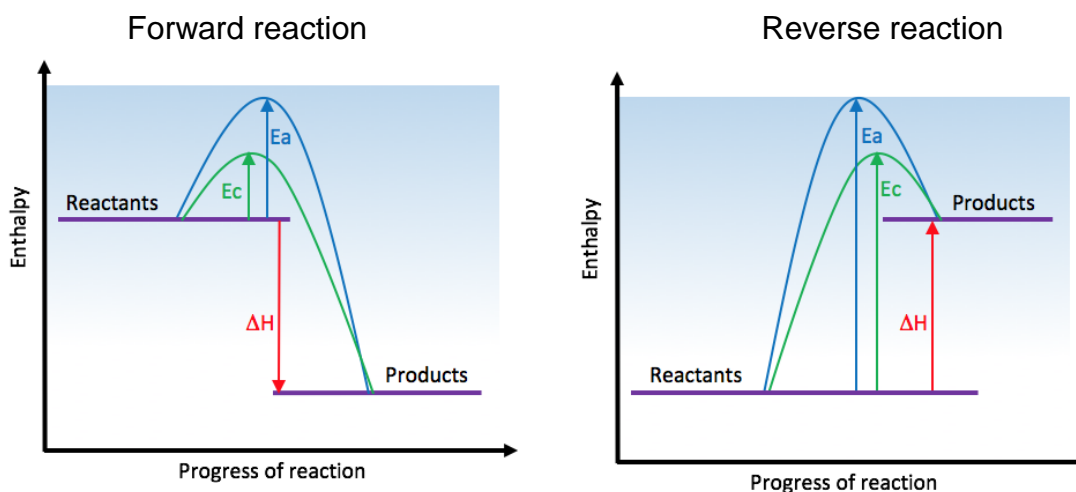
Decreasing temperature:

- **Equilibrium** shifts to the **reactants**
- As this is the **exothermic direction**
- This will **increase temperature** – counteracting the change
- The mixture will become less brown

The equilibrium moves to oppose the change in temperature

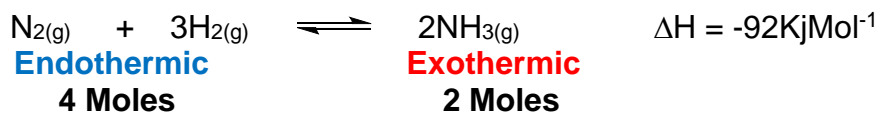


4) The effect of a catalyst on an equilibrium



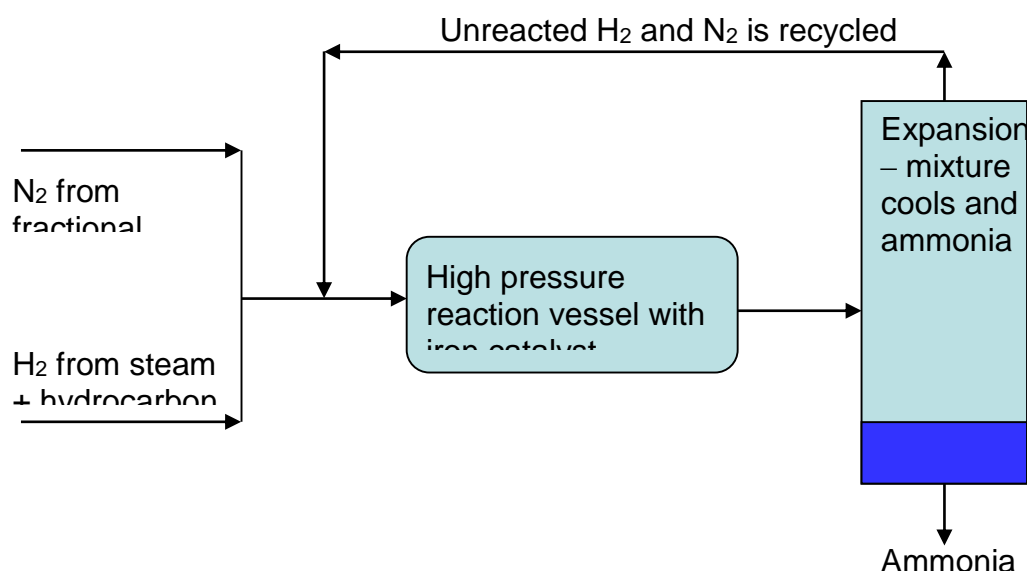
- A catalyst has **no effect** on the **position of the equilibrium**.
- A catalyst **speeds up the forward and reverse reaction** so it will only increase the rate at which equilibrium is achieved.

Compromise: Equilibrium and yield vs Rate:
The Haber process – an industrial process



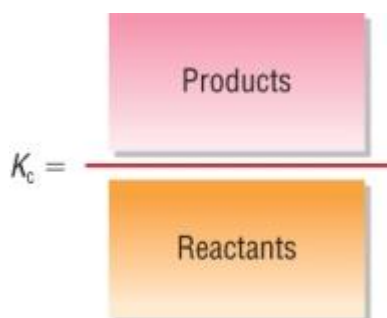
Process	Equilibria	Yield	Rate	Compromise
Temperature	_____	Increase Or Decrease	_____	.
Pressure	_____	Increase Or Decrease	_____	
Catalyst		Increase Or Decrease		
Remove ammonia as it is formed		Increase Or Decrease		

The process:



The equilibrium constant, K_c

- At equilibrium, remember the concentrations of the reactant and products no longer change and are a fixed amount, a constant
- The equilibrium constant is an expression of the relative fixed amounts of **products : reactants** at equilibrium.



The diagram shows a pink box labeled 'Products' above an orange box labeled 'Reactants', with a horizontal line between them. To the left of this diagram is the equation $K_c =$. To the right is the mathematical expression $K_c = \frac{[\text{PRODUCTS}]^p}{[\text{REACTANTS}]^r}$.

- Consider the reaction:



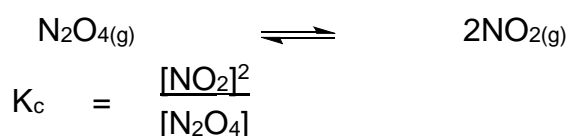
- Where **[A]**, **[B]**, **[C]** and **[D]** are the equilibrium concentrations of reactants and products
- The indices **a, b, c** and **d** are the stoichiometric numbers in the balanced chemical reaction

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

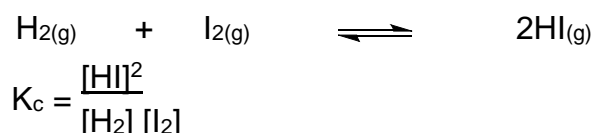
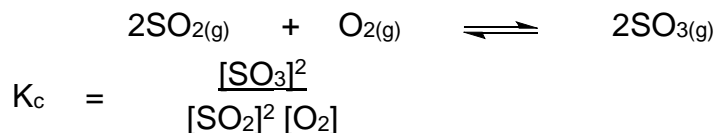
- This expression gives us a mathematical way of looking at the proportions of products and reactants in an equilibrium.
- This means a constant based on concentrations is produced, this is given by - K_c

Writing expressions for K_c :

- At equilibrium the concentrations of NO_2 and N_2O_4 are constant:



Other examples:



Units of K_c

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]^1}$$

$$K_c = \frac{\text{mol dm}^{-3} \times \text{mol dm}^{-3}}{\text{mol dm}^{-3}}$$

$$K_c = \frac{\text{mol dm}^{-3} \times \text{mol dm}^{-3}}{\text{mol dm}^{-3}}$$

$$K_c = \text{mol dm}^{-3}$$

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]}$$

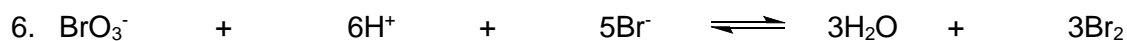
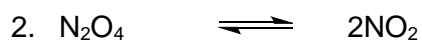
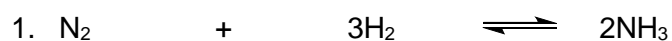
$$K_c = \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})^2 \text{ mol dm}^{-3}}$$

$$K_c = \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})^2 \text{ mol dm}^{-3}}$$

$$K_c = \frac{1}{\text{mol dm}^{-3}}$$

$$K_c = \text{dm}^3 \text{ mol}^{-1}$$

Questions: Write K_c expressions for the following equilibria, for each, work out the units of K_c



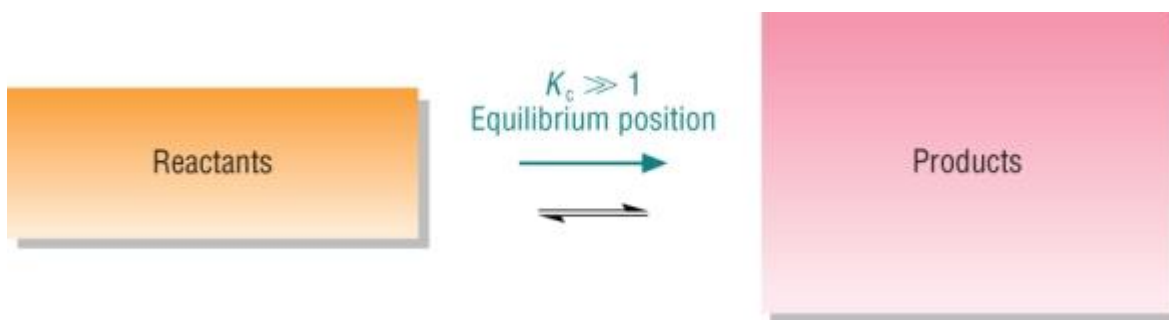
What is the significance of a K_c

- K_c is a mathematical representation of the ratio of **products** : **reactants**.

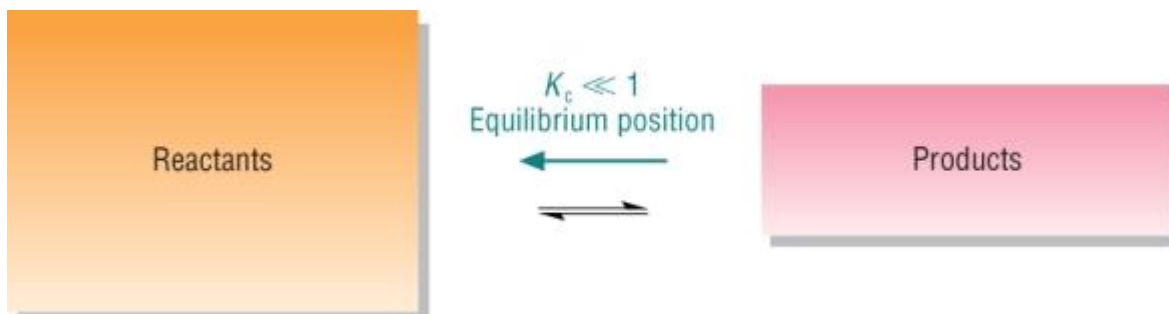
$$K_c = \frac{\text{Products}}{\text{Reactants}}$$

- If the amount of products is equal to reactants, then $K_c = 1$

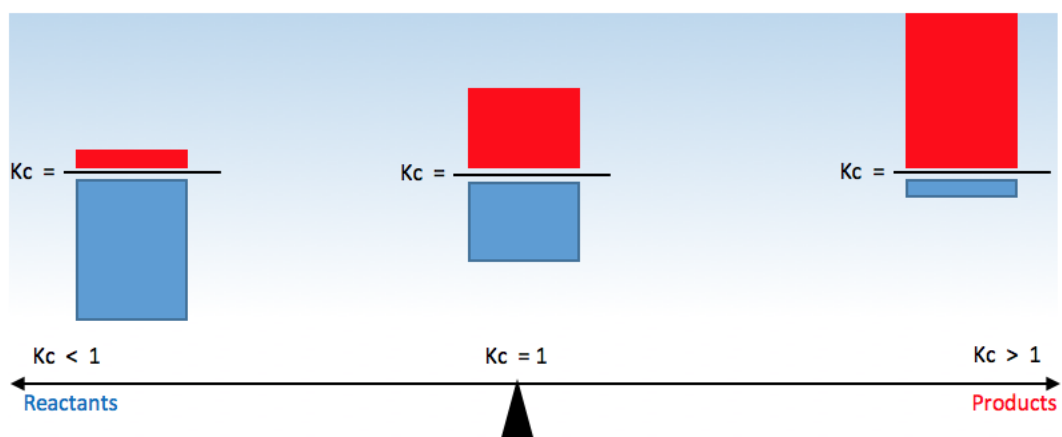
Products favoured: $K_c > 1$



Reactants favoured: $K_c < 1$



Summary:



Calculations using K_c

- The equilibrium expression obviously allows you to calculate K_c if you know the concentrations at equilibrium.
- You can also calculate K_c and equilibrium concentrations knowing the starting concentrations and one of the equilibrium concentrations.

Determining K_c from equilibrium concentrations:

1) Given concentrations at equilibrium

Hydrogen, Iodine, Hydrogen iodide equilibrium:

Reaction	$\text{H}_{2(g)}$	+	$\text{I}_{2(g)}$	\rightleftharpoons	$2\text{HI}_{(g)}$
[Eq]	0.140		0.040		0.320

- Write the **equilibrium expression**, put in the values, **calculate K_c** and work out the **units**:

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2] [\text{I}_2]}$$

$$K_c = \frac{(0.320)^2}{0.140 \times 0.040}$$

$$K_c = 18.3$$

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2] [\text{I}_2]}$$

$$K_c = \frac{\text{mol dm}^{-3} \text{ mol dm}^{-3}}{\text{mol dm}^{-3} \text{ mol dm}^{-3}}$$

$$K_c = \frac{\text{mol dm}^{-3} \cdot \text{mol dm}^{-3}}{\text{mol dm}^{-3} \text{ mol dm}^{-3}}$$

$$K_c = \text{No units}$$

2) Given the number of moles at equilibrium:

N_2O_4 / NO_2 equilibrium in a volume of 2dm^3 .

Reaction	$\text{N}_2\text{O}_4(\text{g})$	\rightleftharpoons	$2\text{NO}_2(\text{g})$
n moles at equilibrium	0.400		3.20

$$[\text{Eq}] = n / V(\text{dm}^3)$$

[Eq]

- As the quantities are given in moles, you have to calculate the equilibrium concentrations
- Write the **equilibrium expression**, put in the values, **calculate K_c** and work out the **units**:

$$K_c = \underline{\hspace{2cm}}$$

$$K_c = \underline{\hspace{2cm}}$$

$$K_c = \underline{\hspace{4cm}}$$

$$K_c = \underline{\hspace{4cm}}$$

$$K_c =$$

$$K_c = \underline{\hspace{4cm}}$$

$$K_c =$$

3) Given moles at the start and equilibrium calculation:

- This time you are told the **mole quantities** at the start and **one equilibrium quantity**.
- Remember to convert to equilibrium concentrations.

Hydrogen, Iodine, Hydrogen iodide equilibrium in a 1 dm³ sealed vessel:

Reaction	H _{2(g)}	+	I _{2(g)}	\rightleftharpoons	2HI _(g)
Stoichiometry	1		1		2
Initial n moles	0.60		0.40		0.0
Reacted					
n moles at equilibrium	0.28				

[Eq]

- Write the **equilibrium expression**, put in the values, **calculate K_c** and work out the **units**:

$$K_c = \underline{\hspace{2cm}}$$

$$K_c = \underline{\hspace{2cm}}$$

$$K_c = \underline{\hspace{4cm}}$$

$$K_c = \underline{\hspace{4cm}}$$

$$K_c =$$

$$K_c = \underline{\hspace{4cm}}$$

$$K_c =$$

4) Calculating a reactant from K_c :

- This time you are told K_c at the start and **initial moles and equilibrium moles**.
- Remember to convert to equilibrium concentrations.

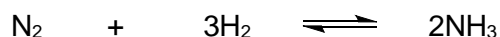
6.00 moles of PCl_3 is mixed with an unknown amount of Cl_2 . 2.00 moles of PCl_5 is made. How many moles of Cl_2 was added? $K_c = 20$. The experiment was carried out in a 2dm^3 flask.

Reaction	$\text{PCl}_{3(g)}$	+	$\text{Cl}_{2(g)}$	\rightleftharpoons	$\text{PCl}_{5(g)}$
Stoichiometry	1		1		1
Initial n moles	6.00		x		0.0
Reacted					
n moles at equilibrium					2.00
[Eq]					

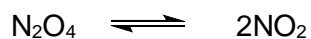
- Write the **equilibrium expression**, put in the values, **calculate K_c** and work out the **units**:

Questions:

1. The concentrations at equilibria are as follows; $0.20 \text{ mol dm}^{-3} \text{ N}_2$ and $0.4 \text{ mol dm}^{-3} \text{ H}_2$ and $0.01 \text{ mol dm}^{-3} \text{ NH}_3$.



- a. Write an equilibrium expression for the above reaction
- b. Calculate K_c for the above equilibria stating any units (7.81×10^{-3})
- c. If the mixture is heated, the equilibrium moves to the products. What does this tell you about the forward reaction, explain your answer?
2. The equilibria between NO_2 and N_2O_4 are allowed to establish in a 2dm^3 sealed vessel:



- a. Write an equilibrium expression for the reaction above
- b. 0.5 moles of N_2O_4 was allowed to reach equilibria. 0.2 moles of NO_2 was found at equilibria. Calculate the amounts of each reactant and product at equilibria
- c. Use your answer to (b) to calculate the value of K_c . Include units in your answer. (0.05)

4. The following equilibrium was established in a 2dm^3 vessel at a particular temperature.
0.20 moles of H_2 was mixed with an unknown amount of I_2 .
At equilibrium 0.24 moles of HI was made.
 $K_c = 10.00$



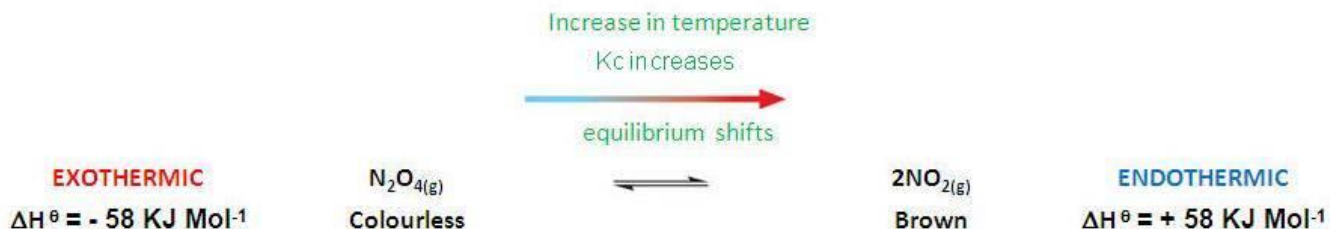
Calculate the number of moles of Iodine present at the start (0.192)

The equilibrium position and K_c

1) Temperature and K_c

- Apply the equilibrium direction movement to work out whether **K_c increases or decreases**:

a) Endothermic reactions:



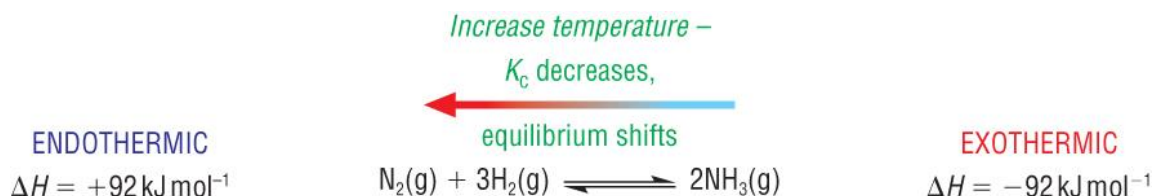
- Increase in temperature** will shift the equilibrium to the **Products** as this is the **endothermic direction**
- There will be **more Products** and **less Reactants**:

$$K_c = \frac{\text{Products}}{\text{Reactants}}$$

- Top number increases
- Bottom number decreases

K_c increases

b) Exothermic reactions:



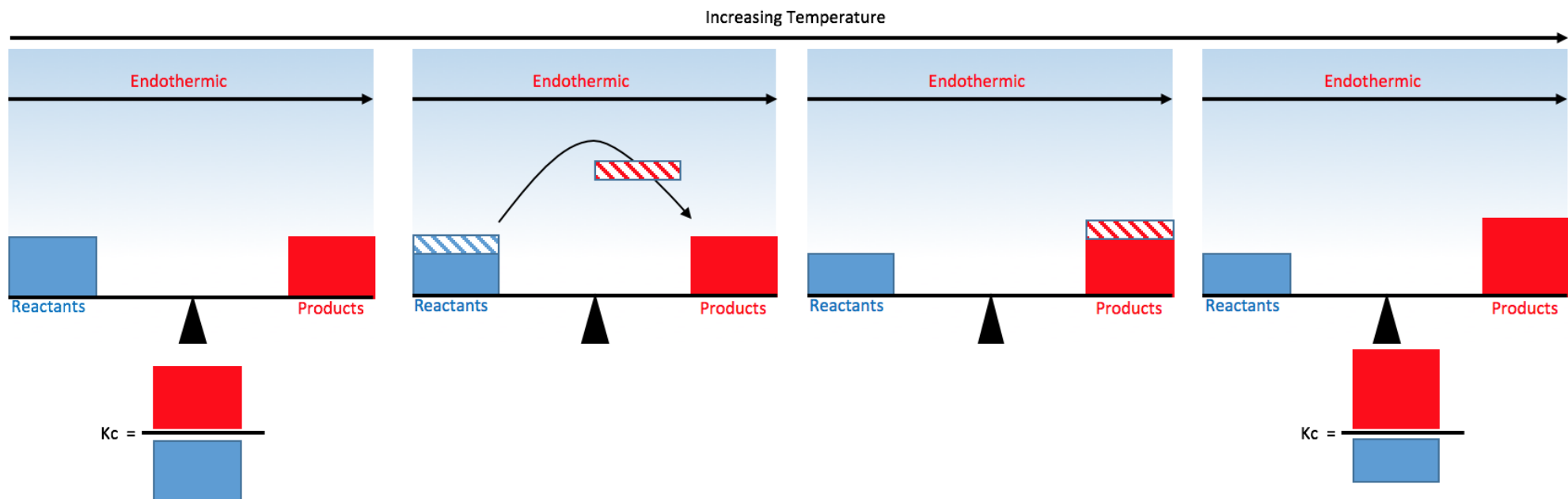
- Increase in temperature** will shift the equilibrium to the **Reactants** as this is the **endothermic direction**
- There will be **more Reactants** and **less Products**:

$$K_c = \frac{\text{Products}}{\text{Reactants}}$$

- Top number decreases
- Bottom number increases

K_c decreases

A visual representation:



Increasing the temperature moves the equilibrium to the products as this is the endothermic direction and will reduce the temperature

In doing so reactants are converted to products

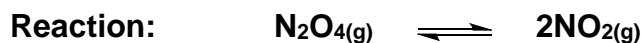
Amount of reactants decrease and amount of products increase

K_c therefore increases

2) Changes in concentration:

A change in Concentration has no effect on the equilibrium constant.

- Remember if a reactant / product is added the equilibrium shifts to the opposite direction to keep the 'proportions' the same - **K_c is unchanged**:



Initially: (keeping the numbers simple)

$$[\text{NO}_2] = 1.0 \text{ Mol dm}^{-3}$$

$$[\text{NO}_2] = 1.0 \text{ Mol dm}^{-3}$$

→ Double $[\text{N}_2\text{O}_4]$ →

$$[\text{N}_2\text{O}_4] = 1.0 \text{ Mol dm}^{-3}$$

$$[\text{N}_2\text{O}_4] = 2.0 \text{ Mol dm}^{-3}$$

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

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

$$K_c = \frac{(1.0)^2}{1.0}$$

$$K_c = \frac{(1.0)^2}{2.0}$$

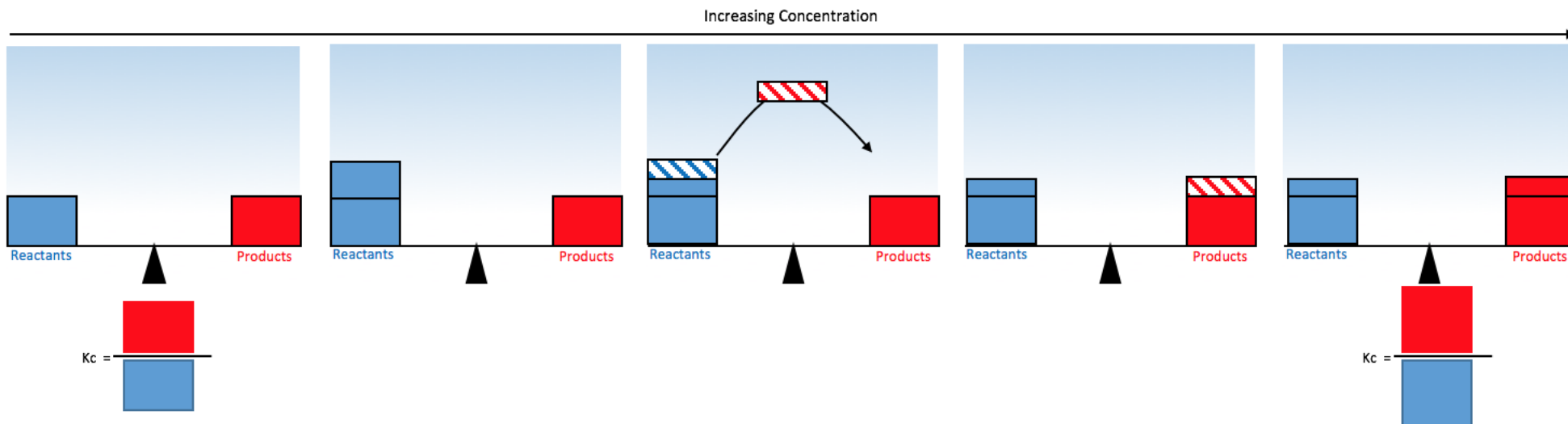
$$K_c = 1.0 \text{ Mol dm}^{-3}$$

$$K_c = 0.5 \text{ Mol dm}^{-3}$$

← Equilibria shifts to bring K_c back to 1.0 ←

- If the concentration of $[\text{N}_2\text{O}_4]$ are doubled, the system is no longer at equilibrium.
- To bring K_c back from **0.5** to **1.0**:
- The system must **increase $[\text{NO}_2]$ and decrease $[\text{N}_2\text{O}_4]$**
- Remember if a reactant / product is added the equilibrium shifts to the opposite direction to keep the 'proportions' the same - **K_c is unchanged**:

A visual representation:



Adding more reactants increases the concentration of the reactants.

Equilibrium converts a proportion of the added reactants to products in order to reduce the concentration of the reactants and increase the concentration of the products

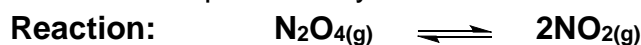
In doing so the proportions of reactants and products are re-established to the same proportions as at the start

K_c remains constant

3) Changes in Pressure: (keeping the numbers simple)

A change in Pressure has no effect on the equilibrium constant.

- If **pressure is doubled** - the **volume is halved** - meaning that the **concentrations** will have **doubled**
- Remember equilibria only shifts if there are more moles of gas on one side.



$$[\text{NO}_2] = 1.0 \text{ Mol dm}^{-3}$$

$$[\text{NO}_2] = 2.0 \text{ Mol dm}^{-3}$$

x2 pressure, x2 []

$$[\text{N}_2\text{O}_4] = 1.0 \text{ Mol dm}^{-3}$$

$$[\text{N}_2\text{O}_4] = 2.0 \text{ Mol dm}^{-3}$$

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

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

$$K_c = \frac{(1.0)^2}{1.0}$$

$$K_c = \frac{(2.0)^2}{2.0}$$

Effect on $[\text{NO}_2]^2$, which is x4

$$K_c = \frac{(1.0)^2}{1.0}$$

$$K_c = \frac{4.0}{2.0}$$

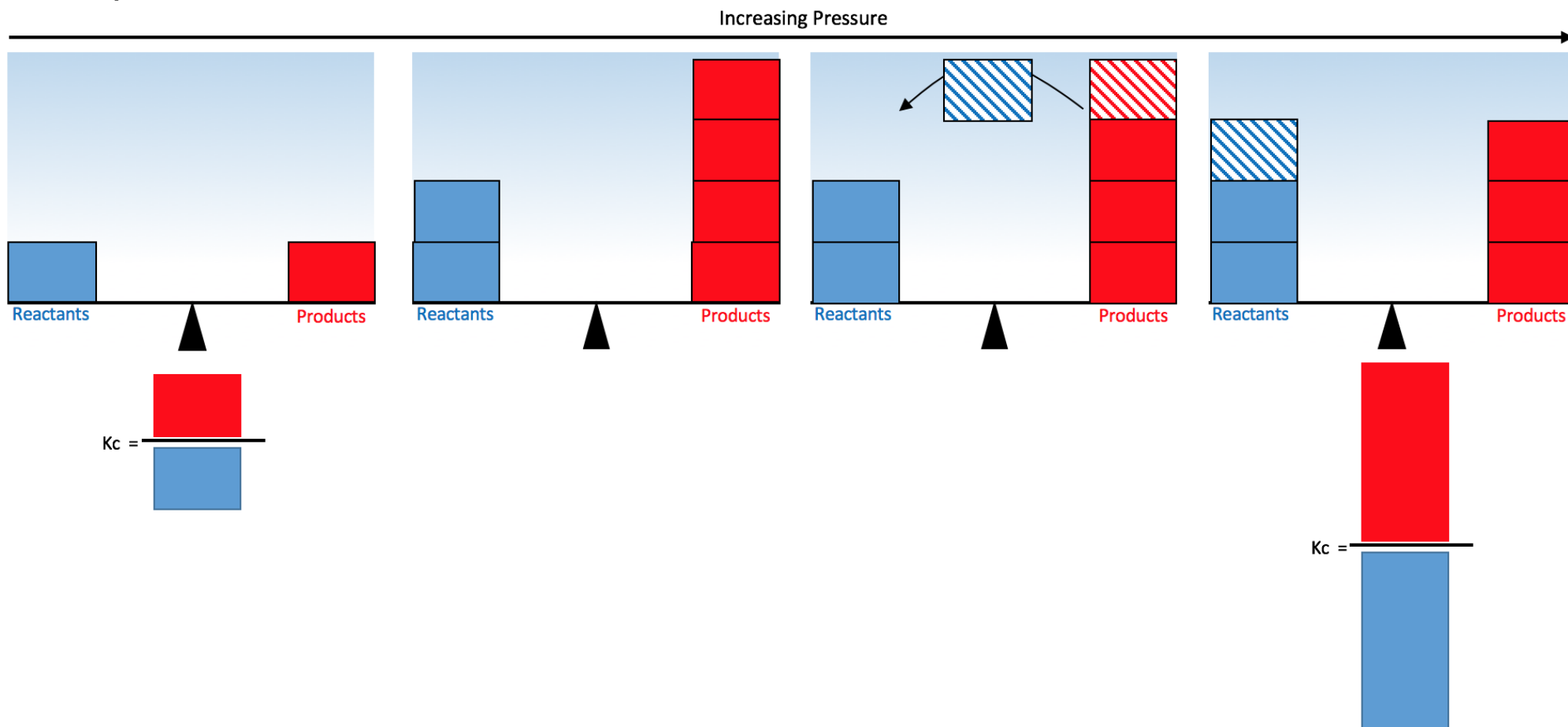
$$K_c = 1.0 \text{ Mol dm}^{-3}$$

$$K_c = 2.0 \text{ Mol dm}^{-3}$$

← Equilibria shifts to bring K_c back to 1.0 ←

- If the pressure is doubled, the system is no longer at equilibrium.
- To bring K_c back from **2.0** to **1.0**:
- The system must **increase $[\text{NO}_2]$ and decrease $[\text{N}_2\text{O}_4]$**
- Remember if a reactant / product is added the equilibrium shifts to the opposite direction to keep the 'proportions' the same - **K_c is unchanged**:

A visual representation:



If the pressure is doubled, then the volume halves. This doubles the concentration of reactants and products, $[\text{NO}_2]$ and $[\text{N}_2\text{O}_4]$

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$
 The expression shows that:
 Effect on the products is $x2^2 = x4$
 Effect on reactants is $x2$

The equilibria now shifts to the side with fewer moles of gas

K_c remains constant

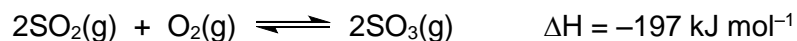
How does the presence of a catalyst affect K_c ?

A catalyst has no effect on the equilibrium constant.

- A catalyst speeds up both the forward and reverse reaction.
- Equilibrium is achieved more quickly.

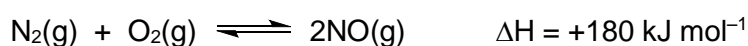
Questions:

1. Consider the following equilibria:



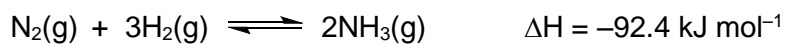
- Explain how you know that the forward reaction is exothermic?
- Explain what happens to the equilibria if the temperature is increased?
- What happens to the concentration of the reactants, explain your answer?
- What happens to the concentration of the products, explain your answer?
- What effect if any will this have on the value of K_c ?

2. The reaction between nitrogen and oxygen



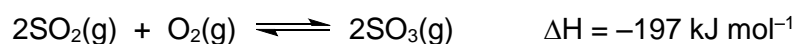
How will K_c change by increasing temperature? Explain your answer fully

3. Manufacture of ammonia



How will K_c change by decreasing temperature? Explain your answer fully

4. Consider the following equilibria:



a) Explain what happens to the equilibria and the value of K_c if the temperature is increased?

b) Explain what happens to the equilibria and the value of K_c if more SO_2 is added?

c) Explain what happens to the equilibria and the value of K_c if the pressure is doubled?

d) Explain what happens to the equilibria and the value of K_c if a catalyst is added?