1.6 Chemical equilibria and Le Chatelier's principle

Reversible reactions:

- Consider the reaction:

$$Mg_{(s)} + H_2SO_{4(aq)} \rightarrow MgSO_{4(aq)} + H_{2(g)}$$

- 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 $\rightleftharpoons$

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

Characteristics of the dynamic equilibrium

1) 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.

2) Equilibrium can be approached from **either direction**. The products can be used as the reactants to set up the equilibrium – reversible reactions.

3) Equilibrium is a **dynamic state** – At equilibrium the rate in both directions **must** be the same.

4) 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:

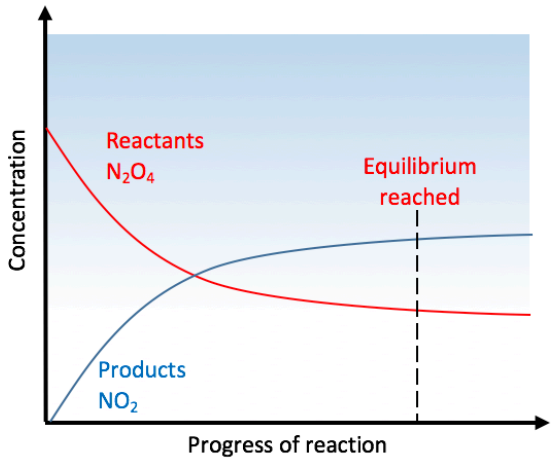
1) Changing the concentration of reactants or products

2) Changing the pressure (if gases involved)

3) Changing temperature

- The effects of these changes can be predicted:

Approaching equilibrium



$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

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:

$$\underset{}{H_{2(g)}} + \underset{\textbf{Purple}}{I_{2(g)}} \rightleftharpoons \underset{\textbf{Colourless}}{2HI_{(g)}}$$

Increasing concentration:
- **Adding H_2** – **increases the concentration of H_2**
- **Equilibrium** shifts to the **products**
- **To reduce the concentration** of the **H_2 – counteracting the change**
- The mixture will become less purple

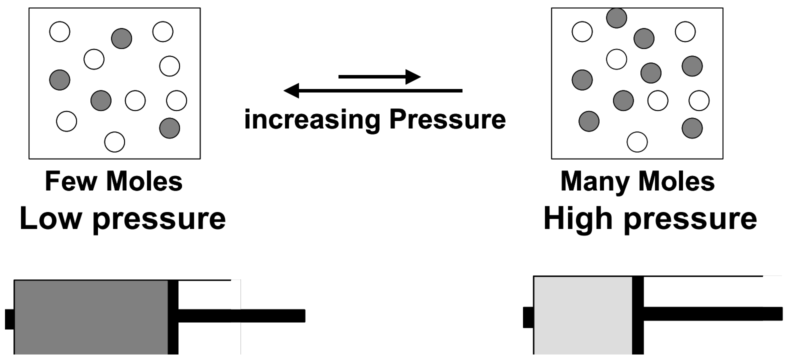
Decreasing concentration:
- **Removing I_2** – **decreases the concentration of I_2**
- **Equilibrium** shifts to the **reactants**
- **To increase the concentration** of the **I_2 – counteracting the change**
- The mixture will become more purple

The equilibrium moves to oppose the change in concentration

2) Changing pressure – gases only

Increasing pressure:

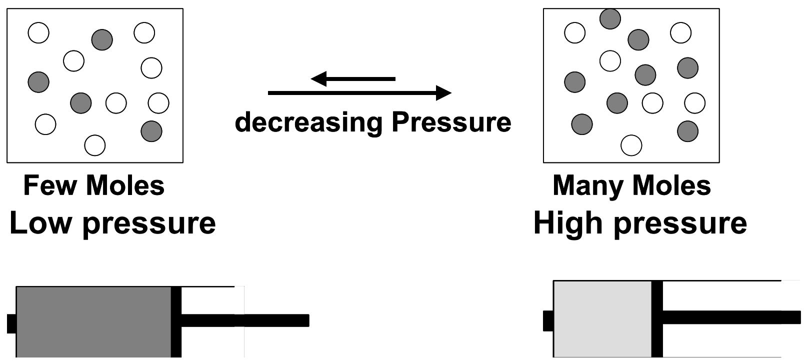
N_2O_4	$\rightleftharpoons$	$2NO_2$
Colourless		**Brown**
1 Mole		**2 Moles**



- **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

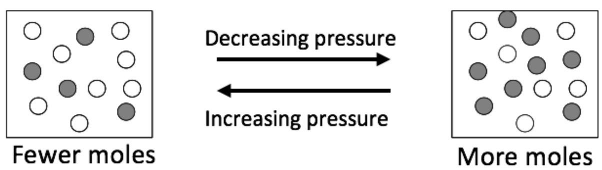
Decreasing pressure:

N_2O_4	$\rightleftharpoons$	$2NO_2$
Colourless		**Brown**
1 Mole		**2 Moles**



- **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:

$$N_2O_4 \rightleftharpoons 2NO_2 \qquad \Delta H^{\theta} = +58 \text{ kj mol}^{-1}$$

Colourless — **Brown**

Exothermic — **Endothermic**

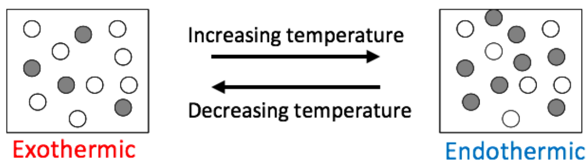
Increasing temperature:

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

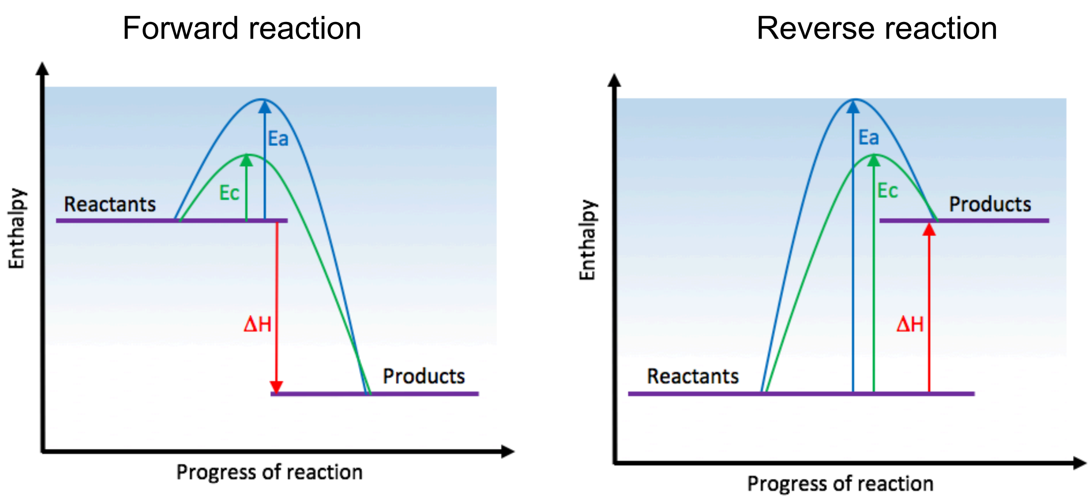
Decreasing temperature:

- **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.

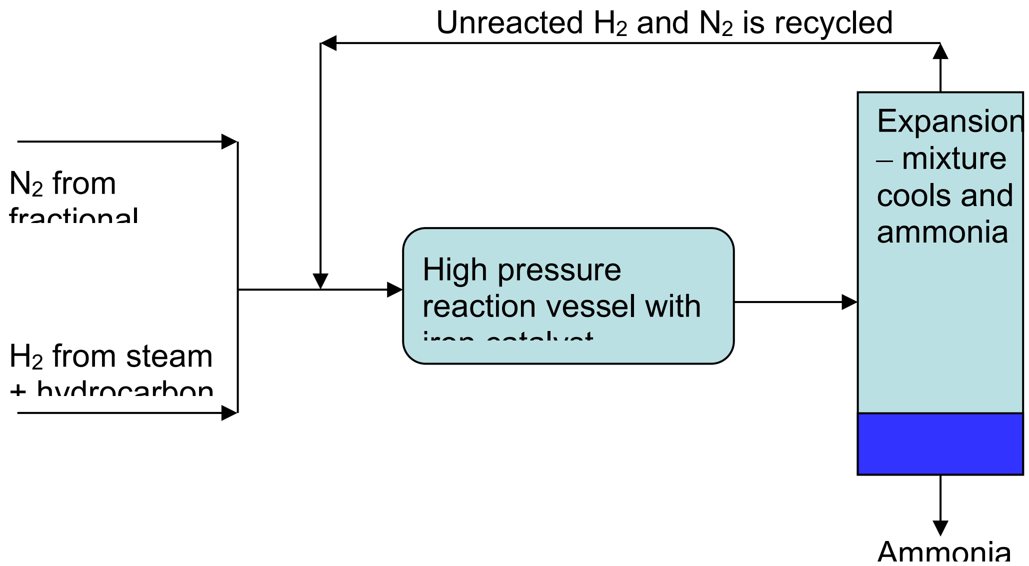
Compromise: Equilibrium and yield vs Rate:
The Haber process – an industrial process

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H = -92KjMol^{-1}$$

Endothermic — **Exothermic**
4 Moles — **2 Moles**

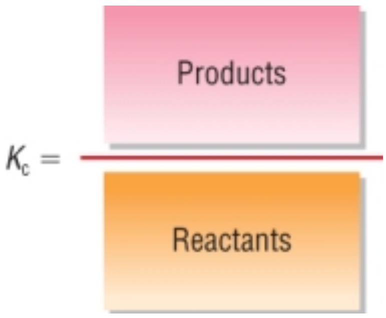
Process	Equilibria	Yield	Rate	Compromise
Temperature	______________	Increase Or Decrease	______________	.
Pressure	______________	Increase Or Decrease	______________	
Catalyst		Increase Or Decrease		
Remove ammonia as it is formed		Increase Or Decrease		

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.



$$K_c = \frac{[\mathrm{PRODUCTS}]^p}{[\mathrm{REACTANTS}]^r}$$

- Consider the reaction:

$$aA + bB \rightleftharpoons cC + dD$$

- 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:

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

Other examples:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

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

Units of K_c

$$K_c = \frac{[NO_2]^2}{[N_2O_4]^1} \qquad K_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

$$K_c = \frac{mol\ dm^{-3} \times mol\ dm^{-3}}{mol\ dm^{-3}} \qquad K_c = \frac{(mol\ dm^{-3})^2}{(mol\ dm^{-3})^2 \quad mol\ dm^{-3}}$$

$$K_c = \frac{mol\ dm^{-3} \times \cancel{mol\ dm^{-3}}}{\cancel{mol\ dm^{-3}}} \qquad K_c = \frac{\cancel{(mol\ dm^{-3})^2}}{\cancel{(mol\ dm^{-3})^2} \quad mol\ dm^{-3}}$$

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

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

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

1. $N_2 + 3H_2 \rightleftharpoons 2NH_3$

2. $N_2O_4 \rightleftharpoons 2NO_2$

3. $2HI \rightleftharpoons H_2 + I_2$

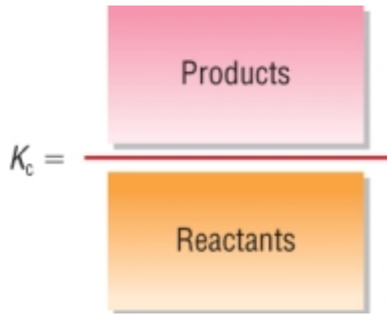
4. $2SO_2 + O_2 \rightleftharpoons 2SO_3$

5. $2A + B_2 \rightleftharpoons 2AB$

6. $BrO_3^- + 6H^+ + 5Br^- \rightleftharpoons 3H_2O + 3Br_2$

What is the significance of a K_c

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

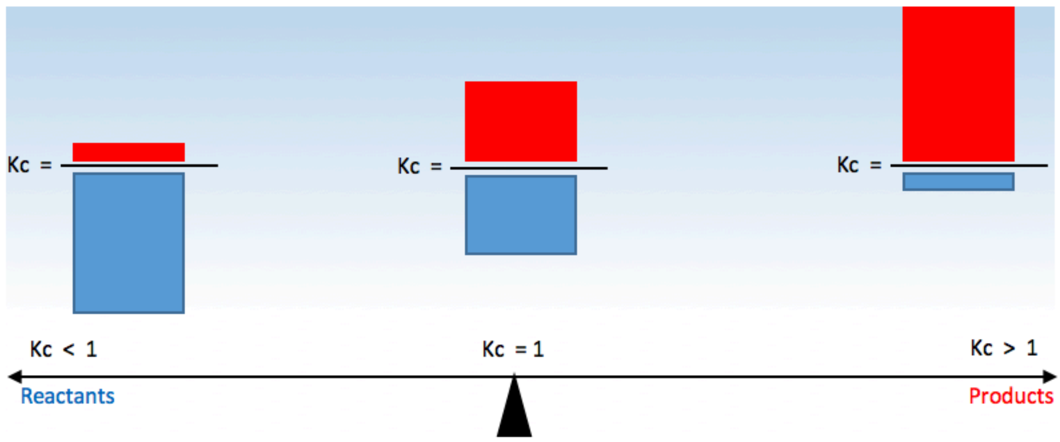


- If the amount of products is equal to reactants, then **K_c = 1**

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	$H_{2(g)}$	+	$I_{2(g)}$	$\rightleftharpoons$	$2HI_{(g)}$
[Eq]	0.140		0.040		0.320

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

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

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

$$K_c = 18.3$$

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

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

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

K_c = No units

2) Given the number of moles at equilibrium:

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

Reaction	$N_2O_{4(g)}$	$\rightleftharpoons$	$2NO_{2(g)}$
n moles at equilibrium	0.400		3.20
[Eq] = n / V(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 = ________ K_c = __________

K_c = __________________ K_c = _____________________

K_c = K_c = _____________________

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 dm^3 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 = ____________

K_c = ____________________

K_c =

K_c = __________

K_c = ____________________

K_c = ____________________

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? Kc = 20. The experiment was carried out in a 2dm^3 flask.

Reaction	$PCl_{3(g)}$	+	$Cl_{2(g)}$	$\rightleftharpoons$	$PCl_{5(g)}$
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 mol dm^{-3} N_2 and 0.4 mol dm^{-3} H_2 and 0.01 mol dm^{-3} NH_3.

$$N_2 \quad + \quad 3H_2 \rightleftharpoons 2NH_3$$

   a. Write an equilibrium expression for the above reaction

   b. Calculate Kc for the above equilibria stating any units (7.81 x 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:

$$N_2O_4 \rightleftharpoons 2NO_2$$

   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 Kc. Include units in your answer. (0.05)

3. The equilibria between ethanol and propanoic acid are allowed to establish:

Ethanol	+	Propanoic acid	$\rightleftharpoons$	Ethyl Propanoate	+	Water
CH_3CH_2OH	+	CH_3CH_2COOH	$\rightleftharpoons$	$CH_3CH_2COOCH_2CH_3$	+	H_2O

a. Write an equilibrium expression for the reaction above

b. 0.1 moles of ethanol was added to 0.2 moles of propanoic acid. At equilibria 0.005 moles of each of the products was formed. Calculate the amounts of each reactant and product at equilibria – Use a table

HINT: When calculating Kc, use 'V' as volume to calculate the concentrations at equilibrium

c. Use your answer to (b) to calculate the value of Kc. Include units. (1.35×10^{-3})
HINT: Put the concentrations with 'V' into the expression, what happens to 'V'

Explain why on this calculation you could use moles at equilibrium instead of concentrations at equilibrium.

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.
   Kc = 10.00

$$H_{2(g)} \quad + \quad I_{2(g)} \quad \rightleftharpoons \quad 2HI_{(g)}$$

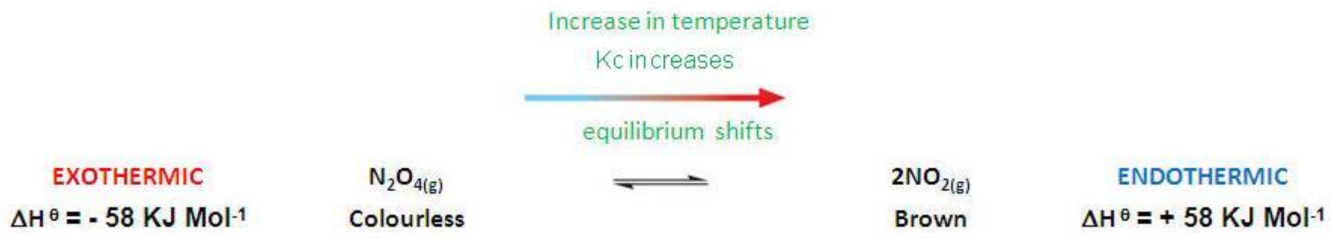
Calculate the number of moles of Iodine present at the start (0.192)

<u>**The equilibrium position and K_c**</u>

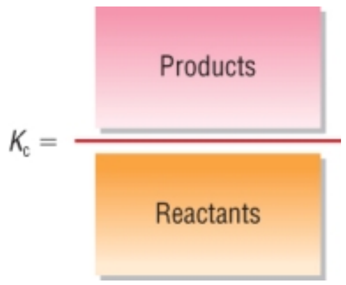
1) Temperature and K_c

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

a) Endothermic reactions:



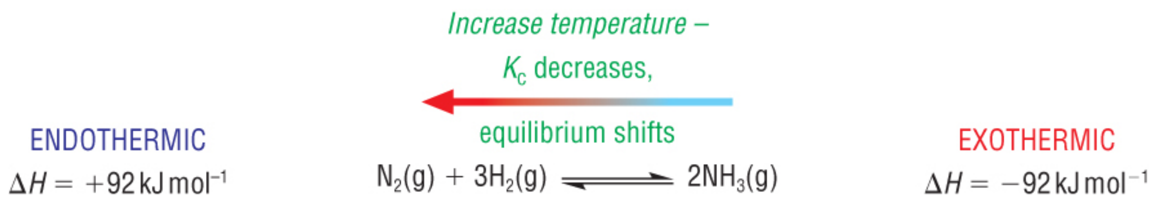
- **Increase in temperature** will shift the equilibrium to the **Products** as this is the **endothermic direction**
- There will be **more Products** and **less Reactants**:



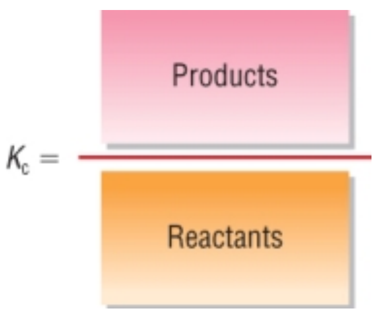
- Top number increases
- Bottom number decreases

K_c increases

b) Exothermic reactions:



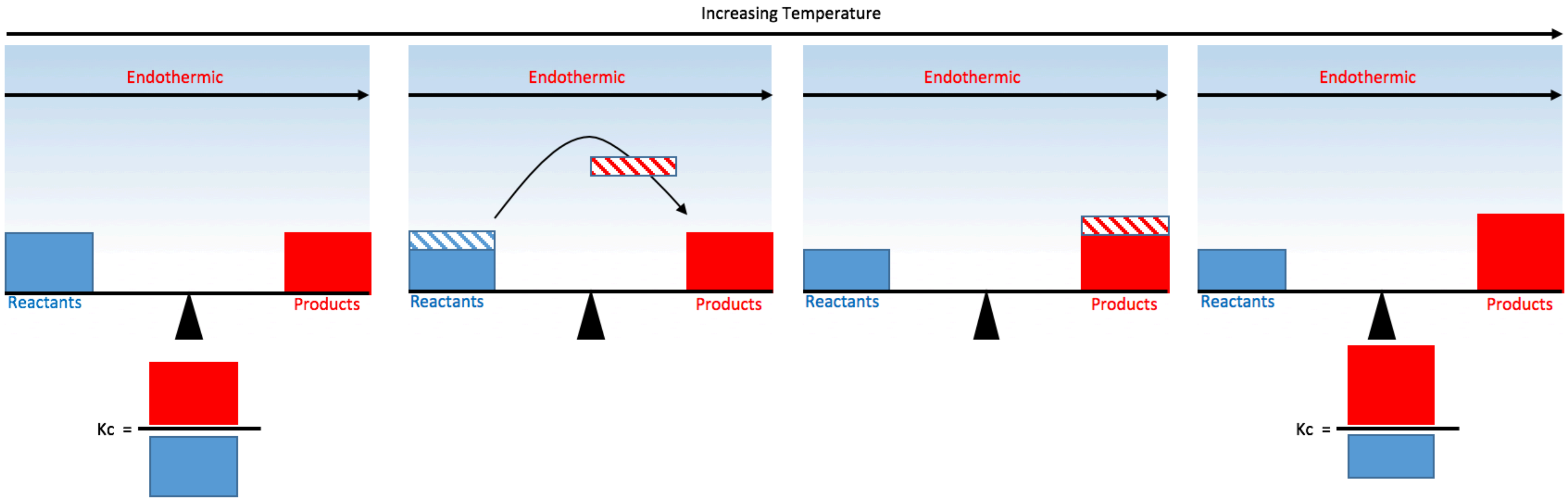
- **Increase in temperature** will shift the equilibrium to the **Reactants** as this is the endothermic direction
- There will be **more Reactants** and **less Products**:



- 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

Kc 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**:

Reaction: $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

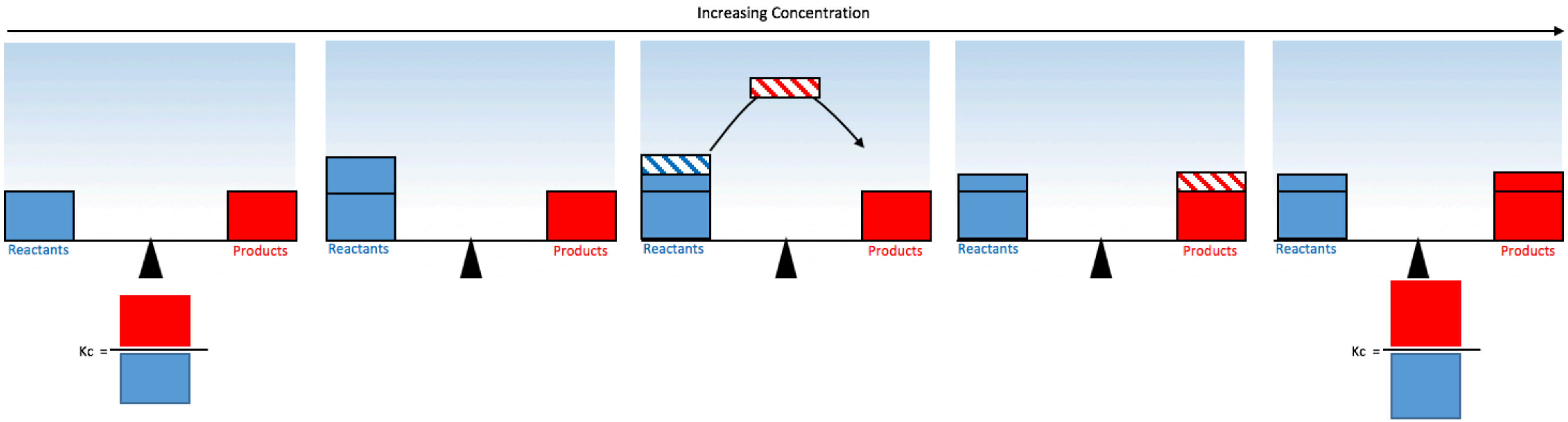
Initially: (keeping the numbers simple)

Initially		After
$[NO_2]$ = 1.0 Mol dm^{-3}	→ Double $[N_2O_4]$ →	$[NO_2]$ = 1.0 Mol dm^{-3}
$[N_2O_4]$ = 1.0 Mol dm^{-3}		$[N_2O_4]$ = 2.0 Mol dm^{-3}
$K_c = \frac{[NO_2]^2}{[N_2O_4]}$		$K_c = \frac{[NO_2]^2}{[N_2O_4]}$
$K_c = \frac{(1.0)^2}{1.0}$		$K_c = \frac{(1.0)^2}{2.0}$
K_c = 1.0 Mol dm^{-3}		K_c = 0.5 Mol dm^{-3}

← Equilibria shifts to bring K_c back to 1.0 ←

- If the concentration of $[N_2O_4]$ are doubled, the system is no longer at equilibrium.
- To bring **K_c** back from **0.5** to **1.0:**
- The system must **increase $[NO_2]$ and decrease $[N_2O_4]$**
- 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.

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

In doing so the proportions of reactants and products are re establish to the same proportions at at the start

Kc 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.

Reaction: $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

$[NO_2]$ = 1.0 Mol dm^{-3} | $[NO_2]$ = 2.0 Mol dm^{-3}

x2 pressure, x2 [ ]

$[N_2O_4]$ = 1.0 Mol dm^{-3} | $[N_2O_4]$ = 2.0 Mol dm^{-3}

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} \qquad K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

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

Effect on $[NO_2]^2$, which is x4

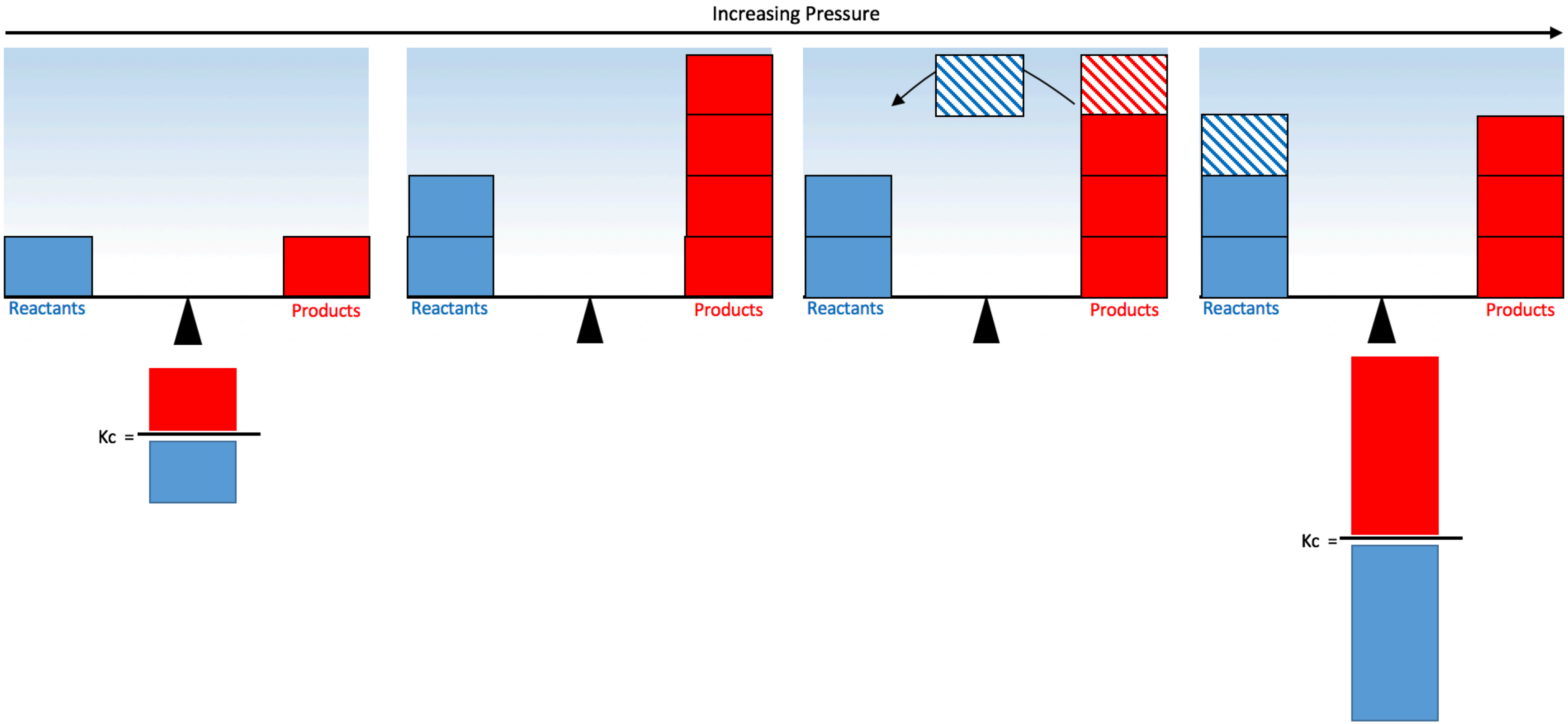
$$K_c = \frac{(1.0)^2}{1.0} \qquad K_c = \frac{4.0}{2.0}$$

$$K_c = 1.0 \text{ Mol dm}^{-3} \qquad K_c = 2.0 \text{ Mol dm}^{-3}$$

← 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 $[NO_2]$ and decrease $[N_2O_4]$**
- 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, $[NO_2]$ and $[N_2O_4]$

$K_c = \frac{[NO_2]^2}{[N_2O_4]}$
The expression shows that:
Effect on the products is $\times 2^2 = \times 4$
Effect on reactants is $\times 2$

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

Kc 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:

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

a) Explain how you know that the forward reaction is exothermic?

b) Explain what happens to the equilibria if the temperature is increased?

c) What happens to the concentration of the reactants, explain your answer?

d) What happens to the concentration of the products, explain your answer?

e) What effect if any will this have on the value of Kc?

2. The reaction between nitrogen and oxygen

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad \Delta H = +180 \text{ kJ mol}^{-1}$$

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

3. Manufacture of ammonia

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92.4 \text{ kJ mol}^{-1}$$

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

4. Consider the following equilibria:

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

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

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

c) Explain what happens to the equilibria and the value of Kc if the pressure id doubled?

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