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Tutorials for IB Chemistry

Topic 7 Equilibrium SL

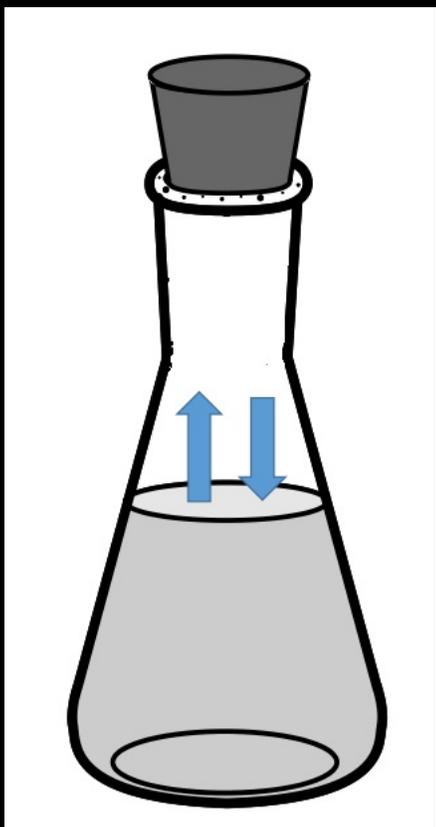
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Physical equilibrium

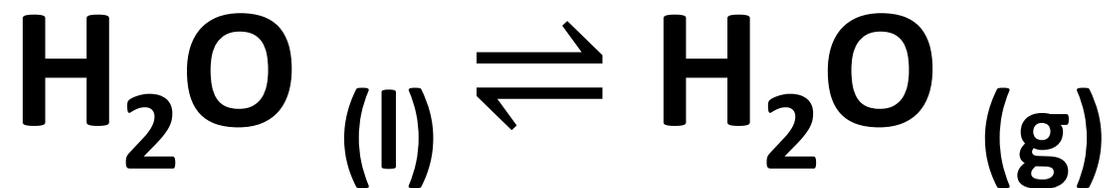
Physical equilibrium

Physical equilibrium differs from chemical equilibrium in that it involves a change of state rather than a chemical reaction.



The flask is a closed system (matter cannot escape).

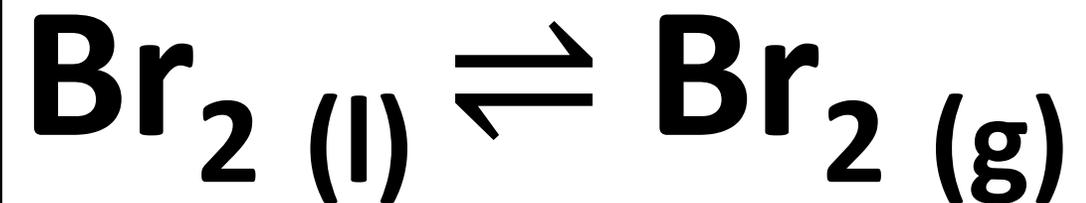
At equilibrium the rate of evaporation is equal to the rate of condensation (liquid level remains constant).



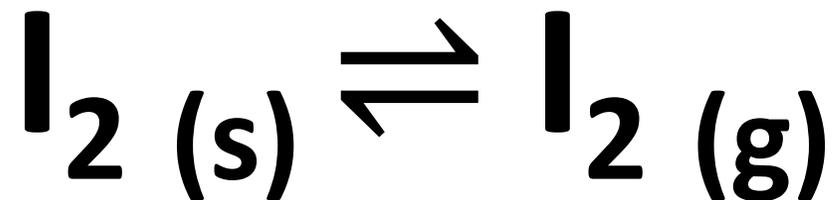
Physical equilibrium

Other examples of physical equilibrium:

Evaporation of bromine.



Sublimation of iodine.

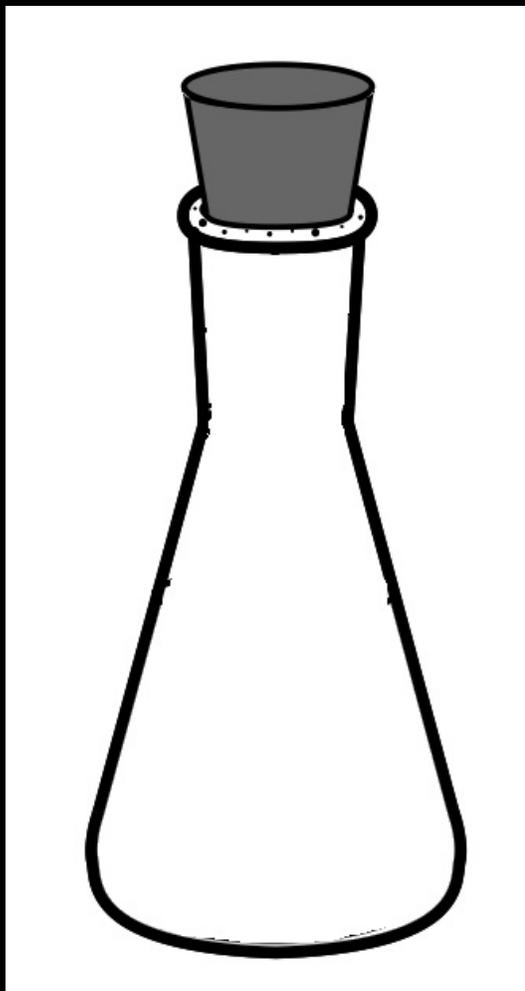


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Dynamic equilibrium

Dynamic equilibrium



Closed system

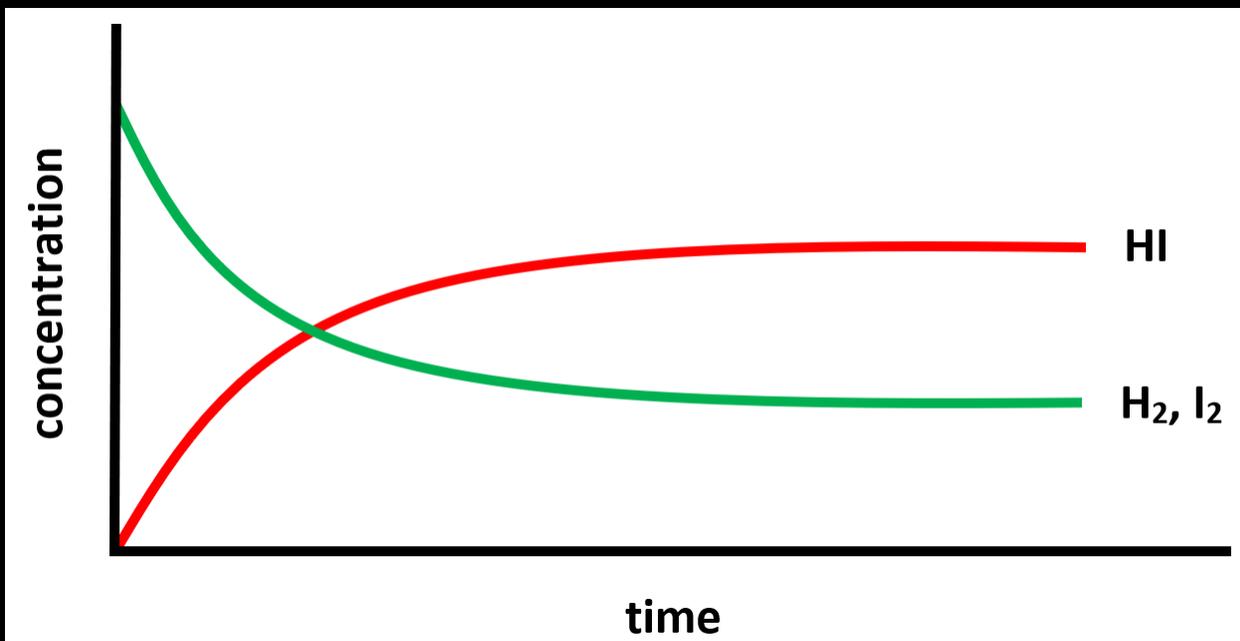
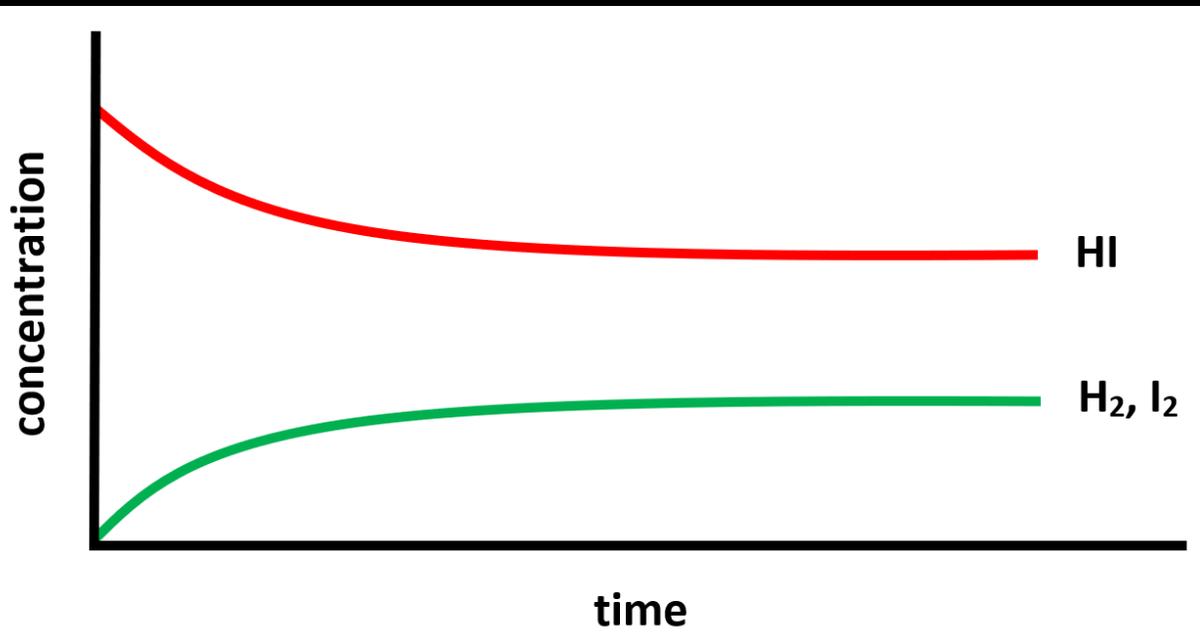
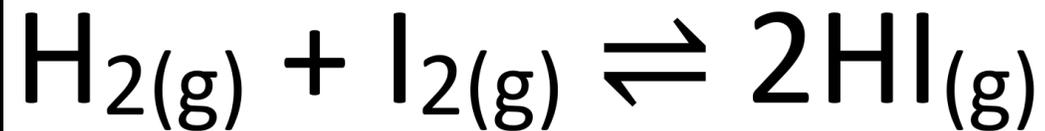
Forward reaction



Reverse reaction

At equilibrium the rate of the forward reaction is equal to the rate of the reverse reaction.

Dynamic equilibrium

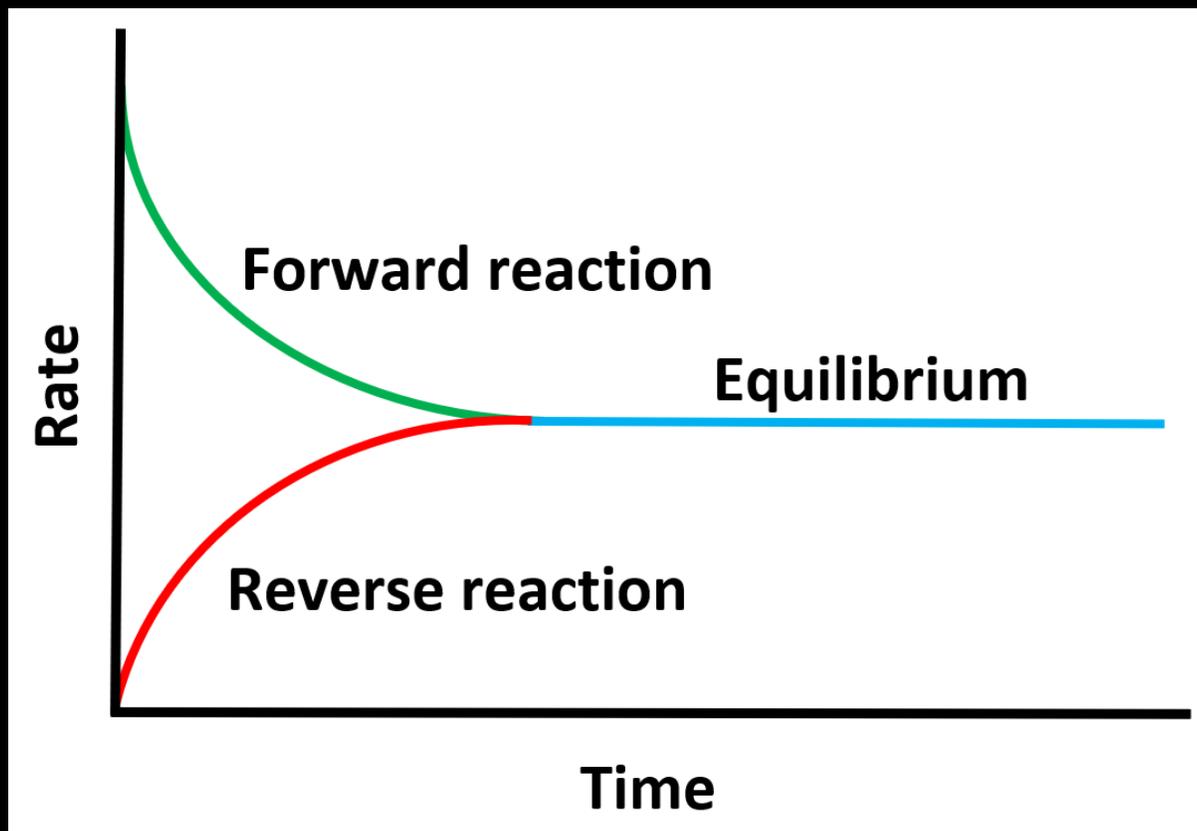


**Equilibrium can be reached from either direction.
Concentrations of reactants and products are constant
(not equal).**

Dynamic equilibrium

For a reaction at equilibrium:

- the rate of the forward reaction is equal to the rate of the reverse reaction.



Dynamic equilibrium

For a reaction at equilibrium:

- **the rate of the forward reaction is equal to the rate of the reverse reaction.**
- **the concentrations of reactants and products remain constant (but not equal).**
- **there is no change in macroscopic properties (such as colour).**
- **equilibrium can be reached from either direction.**

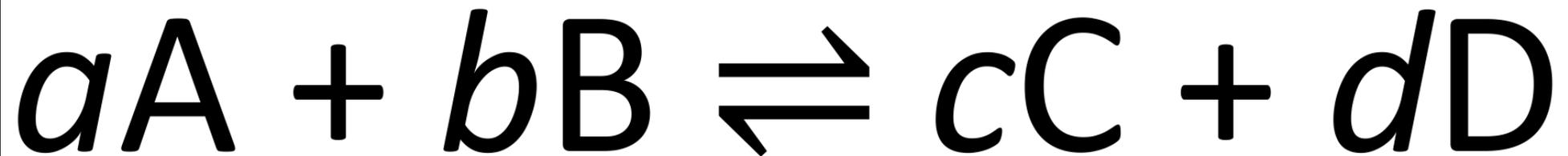
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Equilibrium constant K_c

Equilibrium constant K_c

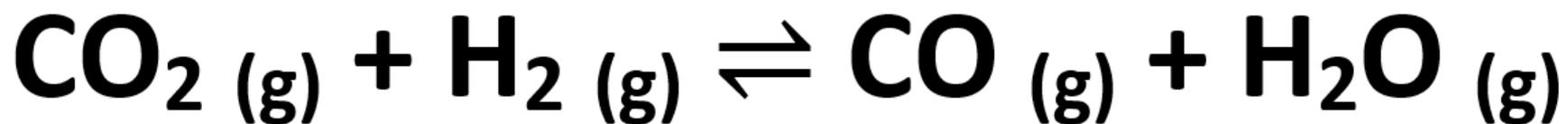
The equilibrium constant K_c is a constant for a reaction at a specific temperature (temperature dependent). Its value gives an idea of how far a reaction proceeds.



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

Equilibrium constant K_c

Calculate the equilibrium constant, K_c , for the reaction shown, if 0.0954 mol of CO_2 , 0.0454 mol of H_2 , 0.0046 mol of CO , and 0.0046 mol of H_2O vapor were present in a 1.00 dm^3 reaction vessel at equilibrium (at 440°C).



Species	Equilibrium concentrations (mol dm^{-3})
CO_2	$0.0954 / 1.00 = 0.0954$
H_2	$0.0454 / 1.00 = 0.0454$
CO	$0.0046 / 1.00 = 0.0046$
H_2O	$0.0046 / 1.00 = 0.0046$

Equilibrium constant K_c

Calculate the equilibrium constant, K_c , for the reaction shown, if 0.0954 mol of CO_2 , 0.0454 mol of H_2 , 0.0046 mol of CO , and 0.0046 mol of H_2O vapor were present in a 1.00 dm^3 reaction vessel at equilibrium (at 440°C).



$$K_c = \frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]}$$

$$K_c = \frac{[0.0046][0.0046]}{[0.0954][0.0454]} = 0.0049$$

Equilibrium constant K_c

Reaction	K_c value (at 298 K)	Position of equilibrium
$\text{CaCO}_{3(s)} \rightarrow \text{CaO}_{(s)} + \text{CO}_{2(g)}$	1.9×10^{-23}	Lies to the left (forward reaction hardly proceeds)
$2\text{H}_{2(g)} + \text{O}_{2(g)} \rightarrow 2\text{H}_2\text{O}_{(g)}$	3.2×10^{81}	Lies to the right (goes to completion)
$\text{N}_2\text{O}_{4(g)} \rightleftharpoons 2\text{NO}_{2(g)}$	4.61×10^{-3}	Lies to the left – reaction mixture contains mostly reactants
$\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$	640	Lies to the right – reaction mixture contains mostly products

Equilibrium constant K_c

Magnitude of K_c	Extent of reaction
$K_c > 1$	Equilibrium lies to the right – equilibrium mixture contains higher concentration of products
$K_c = 1$	Equilibrium mixture contains equal concentrations of reactants and products
$K_c < 1$	Equilibrium lies to the left – equilibrium mixture contains higher concentration of reactants

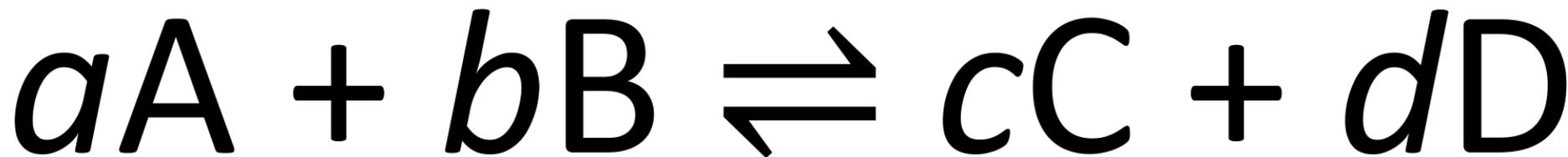
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Reaction quotient Q

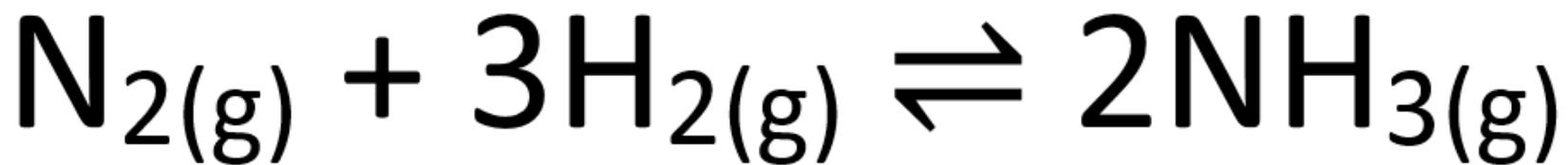
Reaction quotient Q

The reaction quotient Q measures the relative amounts of reactants and products at a point in time. It is expressed with non-equilibrium concentrations.



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

Q and direction of reaction



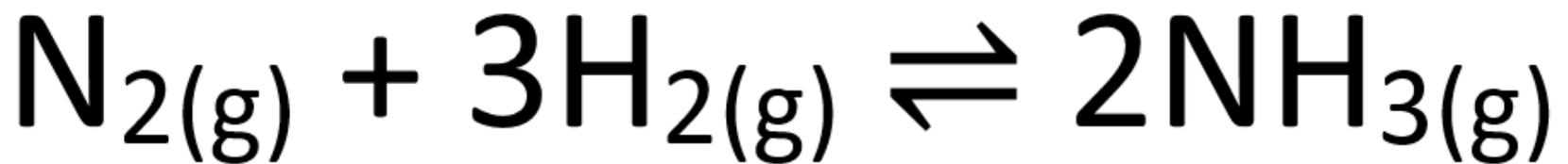
$$K_c = 6.09 \text{ at } 350 \text{ }^\circ\text{C}$$

Species	Concentration at time t (mol dm ⁻³)
N ₂	0.814
H ₂	0.422
NH ₃	0.372

$$Q = \frac{[0.372]^2}{[0.814][0.422]^3} = 2.26$$

$Q < K_c$ – the reaction will proceed to the right to increase the value of Q .

Q and direction of reaction



$$K_c = 6.09 \text{ at } 623 \text{ K}$$

Species	Concentration at time t (mol dm ⁻³)
N ₂	0.841
H ₂	0.523
NH ₃	1.32

$$Q = \frac{[1.32]^2}{[0.841][0.523]^3} = 14.5$$

$Q > K_c$ – the reaction will proceed to the left to decrease the value of Q .

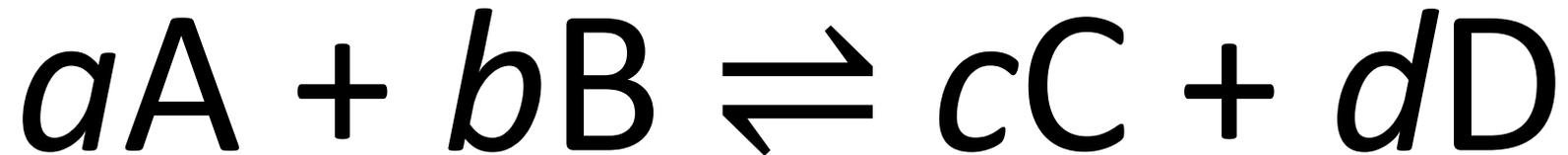
Summary

Q vs K_c	Direction of reaction	Change in Q
$Q > K_c$	To the left (reactants side)	Decrease
$Q < K_c$	To the right (products side)	Increase
$Q = K_c$	Reaction is at equilibrium	No change

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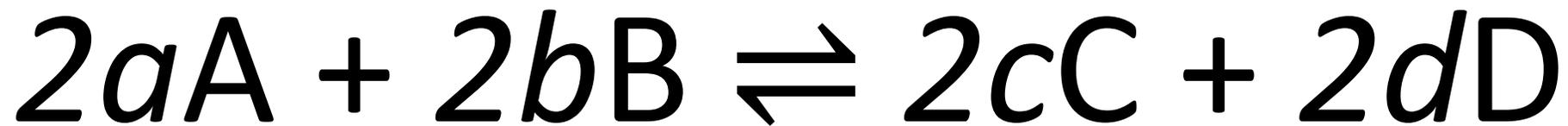
Changes to K_c for the same
reaction at the same
temperature



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

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

The K_c for the reverse reaction is the reciprocal of the K_c for the forward reaction ($1/K_c$).



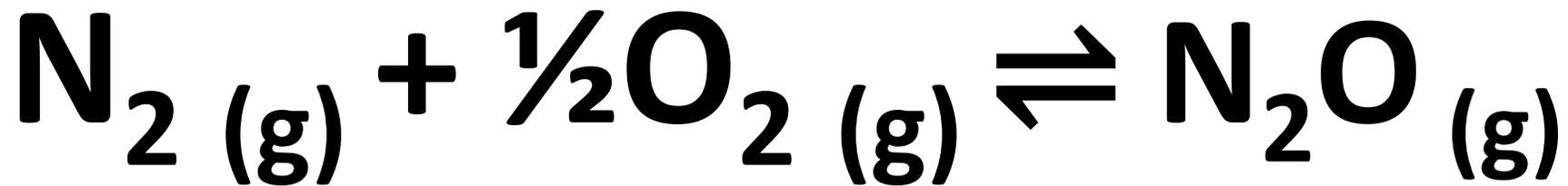
$$K_c = \frac{[C]^{2c} [D]^{2d}}{[A]^{2a} [B]^{2b}}$$

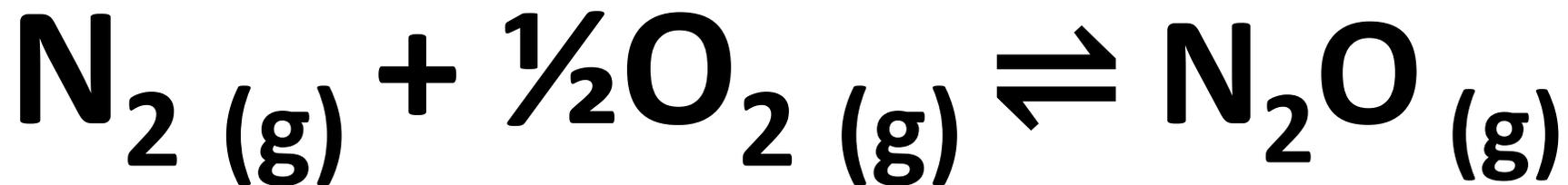
If the coefficients are doubled, the K_c is squared.

If the coefficients are halved, take the square root of the K_c .



The K_c value for the above reaction at a particular temperature is x . What is the K_c for the following reaction at the same temperature?





$$K_c = \sqrt{\frac{1}{x}}$$

Summary (note that these changes are for the same reaction at the same temperature).

Change to reaction	Effect on K_c
Reaction is reversed	$\frac{1}{K_c}$
Coefficients are doubled	K_c^2
Coefficients are halved	$\sqrt{K_c}$

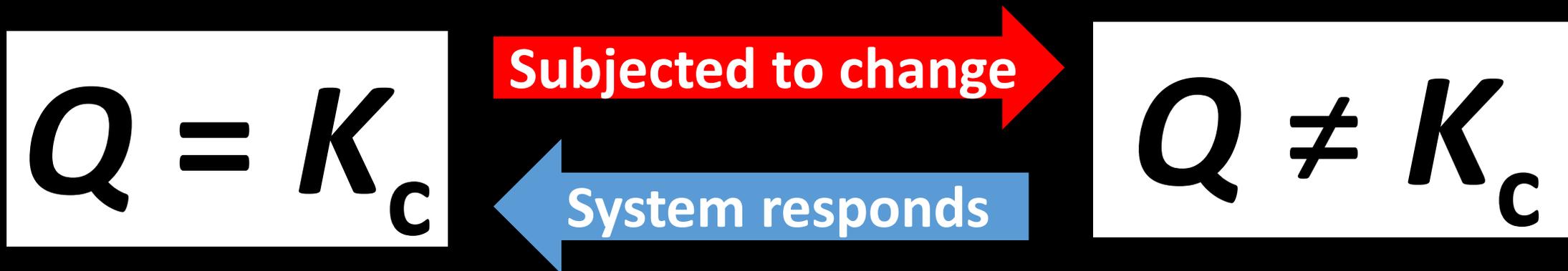
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**Le Chatelier's principle
(concentration and
pressure)**

Le Chatelier's principle

'When a system at equilibrium is subjected to a change, the system will respond to minimize the effect of the change.'

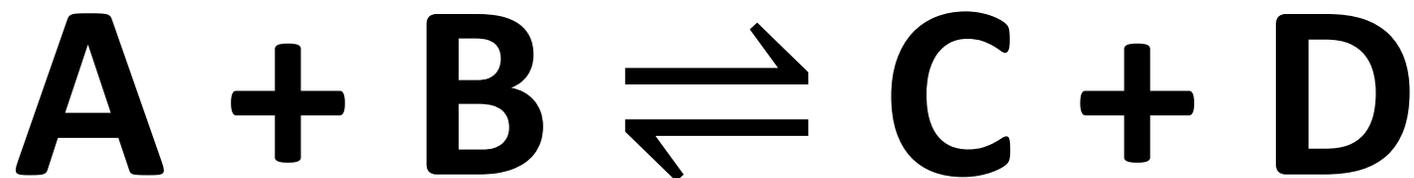


Changes made to the system can be changes in concentration, pressure or temperature.

Le Chatelier's principle

The equilibrium position can shift to the right or to the left.

The equilibrium position shifts to the right (products side)



The equilibrium position shifts to the left (reactants side)

Changes in concentration

Predict in which direction the equilibrium position will shift when the concentration of H_2 is increased.



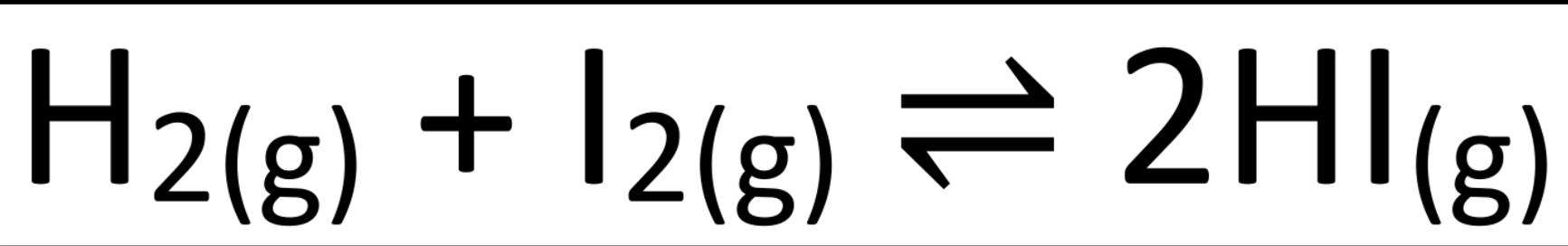
Equilibrium shifts to the right (products side)



The equilibrium position shifts to the right to 'use up' the added H_2 (K_c doesn't change).

Changes in concentration

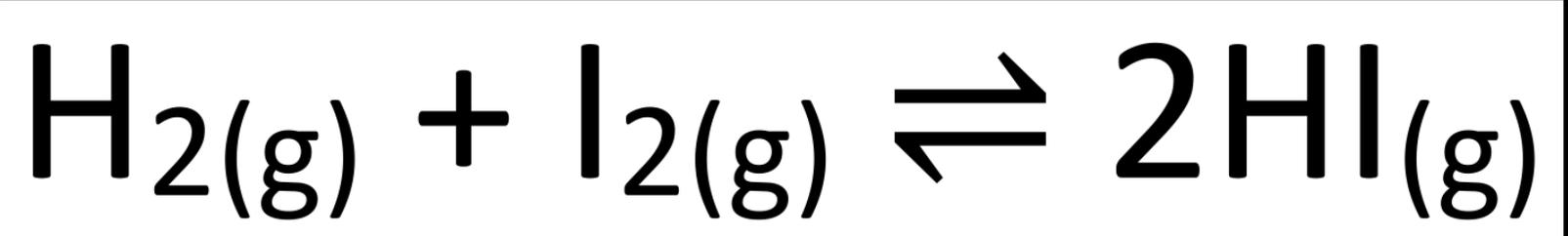
Predict in which direction the equilibrium position will shift when the concentration of HI is increased.



 Equilibrium shifts to the left (reactants side)

The equilibrium position shifts to the left to 'use up' the added HI (K_c doesn't change).

Changes in concentration

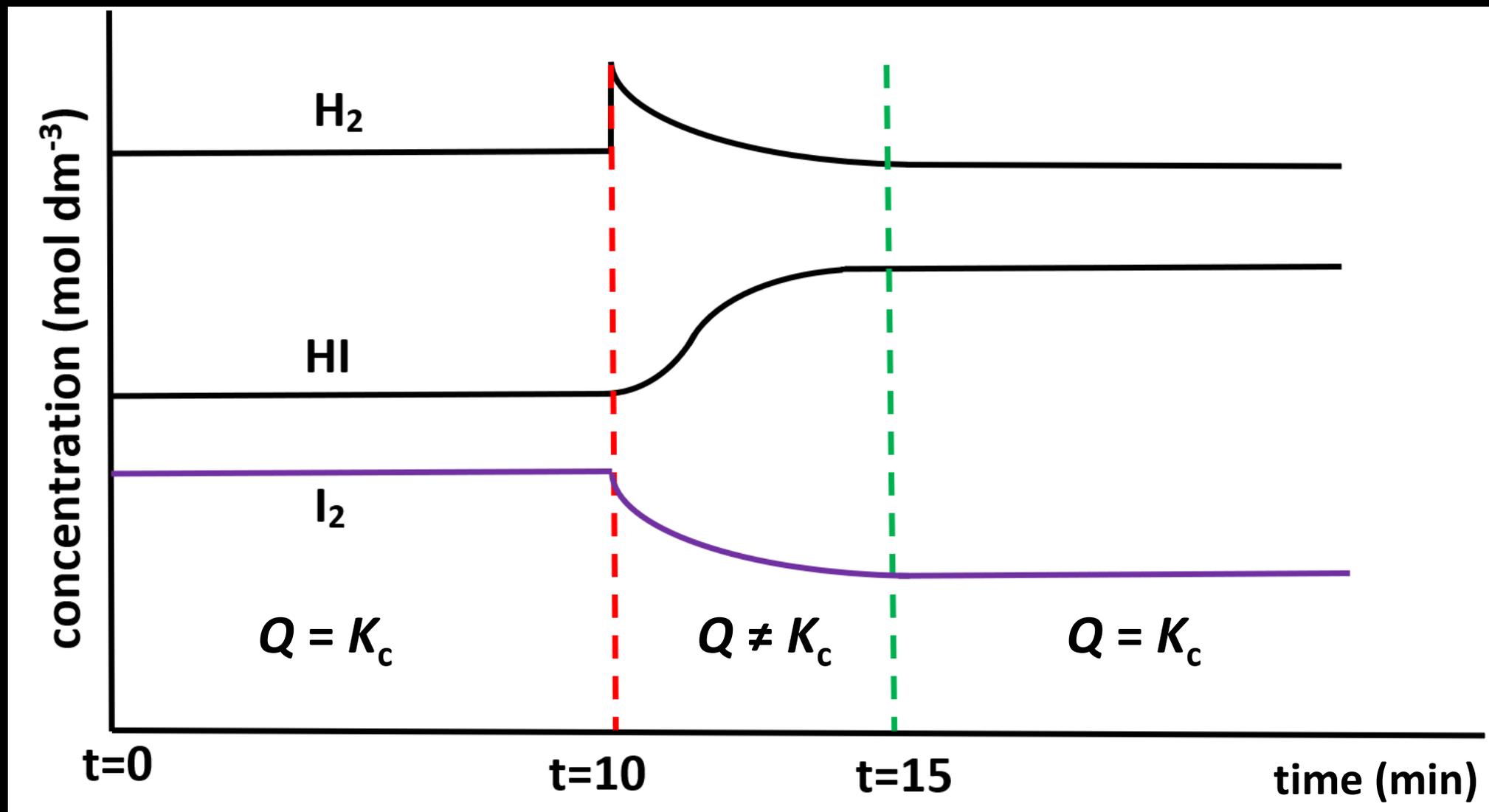


$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

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

Increasing the $[\text{H}_2]$ makes $Q < K_c$ (not at equilibrium).
The equilibrium position shifts to the right, increasing the $[\text{HI}]$ and decreasing the $[\text{H}_2]$ until $Q = K_c$

Changes in concentration



Summary

Change to system at equilibrium	Change in equilibrium position	Value of K_c
Increase concentration of reactants	shifts to right (products side)	No change
Decrease concentration of products	shifts to right (products side)	No change
Decrease concentration of reactants	shifts to left (reactants side)	No change
Increase concentration of products	shifts to left (reactants side)	No change

Changes in pressure

The pressure of a system can be changed by:

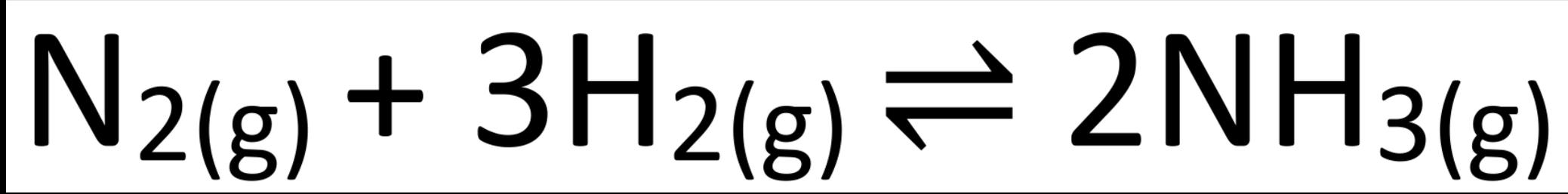
- Adding or removing a reactant or product
- Changing the volume of the reaction vessel

$$PV = k$$

Boyle's law: pressure and volume are inversely proportional (at constant temperature).

Changes in pressure only have an effect on the equilibrium position when there are different amounts of **gaseous molecules** in the reactants and products.

Changes in pressure



4 moles of gas on
reactants side (more
gaseous molecules)

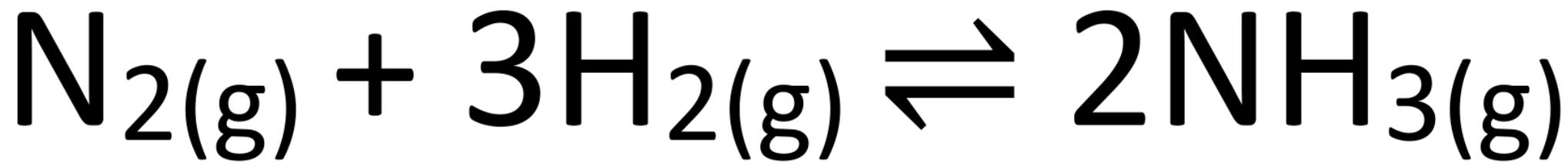
2 moles of gas on
products side (fewer
gaseous molecules)

Position of equilibrium shifts to side with fewer number of gaseous molecules results in a decrease in pressure.

Position of equilibrium shifts to side with greater number of gaseous molecules results in an increase in pressure.

Changes in pressure

Predict in which direction the equilibrium position will shift when the pressure is increased.

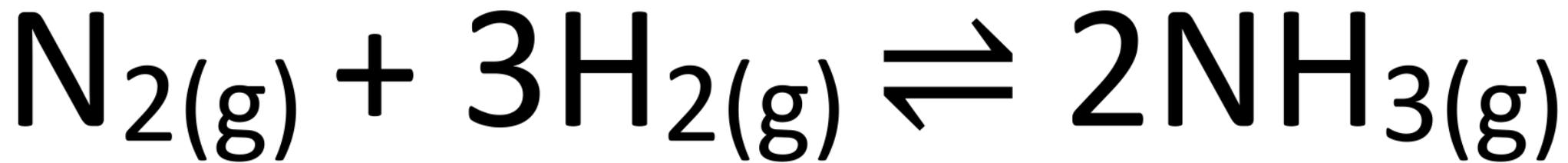


Equilibrium shifts to the right (products side)

Equilibrium position will shift to the right because there are **fewer gaseous molecules** on the products side, which lowers the pressure (K_c doesn't change).

Changes in pressure

Predict in which direction the equilibrium position will shift when the pressure is decreased.

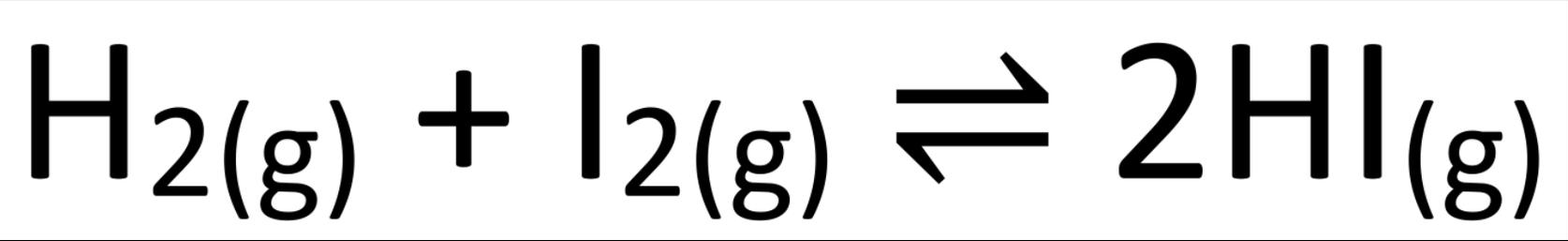


Equilibrium shifts to left (reactants side)

Equilibrium position will shift to the left because there are more **gaseous molecules** on the reactants side, which increases the pressure (K_c doesn't change).

Changes in pressure

Changes in pressure when there are the same number of **gaseous molecules** in the reactants and products.



2 moles of gas on
reactants side

2 moles of gas on
products side

Position of equilibrium will not change because there are the same number of **gaseous molecules** on both sides of the equation.

Summary

Change to system at equilibrium	Change in equilibrium position	Value of K_c
Increase in pressure	shifts to side with fewer gaseous molecules	No change
Decrease in pressure	shifts to side with more gaseous molecules	No change
Change in pressure when equal number of gaseous molecules in the reactants and products	No change	No change

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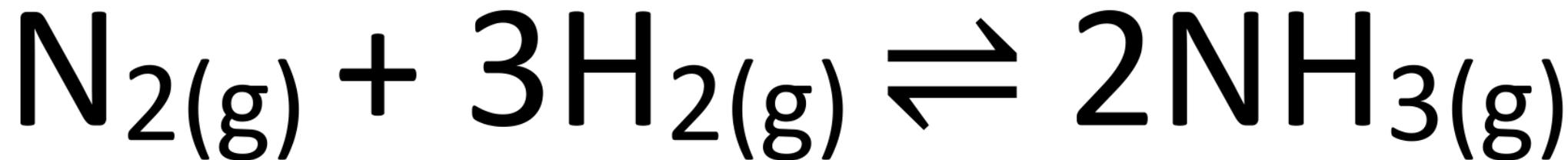
**Le Chatelier's principle
(temperature)**

Changes in temperature

Changes in temperature cause a change in the equilibrium position and in the value of the equilibrium constant K_c .

Forward reaction is exothermic

$\Delta H = -92$
 kJ mol^{-1}

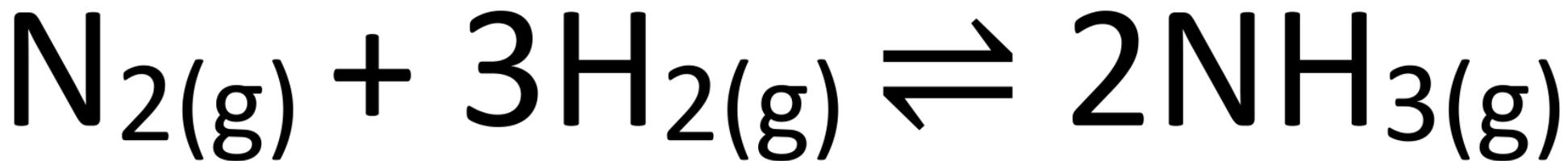


$\Delta H = +92$
 kJ mol^{-1}

Reverse reaction is endothermic

Changes in temperature

Predict in which direction the equilibrium position will shift when the temperature is increased.



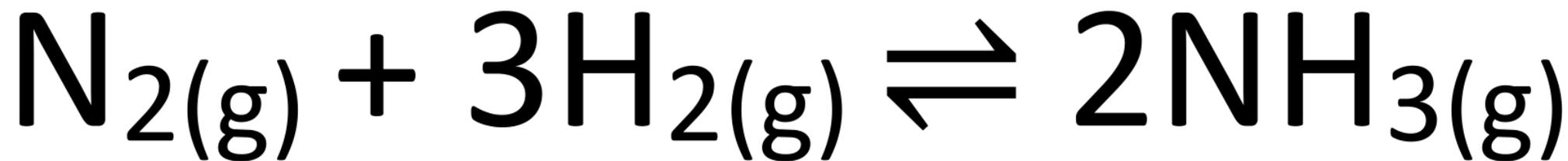
$\Delta H = +92.4$
 kJ mol^{-1}

Equilibrium shifts to left (reactants side)

The system will absorb the extra heat favouring the reverse reaction because it is endothermic.

Changes in temperature

Predict in which direction the equilibrium position will shift when the temperature is decreased.



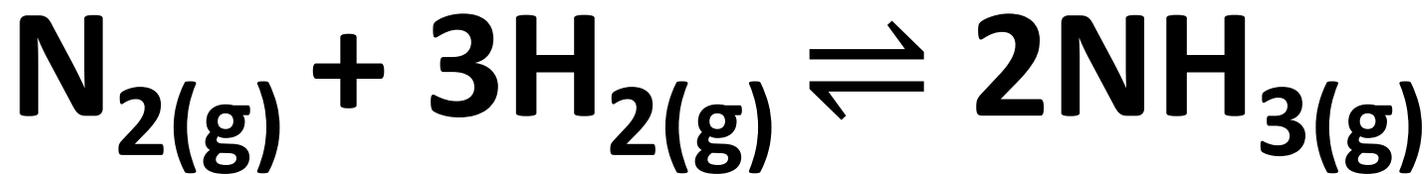
Equilibrium shifts to the right (products side)

$\Delta H = -92.4$
 kJ mol^{-1}

The system will produce heat favouring the forward reaction because it is exothermic.

Temperature and K_c

For an exothermic reaction, increasing the temperature shifts the equilibrium position to the left and **decreases** the value of the K_c



$$\Delta H = -92 \text{ kJ mol}^{-1}$$

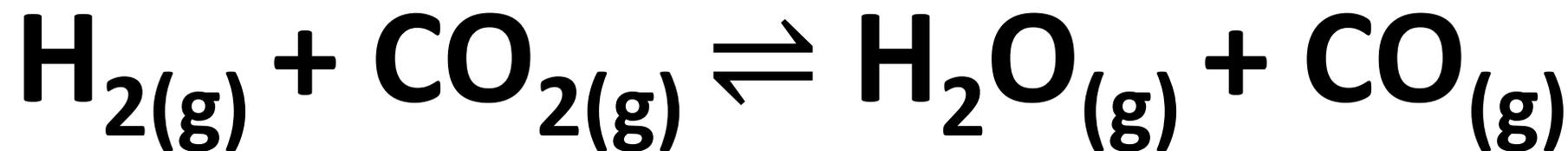
$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$



The value of the K_c decreases.

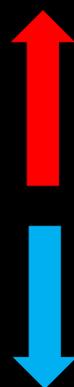
Temperature and K_c

For an endothermic reaction, increasing the temperature shifts the equilibrium position to the right and **increases** the value of the K_c



$$\Delta H = +41 \text{ kJ mol}^{-1}$$

$$K_c = \frac{[\text{H}_2\text{O}][\text{CO}]}{[\text{CO}_2][\text{H}_2]}$$



The value of the K_c increases.

Summary

For exothermic reactions ($\Delta H = \text{negative}$)

Change in temperature	Change in equilibrium position	Value of K_c
increase temperature	shifts to left (reactants side)	decreases
decrease temperature	shifts to right (products side)	increases

Summary

For endothermic reactions ($\Delta H = \text{positive}$)

Change in temperature	Change in equilibrium position	Value of K_c
increase temperature	shifts to right (products side)	increases
decrease temperature	shifts to left (reactants side)	decreases

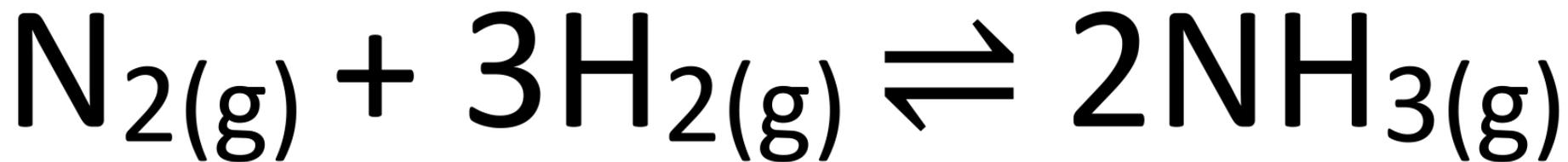
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**Equilibrium and
catalysts**

Adding a catalyst

The catalyst used in the Haber process is powdered iron.



A catalyst increases the rate of the forward and reverse reactions by the same amount.

A catalyst does not change the equilibrium position or the value of the K_c

A catalyst allows equilibrium to be reached more quickly.