# 1 Chemical equilibrium

**Chemical equilibrium** is a dynamic equilibrium when the rate of the forward reaction equals the rate of the reverse reaction for a reversible reaction in a closed system.

isolated from the surroundings no reagents can escape

reverse reaction can take place

#### $N_2 + 3H_2 \rightleftharpoons 2NH_3$ $N_2$ and $H_2$ is sealed in a container:

Initially:	Over time:	Eventually:
$\begin{array}{l} \mbox{High [N_2] and [H_2]} \\ \rightarrow \mbox{Forward reaction fast} \\ [NH_3] = 0 \\ \rightarrow \mbox{ No reverse reaction} \end{array}$		Chemical equilibrium reached Forward and reverse reaction at the same rate. [N <sub>2</sub> ], [H <sub>2</sub> ] & [NH <sub>3</sub> ] constant.

Draw reaction rate vs time graphs for both reactions:

Reaction rate

time(s)

## Equilibrium constant (K<sub>c</sub>)

The equilibrium constant is the ratio of concentration of the products to the concentration of the reactants in the equilibrium mixture and the value holds only for a **specific temperature**.

 $aA + bB \rightleftharpoons cC + dD$   $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ 

Square brackets [ ] represent concentrations and  $K_c$  has no unit. **Pure solids and liquids/solvents** are left out.

 $\mathbf{K}_c > \mathbf{1}$ : More products than reactants in the equilibrium mixture.

 $\mathbf{K}_{c}$  < 1: More reactants than products in the equilibrium mixture.

# **QUESTION 1**

1.1 Write equations for the equilibrium constant for each of the following reactions:

$2H_2O_2(aq) \rightleftharpoons 2H_2O(l) + O_2(g)$	
$AgCI(s) \implies Ag^+(aq) + CI^-(aq)$	
$6\text{CO}_2(g) + 6\text{H}_2\text{O}(I) \rightleftharpoons \text{C}_6\text{H}_{12}\text{O}_6(s) + 6\text{O}_2(g)$	

1.2

Ammonia is prepared according to the following reaction:

$$3H_2(g) + N_2(g) \Rightarrow 2NH_3(g)$$

At a high temperature an equilibrium mixture for the above endothermic reaction has the following concentrations:

$$\begin{split} [\text{NH}_3] &= 2 \, \text{mol/dm}^3 \\ [\text{H}_2] &= 1,5 \, \text{mol/dm}^3 \\ [\text{N}_2] &= 0,5 \, \text{mol/dm}^3 \end{split}$$

Calculate the equilibrium constant ( $K_c$ ) for the reaction at this temperature.

## 1.3 Hydrogen iodide can be produced by the following reversible reaction:

 $H_2(g) + I_2(g) \implies 2HI(g)$   $K_c = 56,00 \text{ at } 425^{\circ}C$ 

At a certain time during the reaction the concentrations in the container are:

$$\label{eq:H2} \begin{split} [\mathsf{H}_2] &= 1{,}5\,\text{mol/dm}^3\\ [\mathsf{I}_2] &= 1{,}0\,\text{mol/dm}^3 \end{split}$$

 $[HI] = 2.5 \, \text{mol/dm}^3$ 

Do a calculation to determine if the reaction has reached chemical equilibrium.

1.4 Consider the following reaction:  $2A(g) + B(g) \Rightarrow C(g)$ .

12 mol A and 10 mol B are sealed in a 2 dm<sup>3</sup> container. At equilibrium there are 4 mole of A in the container. Calculate the  $K_c$  value.

Reaction		
Mole initially		
Mole react		
Mole at equilibrium		
Concentration at equilibrium $c = \frac{n}{\nabla}$		

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### Le Chatelier's Principle:

When the equilibrium in a closed system is disturbed, the system will re-instate a new equilibrium by favouring the reaction that will oppose the disturbance.

The following dynamic equilibrium is reached in a closed container:

 $2A(g) + B(s) \hookrightarrow 2C(g) + D(g)$   $\Delta H$  is negative

$$\mathsf{K}_{\mathsf{c}} = \frac{[\mathsf{C}]^2[\mathsf{D}]}{[\mathsf{A}]^2}$$

$$c = \frac{n}{v}$$

#### If A is added to the mixture in the container:

Disturbance: [A] increases. According to Le Chatelier's principle the system reacts to decrease the [A]. The forward reaction is favoured. (Use A) More C and D is produced.  $K_c$  remains the same.

#### If C is added to the mixture in the container:

Disturbance: [C] increases. According to Le Chatelier's principle the system reacts to decrease the [C] . The reverse reaction is favoured. (Use C) D decreases.  $K_c$  remains the same.

#### If A is removed from the mixture in the container:

Disturbance: [A] decreases. According to Le Chatelier's principle the system reacts to increase [A] . The reverse reaction is favoured (make A). C and D decreases.  $K_c$  remains the same.

#### B(s) is added:

Solid has no effect on equilibrium.

#### If the volume of the container is decreased:

Disturbance: pressure increases (Boyle's Law). According to Le Chatelier's principle the system reacts to lower the pressure. Reacts to produce less moles of gas. Reverse reaction is favoured. C and D decreases.  $K_c$  remains the same.

#### If the temperature is increased:

Disturbance: Temperature increases. According to Le Chatelier's principle the system reacts to decrease the temperature. Endothermic reaction is favoured (uses energy). ( $\Delta$ H is negative  $\therefore$  forward reaction exothermic.) The reverse reaction is favoured. C and D decreases. K<sub>c</sub> decreases.

#### Catalyst is added:

No effect on equilibrium. The rate of both reactions increase **equally**.

Favoured does not indicate that the reaction happens faster than before, but that it happens faster than the reaction in the opposite direction.

Action	Disturbance	Explanation
Adding acid	[H <sup>+</sup> ] increases	Acid donates H <sup>+</sup>
Adding base	[H <sup>+</sup> ] decreases	Base reacts with H <sup>+</sup>
Adding AgNO <sub>3</sub>	[Cl <sup>-</sup> ] decreases	$Ag^+ + CI^- \rightarrow AgCI(s)$ precipitate
Adding $BaCl_2$ or $Ba(NO_3)_2$	$[SO_4^{-2}]$ decreases	$Ba^{+2} + SO_4^{-2} \longrightarrow BaSO_4(s)$ precipitate

The colours of compounds with transition elements are well-known. For example, consider the following equation of a reversible reaction:

$$\underbrace{\overbrace{2CrO_{4}^{2^{-}}(aq)}^{\text{yellow}} + 2H^{+}(aq) \iff \underbrace{cr_{2}O_{7}^{2^{-}}(aq)}^{\text{orange}} + H_{2}O(\ell)$$

- 1. Write down an expression for te equilibrium constant.
- 2. How will the equilibrium constant (K<sub>c</sub>) be influenced in the following situations:
  - a) sodium chromate ( $Na_2CrO_4$ ) is added.
  - b) Hydrochloric acid is added.
  - c) Sodium hydoxide is added
- 3. Explain in detail how the colour of the solution will be influenced when sodium hydroxide is added.



# $2A(g) + B(g) \Rightarrow 3C(g) + D(g)$

	A and B into container	A added	B removed	D added
Disturbance				
Le Chatelier: System reacts to				
The … reaction is favoured				
[C]				
K <sub>c</sub>				

Reaction rate					

Concentrations

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# $\Delta$ H < 0

Volume doubled	Temperatuur increased	Temperarature decreased	Catalyst added

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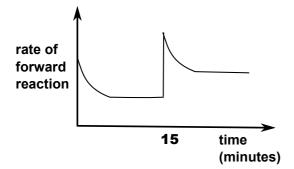
# Le Chatelier, Temperature and Equilibrium constants

### **QUESTION 2**

#### Choose the correct word in the brackets:

- 2.1 The following reaction is at equilibrium at 400K:  $A_2(g) + 3B_2(g) \implies 2AB_3(g) \qquad \Delta H < 0$ If the temperature is increased to 600 K the K<sub>c</sub>-value will (increase/decrease/stay the same).
- 2.2 A mixture of NO and Br<sub>2</sub> is placed in a container. The following traction occurs:  $2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$

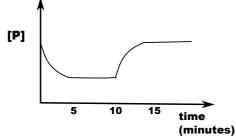
After 5 minutes chemical equilibrium is reached. The following graph shows how the rate of the forward reaction changes with time:

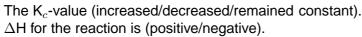


After 15 s the temperature was (increased/decreased) and the  $K_c$ =value (increased/fecreased/remained constant).

2.3 P and Q are sealed in a container and the following chemical equilibrium is reached after 5 minutes at 500 K:  $P(g) + 2Q(g) \rightleftharpoons R(g)$ 

After 10 minutes the temperature is increased to 600 K and after 5 minutes a new chemical equilibrium is established. The following graph shows the change in concentration with time.

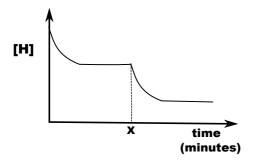




2.4 The following reaction mixture turns more red when the temperature is increased:  $\underbrace{3H(g)}_{pink} \rightleftharpoons \underbrace{2F(g)}_{red} + 2D(g)$ 

When the temperature is increased the equilibrium constant (increases/decreases).  $\Delta H$  is (positive/negative).

2.5 The following reaction reached chemical equilibrium in a closed container: 2H(g) + I(g)  $\rightleftharpoons$  2 K(g)  $\Delta$ H < 0



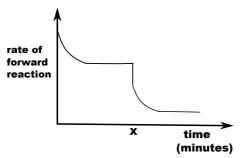
At time X the temperature was (increased/decreased) and the  $K_c$ -value (increases/decreases/remains constant).

2.6 The following reaction is in chemical equilibrium:  $\underbrace{3M(g)}_{green} \rightleftharpoons \underbrace{2N(g)}_{blue} + 2P(g)$ 

When the temperature increases the mixture turns more blue.

 $\Delta H$  is (positive/negative).

2.7 The following reaction reached chemical equilibrium in a closed container:  $2X(g) + Y(g) \rightleftharpoons Z(g) + 2A(g)$ 



After time X the  $K_c$  value is (larger/smaller) than before. The heat of the reaction is (positive/negative).  $2A(g) + B(g) \rightleftharpoons 3C(g) + D(g)$   $\Delta H < 0$  forwards exothermic

Catalyst added	۶۲ Su	constant			
Temperature decreased	Ť	⊥↓	exothermic forward	Ļ	~
Temperature increased	T↑	Ť⊥	endothermic reverse	1	$\rightarrow$
Volume doubled	, ⊐	P	more mol gas forward	Ļ	constant
D added	[D]↑	↑[a]	reverse	$\rightarrow$	constant
B removed	[B]	[B]↑	reverse	$\rightarrow$	constant
A added	[A]↑	[A]	forward	Ļ	constant
A and B in a container					
	Disturbance	Le Chatelier's principle: the system reacts to	The reaction is favoured	[C] will	Kc

