Chemical Equilibrium

A **reversible reaction** is a reaction that can, and does, occur in both directions.

Chemical Equilibrium is a state of dynamic balance in which the rate of forward reaction equals the rate of the backward reaction.

In a **dynamic state** the reactants are continuously forming products and the products are continuously forming reactants.

In a **dynamic equilibrium** the rate of the forward reaction equals the rate of the backward reaction

Le Châtelier's principle states that when a system at equilibrium is disturbed by a stress, the system shifts in equilibrium to relieve the stress applied.

(A **stress** is a change in conditions for the reaction)

Conditions which affect equilibrium position

a) **Concentration**

- Increasing the concentration of a reactant will increase the rate of the forward reaction. The rate of the forward reaction increases as the system attempts to reduce the concentration of the reactant as close to the original concentration as possible.
- Decreasing the concentration of a reactant (i.e. removing some of it) will increase the rate of the backward reaction until the concentration of the reactant returns as close to its original concentration as possible.

b) **Pressure**

- An increase in pressure (i.e. decreasing the volume of the container) will cause the reaction to shift in the direction that reduces/relieves pressure, i.e. the side of the equation with a fewer number of gas molecules.
- A decrease in pressure will cause the reaction to shift in the direction with the greater number of molecules. This is done in order to try and return the pressure in the container to its original value by creating more molecules.

***Note** if there is the same number of molecules on either side of the equation then a change in pressure will have no effect on the equilibrium position *

c) **Temperature**

The shift in equilibrium caused by a change in temperature depends whether the reaction is exothermic or endothermic

Exothermic describes a process that releases energy in the form of heat (negative ΔH)

Endothermic describes a process that takes in energy in the form of heat (positive ΔH)

- Increasing temperature will cause an exothermic reaction to be driven backwards
- Increasing temperature will cause an endothermic reaction to be driven forward

*Note

A **catalyst** speeds up the rate at which equilibrium is reached but does not change the position of equilibrium*

The Haber process

The manufacture of ammonia (NH_3) for the fertiliser industry

$$N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)} \qquad \Delta H = -92.4\ kJmol^{-1}$$

Less molecules on this side

The minus sign tells us that the forward reaction is **exothermic**

Le Châtelier's principle predicts that the yield of NH_3 is maximised by:

1. **High pressure** - increasing pressure causes the reaction to shift to the right as there are fewer molecules on this side. (The higher the pressure the better, but >200atm is too expensive to maintain and safety issues, e.g. gas leaks and explosions, arise).
2. **Low temperature** - the production of ammonia is exothermic and so lowering the temperature will cause the reaction to shift to the right, i.e. producing more ammonia. (However, lowering the temperature slows down the rate of the reaction and so a compromise temperature of 500°C is used).

The Contact process

The manufacture of sulfuric acid

$$2SO_{2(g)} + O_{2(g)} \overset{(V_2O_5)}{\Leftrightarrow} 2SO_{3(g)} \qquad \Delta H = -196 kJmol^{-1}$$

Le Châtelier's principle predicts the yield of $S0_3$ is maximised by:

1. **High pressure** - increasing pressure causes the reaction to shift to the right as there are fewer molecules on the right. However, high pressure is expensive to maintain and it liquefies the sulfur trioxide so a compromise pressure of 2 atms is used.
2. **Low temperatures** - since the forward reaction is exothermic, lowering temperature will cause the reaction to shift to the right, producing a greater amount of sulfur trioxide. (However, lowering the temperature slows down the rate of the reaction and so a compromise temperature of 450°C is used).

The Equilibrium constant (K_c)

- The equilibrium constant gives us an idea of how far the equilibrium has gone to completion (i.e. to the right). A high k_c value means that the concentration of the products is much greater than the concentration of the reactants.
- The value of k_c tells us how far a reaction at equilibrium has gone to completion but not how fast the reaction goes
- K_c is temperature dependent, since changing the temperature shifts the equilibrium in a particular direction. Temperature is the only factor that effects the value of k_c (while changing pressure does change the number of moles of each substance present, in accordance with le Châtelier's principle, the accompanying change in volume balances this out and so the same value of k_c is obtained).
- If the reaction is reversed (i.e. the products are considered the reactants and the reactants are considered to be the products) then,

$$K_c \text{ of the reversed reaction} = \frac{1}{\text{Kc of original reaction}}$$

Writing the equilibrium constant (k_c) expression

Reaction equation:

$$aA + bB \Leftrightarrow cC + dD$$

number of moles

product

square brackets means concentration

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

products

reactants

Equilibrium constant

Indices = moles of each substance

N.B. **multiply** these not add

(number in front of element in chemical equation)

E.g. The Haber process equilibrium

$$N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)}$$

$$k_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Sample Exam Questions

2018 Q9

Q9. (a) A state in which the rate of the forward reaction equals the rate of the reverse reaction

(b)

$$\frac{[COCl_2]}{[CO][Cl_2]}$$

(c)(i) *State:* the mixture turns less green (more colourless)
Explain: When pressure is increased, the equilibrium shifts to the side with less molecules, which is the right hand side
(ii) *State:* Less yield of phosgene
Explain: -High temperatures favour endothermic reactions, which is the reverse reaction.
-The equilibrium shifts left to oppose the stress.
(iii) *State:* no effect
Explain: -K_c value is constant at constant temperature.
-Only temperature affects K_c value.
-The charcoal catalyst will alter the rate of the forward and reverse reactions equally.
(d) 85% of the chlorine had reacted at equilibrium
100 – 85 = 15% chlorine left
(0.2 ÷ 100) × 15 = 0.03 moles chlorine present at equilibrium

	CO	**+**	**Cl_2**	**⇌**	**$COCl_2$**
At start:	0.2 ÷ 12 = ***0.0167 moles***		0.2 ÷ 12 = ***0.0167 moles***		***0 moles***
At equilibrium:	0.03 ÷ 12 = ***0.0025 moles***		0.03 ÷ 12 = ***0.0025 moles***		(0.2 – 0.03) ÷ 12 = ***0.0142 moles***

K_c = 0.0142 ÷ (0.0025 × 0.0025) = **2272**
(e) -Low temperatures are uneconomical because they slow down the rate of the reaction.
-High pressures are unsafe due to risk of explosions

2017 Q7

Q7. (a)*Chemical equilibrium:* a state in which the rate of the forward reaction equals the rate of the reverse reaction
Dynamic: both the forward and reverse reaction are continuous
Le Châtelier's principle: If a stress is placed on a system at equilibrium, the system will adjust to relieve the stress
(b)

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

(c)

	N_2O_4	⇌	$2NO_2$
At start:	1m÷10 = ***0.1 m***		***0m***
At equilibrium:	(1 – x) ÷ 10 m		2x ÷ 10 m

$$\frac{\left[\frac{2x}{10}\right]^2}{\left[\frac{1-x}{10}\right]} = 0\cdot2$$

Multiply everything by 10:

$$\frac{[2x]^2}{[1-x]} = 2$$

Cross multiply:

$$4x^2 = 2(1-x)$$

$$4x^2 = 2 - 2x$$

$$4x^2 + 2x - 2 = 0$$

Use the –b formula:

$$\frac{-b\pm\sqrt{b^2-4ac}}{2a}$$

$$\frac{-2\pm\sqrt{4+32}}{8}$$

$$\frac{-2\pm6}{8} = \frac{4}{8} = \frac{1}{2}$$

x cannot be negative
x = 0.5

For N_2O_4: (1 – 0.5) ÷ 10 = **0.05 M**
For NO_2: (2 × 0.5) ÷ 10 = **0.1 M**
(d) -When temperature was increased, the equilibrium shifted right (the colour turned darker)
-Increased temperature favours endothermic reactions, therefore the forward reaction (the decomposition of denitrogen tetroxide) is endothermic
(e) -There is no change in Kc value
-Kc value is constant at constant temperature. Only a change in temperature results in a change of Kc value.

2016 Q7

a) Le Châtelier's principle states that when a system at equilibrium is disturbed by a stress the system shifts in equilibrium to relieve the stress applied.

- *i) Low temperatures -*
  As the forward reaction is exothermic and thus generates heat, lowering the temperature will result in the equilibrium to shift in favour of the forward reaction in order to restore the temperature conditions as close to the original temperature as possible, and as a result increasing the yield of sulfur trioxide
- *ii) High pressure -*
  In accordance with Le Châtelier's principle, an increase in pressure will favour the reaction that brings about a reduction in volume. In this case, a fewer number of molecules lies on the right-hand side of the equation and so increasing pressure will shift the reaction in this direction and thus increase the yield of sulfur trioxide

Low temperatures are not used industrially as lowering the temperature slows down the rate of the reaction

b) A catalyst would have no effect on the equilibrium yield of SO3. This is because a catalyst only speeds up the rate at which equilibrium is reached; it does not change the position of equilibrium

c) i)

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

ii) **Calculating k_c**

Step 1: *since k_c is calculated using concentrations in moles per litre, all quantities must be converted into moles and the concentration of moles in the 50 litre container must be calculated in terms of concentration in moles per litre*

96g of SO_2 $\longrightarrow$ Relative molecular mass (M_r) of $SO_2 = 64$

$96 \div 64 = 1.5$ moles

⇨ 1.5 moles of SO_2 were placed in the container

24g of O_2 $\longrightarrow$ M_r of $O_2 = 32$

$24 \div 32 = .75$ moles

⇨ .75 moles of O_2 were placed in the container

112g of SO_3 $\longrightarrow$ M_r of $SO_3 = 80$

$112 \div 80 = 1.4$ moles

⇨ 1.4 moles of SO_3 were present in the container at equilibrium

Step 2: *Use a table to calculate the concentration of reactants and products at equilibrium*

	$2SO_2$	O_2	$2SO_3$
Start	1.5 moles	.75 moles	-
Equilibrium	1.5 – 1.4	.75 - .7	1.4 moles
	.1 moles	.05 moles	1.4 moles
Divide by 50 to calculate concentration in **moles per litre** at equilibrium	2×10^{-3}	1×10^{-3}	.028

Step 3: *Calculate k_c using the expression in part c) i)*

$$k_c = \frac{[.028]^2}{[2x10^{-3}]^2[1x10^{-3}]}$$

$$k_c = 196{,}000$$

2014 Q9

a)

$$k_c = \frac{[N_2][O_2]}{[NO]^2}$$

b) Given that k_c = 20.25, this value can be substituted into the expression above. We then let the concentration of N_2 equal 'x' and solve.

	2NO	N_2	O_2
Start	2 moles	-	-
Equilibrium	(2 – 2x) moles	x moles	x moles

***Note** since there is no mention of the volume of the container in the question, it can be assumed that the concentration is given in moles per litre**

$$20.25 = \frac{(x)(x)}{(2-2x)^2}$$

$$20.25 = \frac{x^2}{(4x^2 - 8x + 4)}$$

$$81x^2 - 162x + 81 = x^2$$

$$80x^2 - 162x + 81 = 0$$

$$(10x-9)\ (8x-9) = 0$$

This value cannot be true since at equilibrium (2-2x) moles of NO exist in the container. This would result in a negative value for the number of moles of NO. It is not possible to have a negative number of moles of a substance *c) i) Le Châtelier's principle states that when a system at equilibrium is disturbed by a stress the system shifts in equilibrium to relieve the stress applied.*

ii) i) An increase in temperature would result in a smaller value for Kc. Since the backward reaction is endothermic, an increase in temperature would result in a shift in equilibrium in this direction as the system attempts to restore temperatures to their original value by removing heat. As a result the yield of product would be reduced and so the value for Kc would be smaller.

ii) An increase in pressure would have no effect on the value for Kc. Since an equal number of molecules lie on either side of the equation, a change in pressure would have no effect on the equilibrium position and hence the value for Kc would not change.